

There is a fact, or if you wish, a law, governing all natural phenomena that are known to date. There is no known exception to this law—it is exact as far as we know. The law is called the conservation of energy. It states that there is a certain quantity, which we call energy, that does not change in the manifold changes which nature undergoes.

—RICHARD P. FEYNMAN (1918–1988)

CHAPTER

7

Thermochemistry

We have spent the first few chapters of this book examining one of the two major components of our universe—matter. We now turn our attention to the other major component—energy. As far as we know, matter and energy—which can be interchanged but not destroyed—make up the physical universe. Unlike matter, energy is not something we can touch or hold in our hand, but we experience it in many ways. The warmth of sunlight, the feel of wind on our faces, and the force that presses us back when a car accelerates are all manifestations of energy and its interconversions. And of course energy is critical to society and to the world. The standard of living around the globe is strongly correlated with the access to and use of energy resources. Most of those resources, as we shall see, are chemical ones, and we can understand their advantages as well as their drawbacks in terms of chemistry.



A chemical hand warmer contains substances that react to emit heat.

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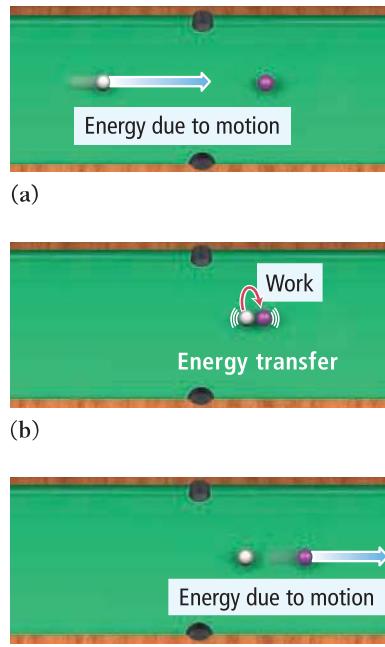
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7.1 Chemical Hand Warmers

My family loves to snowboard. However, my wife hates being cold (with a passion), especially in her hands and toes. Her solution is the chemical hand warmer, a small pouch that comes sealed in a plastic package. She opens the package and places the pouch in her glove or boot. The pouch slowly warms up and keeps her hand (or foot) warm all day long.

Warming your hands with chemical hand warmers involves many of the principles of **thermochemistry**, the study of the relationships between chemistry and energy. When you open the package that contains the hand warmer, the contents are exposed to air, and an *exothermic reaction* occurs. Most hand warmers use the oxidation of iron as the exothermic reaction:



▲ (a) A rolling billiard ball has energy due to its motion. (b) When the ball collides with a second ball, it does work, transferring energy to the second ball. (c) The second ball has energy as it rolls away from the collision.

Breaking chemical bonds always takes energy. The reactions that produce energy involve breaking weak bonds and forming stronger bonds.

The useful product of this reaction is not a substance—it is *heat*. We'll define heat more carefully later, but heat is what you feel when you touch something that is warmer than your hand (in this case, the hand warmer). Although some of the heat is lost through the minute openings in your gloves (which is why my wife prefers mittens, which have fewer openings), most of it is transferred to your hands and to the pocket of air surrounding your hands, resulting in a temperature increase. The magnitude of the temperature increase depends on the size of the hand warmer and the size of your glove (as well as some other details). But in general, the size of the temperature increase is proportional to the amount of heat released by the reaction.

In this chapter, we examine the relationship between chemical reactions and energy. Specifically, we look at how chemical reactions can *exchange* energy with their surroundings and how we can quantify the magnitude of those exchanges. These kinds of calculations are important, not only for chemical hand warmers, but also for many other important processes such as the production of energy.

7.2

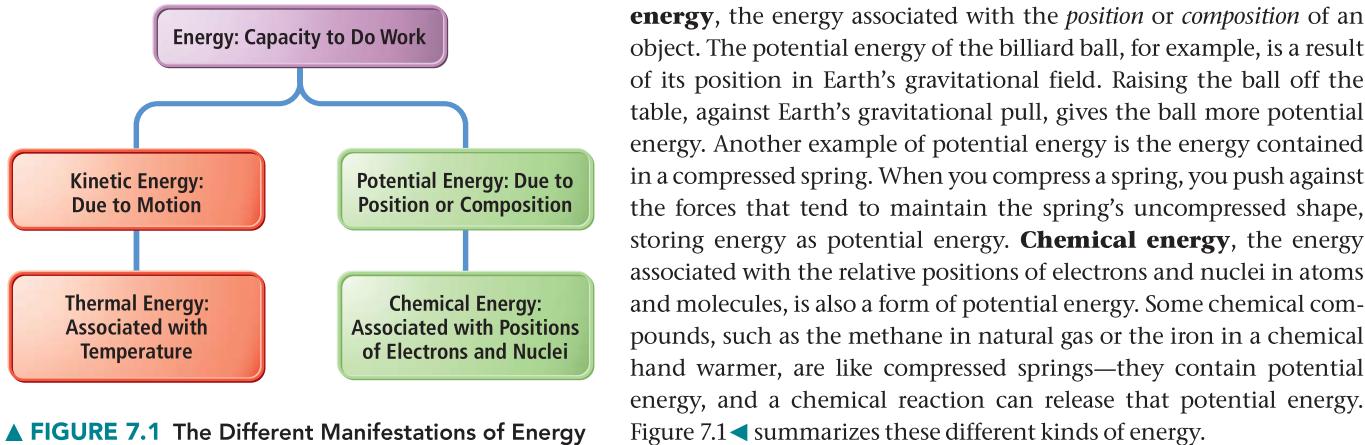
The Nature of Energy: Key Definitions

Recall that we briefly examined energy in Section 1.5. We defined **energy** as the capacity to do work and defined **work** as the result of a force acting through a distance. When you push a box across the floor, you have done work. Consider another example of work: a billiard ball rolling across a billiard table and colliding straight on with a second, stationary billiard ball. The rolling ball has *energy* due to its motion. When it collides with another stationary ball, it does *work* on it, resulting in the *transfer* of energy from one ball to the other. The second billiard ball absorbs the energy and begins to roll across the table.

As we just saw with chemical hand warmers, energy can also be transferred through **heat**, the flow of energy caused by a temperature difference. For example, if you hold a cup of coffee in your hand, energy is transferred, in the form of heat, from the hot coffee to your cooler hand. Think of *energy* as something that an object or set of objects possesses. Think of *heat* and *work* as ways that objects or sets of objects *exchange* energy.

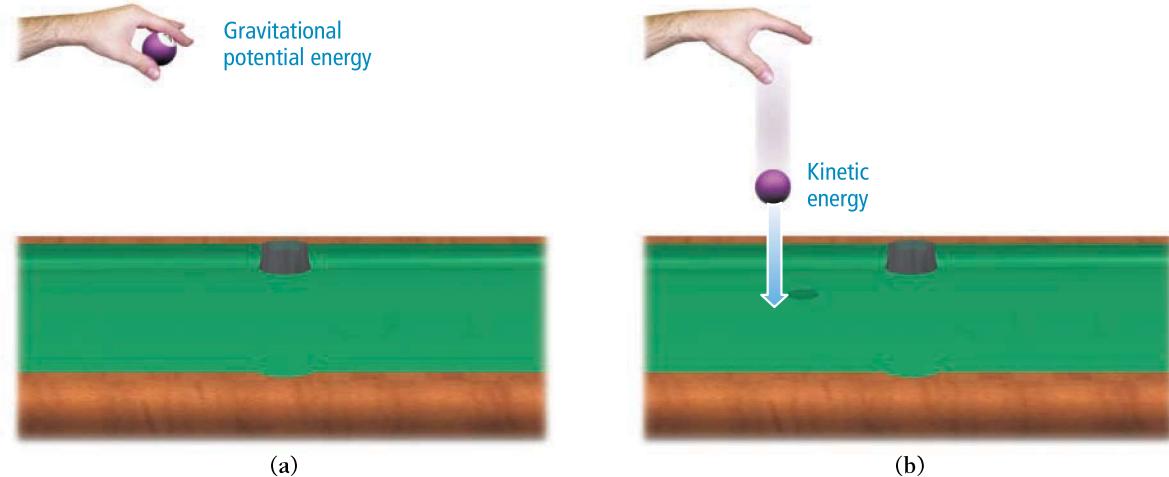
Types of Energy

The energy contained in a rolling billiard ball is an example of **kinetic energy**, the energy associated with the *motion* of an object. The energy contained in a hot cup of coffee is **thermal energy**, the energy associated with the *temperature* of an object. Thermal energy is actually a type of kinetic energy because it arises from the motions of atoms or molecules within a substance. If you raise a billiard ball off the table, you increase its **potential energy**, the energy associated with the *position* or *composition* of an object. The potential energy of the billiard ball, for example, is a result of its position in Earth's gravitational field. Raising the ball off the table, against Earth's gravitational pull, gives the ball more potential energy. Another example of potential energy is the energy contained in a compressed spring. When you compress a spring, you push against the forces that tend to maintain the spring's uncompressed shape, storing energy as potential energy. **Chemical energy**, the energy associated with the relative positions of electrons and nuclei in atoms and molecules, is also a form of potential energy. Some chemical compounds, such as the methane in natural gas or the iron in a chemical hand warmer, are like compressed springs—they contain potential energy, and a chemical reaction can release that potential energy. Figure 7.1 summarizes these different kinds of energy.



▲ FIGURE 7.1 The Different Manifestations of Energy

Energy Transformation I



▲ FIGURE 7.2 Energy Transformation: Potential and Kinetic Energy I (a) A billiard ball held above the table has gravitational potential energy. (b) When the ball is released, the potential energy is transformed into kinetic energy, the energy of motion.

Energy Conservation and Energy Transfer

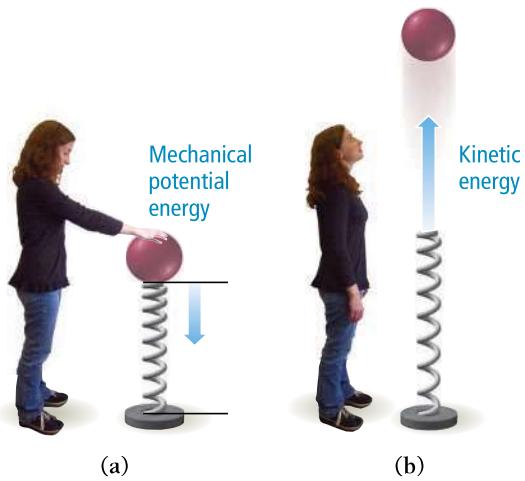
The **law of conservation of energy** states that *energy can be neither created nor destroyed*. However, energy can be transferred from one object to another, and it can assume different forms. For example, if you drop a raised billiard ball, some of its potential energy becomes kinetic energy as the ball falls toward the table, as shown in Figure 7.2▲. If you release a compressed spring, the potential energy becomes kinetic energy as the spring expands outward, as shown in Figure 7.3▼. When iron reacts with oxygen within a chemical hand warmer, the chemical energy of the iron and oxygen becomes thermal energy that increases the temperature of your hand and glove.

A good way to understand and track energy changes is to define the **system** under investigation. For example, the system may be the chemicals in a beaker, or it may be the iron reacting in a hand warmer. The system's **surroundings** are everything with which the system can exchange energy. If we define the chemicals in a beaker as the system, the surroundings may include the water in which the chemicals are dissolved (for aqueous solutions), the beaker itself, the lab bench on which the beaker sits, the air in the room, and so on. For the iron in the hand warmer, the surroundings include your hand, your glove, the air in the glove, and even the air outside of the glove.

In an energy exchange, energy transfers between the system and the surroundings, as shown in Figure 7.4►. If the system loses energy, the surroundings gain the same exact amount of energy, and vice versa. When the iron within the chemical hand warmer reacts, the system loses energy to the surroundings, producing the desired temperature increase within your gloves.

Einstein showed that it is mass-energy that is conserved; one can be converted into the other. This equivalence becomes important in nuclear reactions, discussed in Chapter 21. In ordinary chemical reactions, however, the interconversion of mass and energy is not a significant factor, and we can regard mass and energy as independently conserved.

Energy Transformation II



Units of Energy

We can deduce the units of energy from the definition of kinetic energy. An object of mass m , moving at velocity v , has a kinetic energy KE given by the equation:

$$KE = \frac{1}{2}mv^2 \quad [7.1]$$

kg m/s

▲ FIGURE 7.3 Energy Transformation: Potential and Kinetic Energy II (a) A compressed spring has potential energy. (b) When the spring is released, the potential energy is transformed into kinetic energy.

► FIGURE 7.4 Energy Transfer If a system and surroundings had energy gauges (which measure energy content in the way a fuel gauge measures fuel content), an energy transfer in which the system transfers energy to the surroundings would result in a decrease in the energy content of the system and an increase in the energy content of the surroundings. The total amount of energy, however, must be conserved.

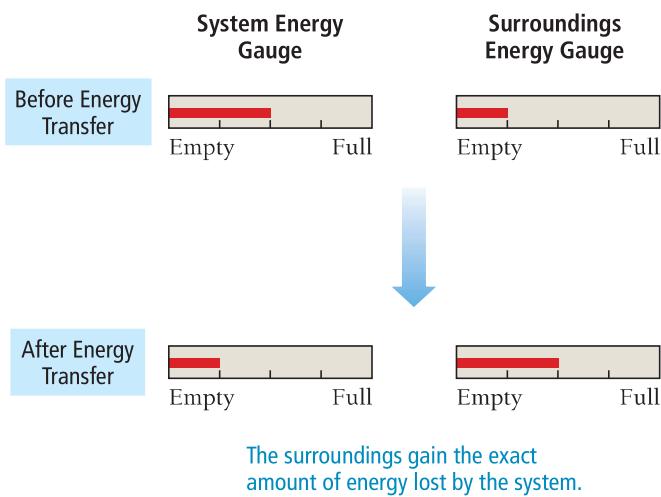


$3.6 \times 10^4 \text{ J or } 0.01 \text{ kWh}$
used in 1 hour

▲ A watt (W) is 1 J/s, so a 10-W lightbulb uses 10 J every second or $3.6 \times 10^4 \text{ J}$ every hour.

The “calorie” referred to on all nutritional labels (regardless of the capitalization) is always the capital C Calorie.

Energy Transfer



The SI unit of mass is the kg, and the unit of velocity is m/s. The SI unit of energy is therefore $\text{kg} \cdot \text{m}^2/\text{s}^2$, defined as the **joule (J)**, named after the English scientist James Joule (1818–1889).

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

One joule is a relatively small amount of energy—for example, a 10-watt lightbulb uses $3.6 \times 10^4 \text{ J}$ in 1 hour. Therefore, we often use the kilojoule (kJ) in our energy discussions and calculations ($1 \text{ kJ} = 1000 \text{ J}$). A second commonly used unit of energy is the **calorie (cal)**, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1 °C. The current definition is $1 \text{ cal} = 4.184 \text{ J}$ (exact); a calorie is a larger unit than a joule. A related energy unit is the nutritional, or uppercase “C” **Calorie (Cal)**, equivalent to 1000 lowercase “c” calories. The Calorie is the same as a kilocalorie (kcal): $1 \text{ Cal} = 1 \text{ kcal} = 1000 \text{ cal}$. Electricity bills typically are based on another, even larger, energy unit, the **kilowatt-hour (kWh)**: $1 \text{ kWh} = 3.60 \times 10^6 \text{ J}$. Electricity costs \$0.08–\$0.18 per kWh. Table 7.1 lists various energy units and their conversion factors. Table 7.2 shows the amount of energy required for various processes.

TABLE 7.1 ■ Energy Conversion Factors*

| | |
|---------------------------------------|--------------------------------|
| 1 calorie (cal) | = 4.184 joules (J) |
| 1 Calorie (Cal) or kilocalorie (kcal) | = 1000 cal = 4184 J |
| 1 kilowatt-hour (kWh) | = $3.60 \times 10^6 \text{ J}$ |

*All conversion factors in this table are exact.

TABLE 7.2 ■ Energy Uses in Various Units

| Unit | Amount Required to Raise Temperature of 1 g of Water by 1 °C | Amount Required to Light 10-W Bulb for 1 Hour | Amount Used by Human Body in Running 1 Mile (Approximate) | Amount Used by Average U.S. Citizen in 1 Day |
|---------------------|--|---|---|--|
| joule (J) | 4.18 | 3.60×10^4 | 4.2×10^5 | 9.0×10^8 |
| calorie (cal) | 1.00 | 8.60×10^3 | 1.0×10^5 | 2.2×10^8 |
| Calorie (Cal) | 0.00100 | 8.60 | 100 | 2.2×10^5 |
| kilowatt-hour (kWh) | 1.16×10^{-6} | 0.0100 | 0.12 | 2.5×10^2 |

7.3

The First Law of Thermodynamics: There Is No Free Lunch

Thermodynamics is the general study of energy and its interconversions. The laws of thermodynamics are among the most fundamental in all of science, governing virtually every process that involves change. The **first law of thermodynamics** is the law of energy conservation, which we state as follows:

The total energy of the universe is constant.

In other words, since energy is neither created nor destroyed, and since the universe does not exchange energy with anything else, its energy content does not change.

The first law has many implications: the most important one is that with energy, you cannot get something for nothing. The best you can do with energy is break even—there is no free lunch. According to the first law, a device that would continually produce energy with no energy input, sometimes known as a *perpetual motion machine*, cannot exist. Occasionally, the media report or speculate on the discovery of a machine that can produce energy without the need for energy input. For example, you may have heard someone propose an electric car that recharges itself while driving, or a new motor that can create additional usable electricity as well as the electricity to power itself. Although some hybrid (electric and gasoline-powered) vehicles can capture energy from braking and use that energy to recharge their batteries, they could never run indefinitely without additional fuel. As for the motor that powers an external load as well as itself—no such thing exists. Our society has a continual need for energy, and as our current energy resources dwindle, new energy sources will be required. But those sources, whatever they may be, must follow the first law of thermodynamics—energy is always conserved.

Internal Energy

The **internal energy (E)** of a system is *the sum of the kinetic and potential energies of all of the particles that compose the system*. Internal energy is a **state function**, which means that its value depends *only on the state of the system*, not on how the system arrived at that state.



CHEMISTRY IN YOUR DAY | Redheffer's Perpetual Motion Machine

In 1812, a man named Charles Redheffer appeared in Philadelphia with a machine that he claimed could run forever without any energy input—a perpetual motion machine. He set up the machine on the edge of town and charged admission to view it. He also appealed to the city for money to build a larger version of the machine. When city commissioners came out to inspect the machine, Redheffer did his best to keep them from viewing it too closely. Nonetheless, one of the commissioners noticed something suspicious: the gears that supposedly ran to an external driveshaft were cut in the wrong direction. The driveshaft that the machine was allegedly powering was instead powering the machine. The city commissioners hired a local engineer and clockmaker named Isaiah Lukens to make a similar machine to expose Redheffer's deception. Lukens's machine was even more ingenious than Redheffer's, and Redheffer left Philadelphia exposed as a fraud.

Redheffer was persistent, however, and took his machine to New York. In 1813, during a public display of the machine, the famous mechanical engineer Robert Fulton (1765–1815)—who had demonstrated the first successful steamboat six years earlier—noticed a rhythm to the machine's motion. It seemed to speed up and slow down at regular intervals. Fulton knew that such rhythmic motion is indicative of motion generated by a manual crank. He knocked away some boards in a wall next to the machine and discovered a long belt that led to an enclosed room where, indeed, an old man sat turning a crank. Redheffer's machine—like many other perpetual motion machines throughout history—was again exposed as a hoax.

QUESTION Can you think of any recent claims of perpetual motion or limitless free energy?

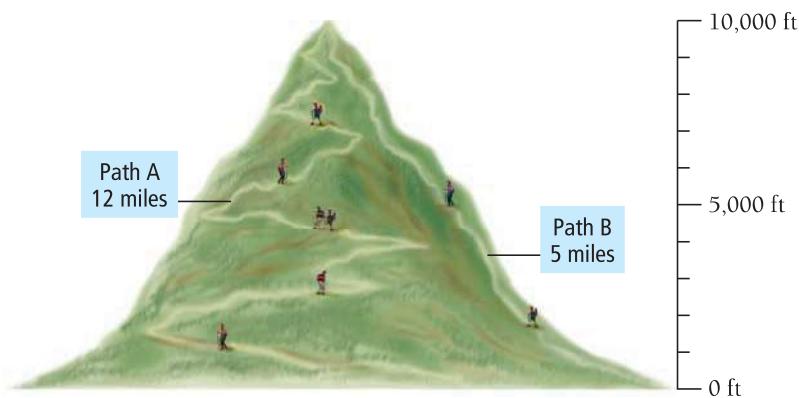
WATCH NOW!**KEY CONCEPT VIDEO 7.3**

The First Law of Thermodynamics



► **FIGURE 7.5** Altitude as a State Function

A State Function
Change in altitude depends only on the difference between the initial and final values, not on the path taken.



The state of a chemical system is specified by parameters such as temperature, pressure, concentration, and physical state (solid, liquid, or gas). Consider the mountain-climbing analogy depicted in Figure 7.5▲. The elevation at any point during a mountain climb is analogous to a state function. For example, when we reach 10,000 ft, our elevation is 10,000 ft, no matter how we got there. The distance we traveled to get there, by contrast, is not a state function; we could have climbed the mountain by any number of routes, each requiring us to cover a different distance.

Since state functions depend only on the state of the system, the value of a *change* in a state function is always the difference between its final and initial values. If we start climbing a mountain at an elevation of 3000 ft and reach the summit at 10,000 ft, then our elevation change is 7000 ft ($10,000 \text{ ft} - 3000 \text{ ft}$), regardless of what path we traveled.

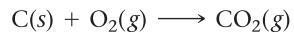
Like an altitude change, an internal energy change (ΔE) is determined by the difference in internal energy between the final and initial states:

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

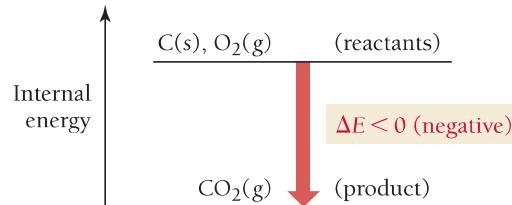
In a chemical system, the reactants constitute the initial state and the products constitute the final state. So ΔE is the difference in internal energy between the products and the reactants:

$$\Delta E = E_{\text{products}} - E_{\text{reactants}} \quad [7.2]$$

For example, consider the reaction between carbon and oxygen to form carbon dioxide:

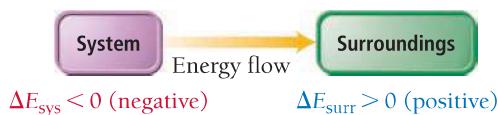


Just as we can portray the changes that occur when climbing a mountain with an *altitude* diagram that depicts the *altitude* before and after the climb (see Figure 7.5), we can portray the energy changes that occur during a reaction with an *energy* diagram, which compares the *internal energy* of the reactants and the products:



The vertical axis of the diagram is *internal energy*, which increases as we move up on the diagram. For this reaction, the reactants are *higher* on the diagram than the products because they have higher internal energy. As the reaction occurs, the reactants become products, which have lower internal energy. Therefore, energy is given off by the reaction and ΔE (that is, $E_{\text{products}} - E_{\text{reactants}}$) is *negative*.

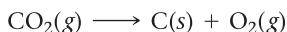
Where does the energy lost by the reactants (as they transform to products) go? If we define the thermodynamic *system* as the reactants and products of the reaction, then energy flows *out of the system* and *into the surroundings*.



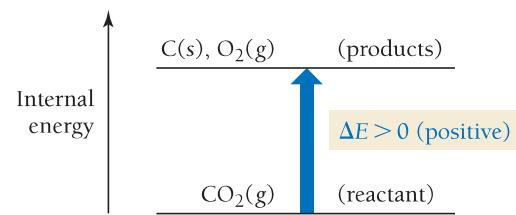
According to the first law, energy must be conserved. Therefore, the amount of energy lost by the system must exactly equal the amount gained by the surroundings:

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}} \quad [7.3]$$

Now, suppose the reaction is reversed:



The energy-level diagram is nearly identical, with one important difference: $\text{CO}_2(g)$ is now the reactant and $\text{C}(s)$ and $\text{O}_2(g)$ are the products. Instead of decreasing in energy as the reaction occurs, the system increases in energy as shown at right. In this reversed reaction, ΔE is *positive*, and energy flows *into the system* and *out of the surroundings*:

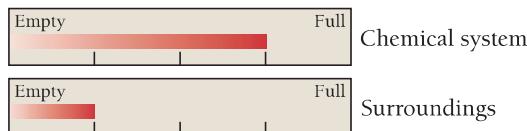


Summarizing Energy Flow:

- If the reactants have a higher internal energy than the products, ΔE_{sys} is negative and energy flows out of the system into the surroundings.
- If the reactants have a lower internal energy than the products, ΔE_{sys} is positive and energy flows into the system from the surroundings.

We can think of the internal energy of the system in the same way we think about the balance in a checking account. Energy flowing *out of* the system is like a withdrawal and therefore carries a negative sign. Energy flowing *into* the system is like a deposit and carries a positive sign.

SYSTEM AND SURROUNDINGS Consider these fictitious internal energy gauges that describe the initial conditions for a chemical system and its surroundings:

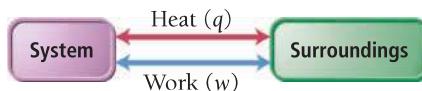


Which energy gauges correspond to the final conditions following an energy exchange in which ΔE_{sys} is negative?

- | | |
|------------|------------|
| <p>(a)</p> | <p>(b)</p> |
| <p>(c)</p> | |

Heat and Work

As we discussed in Section 7.2, a system can exchange energy with its surroundings through *heat* and *work*:



According to the first law of thermodynamics, the change in the internal energy of the system (ΔE) is the sum of the heat transferred (q) and the work done (w):

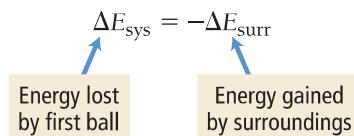
$$\Delta E = q + w \quad [7.4]$$

In Equation 7.4, and from this point forward, we follow the standard convention that ΔE (with no subscript) refers to the internal energy change of the *system*. As shown in Table 7.3, energy entering the system through heat or work carries a positive sign, and energy leaving the system through heat or work carries a negative sign. Recall our checking account analogy. The system is like the checking account—withdrawals are negative and deposits are positive.

TABLE 7.3 ■ Sign Conventions for q , w , and ΔE

| | | |
|--|---------------------------------------|---|
| q (heat) | + system gains thermal energy | - system loses thermal energy |
| w (work) | + work done on the system | - work done by the system |
| ΔE (change in internal energy) | + energy flows <i>into</i> the system | - energy flows <i>out of</i> the system |

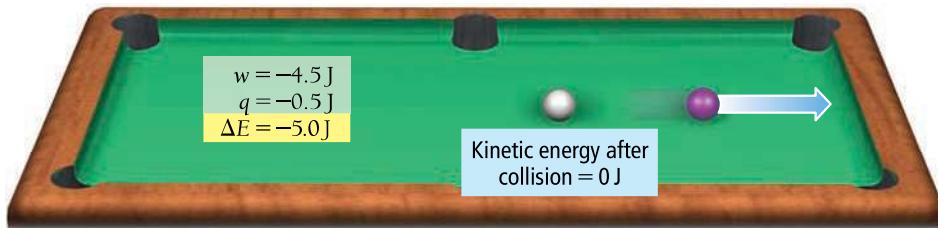
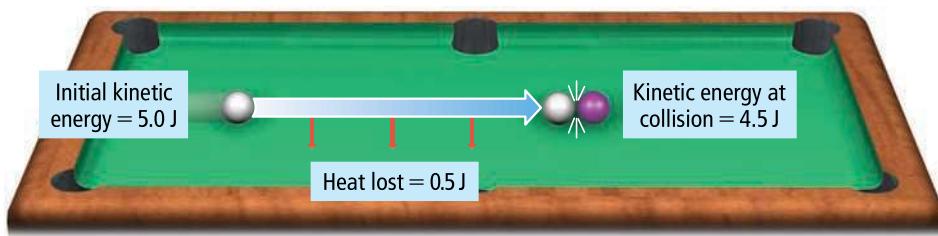
We can define our system as the previously discussed billiard ball rolling across a pool table. The rolling ball has a certain initial amount of kinetic energy. When it reaches the other end of the table, the rolling ball collides head-on with a second ball. Assume that the first ball loses all of its kinetic energy so that it remains completely still (it has no kinetic energy) at the point of collision. The total change in internal energy (ΔE) for the first ball is the difference between its initial kinetic energy and its final kinetic energy (which is zero); the first billiard ball lost all of its energy. What happened to that energy? According to the first law, it must have been transferred to the surroundings. In fact, the energy lost by the system must *exactly equal* the amount gained by the surroundings:



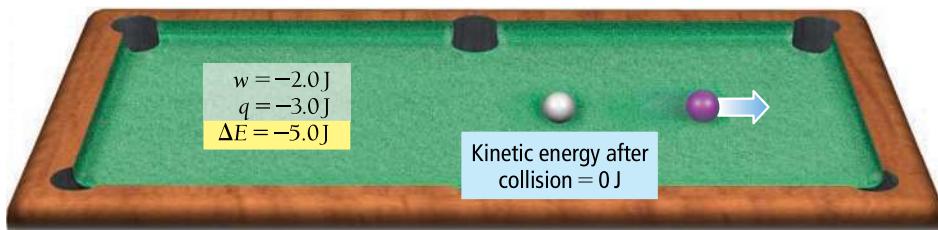
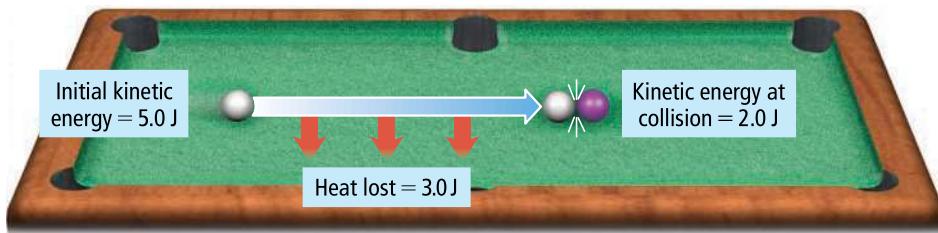
The surroundings include both the pool table and the second ball. The pool table absorbs some of the ball's kinetic energy as the ball rolls down the table. Minute bumps on the table surface cause friction, which slows the ball down by converting kinetic energy to heat (q). The second ball absorbs some of the ball's kinetic energy in the form of work (w) upon collision.

Although it is always the case that $\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$, the exact amount of *work* done on the second ball depends on the quality of the billiard table. On a smooth, high-quality billiard table, the amount of energy lost to friction is relatively small, as illustrated in Figure 7.6(a)►. The speed of the first ball is not reduced by much as it travels across the table, and a great deal of its original kinetic energy is available to perform work when it collides with the second ball. In contrast, on a rough, poor-quality table, the ball loses much of its initial kinetic energy as heat, leaving only a relatively small amount available for work, as illustrated in Figure 7.6(b)►.

Notice that the respective amounts of energy converted to heat and work depend on the details of the pool table and the path taken, while the change in internal energy of the rolling ball does not. Because internal energy is a state function, the value of ΔE for the process in which the ball moves across the table and collides with another ball depends



(a) Smooth table



(b) Rough table

▲ FIGURE 7.6 Energy, Work, and Heat (a) On a smooth table, most of the first billiard ball's initial kinetic energy is transferred to the second ball as work. Only a small amount is lost to heat. (b) On a rough table, most of the first billiard ball's initial kinetic energy is lost to heat. Only a small amount is left to do work on the second billiard ball.

only on the ball's initial and final kinetic energy. Work and heat, however, are *not* state functions; therefore, the values of q and w depend on the details of the ball's journey across the table. On the smooth table, w is greater in magnitude than q ; on the rough table, q is greater in magnitude than w . However, ΔE (the sum of q and w) is constant.

HEAT AND WORK

Which heat exchange is best classified as work?

- (a) An ice cube melts and cools the surrounding beverage.
- (b) A metal cylinder is rolled up a ramp.
- (c) Steam condenses on skin, causing a burn.



ANSWER NOW!



EXAMPLE 7.1 Internal Energy, Heat, and Work

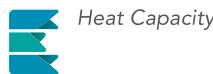
A potato cannon provides a good example of the heat and work associated with a chemical reaction. In a potato cannon, a potato is stuffed into a long cylinder that is capped on one end and open at the other. Some kind of fuel is introduced under the potato at the capped end—usually through a small hole—and ignited. The potato shoots out of the cannon, sometimes flying hundreds of feet, and the cannon emits heat to the surroundings. If the burning of the fuel performs 855 J of work on the potato and produces 1422 J of heat, what is ΔE for the burning of the fuel? (Note: A potato cannon can be dangerous and should not be constructed without proper training and experience.)

SOLUTION

To solve the problem, substitute the values of q and w into the equation for ΔE . Since work is done by the system on the surroundings, w is negative. Similarly, because heat is released by the system to the surroundings, q is also negative.

$$\begin{aligned}\Delta E &= q + w \\ &= -1422 \text{ J} - 855 \text{ J} \\ &= -2277 \text{ J}\end{aligned}$$

FOR PRACTICE 7.1 A cylinder and piston assembly (defined as the system) is warmed by an external flame. The contents of the cylinder expand, doing work on the surroundings by pushing the piston outward against the external pressure. If the system absorbs 559 J of heat and does 488 J of work during the expansion, what is the value of ΔE ?

WATCH NOW!**KEY CONCEPT VIDEO 7.4****7.4****Quantifying Heat and Work**

In the previous section, we calculated ΔE based on *given values of q and w* . We now turn to *calculating q (heat) and w (work)* based on changes in temperature and volume.

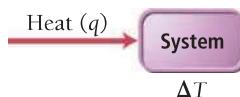
Heat

Recall from Section 7.2 that *heat* is the exchange of thermal energy between a system and its surroundings caused by a temperature difference. Notice the distinction between heat and temperature. Temperature is a *measure* of the average thermal energy within a sample of matter. Heat is the *transfer* of thermal energy. Thermal energy always flows from matter at higher temperatures to matter at lower temperatures. For example, a hot cup of coffee transfers thermal energy—as heat—to the lower-temperature surroundings as it cools down. Imagine a world where the cooler surroundings actually got colder as they transferred thermal energy to the hot coffee, which got hotter. Such a world exists only in our imaginations (or in the minds of science fiction writers) because the spontaneous transfer of heat from a hotter object to a colder one is a fundamental principle of our universe—no exception has ever been observed. The thermal energy in the molecules that compose the hot coffee distributes itself to the molecules in the surroundings. The heat transfer from the coffee to the surroundings stops when the two reach the same temperature, a condition called **thermal equilibrium**. At thermal equilibrium, there is no additional net transfer of heat.

The reason for this one-way transfer is related to the second law of thermodynamics, which we discuss in Chapter 19.

Temperature Changes and Heat Capacity

When a system absorbs heat (q), its temperature changes by ΔT :



$$\Delta T$$

Experiments show that the heat absorbed by a system and its corresponding temperature change are directly proportional: $q \propto \Delta T$. The constant of proportionality between q and ΔT is the system's *heat capacity* (C), a measure of the system's ability to absorb thermal energy without undergoing a large change in temperature.

$$q = C \times \Delta T \quad [7.5]$$

Heat capacity

Notice that the higher the heat capacity of a system, the smaller the change in temperature for a given amount of absorbed heat. We define the **heat capacity (C)** of a system as the quantity of heat required to change its temperature by $1\text{ }^{\circ}\text{C}$. As we can see by solving Equation 7.5 for heat capacity, the units of heat capacity are those of heat (typically J) divided by those of temperature (typically $^{\circ}\text{C}$):

$$C = \frac{q}{\Delta T} = \frac{\text{J}}{\text{ }^{\circ}\text{C}}$$

In order to understand two important concepts related to heat capacity, imagine putting a steel saucepan on a kitchen flame. The saucepan's temperature rises rapidly as it absorbs heat from the flame. However, if you add some water to the saucepan, the temperature rises more slowly. Why? The first reason is that when you add the water, the same amount of heat must now warm more matter, so the temperature rises more slowly. In other words, heat capacity is an extensive property—it depends on the amount of matter being heated (see Section 1.6). The second (and more fundamental) reason is that water is more resistant to temperature change than steel—water has an intrinsically higher capacity to absorb heat without undergoing a large temperature change. The measure of the *intrinsic capacity* of a substance to absorb heat is its **specific heat capacity (C_s)**, the amount of heat required to raise the temperature of *1 gram* of the substance by $1\text{ }^{\circ}\text{C}$. The units of specific heat capacity (also called *specific heat*) are $\text{J/g} \cdot ^{\circ}\text{C}$. Table 7.4 lists the values of the specific heat capacity for several substances. Heat capacity is sometimes reported as **molar heat capacity**, the amount of heat required to raise the temperature of *1 mole* of a substance by $1\text{ }^{\circ}\text{C}$. The units of molar heat capacity are $\text{J/mol} \cdot ^{\circ}\text{C}$. We can see from these definitions that *specific* heat capacity and *molar* heat capacity are intensive properties—they depend on the *kind* of substance being heated, not on the amount.

Notice that water has the highest specific heat capacity of all the substances in Table 7.4—changing the temperature of water requires a lot of heat. If you have ever experienced the drop in temperature that occurs when traveling from an inland region to the coast during the summer, you have experienced the effects of water's high specific heat capacity. On a summer's day in California, for example, the temperature difference between Sacramento (an inland city) and San Francisco (a coastal city) may be as large as $18\text{ }^{\circ}\text{C}$ ($30\text{ }^{\circ}\text{F}$)—San Francisco enjoys a cool $20\text{ }^{\circ}\text{C}$ ($68\text{ }^{\circ}\text{F}$), while Sacramento bakes at nearly $38\text{ }^{\circ}\text{C}$ ($100\text{ }^{\circ}\text{F}$). Yet the intensity of sunlight falling on these two cities is the same. Why the large temperature difference? San Francisco sits on a peninsula, surrounded by the water of the Pacific Ocean. Water, with its high heat capacity, absorbs much of the sun's heat without undergoing a large increase in temperature, keeping San Francisco cool. Sacramento, by contrast, is about 160 km (100 mi) inland. The land surrounding Sacramento, with its low heat capacity, undergoes a large increase in temperature as it absorbs a similar amount of heat.

Similarly, only two U.S. states have never recorded a temperature above $100\text{ }^{\circ}\text{F}$. One of them is obvious: Alaska. It is too far north to get that hot. The other one, however, may come as a surprise. It is Hawaii. The high heat capacity of the water that surrounds the only island state moderates the temperature, preventing Hawaii from ever getting too hot.

We can use the specific heat capacity of a substance to quantify the relationship between the amount of heat added to a given amount of the substance and the corresponding temperature increase. The following equation relates these quantities:

$$\text{Heat (J)} \rightarrow q = m \times C_s \times \Delta T \quad [7.6]$$

Temperature
change ($^{\circ}\text{C}$)

Mass (g) Specific heat
capacity $\text{J/g} \cdot ^{\circ}\text{C}$

where q is the amount of heat in J, m is the mass of the substance in g, C_s is the specific heat capacity in $\text{J/g} \cdot ^{\circ}\text{C}$, and ΔT is the temperature change in $^{\circ}\text{C}$. Example 7.2 demonstrates the use of this equation.

TABLE 7.4 ■ Specific Heat Capacities of Some Common Substances

| Substance | Specific Heat Capacity, C_s (J/g \cdot $^{\circ}\text{C}$)* |
|------------------|--|
| Elements | |
| Lead | 0.128 |
| Gold | 0.128 |
| Silver | 0.235 |
| Copper | 0.385 |
| Iron | 0.449 |
| Aluminum | 0.903 |
| Compounds | |
| Ethanol | 2.42 |
| Water | 4.18 |
| Materials | |
| Glass (Pyrex) | 0.75 |
| Granite | 0.79 |
| Sand | 0.84 |

*At 298 K .



▲ The high heat capacity of the water surrounding San Francisco results in relatively cool summer temperatures.

Δ T in $^{\circ}\text{C}$ is equal to ΔT in K, but not equal to ΔT in $^{\circ}\text{F}$ (Section 1.6).

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 7.2

EXAMPLE 7.2 Temperature Changes and Heat Capacity

Suppose you find a penny (minted before 1982, when pennies were almost entirely copper) in the snow.

How much heat is absorbed by the penny as it warms from the temperature of the snow, which is $-8.0\text{ }^{\circ}\text{C}$, to the temperature of your body, $37.0\text{ }^{\circ}\text{C}$? Assume the penny is pure copper and has a mass of 3.10 g.

SORT You are given the mass of copper as well as its initial and final temperature. You are asked to find the heat required for the given temperature change.

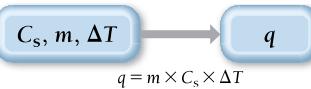
GIVEN: $m = 3.10\text{ g}$ copper

$$T_i = -8.0\text{ }^{\circ}\text{C}$$

$$T_f = 37.0\text{ }^{\circ}\text{C}$$

FIND: q

STRATEGIZE The equation $q = m \times C_s \times \Delta T$ gives the relationship between the amount of heat (q) and the temperature change (ΔT).

CONCEPTUAL PLAN**RELATIONSHIPS USED**

$$q = m \times C_s \times \Delta T \text{ (Equation 7.6)}$$

$$C_s = 0.385\text{ J/g} \cdot ^{\circ}\text{C} \text{ (Table 7.4)}$$

SOLVE Gather the necessary quantities for the equation in the correct units and substitute into the equation to calculate q .

SOLUTION

$$\Delta T = T_f - T_i = 37.0\text{ }^{\circ}\text{C} - (-8.0\text{ }^{\circ}\text{C}) = 45.0\text{ }^{\circ}\text{C}$$

$$q = m \times C_s \times \Delta T$$

$$= 3.10\text{ g} \times 0.385\frac{\text{J}}{\text{g} \cdot ^{\circ}\text{C}} \times 45.0\text{ }^{\circ}\text{C} = 53.7\text{ J}$$

CHECK The units (J) are correct for heat. The sign of q is *positive*, as it should be because the penny *absorbed* heat from the surroundings.

FOR PRACTICE 7.2 To determine whether a shiny gold-colored rock is actually gold, a chemistry student decides to measure its heat capacity. She first weighs the rock and finds it has a mass of 4.7 g. She then finds that upon absorption of 57.2 J of heat, the temperature of the rock rises from $25\text{ }^{\circ}\text{C}$ to $57\text{ }^{\circ}\text{C}$. Find the specific heat capacity of the substance composing the rock and determine whether the value is consistent with the rock being pure gold.

FOR MORE PRACTICE 7.2 A 55.0-g aluminum block initially at $27.5\text{ }^{\circ}\text{C}$ absorbs 725 J of heat. What is the final temperature of the aluminum?

ANSWER NOW!



7.3 Cc Conceptual Connection

THE HEAT CAPACITY OF WATER Suppose you are cold-weather camping and decide to heat some objects to bring into your sleeping bag for added warmth. You place a large water jug and a rock of equal mass near the fire. Over time, both the rock and the water jug warm to about $38\text{ }^{\circ}\text{C}$ (100 °F). If you can bring only one into your sleeping bag, which one should you choose to keep you warmer? Why?

- (a) The water, because it will release more heat as it cools.
- (b) The rock, because it will absorb more heat as it cools.
- (c) The rock, because it will release more heat as it cools.
- (d) The water, because it will absorb more heat as it cools.

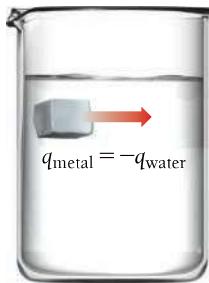
Thermal Energy Transfer

As we noted earlier, when two substances of different temperature are combined, thermal energy flows as heat from the hotter substance to the cooler one. If we assume that the two substances are thermally isolated from everything else, then the heat lost

by one substance exactly equals the heat gained by the other (according to the law of energy conservation). If we define one substance as the system and the other as the surroundings, we can quantify the heat exchange as:

$$q_{\text{sys}} = -q_{\text{surr}}$$

Suppose a block of metal initially at 55 °C is submerged into water initially at 25 °C. Thermal energy transfers as heat from the metal to the water:



The metal becomes colder and the water becomes warmer until the two substances reach the same temperature (thermal equilibrium). The exact temperature change that occurs depends on the masses of the metal and the water and on their specific heat capacities. Since $q = m \times C_s \times \Delta T$, we can arrive at the following relationship:

$$\begin{aligned} q_{\text{metal}} &= -q_{\text{water}} \\ m_{\text{metal}} \times C_{s, \text{metal}} \times \Delta T_{\text{metal}} &= -m_{\text{water}} \times C_{s, \text{water}} \times \Delta T_{\text{water}} \end{aligned}$$

Example 7.3 shows how to work with thermal energy transfer.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 7.3

EXAMPLE 7.3 Thermal Energy Transfer



A 32.5 g cube of aluminum initially at 45.8 °C is submerged into 105.3 g of water at 15.4 °C. What is the final temperature of both substances at thermal equilibrium? (Assume that the aluminum and the water are thermally isolated from everything else.)

SORT You are given the masses of aluminum and water and their initial temperatures. You are asked to find the final temperature.

STRATEGIZE The heat lost by the aluminum (q_{Al}) equals the heat gained by the water ($q_{\text{H}_2\text{O}}$).

Use the relationship between q and ΔT and the given variables to find a relationship between ΔT_{Al} and $\Delta T_{\text{H}_2\text{O}}$.

Use the relationship between ΔT_{Al} and $\Delta T_{\text{H}_2\text{O}}$ (that you just found) along with the initial temperatures of the aluminum and the water to determine the final temperature. Note that at thermal equilibrium, the final temperature of the aluminum and the water is the same, that is, $T_{f, \text{Al}} = T_{f, \text{H}_2\text{O}} = T_f$.

SOLVE

Write the equation for the relationship between the heat lost by the aluminum (q_{Al}) and the heat gained by the water $q_{\text{Al}} = -q_{\text{H}_2\text{O}}$ and substitute $q = m \times C_s \times \Delta T$ for each substance.

GIVEN: $m_{\text{Al}} = 32.5 \text{ g}$ $m_{\text{H}_2\text{O}} = 105.3 \text{ g}$

$T_{i, \text{Al}} = 45.8 \text{ }^\circ\text{C}$; $T_{i, \text{H}_2\text{O}} = 15.4 \text{ }^\circ\text{C}$

FIND: T_f

CONCEPTUAL PLAN $q_{\text{Al}} = -q_{\text{H}_2\text{O}}$

$$m_{\text{Al}}, C_{s, \text{Al}}, m_{\text{H}_2\text{O}}, C_{s, \text{H}_2\text{O}} \rightarrow \Delta T_{\text{Al}} = \text{constant} \times \Delta T_{\text{H}_2\text{O}}$$

$$m_{\text{Al}} \times C_{s, \text{Al}} \times \Delta T_{\text{Al}} = -m_{\text{H}_2\text{O}} \times C_{s, \text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}$$

$$T_{i, \text{Al}}; T_{i, \text{H}_2\text{O}} \rightarrow T_f$$

$$\Delta T_{\text{Al}} = \text{constant} \times \Delta T_{\text{H}_2\text{O}}$$

RELATIONSHIPS USED

$C_{s, \text{H}_2\text{O}} = 4.18 \text{ J/g} \cdot {}^\circ\text{C}$; $C_{s, \text{Al}} = 0.903 \text{ J/g} \cdot {}^\circ\text{C}$ (Table 7.4)

$q = m \times C_s \times \Delta T$ (Equation 7.6)

SOLUTION

$$q_{\text{Al}} = -q_{\text{H}_2\text{O}}$$

$$m_{\text{Al}} \times C_{s, \text{Al}} \times \Delta T_{\text{Al}} = -m_{\text{H}_2\text{O}} \times C_{s, \text{H}_2\text{O}} \times \Delta T_{\text{H}_2\text{O}}$$

—Continued on the next page

Continued—

Substitute the values of m (given) and C_s (from Table 7.4) for each substance and solve the equation for ΔT_{Al} . (Alternatively, you can solve the equation for $\Delta T_{\text{H}_2\text{O}}$.)

Substitute the initial temperatures of aluminum and water into the relationship from the previous step and solve the expression for the final temperature (T_f). Remember that the final temperature for both substances will be the same.

$$32.5 \text{ g} \times \frac{0.903 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \cdot \Delta T_{\text{Al}} = -105.3 \text{ g} \times \frac{4.18 \text{ J}}{\text{J} \cdot ^\circ\text{C}} \cdot \Delta T_{\text{H}_2\text{O}}$$

$$29.348 \cdot \Delta T_{\text{Al}} = -440.15 \cdot \Delta T_{\text{H}_2\text{O}}$$

$$\Delta T_{\text{Al}} = -14.998 \cdot \Delta T_{\text{H}_2\text{O}}$$

$$T_f - T_{i, \text{Al}} = -14.998(T_f - T_{i, \text{H}_2\text{O}})$$

$$T_f = -14.998 \cdot T_f + 14.998 \cdot T_{i, \text{H}_2\text{O}} + T_{i, \text{Al}}$$

$$15.998 \cdot T_f = 14.998 \cdot T_{i, \text{H}_2\text{O}} + T_{i, \text{Al}}$$

$$T_f = \frac{14.998 \cdot T_{i, \text{H}_2\text{O}} + T_{i, \text{Al}}}{15.998} = \frac{14.998 \cdot 15.4 \text{ }^\circ\text{C} + 45.8 \text{ }^\circ\text{C}}{15.998}$$

$$= 17.3 \text{ }^\circ\text{C}$$

CHECK The units $^\circ\text{C}$ are correct. The final temperature of the mixture is closer to the initial temperature of the *water* than the *aluminum*. This makes sense for two reasons: (1) water has a higher specific heat capacity than aluminum, and (2) there is more water than aluminum. Because the aluminum loses the same amount of heat that is gained by the water, the greater mass and specific heat capacity of the water make the temperature change in the water *less than* the temperature change in the aluminum.

FOR PRACTICE 7.3 A block of copper of unknown mass has an initial temperature of $65.4 \text{ }^\circ\text{C}$. The copper is immersed in a beaker containing 95.7 g of water at $22.7 \text{ }^\circ\text{C}$. When the two substances reach thermal equilibrium, the final temperature is $24.2 \text{ }^\circ\text{C}$. What is the mass of the copper block?

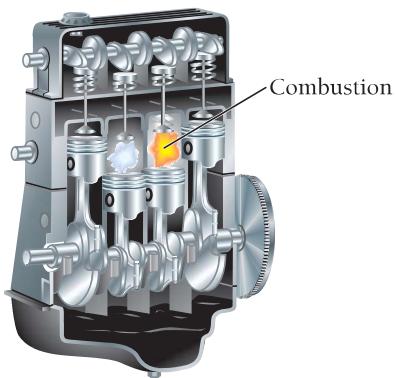
ANSWER NOW!



7.4 Cc Conceptual Connection

THERMAL ENERGY TRANSFER Substances A and B, initially at different temperatures, come in contact with each other and reach thermal equilibrium. The mass of substance A is twice the mass of substance B. The specific heat capacity of substance B is twice the specific heat capacity of substance A. Which statement is true about the final temperature of the two substances once thermal equilibrium is reached?

- (a) The final temperature is closer to the initial temperature of substance A than it is to the initial temperature of substance B.
- (b) The final temperature is closer to the initial temperature of substance B than it is to the initial temperature of substance A.
- (c) The final temperature is exactly midway between the initial temperatures of substances A and B.



▲ The combustion of gasoline within an engine's cylinders does pressure-volume work that ultimately results in the motion of the car.

Work: Pressure–Volume Work

We know that energy transfer can occur via heat (q) or work (w). In Example 7.3, we calculated the *heat* associated with an observed *temperature* change. We now turn to calculating the *work* associated with an observed *volume* change.

Although a chemical reaction can do several different types of work, for now we limit our discussion to **pressure–volume work**. We have already defined work as a force acting through a distance. Pressure–volume work occurs when a force (caused by a change in volume) acts through a distance against an external pressure. For example, pressure–volume work occurs in the cylinder of an automobile engine. The combustion of gasoline causes gases within the cylinders to expand, pushing the piston and ultimately moving the wheels of the car.

We can derive an equation for the value of pressure–volume work from the definition of work as a force (F) acting through a distance (D):

$$w = F \times D$$

[7.7]

When the volume of a cylinder increases (Figure 7.7▼), it pushes against an external force. That external force equals the product of the external pressure (P_{ext}) and area the pressure acts on (A):

$$F = P_{\text{ext}} \times A$$

If we substitute this expression for force into the definition of work given in Equation 7.7, we arrive at the expression:

$$\begin{aligned} w &= F \times D \\ &= P_{\text{ext}} \times A \times D \end{aligned}$$

The distance through which the force acts is the change in the height of the piston as it moves during the expansion (Δh). Substituting Δh for D , we get:

$$w = P_{\text{ext}} \times A \times \Delta h$$

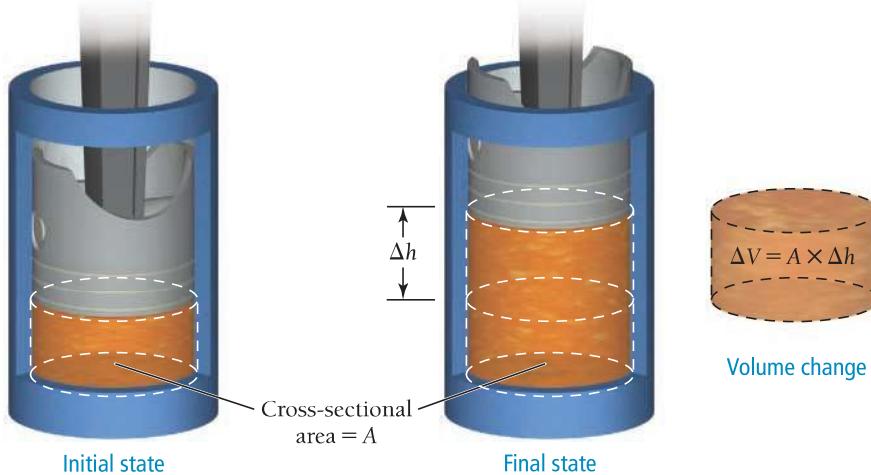
The volume of a cylinder is the area of its base times its height, so $A \times \Delta h$ is actually the change in volume (ΔV) that occurs during the expansion. Thus, the expression for work becomes the *product of the pressure times the change in volume*:

$$w = P_{\text{ext}} \Delta V$$

Still missing from the equation is the *sign* of the work done by the expanding gases. As the volume of the cylinder increases, work is done *on* the surroundings *by* the system, so w should be negative. However, upon expansion, V_2 (the final volume) is greater than V_1 (the initial volume), so ΔV is positive. In order for w to be negative for a positive expansion, we need to add a negative sign to our equation. In other words, w and ΔV must be opposite in sign:

$$w = -P_{\text{ext}} \Delta V \quad [7.8]$$

So the work caused by an expansion of volume is the negative of the pressure that the volume expands against multiplied by the change in volume that occurs during the expansion. The units of the work obtained by using this equation are those of pressure (usually atm) multiplied by those of volume (usually L). To convert between L · atm and J, we use the conversion factor $101.3 \text{ J} = 1 \text{ L} \cdot \text{atm}$.



▲ FIGURE 7.7 Piston Moving within a Cylinder against an External Pressure

PRESSURE-VOLUME WORK A cylinder within a piston expands from a volume of 1.00 L to a volume of 2.00 L against an external pressure of 1.00 atm. How much work (in J) was done by the expansion?

- (a) 1.00 J (b) -1.00 J (c) 101 J (d) -101 J

The force in this equation must be a constant force.

7.5
Cc
Conceptual Connection

ANSWER NOW!



EXAMPLE 7.4 Pressure–Volume Work

To inflate a balloon, you must do pressure–volume work on the surroundings. If you inflate a balloon from a volume of 0.100 L to 1.85 L against an external pressure of 1.00 atm, how much work is done (in joules)?

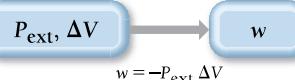
SORT You know the initial and final volumes of the balloon and the pressure against which it expands. The balloon and its contents are the system.

GIVEN: $V_1 = 0.100\text{L}$
 $V_2 = 1.85\text{L}$
 $P = 1.00\text{atm}$

FIND: w

STRATEGIZE The equation $w = -P_{\text{ext}} \Delta V$ specifies the amount of work done during a volume change against an external pressure.

CONCEPTUAL PLAN



SOLVE To solve the problem, calculate the value of ΔV and substitute it, together with P_{ext} , into the equation.

SOLUTION

$$\begin{aligned}\Delta V &= V_2 - V_1 \\ &= 1.85\text{ L} - 0.100\text{ L} \\ &= 1.75\text{ L} \\ w &= -P_{\text{ext}} \Delta V \\ &= -1.00\text{ atm} \times 1.75\text{ L} \\ &= -1.75\text{ L} \cdot \text{atm}\end{aligned}$$

Convert the units of the answer ($\text{L} \cdot \text{atm}$) to joules using $101.3\text{ J} = 1\text{ L} \cdot \text{atm}$.

$$-1.75\text{ L} \cdot \text{atm} \times \frac{101.3\text{ J}}{1\text{ L} \cdot \text{atm}} = -177\text{ J}$$

CHECK The units (J) are correct for work. The sign of the work is negative, as it should be for an expansion: work is done on the surroundings by the expanding balloon.

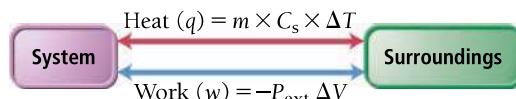
FOR PRACTICE 7.4 A cylinder equipped with a piston expands against an external pressure of 1.58 atm. If the initial volume is 0.485 L and the final volume is 1.245 L, how much work (in J) is done?

FOR MORE PRACTICE 7.4 When fuel is burned in a cylinder equipped with a piston, the volume expands from 0.255 L to 1.45 L against an external pressure of 1.02 atm. In addition, 875 J is emitted as heat. What is ΔE for the burning of the fuel?

7.5

Measuring ΔE for Chemical Reactions: Constant-Volume Calorimetry

We now have a complete picture of how a system exchanges energy with its surroundings via heat and pressure–volume work:



Recall from Section 7.3 that the change in internal energy that occurs during a chemical reaction (ΔE) is a measure of *all of the energy* (heat and work) exchanged with the surroundings ($\Delta E = q + w$). Therefore, we can measure the changes in temperature (to calculate heat) and the changes in volume (to calculate work) that occur during a chemical reaction, and then sum them together to calculate ΔE . However, an easier way to obtain the value of ΔE for a chemical reaction is to force all of the energy change associated with a reaction to manifest itself as heat rather than work. We can then measure the temperature change caused by the heat flow.

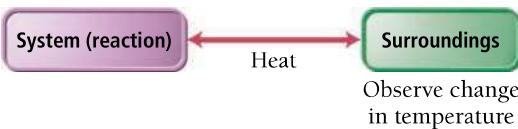
Recall that $\Delta E = q + w$ and that $w = -P_{\text{ext}} \Delta V$. If a reaction is carried out at constant volume, then $\Delta V = 0$ and $w = 0$. The heat evolved (or given off), called the *heat at constant volume* (q_v), is then equal to ΔE_{rxn} :

$$\Delta E_{\text{rxn}} = q_v + w$$

Equals zero
at constant volume

$$\Delta E_{\text{rxn}} = q_v \quad [7.9]$$

We can measure the heat evolved in a chemical reaction using *calorimetry*. In **calorimetry**, we measure the thermal energy exchanged between the reaction (defined as the system) and the surroundings by observing the change in temperature of the surroundings:



The magnitude of the temperature change in the surroundings depends on the magnitude of ΔE for the reaction and on the heat capacity of the surroundings.

Figure 7.8 shows a **bomb calorimeter**, a piece of equipment that measures ΔE for combustion reactions. In a bomb calorimeter, the reaction occurs in a sealed container called a *bomb*, which ensures that the reaction occurs at constant volume. To use a bomb calorimeter, we put the sample to be burned (of known mass) into a cup equipped with an ignition wire. We then seal the cup into the bomb, which is filled with oxygen gas, and place the bomb in a water-filled, insulated container. The container is equipped with a stirrer and a thermometer. Finally, we ignite the sample with a wire coil and monitor the temperature with the thermometer. The temperature change (ΔT) is related to the heat absorbed by the entire calorimeter assembly (q_{cal}) by the equation:

$$q_{\text{cal}} = C_{\text{cal}} \times \Delta T \quad [7.10]$$

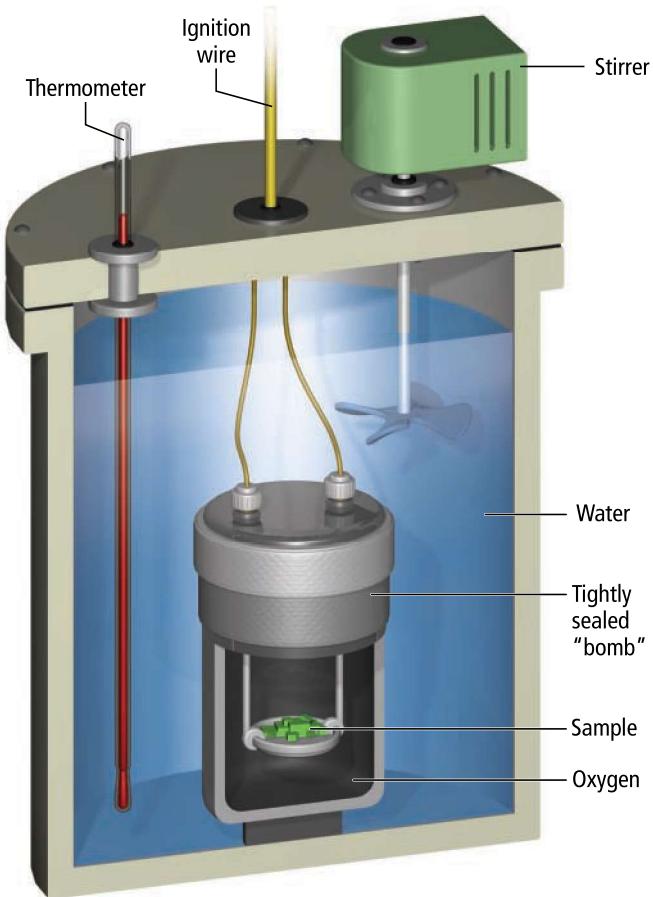
where C_{cal} is the heat capacity of the entire calorimeter assembly (which is usually determined in a separate measurement involving the burning of a substance that gives off a known amount of heat). If no heat escapes from the calorimeter, the amount of heat *gained by* the calorimeter exactly equals that *released by* the reaction (the two are equal in magnitude but opposite in sign):

$$q_{\text{cal}} = -q_{\text{rxn}} \quad [7.11]$$

Since the reaction occurs under conditions of constant volume, $q_{\text{rxn}} = q_v = \Delta E_{\text{rxn}}$. This measured quantity is the change in the internal energy of the reaction for the specific amount of reactant burned. To get ΔE_{rxn} per mole of a particular reactant—a more general quantity—we divide by the number of moles that actually reacted, as demonstrated in Example 7.5.

The Bomb Calorimeter

A bomb calorimeter measures changes in internal energy for combustion reactions.



▲ FIGURE 7.8 The Bomb Calorimeter

The heat capacity of the calorimeter, C_{cal} , has units of energy over temperature; its value accounts for all of the heat absorbed by all of the components within the calorimeter (including the water).

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 7.5

EXAMPLE 7.5 Measuring ΔE_{rxn} in a Bomb Calorimeter

When 1.010 g of sucrose ($C_{12}H_{22}O_{11}$) undergoes combustion in a bomb calorimeter, the temperature rises from 24.92°C to 28.33°C . Find ΔE_{rxn} for the combustion of sucrose in kJ/mol sucrose. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 4.90 kJ/ $^\circ\text{C}$. (You can ignore the heat capacity of the small sample of sucrose because it is negligible compared to the heat capacity of the calorimeter.)



SORT You are given the mass of sucrose, the heat capacity of the calorimeter, and the initial and final temperatures. You are asked to find the change in internal energy for the reaction.

GIVEN: 1.010 g $C_{12}H_{22}O_{11}$
 $T_i = 24.92^\circ\text{C}$
 $T_f = 28.33^\circ\text{C}$
 $C_{cal} = 4.90 \text{ kJ}/^\circ\text{C}$

FIND: ΔE_{rxn}

STRATEGIZE The conceptual plan has three parts. In the first part, use the temperature change and the heat capacity of the calorimeter to find q_{cal} .

In the second part, use q_{cal} to get q_{rxn} (which just involves changing the sign). Since the bomb calorimeter ensures constant volume, q_{rxn} is equivalent to ΔE_{rxn} for the amount of sucrose burned.

In the third part, divide q_{rxn} by the number of moles of sucrose to determine ΔE_{rxn} per mole of sucrose.

CONCEPTUAL PLAN

$$C_{cal}, \Delta T \longrightarrow q_{cal}$$

$$q_{cal} = C_{cal} \times \Delta T$$

$$q_{cal} \longrightarrow q_{rxn}$$

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

$$\Delta E_{rxn} = \frac{q_{rxn}}{\text{mol } C_{12}H_{22}O_{11}}$$

RELATIONSHIPS USED

$$q_{cal} = C_{cal} \times \Delta T = -q_{rxn}$$

molar mass $C_{12}H_{22}O_{11} = 342.3 \text{ g/mol}$

SOLVE Gather the necessary quantities in the correct units and substitute these into the equation to calculate q_{cal} .

SOLUTION

$$\Delta T = T_f - T_i$$

$$= 28.33^\circ\text{C} - 24.92^\circ\text{C} = 3.41^\circ\text{C}$$

$$q_{cal} = C_{cal} \times \Delta T$$

$$q_{cal} = 4.90 \frac{\text{kJ}}{^\circ\text{C}} \times 3.41^\circ\text{C} = 16.7 \text{ kJ}$$

$$q_{rxn} = -q_{cal} = -16.7 \text{ kJ}$$

$$\Delta E_{rxn} = \frac{q_{rxn}}{\text{mol } C_{12}H_{22}O_{11}}$$

$$= \frac{-16.7 \text{ kJ}}{1.010 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}}}$$

$$= -5.66 \times 10^3 \text{ kJ/mol } C_{12}H_{22}O_{11}$$

Find q_{rxn} by taking the negative of q_{cal} .

Find ΔE_{rxn} per mole of sucrose by dividing q_{rxn} by the number of moles of sucrose (calculated from the given mass of sucrose and its molar mass).

CHECK The units of the answer (kJ) are correct for a change in internal energy. The sign of ΔE_{rxn} is negative, as it should be for a combustion reaction that gives off energy.

FOR PRACTICE 7.5 When 1.550 g of liquid hexane (C_6H_{14}) undergoes combustion in a bomb calorimeter, the temperature rises from 25.87°C to 38.13°C . Find ΔE_{rxn} for the reaction in kJ/mol hexane. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 5.73 kJ/ $^\circ\text{C}$.

FOR MORE PRACTICE 7.5 The combustion of toluene has a ΔE_{rxn} of $-3.91 \times 10^3 \text{ kJ/mol}$. When 1.55 g of toluene (C_7H_8) undergoes combustion in a bomb calorimeter, the temperature rises from 23.12°C to 37.57°C . Find the heat capacity of the bomb calorimeter.

7.6

Enthalpy: The Heat Evolved in a Chemical Reaction at Constant Pressure

We have just seen that when a chemical reaction occurs in a sealed container under conditions of constant volume, the energy evolves only as heat. However, when a chemical reaction occurs open to the atmosphere under conditions of constant pressure—such as a reaction occurring in an open beaker or the burning of natural gas on a stove—the energy can evolve as both heat and work. As we have also seen, ΔE_{rxn} is a measure of the *total energy change* (both heat and work) that occurs during the reaction. However, in many cases, we are interested only in the heat exchanged, not the work done. For example, when we burn natural gas on a stove to cook food, we do not really care how much work the combustion reaction does on the atmosphere by expanding against it—we just want to know how much heat is given off to cook the food. Under conditions of constant pressure, a thermodynamic quantity called *enthalpy* represents exactly this.

We define the **enthalpy (H)** of a system as the sum of its internal energy and the product of its pressure and volume:

$$H = E + PV \quad [7.12]$$

Since internal energy, pressure, and volume are all state functions, enthalpy is also a state function. The *change in enthalpy* (ΔH) for any process occurring under constant pressure is given by the expression:

$$\Delta H = \Delta E + P\Delta V \quad [7.13]$$

To better understand this expression, we can interpret the two terms on the right with the help of relationships already familiar to us. We saw previously that $\Delta E = q + w$. If we represent the heat at constant pressure as q_p , then the change in internal energy at constant pressure is $\Delta E = q_p + w$. In addition, from our definition of pressure-volume work, we know that $P_{\text{ext}} \Delta V = -w$. Substituting these expressions into the expression for ΔH gives us the following expression:

$$\begin{aligned} \Delta H &= \Delta E + P\Delta V \\ &= (q_p + w) + P\Delta V \\ &= q_p + w - w \\ \Delta H &= q_p \end{aligned} \quad [7.14]$$

We can see that ΔH is equal to q_p , the heat at constant pressure.

Conceptually (and often numerically), ΔH and ΔE are similar: they both represent changes in a state function for the system. However, ΔE is a measure of *all of the energy* (heat and work) exchanged with the surroundings, while ΔH is a measure of only the heat exchanged under conditions of constant pressure. For chemical reactions that do not exchange much work with the surroundings—that is, those that do not cause a large change in reaction volume as they occur— ΔH and ΔE are nearly identical in value. For chemical reactions that produce or consume large amounts of gas, and therefore result in large volume changes, ΔH and ΔE may differ slightly in value.

THE DIFFERENCE BETWEEN ΔH AND ΔE Lighters are usually fueled by butane (C_4H_{10}). When 1 mol of butane burns at constant pressure, it produces 2658 kJ of heat and does 3 kJ of work. What are the values of ΔH and ΔE for the combustion of one mole of butane?

- (a) $\Delta H = -2658 \text{ kJ}$; $\Delta E = -2655 \text{ kJ}$
- (b) $\Delta H = -2658 \text{ kJ}$; $\Delta E = -3 \text{ kJ}$
- (c) $\Delta H = -2658 \text{ kJ}$; $\Delta E = -2661 \text{ kJ}$
- (d) $\Delta H = 2658 \text{ kJ}$; $\Delta E = 2661 \text{ kJ}$

WATCH NOW!

KEY CONCEPT VIDEO 7.6



The Change in Enthalpy for a Chemical Reaction

7.6

Cc

Conceptual Connection

ANSWER NOW!



The signs of ΔH and ΔE follow the same conventions. A positive ΔH indicates that heat flows into the system as the reaction occurs. A chemical reaction with a positive ΔH , called an **endothermic reaction**, absorbs heat from its surroundings.

► The reaction that occurs in a chemical cold pack is endothermic—it absorbs energy from the surroundings. The combustion of natural gas is an exothermic reaction—it releases energy to the surroundings.



The reaction that occurs in a chemical cold pack, often used to ice athletic injuries, is a good example of an endothermic reaction. When you break the barrier separating the reactants in a chemical cold pack, the substances mix, react, and absorb heat from the surroundings. The surroundings—including, say, your bruised wrist—get *colder* because they *lose* energy as the cold pack absorbs it.

A chemical reaction with a negative ΔH , called an **exothermic reaction**, gives off heat to its surroundings. The reaction that occurs in the chemical hand warmer discussed in Section 7.1 is a good example of an exothermic reaction. When the reaction takes place, heat is given off into the surroundings (including your hand and glove), making them warmer. The burning of natural gas is another exothermic reaction. As the gas burns, it gives off energy, raising the temperature of its surroundings.

Summarizing Enthalpy:

- The value of ΔH for a chemical reaction is the amount of heat absorbed or evolved in the reaction under conditions of constant pressure.
- An endothermic reaction has a *positive* ΔH and absorbs heat from the surroundings. An endothermic reaction feels cold to the touch.
- An exothermic reaction has a *negative* ΔH and gives off heat to the surroundings. An exothermic reaction feels warm to the touch.

EXAMPLE 7.6 Exothermic and Endothermic Processes

Identify each process as endothermic or exothermic and indicate the sign of ΔH .

- sweat evaporating from skin
- water freezing in a freezer
- wood burning in a fire

SOLUTION

- Sweat evaporating from skin cools the skin and is therefore endothermic, with a positive ΔH . The skin must supply heat to the perspiration in order for it to continue to evaporate.
- Water freezing in a freezer releases heat and is therefore exothermic, with a negative ΔH . The refrigeration system in the freezer must remove this heat for the water to continue to freeze.
- Wood burning in a fire releases heat and is therefore exothermic, with a negative ΔH .

FOR PRACTICE 7.6 Identify each process as endothermic or exothermic and indicate the sign of ΔH .

- an ice cube melting
- nail polish remover quickly evaporating after it is accidentally spilled on the skin
- gasoline burning within the cylinder of an automobile engine

Exothermic and Endothermic Processes: A Molecular View

When a chemical system undergoes a change in enthalpy, where does the energy come from or go to? For example, we just saw that an exothermic chemical reaction gives off *thermal energy*—what is the source of that energy?

First, we know that the emitted thermal energy *does not* come from the original thermal energy of the system. Recall from Section 7.2 that the thermal energy of a system is the total kinetic energy of the atoms and molecules that compose the system. This kinetic energy *cannot* be the source of the energy given off in an exothermic reaction because if the atoms and molecules that compose the system were to lose kinetic energy, their temperature would necessarily fall—the system would get colder. Yet we know that in exothermic reactions, the temperature of the system and the surroundings rises. So there must be some other source of energy.

Recall also from Section 7.2 that the internal energy of a chemical system is the sum of its kinetic energy and its *potential energy*. This potential energy is the source in an exothermic chemical reaction. Under normal circumstances, chemical potential energy (or simply chemical energy) arises primarily from the electrostatic forces between the protons and electrons that compose the atoms and molecules within the system. In an exothermic reaction, some bonds break and new ones form, and the nuclei and electrons reorganize into an arrangement with lower potential energy. As the atoms rearrange, their potential energy converts into thermal energy, the heat emitted in the reaction. Note that breaking bonds always *absorbs* energy. In an exothermic reaction, weak bonds break and stronger bonds form. It only takes a small amount of energy to break the weak bonds, and a greater amount is given off when the stronger bonds form, resulting in net energy production. In an endothermic reaction, the opposite happens: strong bonds break and weak ones form. The nuclei and electrons reorganize into an arrangement with higher potential energy, absorbing thermal energy in the process.

EXOTHERMIC AND ENDOTHERMIC REACTIONS An endothermic reaction occurs in a flask. What happens to the temperature of the flask?

- (a) The temperature rises.
- (b) The temperature falls.
- (c) The temperature remains unchanged.

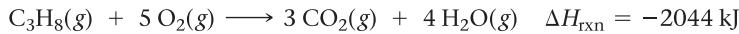


ANSWER NOW!



Stoichiometry Involving ΔH : Thermochemical Equations

The enthalpy change for a chemical reaction, abbreviated ΔH_{rxn} , is also called the **enthalpy of reaction** or **heat of reaction** and depends on the amount of material undergoing the reaction. In other words, the amount of heat generated or absorbed when a chemical reaction occurs depends on the *amounts* of reactants that actually react. We usually specify ΔH_{rxn} in combination with the balanced chemical equation for the reaction. *The magnitude of ΔH_{rxn} reflects the stoichiometric amounts of reactants and products for the reaction as written.* For example, consider the balanced equation and ΔH_{rxn} for the combustion of propane, the main component of LP gas:

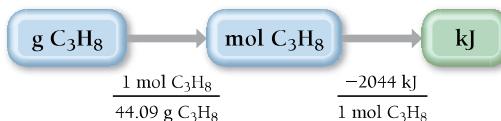


The equation tells us that when 1 mol of C_3H_8 reacts with 5 mol of O_2 to form 3 mol of CO_2 and 4 mol of H_2O , 2044 kJ of heat is emitted. We can write these relationships in the same way that we expressed stoichiometric relationships in Chapter 4, as ratios between two quantities. For example, for the reactants, we write the following ratios:

$$1 \text{ mol C}_3\text{H}_8 : -2044 \text{ kJ} \quad \text{or} \quad 5 \text{ mol O}_2 : -2044 \text{ kJ}$$

The ratios indicate that 2044 kJ of heat evolve when 1 mol of C_3H_8 and 5 mol of O_2 completely react. We can use these ratios to construct conversion factors between amounts of reactants or products and the quantity of heat emitted (for exothermic reactions) or

absorbed (for endothermic reactions). To find out how much heat is emitted upon the combustion of a certain mass in grams of C₃H₈, we work with the following conceptual plan:



We use the molar mass to convert between grams and moles, and the stoichiometric relationship between moles of C₃H₈ and the heat of reaction to convert between moles and kilojoules, as demonstrated in Example 7.7.

ANSWER NOW!

7.8

Cc

Conceptual Connection



THERMOCHEMICAL EQUATIONS

Consider the following thermochemical equation:



What is the heat associated with the reaction of 6 moles of A?

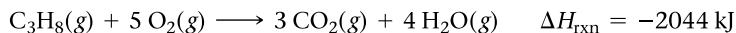
- (a) -51.0 J (b) -306 J (c) -153 J (d) 153 J

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 7.7

EXAMPLE 7.7 Stoichiometry Involving ΔH

An LP gas tank in a home barbecue contains 13.2 kg of propane, C₃H₈. Calculate the heat (in kJ) associated with the complete combustion of all of the propane in the tank.



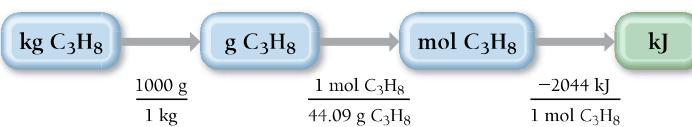
SORT You are given the mass of propane and asked to find the heat evolved in its combustion.

GIVEN: 13.2 kg C₃H₈

FIND: q

STRATEGIZE Starting with kg C₃H₈, convert to g C₃H₈ and then use the molar mass of C₃H₈ to find the number of moles. Next, use the stoichiometric relationship between mol C₃H₈ and kJ to determine the heat evolved.

CONCEPTUAL PLAN



RELATIONSHIPS USED

$$1000 \text{ g} = 1 \text{ kg}$$

$$\text{molar mass C}_3\text{H}_8 = 44.09 \text{ g/mol}$$

$$1 \text{ mol C}_3\text{H}_8 : -2044 \text{ kJ} \text{ (from balanced equation)}$$

SOLVE Follow the conceptual plan to solve the problem. Begin with 13.2 kg C₃H₈ and multiply by the appropriate conversion factors to arrive at kJ.

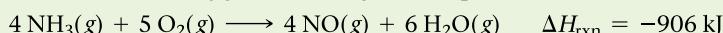
SOLUTION

$$13.2 \text{ kg C}_3\text{H}_8 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{-2044 \text{ kJ}}{1 \text{ mol C}_3\text{H}_8}$$

$$= -6.12 \times 10^5 \text{ kJ}$$

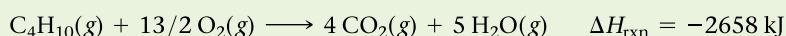
CHECK The units of the answer (kJ) are correct for energy. The answer is negative, as it should be for heat evolved by the reaction.

FOR PRACTICE 7.7 Ammonia reacts with oxygen according to the equation:



Calculate the heat (in kJ) associated with the complete reaction of 155 g of NH₃.

FOR MORE PRACTICE 7.7 What mass of butane in grams is necessary to produce 1.5×10^3 kJ of heat? What mass of CO₂ is produced?



7.7

Constant-Pressure Calorimetry: Measuring ΔH_{rxn}

For many aqueous reactions, we can measure ΔH_{rxn} fairly simply using the **coffee-cup calorimeter** shown in Figure 7.9►. The calorimeter consists of two Styrofoam coffee cups, one inserted into the other, to provide insulation from the laboratory environment. The calorimeter is equipped with a thermometer and a stirrer. The reaction occurs in a specifically measured quantity of solution within the calorimeter, so that the mass of the solution is known. During the reaction, the heat evolved (or absorbed) causes a temperature change in the solution, which the thermometer measures. If we know the specific heat capacity of the solution, normally assumed to be that of water, we can calculate q_{soln} , the heat absorbed by or lost from the solution (which is acting as the surroundings) using the equation:

$$q_{soln} = m_{soln} \times C_{s, soln} \times \Delta T$$

The insulated calorimeter prevents heat from escaping, so we assume that the heat gained by the solution equals that lost by the reaction (or vice versa):

$$q_{rxn} = -q_{soln}$$

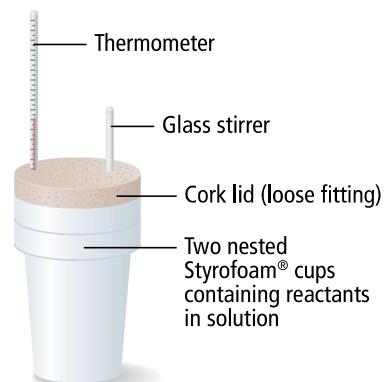
Because the reaction happens under conditions of constant pressure (open to the atmosphere), $q_{rxn} = q_p = \Delta H_{rxn}$. This measured quantity is the heat of reaction for the specific amount (which is measured ahead of time) of reactants that react. To find ΔH_{rxn} per mole of a particular reactant—a more general quantity—we divide by the number of moles that actually reacted, as demonstrated in Example 7.8.

Summarizing Calorimetry:

- Bomb calorimetry occurs at constant *volume* and measures ΔE for a reaction.
- Coffee-cup calorimetry occurs at constant *pressure* and measures ΔH for a reaction.

The Coffee-Cup Calorimeter

A coffee cup calorimeter measures enthalpy changes for chemical reactions in solution.



▲ FIGURE 7.9 The Coffee-Cup Calorimeter

The equation $q_{rxn} = -q_{soln}$ assumes that no heat is lost to the calorimeter itself. If heat absorbed by the calorimeter is accounted for, the equation becomes $q_{rxn} = -(q_{soln} + q_{cal})$.

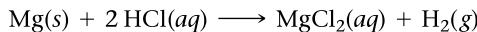
WATCH NOW!

INTERACTIVE WORKED EXAMPLE 7.8



EXAMPLE 7.8 Measuring ΔH_{rxn} in a Coffee-Cup Calorimeter

Magnesium metal reacts with hydrochloric acid according to the balanced equation:



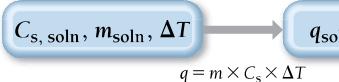
In an experiment to determine the enthalpy change for this reaction, 0.158 g of Mg metal is combined with enough HCl to make 100.0 mL of solution in a coffee-cup calorimeter. The HCl is sufficiently concentrated so that the Mg completely reacts. The temperature of the solution rises from 25.6 °C to 32.8 °C as a result of the reaction. Find ΔH_{rxn} for the reaction as written. Use 1.00 g/mL as the density of the solution and $C_{s, soln} = 4.18 \text{ J/g} \cdot \text{°C}$ as the specific heat capacity of the solution.

SORT You are given the mass of magnesium, the volume of solution, the initial and final temperatures, the density of the solution, and the heat capacity of the solution. You are asked to find the change in enthalpy for the reaction.

GIVEN: 0.158 g Mg
100.0 mL soln
 $T_i = 25.6 \text{ }^\circ\text{C}$
 $d = 1.00 \text{ g/mL}$
 $T_f = 32.8 \text{ }^\circ\text{C}$
 $C_{s, soln} = 4.18 \text{ J/g} \cdot \text{°C}$

FIND: ΔH_{rxn}

CONCEPTUAL PLAN



STRATEGIZE The conceptual plan has three parts. In the first part, use the temperature change and the other given quantities, together with the equation $q = m \times C_s \times \Delta T$, to find q_{soln} .

In the second part, use q_{soln} to get q_{rxn} (which simply involves changing the sign). Because the pressure is constant, q_{rxn} is equivalent to ΔH_{rxn} for the amount of magnesium that reacts.

In the third part, divide q_{rxn} by the number of moles of magnesium to determine ΔH_{rxn} per mole of magnesium.

$$\Delta H_{rxn} = \frac{q_{rxn}}{\text{mol Mg}}$$

RELATIONSHIPS USED
 $q = m \times C_s \times \Delta T$
 $q_{rxn} = -q_{soln}$

—Continued on the next page

Continued—

SOLVE Gather the necessary quantities in the correct units for the equation $q = m \times C_s \times \Delta T$ and substitute these into the equation to calculate q_{soln} . Notice that the sign of q_{soln} is positive, indicating that the solution absorbed heat from the reaction.

Find q_{rxn} by taking the negative of q_{soln} . Notice that q_{rxn} is negative, as you expect for an exothermic reaction.

Finally, find ΔH_{rxn} per mole of magnesium by dividing q_{rxn} by the number of moles of magnesium that reacts. Find the number of moles of magnesium from the given mass of magnesium and its molar mass.

Since the stoichiometric coefficient for magnesium in the balanced chemical equation is 1, the calculated value represents ΔH_{rxn} for the reaction as written.

CHECK The units of the answer (J) are correct for the change in enthalpy of a reaction. The sign is negative, as you expect for an exothermic reaction.

FOR PRACTICE 7.8 The addition of hydrochloric acid to a silver nitrate solution precipitates silver chloride according to the reaction:



When 50.0 mL of 0.100 M AgNO_3 is combined with 50.0 mL of 0.100 M HCl in a coffee-cup calorimeter, the temperature changes from 23.40 °C to 24.21 °C. Calculate ΔH_{rxn} for the reaction as written. Use 1.00 g/mL as the density of the solution and $C = 4.18 \text{ J/g} \cdot ^\circ\text{C}$ as the specific heat capacity.

ANSWER NOW!



7.9 Cc Conceptual Connection

CONSTANT-PRESSURE VERSUS CONSTANT-VOLUME CALORIMETRY

The same reaction, with exactly the same amount of reactant, is conducted in a bomb calorimeter and in a coffee-cup calorimeter. In one of the calorimeters, $q_{\text{rxn}} = -12.5 \text{ kJ}$ and in the other $q_{\text{rxn}} = -11.8 \text{ kJ}$. Which value was obtained in the bomb calorimeter? (Assume that the reaction has a positive ΔV in the coffee-cup calorimeter.)

(a) $q_{\text{rxn}} = -12.5 \text{ kJ}$

(b) $q_{\text{rxn}} = -11.8 \text{ kJ}$

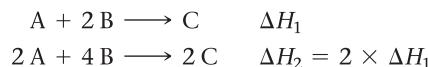
7.8

Relationships Involving ΔH_{rxn}

The change in enthalpy for a reaction is always associated with a *particular* reaction. If we change the reaction in well-defined ways, then ΔH_{rxn} also changes in well-defined ways. We now turn our attention to three quantitative relationships between a chemical equation and ΔH_{rxn} .

1. If a chemical equation is multiplied by some factor, then ΔH_{rxn} is also multiplied by the same factor.

Recall from Section 7.6 that ΔH_{rxn} is an extensive property; it depends on the quantity of reactants undergoing reaction. Recall also that ΔH_{rxn} is usually reported for a reaction involving stoichiometric amounts of reactants. For example, for a reaction $A + 2B \longrightarrow C$, ΔH_{rxn} is typically reported as the amount of heat emitted or absorbed when 1 mol A reacts with 2 mol B to form 1 mol C. Therefore, if a chemical equation is multiplied by a factor, then ΔH_{rxn} is also multiplied by the same factor. For example,

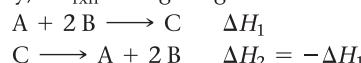


2. If a chemical equation is reversed, then ΔH_{rxn} changes sign.

Recall from Section 7.6 that ΔH_{rxn} is a state function, which means that its value depends only on the initial and final states of the system.

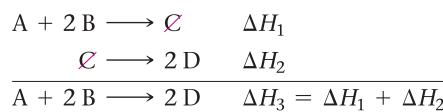
$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

When a reaction is reversed, the final state becomes the initial state and vice versa. Consequently, ΔH_{rxn} changes sign:



3. If a chemical equation can be expressed as the sum of a series of steps, then ΔH_{rxn} for the overall equation is the sum of the heats of reaction for each step.

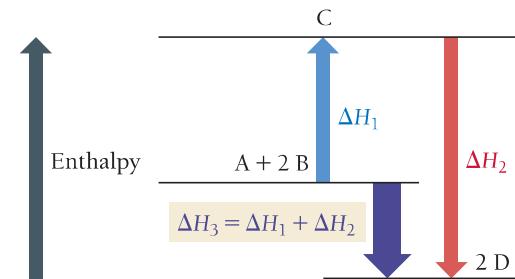
This last relationship, known as **Hess's law**, also follows from the enthalpy of reaction being a state function. Since ΔH_{rxn} is dependent only on the initial and final states, and not on the pathway the reaction follows, ΔH obtained from summing the individual steps that lead to an overall reaction must be the same as ΔH for that overall reaction. For example,



We illustrate Hess's law with the energy-level diagram in Figure 7.10.

Hess's Law

The change in enthalpy for a stepwise process is the sum of the enthalpy changes of the steps.



▲ FIGURE 7.10 Hess's Law

RELATIONSHIPS INVOLVING ΔH_{rxn}

Consider the following chemical equation:



What is ΔH_{rxn} for the reaction $2C \longrightarrow 4A + 2B$?

- (a) 122 J (b) -122 J (c) 244 J (d) -244 J

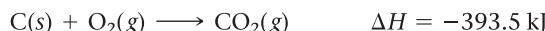
ANSWER NOW!



These three quantitative relationships make it possible to determine ΔH for a reaction without directly measuring it in the laboratory. (For some reactions, direct measurement can be difficult.) If we can find related reactions (with known ΔH 's) that sum to the reaction of interest, we can find ΔH for the reaction of interest. For example, the following reaction between C(s) and H₂O(g) is an industrially important method of generating hydrogen gas:



We can find ΔH_{rxn} from the following reactions that have known ΔH 's:



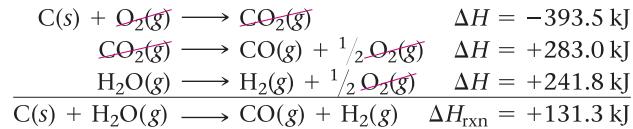
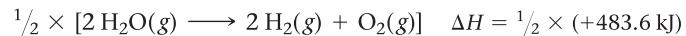
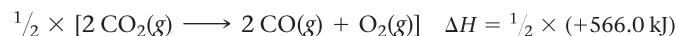
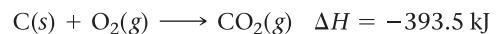
To get the overall reaction of interest, we just have to determine how to sum these reactions. We do this by manipulating the reactions with known ΔH 's in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

Since the first reaction has $C(s)$ as a reactant, and the reaction of interest also has $C(s)$ as a reactant, we write the first reaction unchanged.

The second reaction has 2 mol of $\text{CO}(g)$ as a reactant. However, the reaction of interest has 1 mol of $\text{CO}(g)$ as a product. Therefore, we reverse the second reaction, change the sign of ΔH , and multiply the reaction and ΔH by $\frac{1}{2}$.

In the third reaction $\text{H}_2(g)$ is a reactant. In the reaction of interest, however, $\text{H}_2(g)$ is a product. Therefore, we reverse the equation and change the sign of ΔH . In addition, to obtain coefficients that match the reaction of interest, and to cancel O_2 , we must multiply the reaction and ΔH , by $\frac{1}{2}$.

Lastly, we rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest. ΔH for the reaction of interest is the sum of the ΔH 's for the steps.

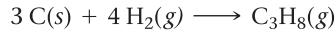


WATCH NOW!

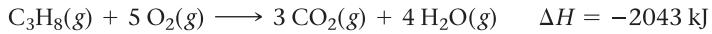
INTERACTIVE WORKED EXAMPLE 7.9

EXAMPLE 7.9 Hess's Law

Find ΔH_{rxn} for the reaction:



Use these reactions with known ΔH 's:

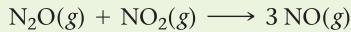


SOLUTION

To work this and other Hess's law problems, manipulate the reactions with known ΔH 's in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

| | |
|--|---|
| The first reaction has C_3H_8 as a reactant, and the reaction of interest has C_3H_8 as a product, so reverse the first reaction and change the sign of ΔH . | $3\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \longrightarrow \text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \quad \Delta H = +2043 \text{ kJ}$ |
| The second reaction has C as a reactant and CO_2 as a product, just as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. You need to multiply this equation and its ΔH by 3. | $3 \times [\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)] \quad \Delta H = 3 \times (-393.5 \text{ kJ})$ |
| The third reaction has $\text{H}_2(g)$ as a reactant, as required. However, the coefficient for H_2 is 2, and in the reaction of interest, the coefficient for H_2 is 4. Multiply this reaction and its ΔH by 2. | $2 \times [2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(g)] \quad \Delta H = 2 \times (-483.6 \text{ kJ})$ |
| Rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest. ΔH for the reaction of interest is the sum of the ΔH 's for the steps. | $\begin{array}{rcl} \cancel{3\text{CO}_2(g)} + \cancel{4\text{H}_2\text{O}(g)} \longrightarrow \text{C}_3\text{H}_8(g) + \cancel{5\text{O}_2(g)} & & \Delta H = +2043 \text{ kJ} \\ 3\text{C}(s) + \cancel{3\text{O}_2(g)} \longrightarrow \cancel{3\text{CO}_2(g)} & & \Delta H = -1181 \text{ kJ} \\ 4\text{H}_2(g) + \cancel{2\text{O}_2(g)} \longrightarrow \cancel{4\text{H}_2\text{O}(g)} & & \Delta H = -967.2 \text{ kJ} \\ \hline 3\text{C}(s) + 4\text{H}_2(g) \longrightarrow \text{C}_3\text{H}_8(g) & & \Delta H_{\text{rxn}} = -105 \text{ kJ} \end{array}$ |

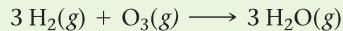
FOR PRACTICE 7.9 Find ΔH_{rxn} for the reaction:



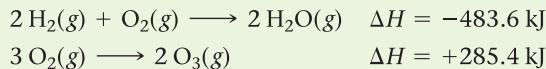
Use these reactions with known ΔH 's:



FOR MORE PRACTICE 7.9 Find ΔH_{rxn} for the reaction:



Use these reactions with known ΔH 's:



7.9

Determining Enthalpies of Reaction from Standard Enthalpies of Formation

We have examined two ways to determine ΔH for a chemical reaction: experimentally through calorimetry and inferentially through Hess's law. We now turn to a third and more convenient way to determine ΔH for a large number of chemical reactions: from tabulated *standard enthalpies of formation*.

WATCH NOW!

KEY CONCEPT VIDEO 7.9

 Determining the Enthalpy of Reaction from Standard Enthalpies of Formation

Standard States and Standard Enthalpy Changes

Recall that ΔH is the *change* in enthalpy for a chemical reaction—the difference in enthalpy between the products and the reactants. Because we are interested in changes in enthalpy (and not in absolute values of enthalpy itself), we are free to define the *zero* of enthalpy as conveniently as possible. Returning to our mountain-climbing analogy, a change in altitude (like a change in enthalpy) is an absolute quantity. Altitude itself (like enthalpy), however, is a relative quantity, defined relative to some standard (such as sea level in the case of altitude). We define a similar, albeit slightly more complex, standard for enthalpy. This standard has three parts: the **standard state**, the **standard enthalpy change (ΔH°)**, and the **standard enthalpy of formation (ΔH_f°)**.

1. Standard State

- *For a Gas:* The standard state for a gas is the pure gas at a pressure of exactly 1 atm.
- *For a Liquid or Solid:* The standard state for a liquid or solid is the pure substance in its most stable form at a pressure of 1 atm and at the temperature of interest (often taken to be 25 °C).
- *For a Substance in Solution:* The standard state for a substance in solution is a concentration of exactly 1 M.

The standard state was changed in 1997 to a pressure of 1 bar, which is very close to 1 atm (1 atm = 1.013 bar). Both standards are now in common use.

2. Standard Enthalpy Change (ΔH°)

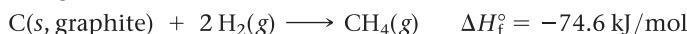
- The change in enthalpy for a process when all reactants and products are in their standard states. The degree sign indicates standard states.

3. Standard Enthalpy of Formation (ΔH_f°)

- *For a Pure Compound:* The change in enthalpy when 1 mol of the compound forms from its constituent elements in their standard states.
- *For a Pure Element in Its Standard State:* $\Delta H_f^\circ = 0$.

The standard enthalpy of formation is also called the **standard heat of formation**.

Assigning the value of zero to the standard enthalpy of formation for an element in its standard state is the equivalent of assigning an altitude of zero to sea level. Once we assume sea level is zero, we can then measure all subsequent changes in altitude relative to sea level. Similarly, we can measure all changes in enthalpy relative to those of pure elements in their standard states. For example, consider the standard enthalpy of formation of methane gas at 25 °C:



For methane, as with most compounds, ΔH_f° is negative. Continuing our analogy, if we think of pure elements in their standard states as being at *sea level*, then most compounds lie *below sea level*. The chemical equation for the enthalpy of formation of a compound is always written to form 1 mol of the compound, so ΔH_f° has the units of kJ/mol. Table 7.5 lists ΔH_f° values for some selected compounds. A more complete list is presented in Appendix IIB.

The carbon in this equation must be graphite (the most stable form of carbon at 1 atm and 25 °C).

TABLE 7.5 ■ Standard Enthalpies (or Heats) of Formation, ΔH_f° , at 298 K

| Formula | ΔH_f° (kJ/mol) | Formula | ΔH_f° (kJ/mol) | Formula | ΔH_f° (kJ/mol) |
|------------------------|-----------------------------|-----------------------------------|-----------------------------|-----------------------|-----------------------------|
| Bromine | | $C_3H_8O(l$, isopropanol) | -318.1 | Oxygen | |
| $Br(g)$ | 111.9 | $C_6H_6(l)$ | 49.1 | $O_2(g)$ | 0 |
| $Br_2(l)$ | 0 | $C_6H_{12}O_6(s$, glucose) | -1273.3 | $O_3(g)$ | 142.7 |
| $HBr(g)$ | -36.3 | $C_{12}H_{22}O_{11}(s$, sucrose) | -2226.1 | $H_2O(g)$ | -241.8 |
| Calcium | | Chlorine | | $H_2O(l)$ | -285.8 |
| $Ca(s)$ | 0 | $Cl(g)$ | 121.3 | Silver | |
| $CaO(s)$ | -634.9 | $Cl_2(g)$ | 0 | $Ag(s)$ | 0 |
| $CaCO_3(s)$ | -1207.6 | $HCl(g)$ | -92.3 | $AgCl(s)$ | -127.0 |
| Carbon | | Fluorine | | Sodium | |
| $C(s$, graphite) | 0 | $F(g)$ | 79.38 | $Na(s)$ | 0 |
| $C(s$, diamond) | 1.88 | $F_2(g)$ | 0 | $Na(g)$ | 107.5 |
| $CO(g)$ | -110.5 | $HF(g)$ | -273.3 | $NaCl(s)$ | -411.2 |
| $CO_2(g)$ | -393.5 | Hydrogen | | $Na_2CO_3(s)$ | -1130.7 |
| $CH_4(g)$ | -74.6 | $H(g)$ | 218.0 | $NaHCO_3(s)$ | -950.8 |
| $CH_3OH(l)$ | -238.6 | $H_2(g)$ | 0 | Sulfur | |
| $C_2H_2(g)$ | 227.4 | Nitrogen | | $S_8(s$, rhombic) | 0 |
| $C_2H_4(g)$ | 52.4 | $N_2(g)$ | 0 | $S_8(s$, monoclinic) | 0.3 |
| $C_2H_6(g)$ | -84.68 | $NH_3(g)$ | -45.9 | $SO_2(g)$ | -296.8 |
| $C_2H_5OH(l)$ | -277.6 | $NH_4NO_3(s)$ | -365.6 | $SO_3(g)$ | -395.7 |
| $C_3H_8(g)$ | -103.85 | $NO(g)$ | 91.3 | $H_2SO_4(l)$ | -814.0 |
| $C_3H_6O(l$, acetone) | -248.4 | $N_2O(g)$ | 81.6 | | |

EXAMPLE 7.10 Standard Enthalpies of Formation

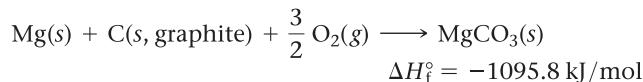
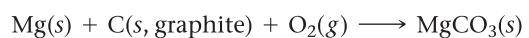
Write equations for the formation of (a) $MgCO_3(s)$ and (b) $C_6H_{12}O_6(s)$ from their respective elements in their standard states. Include the value of ΔH_f° for each equation.

SOLUTION

(a) $MgCO_3(s)$

Write the equation with the elements in $MgCO_3$ in their standard states as the reactants and 1 mol of $MgCO_3$ as the product.

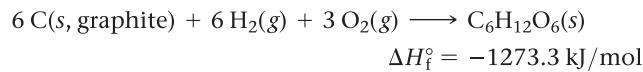
Balance the equation and look up ΔH_f° in Appendix II B. (Use fractional coefficients so that the product of the reaction is 1 mol of $MgCO_3$.)



(b) $C_6H_{12}O_6(s)$

Write the equation with the elements in $C_6H_{12}O_6$ in their standard states as the reactants and 1 mol of $C_6H_{12}O_6$ as the product.

Balance the equation and look up ΔH_f° in Appendix II B.



FOR PRACTICE 7.10 Write equations for the formation of (a) $NaCl(s)$ and (b) $Pb(NO_3)_2(s)$ from their respective elements in their standard states. Include the value of ΔH_f° for each equation.

Calculating the Standard Enthalpy Change for a Reaction

We have just seen that the standard enthalpy of formation corresponds to the *formation* of a compound from its constituent elements in their standard states:



Therefore, the *negative* of the standard enthalpy of formation corresponds to the *decomposition* of a compound into its constituent elements in their standard states:

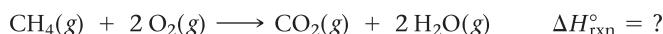


We can use these two concepts—the decomposition of a compound into its elements and the formation of a compound from its elements—to calculate the enthalpy change of any reaction by mentally taking the reactants through two steps. In the first step, we *decompose the reactants* into their constituent elements in their standard states; in the second step, we *form the products* from the constituent elements in their standard states:

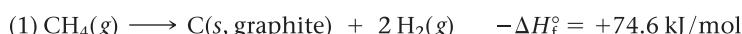
$$\begin{array}{lcl} \text{reactants} \longrightarrow \text{elements} & \Delta H_1 = -\sum \Delta H_f^\circ (\text{reactants}) \\ \text{elements} \longrightarrow \text{products} & \Delta H_2 = +\sum \Delta H_f^\circ (\text{products}) \\ \hline \text{reactants} \longrightarrow \text{products} & \Delta H_{\text{rxn}}^\circ = \Delta H_1 + \Delta H_2 \end{array}$$

In these equations, Σ means sum so that ΔH_1 is the sum of the negatives of the heats of formation of the reactants and ΔH_2 is the sum of the heats of formation of the products.

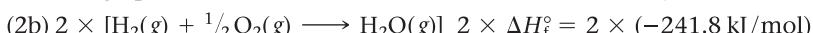
We can demonstrate this procedure by calculating the standard enthalpy change ($\Delta H_{\text{rxn}}^\circ$) for the combustion of methane:



The energy changes associated with the decomposition of the reactants and the formation of the products are shown in Figure 7.11▼. The first step (1) is the decomposition of 1 mol of methane into its constituent elements in their standard states. We can obtain the change in enthalpy for this step by reversing the enthalpy of formation equation for methane and changing the sign of ΔH_f° :



The second step, the formation of the products from their constituent elements, has two parts: (a) the formation of 1 mol CO_2 and (b) the formation of 2 mol H_2O . Because part b forms 2 mol H_2O , we multiply the ΔH_f° for that step by 2:



Calculating the Enthalpy Change for the Combustion of Methane

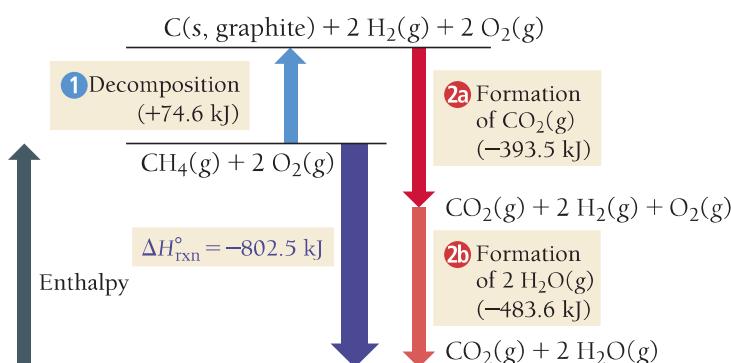
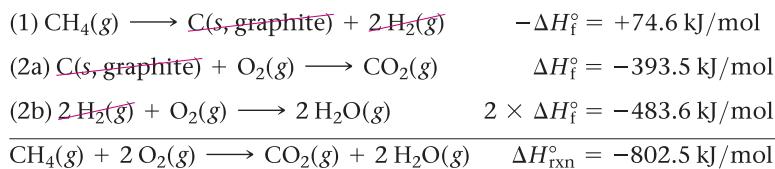


FIGURE 7.11 Enthalpy Change for the Combustion of Methane

As we know from Hess's law, the enthalpy of reaction for the overall reaction is the sum of the enthalpies of reaction of the individual steps:



We can streamline and generalize this process as follows:

To calculate ΔH_{rxn}° , subtract the enthalpies of formation of the reactants multiplied by their stoichiometric coefficients from the enthalpies of formation of the products multiplied by their stoichiometric coefficients.

In the form of an equation:

$$\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants}) \quad [7.15]$$

In this equation, n_p represents the stoichiometric coefficients of the products, n_r represents the stoichiometric coefficients of the reactants, and ΔH_f° represents the standard enthalpies of formation. Keep in mind when using this equation that elements in their standard states have $\Delta H_f^\circ = 0$. Examples 7.11 and 7.12 demonstrate this process.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 7.11

EXAMPLE 7.11 ΔH_{rxn}° and Standard Enthalpies of Formation

Use the standard enthalpies of formation to determine ΔH_{rxn}° for the reaction:



SORT You are given the balanced equation and asked to find the enthalpy of reaction.

GIVEN: $4\text{NH}_3(g) + 5\text{O}_2(g) \longrightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$

FIND: ΔH_{rxn}°

STRATEGIZE To calculate ΔH_{rxn}° from standard enthalpies of formation, subtract the heats of formation of the reactants multiplied by their stoichiometric coefficients from the heats of formation of the products multiplied by their stoichiometric coefficients.

CONCEPTUAL PLAN

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

SOLVE Begin by looking up (in Appendix IIB) the standard enthalpy of formation for each reactant and product. Remember that the standard enthalpy of formation of pure elements in their standard state is zero. Calculate ΔH_{rxn}° by substituting into the equation.

SOLUTION

| Reactant or product | ΔH_f° (kJ/mol, from Appendix IIB) |
|-------------------------|--|
| $\text{NH}_3(g)$ | -45.9 |
| $\text{O}_2(g)$ | 0.0 |
| $\text{NO}(g)$ | +91.3 |
| $\text{H}_2\text{O}(g)$ | -241.8 |

$$\begin{aligned}
 \Delta H_{rxn}^\circ &= \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants}) \\
 &= [4(\Delta H_f^\circ, \text{NO}(g)) + 6(\Delta H_f^\circ, \text{H}_2\text{O}(g))] - [4(\Delta H_f^\circ, \text{NH}_3(g)) + 5(\Delta H_f^\circ, \text{O}_2(g))] \\
 &= [4(+91.3 \text{ kJ}) + 6(-241.8 \text{ kJ})] - [4(-45.9 \text{ kJ}) + 5(0.0 \text{ kJ})] \\
 &= -1085.6 \text{ kJ} - (-183.6 \text{ kJ}) \\
 &= -902.0 \text{ kJ}
 \end{aligned}$$

CHECK The units of the answer (kJ) are correct. The answer is negative, which means that the reaction is exothermic.

FOR PRACTICE 7.11 The thermite reaction, in which powdered aluminum reacts with iron oxide, is highly exothermic.



Use standard enthalpies of formation to determine $\Delta H_{\text{rxn}}^{\circ}$ for the thermite reaction.



► The reaction of powdered aluminum with iron oxide, known as the thermite reaction, releases a large amount of heat.

EXAMPLE 7.12 $\Delta H_{\text{rxn}}^{\circ}$ and Standard Enthalpies of Formation

A city of 100,000 people uses approximately 1.0×10^{11} kJ of energy per day. Suppose all of that energy comes from the combustion of liquid octane (C_8H_{18}) to form gaseous water and gaseous carbon dioxide. Use standard enthalpies of formation to calculate $\Delta H_{\text{rxn}}^{\circ}$ for the combustion of octane and then determine the number of kilograms of octane necessary to provide this amount of energy.

SORT You are given the amount of energy used and asked to find the mass of octane required to produce the energy.

STRATEGIZE The conceptual plan has three parts. In the first part, write a balanced equation for the combustion of octane.

In the second part, calculate $\Delta H_{\text{rxn}}^{\circ}$ from the ΔH_f° 's of the reactants and products.

In the third part, convert from kilojoules of energy to moles of octane using the conversion factor found in step 2, and then convert from moles of octane to mass of octane using the molar mass.

GIVEN: 1.0×10^{11} kJ

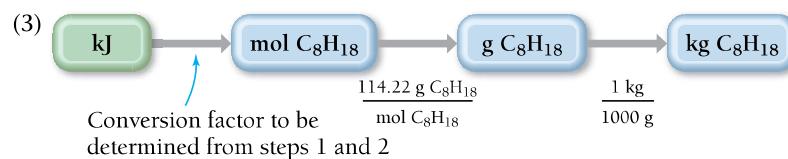
FIND: kg C_8H_{18}

CONCEPTUAL PLAN

(1) Write the balanced equation.



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



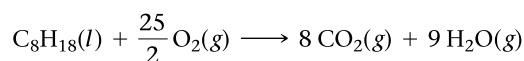
RELATIONSHIPS USED

molar mass $\text{C}_8\text{H}_{18} = 114.22 \text{ g/mol}$

$1 \text{ kg} = 1000 \text{ g}$

SOLVE Begin by writing the balanced equation for the combustion of octane. For convenience, do not clear the $25/2$ fraction in order to keep the coefficient on octane as 1.

SOLUTION STEP 1



Look up (in Appendix IIB) the standard enthalpy of formation for each reactant and product and then calculate $\Delta H_{\text{rxn}}^{\circ}$.

SOLUTION STEP 2

| Reactant or product | ΔH_f° (kJ/mol, from Appendix IIB) |
|------------------------------|--|
| $\text{C}_8\text{H}_{18}(l)$ | -250.1 |
| $\text{O}_2(g)$ | 0.0 |
| $\text{CO}_2(g)$ | -393.5 |
| $\text{H}_2\text{O}(g)$ | -241.8 |

Continued—

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= \sum n_p \Delta H_f^{\circ} (\text{products}) - \sum n_r \Delta H_f^{\circ} (\text{reactants}) \\ &= [8(\Delta H_f^{\circ}, \text{CO}_2(g)) + 9(\Delta H_f^{\circ}, \text{H}_2\text{O}(g))] \\ &\quad - \left[1(\Delta H_f^{\circ}, \text{C}_8\text{H}_{18(l)}) + \frac{25}{2} (\Delta H_f^{\circ}, \text{O}_2(g)) \right] \\ &= [8(-393.5 \text{ kJ}) + 9(-241.8 \text{ kJ})] - \left[1(-250.1 \text{ kJ}) + \frac{25}{2} (0.0 \text{ kJ}) \right] \\ &= -5324.2 \text{ kJ} - (-250.1 \text{ kJ}) \\ &= -5074.1 \text{ kJ}\end{aligned}$$

From steps 1 and 2 build a conversion factor between mol C₈H₁₈ and kJ.

Follow step 3 of the conceptual plan. Begin with $-1.0 \times 10^{11} \text{ kJ}$ (since the city uses this much energy, the reaction must emit it, and therefore the sign is negative) and follow the steps to determine kilograms of octane.

SOLUTION STEP 3

1 mol C₈H₁₈: -5074.1 kJ

$$\begin{aligned}-1.0 \times 10^{11} \text{ kJ} &\times \frac{1 \text{ mol C}_8\text{H}_{18}}{-5074.1 \text{ kJ}} \times \frac{114.22 \text{ g C}_8\text{H}_{18}}{1 \text{ mol C}_8\text{H}_{18}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \\ &= 2.3 \times 10^6 \text{ kg C}_8\text{H}_{18}\end{aligned}$$

CHECK The units of the answer (kg C₈H₁₈) are correct. The answer is positive, as it should be for mass. The magnitude is fairly large, as you would expect since this amount of octane is supposed to provide the energy for an entire city.

FOR PRACTICE 7.12 The chemical hand warmers described in Section 7.1 produce heat when they are removed from their airtight plastic wrappers. Recall that they utilize the oxidation of iron to form iron oxide according to the reaction $4 \text{ Fe}(s) + 3 \text{ O}_2(g) \longrightarrow 2 \text{ Fe}_2\text{O}_3(s)$. Calculate $\Delta H_{\text{rxn}}^{\circ}$ for this reaction and calculate how much heat is produced from a hand warmer containing 15.0 g of iron powder.

7.10

Energy Use and the Environment

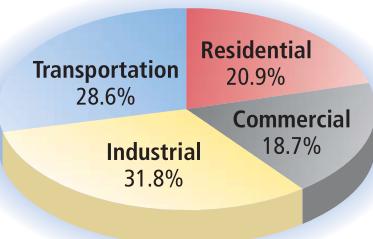
In this chapter, we explored the relationship between chemical reactions and energy changes. As noted earlier, our society derives the majority of its energy from the energy changes associated with burning fossil fuels. Fossil fuels have traditionally been regarded as convenient sources of energy due to their abundance and portability and because they undergo combustion reactions that have large negative enthalpies of reaction (the reactions are highly exothermic). However, the burning of fossil fuels also has some serious environmental impacts.

Energy Consumption

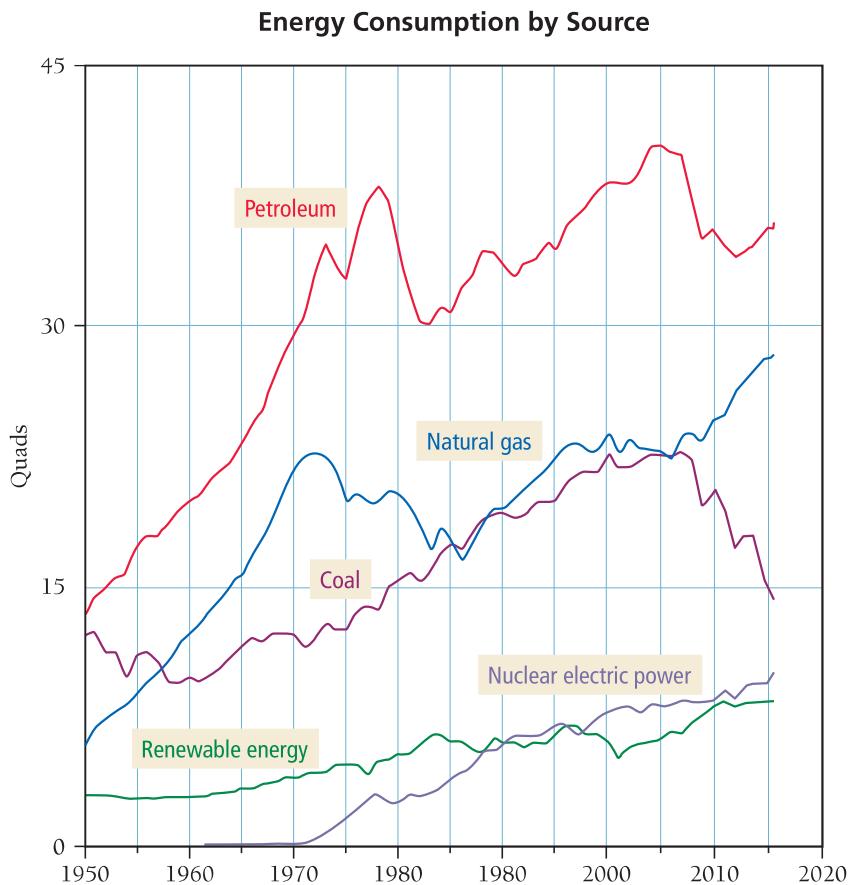
According to the U.S. Department of Energy, the United States currently consumes close to 100 quads (1 quad = 1 quadrillion British thermal units = $1.06 \times 10^{18} \text{ J}$) of energy per year in the categories shown in this chart.

This corresponds to over 100,000 kWh of energy use per person per year. If we used physical laborers to do the equivalent amount of work, each person would need about 120 people. In other words, the average American employs the work output of 120 people, day and night, all year long! For this reason, Americans enjoy one of the highest standards of living in the world. However, our consumption of energy has significant environmental consequences.

Most U.S. energy comes from the combustion of fossil fuels, as shown in Figure 7.12►. Fossil fuels include petroleum, natural gas, and coal, all of which have been considered convenient fuels because they are relatively abundant in Earth's crust (and therefore relatively inexpensive), they are easily transportable, and their combustion is highly exothermic.



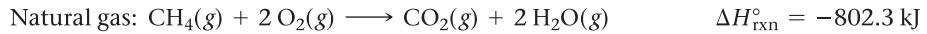
Source: U.S. Energy Information Administration. *Monthly Energy Review*, October 2017 (percentages for the 2016 calendar year).



◀ FIGURE 7.12 Energy Consumption by Source

Source: U.S. Energy Information Administration. *Monthly Energy Review*, October 2017.

The reactions for the combustion of the main or representative components of several fossil fuels, and the associated enthalpies of reaction, are:



Environmental Problems Associated with Fossil Fuel Use

One of the main problems associated with the burning of fossil fuels is that even though they are abundant in Earth's crust, fossil fuels are also finite. Fossil fuels originate from ancient plant and animal life and are a nonrenewable energy source—once they are all burned, they cannot be replenished. At current rates of consumption, oil and natural gas supplies will be depleted in 50 to 100 years. Although there is enough coal to last much longer, it is a dirtier fuel (it produces more pollution), and, because it is a solid, it is less convenient (more difficult to transport and use) than petroleum and natural gas.

The other major problems associated with fossil fuel use stem from the products of combustion. The chemical equations we show in this section for fossil fuel combustion all produce carbon dioxide and water. However, these equations represent the reactions under ideal conditions and do not account for impurities in the fuel, side reactions, and incomplete combustion. When these are taken into account, we can identify three major environmental problems associated with the emissions of fossil fuel combustion: air pollution, acid rain, and global climate change. We discussed acid rain in Chapter 3 (see *Chemistry in the Environment: Acid Rain* in Section 3.6). Here we address air pollution and global climate change, which we first touched on in Section 4.1.

Air Pollution

The air in all major cities in the world is polluted. Pollution comes from a number of sources, including electricity generation, motor vehicle emissions, and industrial waste. There are many different kinds of air pollutants.

Sulfur Oxides (SO_x)

Sulfur oxides include SO_2 and SO_3 , which are produced primarily during coal-fired electricity generation and industrial metal refining. The sulfur oxides are lung and eye irritants that affect the respiratory system and are the main precursors of acid rain (see Section 3.6).

Carbon Monoxide (CO)

Carbon monoxide forms during the incomplete combustion of fossil fuels (petroleum, natural gas, and coal). It is emitted mainly by motor vehicles. In humans and other animals, carbon monoxide displaces oxygen in the blood, forcing the heart and lungs to work harder. At high levels, CO can cause sensory impairment, decreased thinking ability, unconsciousness, and even death.

Nitrogen Oxides (NO_x)

The nitrogen oxides include NO and NO_2 , emitted by motor vehicles, fossil fuel-based electricity generation plants, and any high-temperature combustion process occurring in air. Nitrogen dioxide is an orange-brown gas that causes the dark haze over polluted cities. Nitrogen oxides are eye and lung irritants and precursors of acid rain.

TABLE 7.6 ■ Changes in National Average Pollutant Levels, 1990–2016

| Pollutant | Change (%) in Average Level |
|---------------|-----------------------------|
| SO_2 | -85 |
| CO | -77 |
| NO_2 | -50 |
| O_3 | -22 |

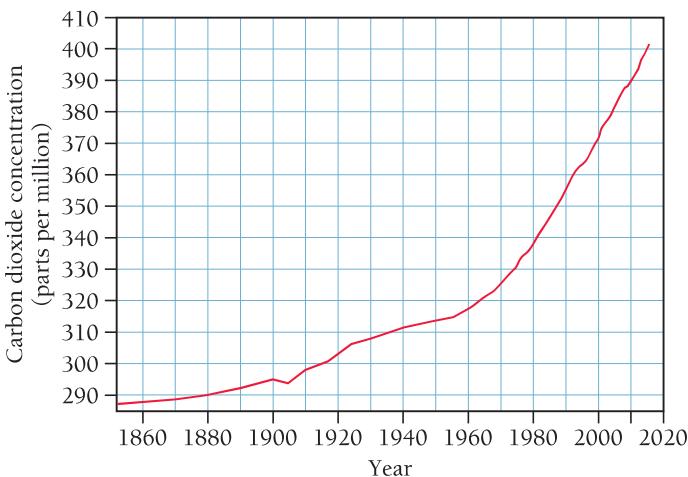
Source: EPA's National Air Trends

Ozone (O_3)

Ozone is produced when some of the products of fossil fuel combustion, especially nitrogen oxides and unburned volatile organic compounds (VOCs), react in the presence of sunlight. The products of this reaction, which include ozone, are called *photochemical smog*. Ozone produced in this way—sometimes called ground-level ozone—should not be confused with upper atmospheric or *stratospheric* ozone. Although ozone is always the same molecule (O_3), stratospheric ozone is a natural part of our environment that protects Earth from harmful ultraviolet light. Stratospheric ozone does not harm humans because we are not directly exposed to it. Ground-level ozone, on the other hand, is a pollutant to which we are directly exposed; it is an eye and lung irritant, and prolonged exposure can cause permanent lung damage.

In the United States, the U.S. Environmental Protection Agency (EPA) has established limits on these pollutants. Beginning in the 1970s, the U.S. Congress passed the Clean Air Act and its amendments, requiring U.S. cities to reduce their pollution and maintain levels below the standards set by the EPA. As a result of this legislation, pollutant levels in U.S. cities have decreased over the last 30 years, even as the number of vehicles has increased. According to the EPA, the levels of the major pollutants in the air of U.S. cities decreased significantly during the period 1990–2016, as shown in Table 7.6.

Atmospheric Carbon Dioxide



▲ FIGURE 7.13 The Rise in Atmospheric Carbon

Dioxide Atmospheric carbon dioxide levels have been steadily increasing as a result of fossil fuel combustion. Source: Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (www.scrippsco2.ucsd.edu/)

Global Climate Change

One of the main products of fossil fuel combustion is carbon dioxide. Carbon dioxide is a greenhouse gas; it allows visible light from the sun to enter Earth's atmosphere, but it prevents heat (in the form of infrared light) from escaping. In doing so, carbon dioxide acts as a blanket, keeping Earth warm, which, in moderation, is a very good thing and allows life as we know it to exist on our planet. However, because of fossil fuel combustion, carbon dioxide levels in the atmosphere have been steadily increasing, as shown in Figure 7.13 ▲. This increase is expected to change the global climate and further raise Earth's average temperature. Current observations suggest that Earth has already warmed by about 0.9°C in the last century due to an approximately 38% increase in atmospheric carbon dioxide. Computer models suggest that the warming could worsen if carbon dioxide emissions are not curbed.

The possible effects of this warming include heightened storm severity, increasing numbers of floods and droughts, major shifts in agricultural zones, rising sea levels and coastal flooding, and profound changes in habitats that could result in the extinction of some plant and animal species.

EXAMPLE 7.13 Fossil Fuels and Climate Change

One way to evaluate fuels with respect to global warming is to determine how much heat they release during combustion relative to how much CO₂ they produce. The greater the heat relative to the amount of CO₂, the better the fuel. Use the combustion reactions of carbon, natural gas, and octane, in combination with the enthalpy of combustion for each reaction (all given earlier), to calculate the heat (in kJ) released by each fuel per 1.00 kg of CO₂ produced.

SORT You are given the mass of CO₂ emitted and asked to find the energy output for three different fuels.

STRATEGIZE First write the thermochemical equations for the combustion of each fuel given in Section 7.10.

The conceptual plan has two parts. In the first part, use the molar mass of CO₂ to convert from mass of CO₂ to moles of CO₂. This step is the same for each fuel.

In the second part, use the stoichiometric relationship between moles of CO₂ produced and kilojoules of energy released to calculate the energy output. Repeat the second part for each fuel using the appropriate stoichiometric relationship from the balanced equations.

SOLVE Begin by converting kg CO₂ to mol CO₂.

Then, for each fuel, convert mol CO₂ to kJ.

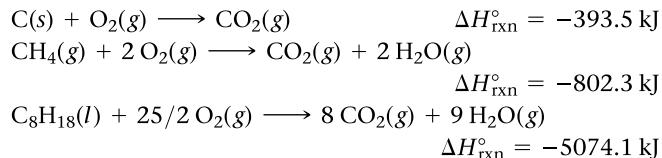
As you can see from the heat released in the production of 1 kg CO₂, natural gas, CH₄, provides the most energy per kg CO₂; therefore, it is the best fuel with respect to climate change.

CHECK Each answer is in kJ, as it should be for heat produced. Each answer is negative, as expected for exothermic combustion reactions.

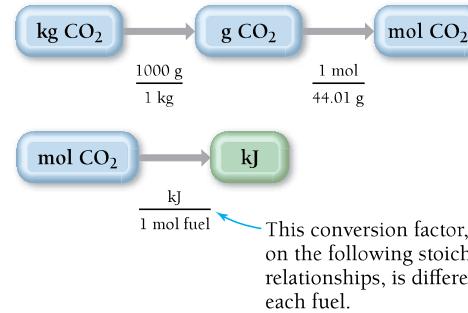
FOR PRACTICE 7.13 What mass of CO₂ (in kilograms) does the combustion of a 15-gallon tank of gasoline release into the atmosphere? Assume the gasoline is pure octane (C₈H₁₈) and that it has a density of 0.70 g/mL.

GIVEN: 1.00 kg CO₂

FIND: kJ



CONCEPTUAL PLAN



STOICHIOMETRIC RELATIONSHIPS

For C: 1 mol CO₂: -393.5 kJ

For CH₄: 1 mol CO₂: -802.3 kJ

For C₈H₁₈: 8 mol CO₂: -5074.1 kJ

OTHER RELATIONSHIPS USED

1 kg = 1000 g

molar mass CO₂ = 44.01 g/mol

SOLUTION

$$1.00 \text{ kg CO}_2 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} = 22.72 \text{ mol CO}_2$$

$$\text{For C: } 22.72 \text{ mol CO}_2 \times \frac{-393.5 \text{ kJ}}{1 \text{ mol CO}_2} = -8.94 \times 10^3 \text{ kJ}$$

$$\text{For CH}_4: 22.72 \text{ mol CO}_2 \times \frac{-802.3 \text{ kJ}}{1 \text{ mol CO}_2} = -1.82 \times 10^4 \text{ kJ}$$

$$\text{For C}_8\text{H}_{18}: 22.72 \text{ mol CO}_2 \times \frac{-5074.1 \text{ kJ}}{8 \text{ mol CO}_2} = -1.44 \times 10^4 \text{ kJ}$$



CHEMISTRY IN THE ENVIRONMENT

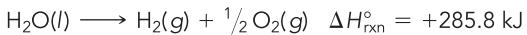
Renewable Energy

Because of their finite supply and environmental impacts, fossil fuels will not be our major source of energy in the future. What will replace them? Although the answer is not clear, several alternative energy technologies are beginning to emerge. Unlike fossil fuels, these technologies are renewable, and we can use them indefinitely.

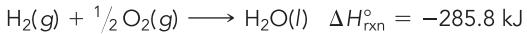
Our planet's greatest source of renewable energy is the sun. If we could capture and harness just a small fraction of the total sunlight falling on Earth, we could meet our energy needs several times over. The main problem with solar energy, however, is diffuseness—the sun's energy falls over an enormous area. How do we concentrate and store it? In California, some of the state's electricity is generated by parabolic troughs, solar power towers, and dish/engines.

These devices use reflective surfaces to focus the sun's energy and produce enough heat to generate electricity. Although the direct cost of generating electricity this way is higher than using fossil fuels, the benefits to the environment are obvious. In addition, with time, the costs are expected to fall.

Another way to capture the sun's energy is in chemical bonds. For example, solar energy could be used to drive the decomposition of water:



The hydrogen gas produced could be stored until needed to provide energy by re-forming water in the reverse reaction:



This reaction can be carried out in an electrochemical device called a fuel cell. In a fuel cell, hydrogen and oxygen gases combine to form water and produce electricity. In 2015, Toyota introduced the Mirai (which means future in Japanese), the first mass-produced fuel cell vehicle. The Mirai has a 300-mile range and produces 153 horsepower. Unlike most electric vehicles (such as the Tesla Model S), a fuel cell vehicle can be refueled instead of recharged. The refueling process only takes a few minutes (compared to recharging, which can take several hours). California has earmarked \$200 million to build a "hydrogen highway," a series of 100 hydrogen refueling stations to be operational by 2020.

Other renewable energy sources are hydroelectric power and wind power. Hydroelectric power plants—which generate



▲ The Toyota Mirai, a fuel cell vehicle that runs on hydrogen gas and produces only water as exhaust.

approximately 7% of U.S. electricity—harness the gravitational potential energy of water held behind a dam. Water is released at a controlled rate. As the released water falls, it acquires kinetic energy that is used to spin turbines, generating electricity. Wind power plants—which produce nearly 5% of U.S. electricity—consist of hundreds of turbines that are spun by the wind to generate electricity. Both of these technologies are cost competitive with fossil fuels, have no emissions, and are completely renewable.

Our energy future will probably involve a combination of these technologies and some new ones, combined with a focus on greater efficiency and conservation. One thing, however, is clear—the future of fossil fuels is limited.



▲ Wind turbines such as these generate nearly 5% of U.S. electricity.



Parabolic troughs



Solar power tower



Dish/engine

▲ The sun's energy, concentrated by reflective surfaces in various arrangements, can produce enough heat to generate electricity.





Self-Assessment Quiz

- Q1.** A chemical system produces 155 kJ of heat and does 22 kJ of work. What is ΔE for the surroundings?

MISSED THIS? Read Section 7.2

a) 177 kJ b) -177 kJ c) 133 kJ d) -133 kJ

Q2. Which sample is most likely to undergo the smallest change in temperature upon the absorption of 100 kJ of heat?

MISSED THIS? Read Section 7.4; Watch KCV 7.4

a) 15 g water b) 15 g lead c) 50 g water d) 50 g lead

Q3. How much heat must be absorbed by a 15.0-g sample of water to raise its temperature from 25.0 °C to 55.0 °C? (For water, $C_s = 4.18 \text{ J/g} \cdot \text{°C}$.)

MISSED THIS? Read Section 7.4; Watch KCV 7.4, IWE 7.2

a) 1.57 kJ b) 1.88 kJ c) 3.45 kJ d) 107 J

Q4. A 12.5-g sample of granite initially at 82.0 °C is immersed into 25.0 g of water initially at 22.0 °C. What is the final temperature of both substances when they reach thermal equilibrium? (For water, $C_s = 4.18 \text{ J/g} \cdot \text{°C}$ and for granite, $C_s = 0.790 \text{ J/g} \cdot \text{°C}$.)

MISSED THIS? Read Section 7.4; Watch KCV 7.4, IWE 7.3

a) 52.0 °C b) $1.55 \times 10^3 \text{ °C}$ c) 15.7 °C d) 27.2 °C

Q5. A cylinder with a moving piston expands from an initial volume of 0.250 L against an external pressure of 2.00 atm. The expansion does 288 J of work on the surroundings. What is the final volume of the cylinder?

MISSED THIS? Read Section 7.4

a) 1.42 L b) 1.17 L c) 144 L d) 1.67 L

Q6. When a 3.80-g sample of liquid octane (C_8H_{18}) is burned in a bomb calorimeter, the temperature of the calorimeter rises by 27.3 °C. The heat capacity of the calorimeter, measured in a separate experiment, is 7.18 kJ/°C. Determine the ΔE for octane combustion in units of kJ/mol octane.

MISSED THIS? Read Section 7.5; Watch IWE 7.5

a) $-5.07 \times 10^3 \text{ kJ/mol}$ b) $5.07 \times 10^3 \text{ kJ/mol}$
c) $-44.4 \times 10^3 \text{ kJ/mol}$ d) $-16.7 \times 10^3 \text{ kJ/mol}$

Q7. Hydrogen gas reacts with oxygen to form water:

$$2 \text{ H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{ H}_2\text{O}(\text{g}) \quad \Delta H = -483.5 \text{ kJ}$$

Determine the minimum mass of hydrogen gas required to produce 226 kJ of heat.

MISSED THIS? Read Section 7.6; Watch KCV 7.6, IWE 7.7

a) 8.63 g b) 1.88 g c) 0.942 g d) 0.935 g

Q8. Manganese reacts with hydrochloric acid to produce manganese(II) chloride and hydrogen gas:

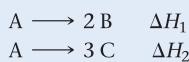
$$\text{Mn}(\text{s}) + 2 \text{ HCl}(\text{aq}) \longrightarrow \text{MnCl}_2(\text{aq}) + \text{H}_2(\text{g})$$

When 0.625 g Mn is combined with enough hydrochloric acid to make 100.0 mL of solution in a coffee-cup calorimeter, all of the Mn reacts, raising the temperature of the solution from 23.5 °C to 28.8 °C. Find ΔH_{rxn} for the reaction as written. (Assume that the specific heat capacity of the solution is 4.18 J/g · °C and the density is 1.00 g/mL.)

MISSED THIS? Read Section 7.7; Watch IWE 7.8

a) -195 kJ b) -3.54 kJ c) -1.22 kJ d) -2.21 kJ

Q9. Consider the reactions:



What is ΔH for the reaction $2 \text{ B} \longrightarrow 3 \text{ C}$?

- MISSED THIS? Read Section 7.8; Watch IWE 7.9**

a) $\Delta H_1 + \Delta H_2$ b) $\Delta H_1 - \Delta H_2$
 c) $\Delta H_2 - \Delta H_1$ d) $2 \times (\Delta H_1 + \Delta H_2)$

Answers: 1. (a) 2. (c) 3. (b) 4. (d) 5. (d) 6. (a) 7. (b) 8. (c) 9. (c) 10. (d) 11. (a) 12. (a) 13. (b) 14. (d) 15. (a)

CHAPTER 7 IN REVIEW

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(267)

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standard enthalpy change

(ΔH°) (289)

standard enthalpy of

formation (ΔH_f°) (289)

standard heat

of formation (289)

CONCEPTS

The Nature of Energy and Thermodynamics (7.2, 7.3)

- Energy, which is measured in the SI unit of joules (J), is the capacity to do work.
- Work is the result of a force acting through a distance.
- Many different kinds of energy exist, including kinetic energy, thermal energy, potential energy, and chemical energy, a type of potential energy associated with the relative positions of electrons and nuclei in atoms and molecules.
- The first law of thermodynamics states that energy can be converted from one form to another, but the total amount of energy is always conserved.
- The internal energy (*E*) of a system is the sum of all of its kinetic and potential energy. Internal energy is a state function, which means that it depends only on the state of the system and not on the pathway by which it got to that state.
- A chemical system exchanges energy with its surroundings through heat (the transfer of thermal energy caused by a temperature difference) or work. The total change in internal energy is the sum of these two quantities.

Heat and Work (7.4)

- We quantify heat with the equation $q = m \times C_s \times \Delta T$. In this expression, C_s is the specific heat capacity, the amount of heat required to change the temperature of 1 g of the substance by 1 °C. Compared to most substances, water has a very high heat capacity—it takes a lot of heat to change its temperature.
- The type of work most characteristic of chemical reactions is pressure-volume work, which occurs when a gas expands against an external pressure. Pressure-volume work can be quantified with the equation $w = -P_{ext} \Delta V$.
- The change in internal energy (ΔE) that occurs during a chemical reaction is the sum of the heat (q) exchanged and the work (w) done: $\Delta E = q + w$.

Enthalpy (7.6)

- The heat evolved in a chemical reaction occurring at constant pressure is the change in enthalpy (ΔH) for the reaction. Like internal energy, enthalpy is a state function.

- An endothermic reaction has a positive enthalpy of reaction; an exothermic reaction has a negative enthalpy of reaction.
- We can use the enthalpy of reaction to stoichiometrically determine the heat evolved when a specific amount of reactant reacts.

Calorimetry (7.5, 7.7)

- Calorimetry is a method of measuring ΔE or ΔH for a reaction.
- In bomb calorimetry, the reaction is carried out under conditions of constant volume, so $\Delta E = q_v$. We can therefore use the temperature change of the calorimeter to calculate ΔE for the reaction.
- When a reaction takes place at constant pressure, energy may be released both as heat and as work.
- In coffee-cup calorimetry, a reaction is carried out under atmospheric pressure in a solution, so $q = \Delta H$. We use the temperature change of the solution to calculate ΔH for the reaction.

Calculating ΔH_{rxn} (7.8, 7.9)

- We can calculate the enthalpy of reaction (ΔH_{rxn}) from known thermochemical data using the following relationships: (a) when a reaction is multiplied by a factor, ΔH_{rxn} is multiplied by the same factor; (b) when a reaction is reversed, ΔH_{rxn} changes sign; and (c) if a chemical reaction can be expressed as a sum of two or more steps, ΔH_{rxn} is the sum of the ΔH 's for the individual steps (Hess's law). We can use these relationships to determine the enthalpy change of an unknown reaction from reactions with known enthalpy changes.
- A second method to calculate ΔH_{rxn} from known thermochemical data involves using tabulated standard enthalpies of formation for the reactants and products of the reaction. These are usually tabulated for substances in their standard states, and the enthalpy of reaction is called the standard enthalpy of reaction (ΔH_{rxn}°). For any reaction, we obtain ΔH_{rxn}° by subtracting the sum of the enthalpies of formation of the reactants multiplied by their stoichiometric coefficients from the sum of the enthalpies of formation of the products multiplied by their stoichiometric coefficients.

Environmental Problems Associated with Fossil Fuel Use (7.10)

- Fossil fuels are nonrenewable fuels; once humans consume them, they cannot be replaced.
- At current rates of consumption, natural gas and petroleum reserves will be depleted in 50–100 years.

- In addition to their limited supply, the products of the combustion of fossil fuels—directly or indirectly formed—contribute to environmental problems including air pollution, acid rain, and global climate change, which involves an increase in Earth's average temperature caused by CO₂ emission.

EQUATIONS AND RELATIONSHIPS

Kinetic Energy (7.2)

$$\text{KE} = \frac{1}{2} mv^2$$

Change in Internal Energy (ΔE) of a Chemical System (7.3)

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

Energy Flow between System and Surroundings (7.3)

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

Relationship between Internal Energy (ΔE), Heat (q), and Work (w) (7.3)

$$\Delta E = q + w$$

Relationship between Heat (q), Temperature (T), and Heat Capacity (C) (7.4)

$$q = C \times \Delta T$$

Relationship between Heat (q), Mass (m), Temperature (T), and Specific Heat Capacity of a Substance (C_s) (7.4)

$$q = m \times C_s \times \Delta T$$

Relationship between Work (w), Force (F), and Distance (D) (7.4)

$$w = F \times D$$

Relationship between Work (w), Pressure (P), and Change in Volume (ΔV) (7.4)

$$w = -P_{\text{ext}} \Delta V$$

Change in Internal Energy (ΔE) of System at Constant Volume (7.5)

$$\Delta E = q_v$$

Heat of a Bomb Calorimeter (q_{cal}) (7.5)

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

Heat Exchange between a Calorimeter and a Reaction (7.5)

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

Relationship between Enthalpy (ΔH), Internal Energy (ΔE), Pressure (P), and Volume (V) (7.6)

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

$$\Delta H = q_p$$

Relationship between Enthalpy of a Reaction ($\Delta H_{\text{rxn}}^\circ$) and the Heats of Formation (ΔH_f°) (7.9)

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

LEARNING OUTCOMES

| Chapter Objectives | Assessment |
|--|---|
| Analyze types of energy and convert between energy units (7.2) | Exercises 33–36 |
| Analyze changes in internal energy in terms of heat and work (7.3) | Example 7.1 For Practice 7.1 Exercises 37–44 |
| Determine heat from temperature changes (7.4) | Example 7.2 For Practice 7.2 For More Practice 7.2 Exercises 45–50 |
| Calculate quantities in thermal energy transfer (7.4) | Example 7.3 For Practice 7.3 Exercises 65–70 |
| Analyze processes involving pressure–volume work (7.4) | Example 7.4 For Practice 7.4 For More Practice 7.4 Exercises 51–54 |
| Analyze energy changes for combustion reactions inside a bomb calorimeter (7.5) | Example 7.5 For Practice 7.5 For More Practice 7.5 Exercises 73–74 |
| Predict endothermic and exothermic processes (7.6) | Example 7.6 For Practice 7.6 Exercises 55–58 |
| Perform stoichiometric calculations involving the enthalpy of reaction (7.6) | Example 7.7 For Practice 7.7 For More Practice 7.7 Exercises 59–64 |
| Analyze enthalpy changes for reactions in a coffee-cup calorimeter (7.7) | Example 7.8 For Practice 7.8 Exercises 71–72, 75–76 |
| Analyze how changes in chemical reactions affect the enthalpy of reaction (7.8) | Example 7.9 For Practice 7.9 For More Practice 7.9 Exercises 77–82 |
| Determine the standard enthalpy change for a reaction using standard enthalpies of formation (7.9) | Examples 7.10, 7.11, 7.12 For Practice 7.10, 7.11, 7.12 Exercises 83–92 |
| Analyze the effects of energy use on the environment (7.10) | Example 7.13 For Practice 7.13 Exercises 93–96 |

EXERCISES

REVIEW QUESTIONS

- Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.
- What is thermochemistry? Why is it important?
 - What is energy? What is work? List some examples of each.
 - What is kinetic energy? What is potential energy? List some examples of each.
 - State the law of conservation of energy. How does it relate to energy exchanges between a thermodynamic system and its surroundings?
 - What is the SI unit of energy? List some other common units of energy.
 - State the first law of thermodynamics. What are its implications?
 - A friend claims to have constructed a machine that creates electricity but requires no energy input. Explain why you should be suspicious of your friend's claim.
 - What is a state function? List some examples of state functions.
 - What is internal energy? Is internal energy a state function?
 - If energy flows out of a chemical system and into the surroundings, what is the sign of ΔE_{system} ?
 - If the internal energy of the products of a reaction is higher than the internal energy of the reactants, what is the sign of ΔE for the reaction? In which direction does energy flow?
 - What is heat? Explain the difference between heat and temperature.
 - How is the change in internal energy of a system related to heat and work?
 - Explain how the sum of heat and work can be a state function, even though heat and work are themselves not state functions.
 - What is heat capacity? Explain the difference between heat capacity and specific heat capacity.
 - Explain how the high specific heat capacity of water can affect the weather in coastal regions.
 - If two objects, A and B, of different temperature come into direct contact, what is the relationship between the heat lost by one object and the heat gained by the other? What is the relationship between the temperature changes of the two objects? (Assume that the two objects do not lose any heat to anything else.)
 - What is pressure-volume work? How is it calculated?
 - What is calorimetry? Explain the difference between a coffee-cup calorimeter and a bomb calorimeter. What is each designed to measure?
 - What is the change in enthalpy (ΔH) for a chemical reaction? How is ΔH different from ΔE ?
 - Explain the difference between an exothermic and an endothermic reaction. Give the sign of ΔH for each type of reaction.
 - From a molecular viewpoint, where does the energy emitted in an exothermic chemical reaction come from? Why does the reaction mixture undergo an increase in temperature even though energy is emitted?
 - From a molecular viewpoint, where does the energy absorbed in an endothermic chemical reaction go? Why does the reaction mixture undergo a decrease in temperature even though energy is absorbed?
 - Is the change in enthalpy for a reaction an extensive property? Explain the relationship between ΔH for a reaction and the amounts of reactants and products that undergo reaction.
 - Explain how the value of ΔH for a reaction changes upon each operation.
 - multiplying the reaction by a factor
 - reversing the reaction
 Why do these relationships hold?
 - What is Hess's law? Why is it useful?
 - What is a standard state? What is the standard enthalpy change for a reaction?
 - What is the standard enthalpy of formation for a compound? For a pure element in its standard state?
 - How do you calculate $\Delta H_{\text{rxn}}^{\circ}$ from tabulated standard enthalpies of formation?
 - What are the main sources of the energy consumed in the United States?
 - What are the main environmental problems associated with fossil fuel use?
 - Explain global climate change. What causes global warming? What is the evidence that global warming is occurring?

PROBLEMS BY TOPIC

Energy Units

33. Convert between energy units.
MISSED THIS? Read Section 7.2
- 534 kWh to J
 - 215 kJ to Cal
 - 567 Cal to J
 - 2.85×10^3 J to cal
34. Convert between energy units.
- 231 cal to kJ
 - 132×10^4 kJ to kcal
 - 4.99×10^3 kJ to kWh
 - 2.88×10^4 J to Cal
35. Suppose that a person eats 2387 Calories per day. Convert this amount of energy into each unit.
- MISSED THIS? Read Section 7.2**
- J
 - kJ
 - kWh
36. A particular frost-free refrigerator uses about 745 kWh of electrical energy per year. Express this amount of energy in each unit.
- J
 - kJ
 - Cal

Internal Energy, Heat, and Work

- 37.** Which statement is true of the internal energy of a system and its surroundings during an energy exchange with a negative ΔE_{sys} ? **MISSED THIS? Read Section 7.3; Watch KCV 7.3**
- The internal energy of the system increases and the internal energy of the surroundings decreases.
 - The internal energy of both the system and the surroundings increases.
 - The internal energy of both the system and the surroundings decreases.
 - The internal energy of the system decreases and the internal energy of the surroundings increases.
- 38.** During an energy exchange, a chemical system absorbs energy from its surroundings. What is the sign of ΔE_{sys} for this process? Explain.
- 39.** Identify each energy exchange as primarily heat or work and determine whether the sign of ΔE is positive or negative for the system. **MISSED THIS? Read Section 7.3; Watch KCV 7.3**
- Sweat evaporates from skin, cooling the skin. (The evaporating sweat is the system.)
 - A balloon expands against an external pressure. (The contents of the balloon is the system.)
 - An aqueous chemical reaction mixture is warmed with an external flame. (The reaction mixture is the system.)
- 40.** Identify each energy exchange as primarily heat or work and determine whether the sign of ΔE is positive or negative for the system.
- A rolling billiard ball collides with another billiard ball. The first billiard ball (defined as the system) stops rolling after the collision.
 - A book falls to the floor. (The book is the system.)
 - A father pushes his daughter on a swing. (The daughter and the swing are the system.)
- 41.** A system releases 622 kJ of heat and does 105 kJ of work on the surroundings. What is the change in internal energy of the system? **MISSED THIS? Read Section 7.3**
- 42.** A system absorbs 196 kJ of heat, and the surroundings do 117 kJ of work on the system. What is the change in internal energy of the system?
- 43.** The gas in a piston (defined as the system) warms and absorbs 655 J of heat. The expansion performs 344 J of work on the surroundings. What is the change in internal energy for the system? **MISSED THIS? Read Section 7.3**
- 44.** The air in an inflated balloon (defined as the system) warms over a toaster and absorbs 115 J of heat. As it expands, it does 77 kJ of work. What is the change in internal energy for the system?

Heat, Heat Capacity, and Work

- 45.** We pack two identical coolers for a picnic, placing 24 12-ounce soft drinks and five pounds of ice in each. However, the drinks that we put into cooler A were refrigerated for several hours before they were packed in the cooler, while the drinks that we put into cooler B were at room temperature. When we open the two coolers three hours later, most of the ice in cooler A is still present, while nearly all of the ice in cooler B has melted. Explain this difference. **MISSED THIS? Read Section 7.4; Watch KCV 7.4**

- 46.** A kilogram of aluminum metal and a kilogram of water are each warmed to 75 °C and placed in two identical insulated containers. One hour later, the two containers are opened, and the temperature of each substance is measured. The aluminum has cooled to 35 °C, while the water has cooled only to 66 °C. Explain this difference.
- 47.** How much heat is required to warm 1.50 L of water from 25.0 °C to 100.0 °C? (Assume a density of 1.0 g/mL for the water.) **MISSED THIS? Read Section 7.3; Watch KCV 7.3, IWE 7.2**
- 48.** How much heat is required to warm 1.50 kg of sand from 25.0 °C to 100.0 °C?
- 49.** Suppose that 25 g of each substance is initially at 27.0 °C. What is the final temperature of each substance upon absorbing 2.35 kJ of heat? **MISSED THIS? Read Section 7.3; Watch KCV 7.3, IWE 7.2**
- gold
 - silver
 - aluminum
 - water
- 50.** An unknown mass of each substance, initially at 23.0 °C, absorbs 1.95×10^3 J of heat. The final temperature is recorded. Find the mass of each substance.
- Pyrex glass ($T_f = 55.4$ °C)
 - sand ($T_f = 62.1$ °C)
 - ethanol ($T_f = 44.2$ °C)
 - water ($T_f = 32.4$ °C)
- 51.** How much work (in J) is required to expand the volume of a pump from 0.0 L to 2.5 L against an external pressure of 1.1 atm? **MISSED THIS? Read Section 7.4**
- 52.** The average human lung expands by about 0.50 L during each breath. If this expansion occurs against an external pressure of 1.0 atm, how much work (in J) is done during the expansion?
- 53.** The air within a piston equipped with a cylinder absorbs 565 J of heat and expands from an initial volume of 0.10 L to a final volume of 0.85 L against an external pressure of 1.0 atm. What is the change in internal energy of the air within the piston? **MISSED THIS? Read Section 7.4**
- 54.** A gas is compressed from an initial volume of 5.55 L to a final volume of 1.22 L by an external pressure of 1.00 atm. During the compression the gas releases 124 J of heat. What is the change in internal energy of the gas?

Enthalpy and Thermochemical Stoichiometry

- 55.** When 1 mol of a fuel burns at constant pressure, it produces 3452 kJ of heat and does 11 kJ of work. What are ΔE and ΔH for the combustion of the fuel? **MISSED THIS? Read Section 7.6**
- 56.** The change in internal energy for the combustion of 1.0 mol of octane at a pressure of 1.0 atm is 5084.3 kJ. If the change in enthalpy is 5074.1 kJ, how much work is done during the combustion?
- 57.** Determine whether each process is exothermic or endothermic and indicate the sign of ΔH . **MISSED THIS? Read Section 7.6; Watch KCV 7.6**
- natural gas burning on a stove
 - isopropyl alcohol evaporating from skin
 - water condensing from steam
- 58.** Determine whether each process is exothermic or endothermic and indicate the sign of ΔH .
- dry ice evaporating
 - a sparkler burning
 - the reaction that occurs in a chemical cold pack used to ice athletic injuries

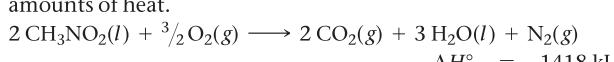
59. Consider the thermochemical equation for the combustion of acetone (C_3H_6O), the main ingredient in nail polish remover:
- $$C_3H_6O(l) + 4 O_2(g) \longrightarrow 3 CO_2(g) + 3 H_2O(g)$$
- $$\Delta H_{rxn}^\circ = -1790 \text{ kJ}$$

If a bottle of nail polish remover contains 177 mL of acetone, how much heat is released by its complete combustion? The density of acetone is 0.788 g/mL.

MISSED THIS? Read Section 7.6; Watch IWE 7.7

60. What mass of natural gas (CH_4) must burn to emit 267 kJ of heat?
- $$CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(g)$$
- $$\Delta H_{rxn}^\circ = -802.3 \text{ kJ}$$

61. Nitromethane (CH_3NO_2) burns in air to produce significant amounts of heat.



How much heat is produced by the complete reaction of 5.56 kg of nitromethane?

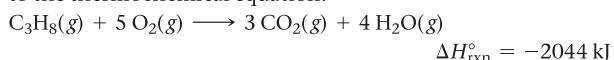
MISSED THIS? Read Section 7.6; Watch IWE 7.7

62. Titanium reacts with iodine to form titanium(III) iodide, emitting heat.



Determine the masses of titanium and iodine that react if 1.55×10^3 kJ of heat is emitted by the reaction.

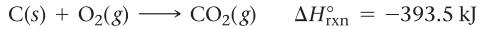
63. The propane fuel (C_3H_8) used in gas barbeques burns according to the thermochemical equation:



If a pork roast must absorb 1.6×10^3 kJ to fully cook, and if only 10% of the heat produced by the barbecue is actually absorbed by the roast, what mass of CO_2 is emitted into the atmosphere during the grilling of the pork roast?

MISSED THIS? Read Section 7.6; Watch IWE 7.7

64. Charcoal is primarily carbon. Determine the mass of CO_2 produced by burning enough carbon (in the form of charcoal) to produce 5.00×10^2 kJ of heat.



Thermal Energy Transfer

65. A silver block, initially at 58.5°C , is submerged into 100.0 g of water at 24.8°C , in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 26.2°C . What is the mass of the silver block?

MISSED THIS? Read Section 7.4; Watch KCV 7.4, IWE 7.3

66. A 32.5-g iron rod, initially at 22.7°C , is submerged into an unknown mass of water at 63.2°C , in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 59.5°C . What is the mass of the water?

67. A 31.1-g wafer of pure gold, initially at 69.3°C , is submerged into 64.2 g of water at 27.8°C in an insulated container. What is the final temperature of both substances at thermal equilibrium?

MISSED THIS? Read Section 7.4; Watch KCV 7.4, IWE 7.3

68. A 2.85-g lead weight, initially at 10.3°C , is submerged in 7.55 g of water at 52.3°C in an insulated container. What is the final temperature of both substances at thermal equilibrium?

69. Two substances, A and B, initially at different temperatures, come into contact and reach thermal equilibrium. The mass of substance A is 6.15 g and its initial temperature is 20.5°C . The mass of substance B is 25.2 g and its initial temperature is 52.7°C . The final temperature of both substances at thermal equilibrium is 46.7°C . If the specific heat capacity of substance B is $1.17 \text{ J/g}\cdot^\circ\text{C}$, what is the specific heat capacity of substance A?

MISSED THIS? Read Section 7.4; Watch KCV 7.4, IWE 7.3

70. A 2.74-g sample of a substance suspected of being pure gold is warmed to 72.1°C and submerged into 15.2 g of water initially at 24.7°C . The final temperature of the mixture is 26.3°C . What is the heat capacity of the unknown substance? Could the substance be pure gold?

Calorimetry

71. Exactly 1.5 g of a fuel burns under conditions of constant pressure and then again under conditions of constant volume. In measurement A the reaction produces 25.9 kJ of heat, and in measurement B the reaction produces 23.3 kJ of heat. Which measurement (A or B) corresponds to conditions of constant pressure? Which one corresponds to conditions of constant volume? Explain.

MISSED THIS? Read Section 7.6

72. In order to obtain the largest possible amount of heat from a chemical reaction in which there is a large increase in the number of moles of gas, should you carry out the reaction under conditions of constant volume or constant pressure? Explain.

73. When 0.514 g of biphenyl ($C_{12}H_{10}$) undergoes combustion in a bomb calorimeter, the temperature rises from 25.8°C to 29.4°C . Find ΔE_{rxn} for the combustion of biphenyl in kJ/mol biphenyl. The heat capacity of the bomb calorimeter, determined in a separate experiment, is $5.86 \text{ kJ}/^\circ\text{C}$.

MISSED THIS? Read Section 7.5; Watch IWE 7.5

74. Mothballs are composed primarily of the hydrocarbon naphthalene ($C_{10}H_8$). When 1.025 g of naphthalene burns in a bomb calorimeter, the temperature rises from 24.25°C to 32.33°C . Find ΔE_{rxn} for the combustion of naphthalene. The heat capacity of the bomb calorimeter, determined in a separate experiment, is $5.11 \text{ kJ}/^\circ\text{C}$.

75. Zinc metal reacts with hydrochloric acid according to the balanced equation:



When 0.103 g of $Zn(s)$ is combined with enough HCl to make 50.0 mL of solution in a coffee-cup calorimeter, all of the zinc reacts, raising the temperature of the solution from 22.5°C to 23.7°C . Find ΔH_{rxn} for this reaction as written. (Use 1.0 g/mL for the density of the solution and $4.18 \text{ J/g}\cdot^\circ\text{C}$ as the specific heat capacity.)

MISSED THIS? Read Section 7.7; Watch IWE 7.8

76. Instant cold packs used to ice athletic injuries on the field contain ammonium nitrate and water separated by a thin plastic divider. When the divider is broken, the ammonium nitrate dissolves according to the endothermic reaction:



In order to measure the enthalpy change for this reaction, 1.25 g of NH_4NO_3 is dissolved in enough water to make 25.0 mL of solution. The initial temperature is 25.8°C and the final temperature (after the solid dissolves) is 21.9°C . Calculate the change in enthalpy for the reaction in kJ . (Use 1.0 g/mL as the density of the solution and $4.18 \text{ J/g}\cdot^\circ\text{C}$ as the specific heat capacity.)

Quantitative Relationships Involving ΔH and Hess's Law

77. For each generic reaction, determine the value of ΔH_2 in terms of ΔH_1 . **MISSED THIS?** Read Section 7.8

- a. $A + B \longrightarrow 2 C \quad \Delta H_1$
 $2 C \longrightarrow A + B \quad \Delta H_2 = ?$
- b. $A + \frac{1}{2}B \longrightarrow C \quad \Delta H_1$
 $2 A + B \longrightarrow 2 C \quad \Delta H_2 = ?$
- c. $A \longrightarrow B + 2 C \quad \Delta H_1$
 $\frac{1}{2}B + C \longrightarrow \frac{1}{2}A \quad \Delta H_2 = ?$

78. Consider the generic reaction:



Determine the value of ΔH for each related reaction.

- a. $3A + 6B \longrightarrow 3C + 9D$ b. $C + 3D \longrightarrow A + 2B$
 c. $\frac{1}{2}C + \frac{3}{2}D \longrightarrow \frac{1}{2}A + B$

79. Calculate ΔH_{rxn} for the reaction:

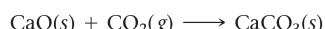


Use the following reactions and given ΔH 's:

- 2 $\text{Fe}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s) \quad \Delta H = -824.2 \text{ kJ}$
 $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H = -282.7 \text{ kJ}$

MISSED THIS? Read Section 7.8; Watch IWE 7.9

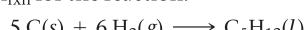
80. Calculate ΔH_{rxn} for the reaction:



Use the following reactions and given ΔH 's:

- $\text{Ca}(s) + \text{CO}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CaCO}_3(s) \quad \Delta H = -812.8 \text{ kJ}$
 $2\text{Ca}(s) + \text{O}_2(g) \longrightarrow 2\text{CaO}(s) \quad \Delta H = -1269.8 \text{ kJ}$

81. Calculate ΔH_{rxn} for the reaction:

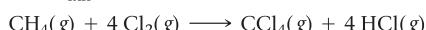


Use the following reactions and given ΔH 's:

- $\text{C}_5\text{H}_{12}(l) + 8\text{O}_2(g) \longrightarrow 5\text{CO}_2(g) + 6\text{H}_2\text{O}(g) \quad \Delta H = -3244.8 \text{ kJ}$
 $\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H = -393.5 \text{ kJ}$
 $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(g) \quad \Delta H = -483.5 \text{ kJ}$

MISSED THIS? Read Section 7.8; Watch IWE 7.9

82. Calculate ΔH_{rxn} for the reaction:



Use the following reactions and given ΔH 's:

- $\text{C}(s) + 2\text{H}_2(g) \longrightarrow \text{CH}_4(g) \quad \Delta H = -74.4 \text{ kJ}$
 $\text{C}(s) + 2\text{Cl}_2(g) \longrightarrow \text{CCl}_4(g) \quad \Delta H = -95.7 \text{ kJ}$
 $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g) \quad \Delta H = -92.3 \text{ kJ}$

Enthalpies of Formation and ΔH

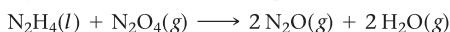
83. Write an equation for the formation of each compound from its elements in their standard states, and find ΔH_f° for each in Appendix IIB. **MISSED THIS?** Read Section 7.9

- a. $\text{NH}_3(g)$ b. $\text{CO}_2(g)$ c. $\text{Fe}_2\text{O}_3(s)$ d. $\text{CH}_4(g)$

84. Write an equation for the formation of each compound from its elements in their standard states, and find $\Delta H_{\text{rxn}}^\circ$ for each in Appendix IIB.

- a. $\text{NO}_2(g)$ b. $\text{MgCO}_3(s)$ c. $\text{C}_2\text{H}_4(g)$ d. $\text{CH}_3\text{OH}(l)$

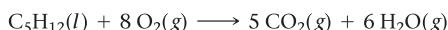
85. Hydrazine (N_2H_4) is a fuel used by some spacecraft. It is normally oxidized by N_2O_4 according to the equation:



Calculate $\Delta H_{\text{rxn}}^\circ$ for this reaction using standard enthalpies of formation.

MISSED THIS? Read Section 7.9; Watch KCV 7.9, IWE 7.11

86. Pentane (C_5H_{12}) is a component of gasoline that burns according to the following balanced equation:



Calculate $\Delta H_{\text{rxn}}^\circ$ for this reaction using standard enthalpies of formation. (The standard enthalpy of formation of liquid pentane is -146.8 kJ/mol .)

87. Use standard enthalpies of formation to calculate $\Delta H_{\text{rxn}}^\circ$ for each reaction.

MISSED THIS? Read Section 7.9; Watch KCV 7.9, IWE 7.11

- a. $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g)$
 b. $\text{CO}(g) + \text{H}_2\text{O}(g) \longrightarrow \text{H}_2(g) + \text{CO}_2(g)$
 c. $3\text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2\text{HNO}_3(aq) + \text{NO}(g)$
 d. $\text{Cr}_2\text{O}_3(s) + 3\text{CO}(g) \longrightarrow 2\text{Cr}(s) + 3\text{CO}_2(g)$

88. Use standard enthalpies of formation to calculate $\Delta H_{\text{rxn}}^\circ$ for each reaction.

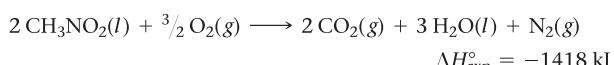
- a. $2\text{H}_2\text{S}(g) + 3\text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l) + 2\text{SO}_2(g)$
 b. $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{SO}_3(g)$
 c. $\text{C}(s) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + \text{H}_2(g)$
 d. $\text{N}_2\text{O}_4(g) + 4\text{H}_2(g) \longrightarrow \text{N}_2(g) + 4\text{H}_2\text{O}(g)$

89. During photosynthesis, plants use energy from sunlight to form glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and oxygen from carbon dioxide and water. Write a balanced equation for photosynthesis and calculate $\Delta H_{\text{rxn}}^\circ$.

MISSED THIS? Read Section 7.9; Watch KCV 7.9, IWE 7.11

90. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) can be made from the fermentation of crops and has been used as a fuel additive to gasoline. Write a balanced equation for the combustion of ethanol and calculate $\Delta H_{\text{rxn}}^\circ$.

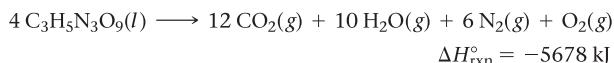
91. Top fuel dragsters and funny cars burn nitromethane as fuel according to the balanced combustion equation:



Calculate the standard enthalpy of formation (ΔH_f°) for nitromethane.

MISSED THIS? Read Section 7.9; Watch KCV 7.9, IWE 7.11

92. The explosive nitroglycerin ($\text{C}_3\text{H}_5\text{N}_3\text{O}_9$) decomposes rapidly upon ignition or sudden impact according to the balanced equation:



Calculate the standard enthalpy of formation (ΔH_f°) for nitroglycerin.

Energy Use and the Environment

93. Determine the mass of CO_2 produced by burning enough of each fuel to produce $1.00 \times 10^2 \text{ kJ}$ of heat. Which fuel contributes least to global warming per kJ of heat produced?

MISSED THIS? Read Sections 7.4, 7.6; KCV 7.4, 7.6, IWE 7.2, 7.7

- a. $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H_{\text{rxn}}^\circ = -802.3 \text{ kJ}$

- b. $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \longrightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \quad \Delta H_{\text{rxn}}^\circ = -2043 \text{ kJ}$

- c. $\text{C}_8\text{H}_{18}(l) + \frac{25}{2}\text{O}_2(g) \longrightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(g) \quad \Delta H_{\text{rxn}}^\circ = -5074.1 \text{ kJ}$

94. Methanol (CH_3OH) has been suggested as a fuel to replace gasoline. Write a balanced equation for the combustion of methanol, find $\Delta H_{\text{rxn}}^\circ$, and determine the mass of carbon dioxide emitted per kJ of heat produced. Use the information from the previous exercise to calculate the same quantity for octane, C_8H_{18} . How does methanol compare to octane with respect to global warming?

95. The citizens of the world burn the fossil fuel equivalent of $7 \times 10^{12} \text{ kg}$ of petroleum per year. Assume that all of this petroleum is in the form of octane (C_8H_{18}) and calculate how much CO_2 (in kg) the world produces from fossil fuel combustion per year. (Hint: Begin by writing a balanced equation for the combustion of octane.) If the atmosphere currently contains approximately $3 \times 10^{15} \text{ kg}$ of CO_2 , how long will it take for the world's fossil fuel combustion to double the amount of atmospheric carbon dioxide?

MISSED THIS? Read Sections 7.4, 7.6; KCV 7.4, 7.6, IWE 7.2, 7.7

- 96.** In a sunny location, sunlight has a power density of about 1 kW/m^2 . Photovoltaic solar cells can convert this power into electricity with 15% efficiency. If a typical home uses 385 kWh of electricity per month, how many square meters of solar cells are required to meet its energy requirements? Assume that electricity can be generated from the sunlight for 8 hours per day.



▲ What area of solar cells do you need to power a home?

CUMULATIVE PROBLEMS

- 97.** The kinetic energy of a rolling billiard ball is given by $\text{KE} = \frac{1}{2}mv^2$. Suppose a 0.17-kg billiard ball is rolling down a pool table with an initial speed of 4.5 m/s. As it travels, it loses some of its energy as heat. The ball slows down to 3.8 m/s and then collides head-on with a second billiard ball of equal mass. The first billiard ball completely stops, and the second one rolls away with a velocity of 3.8 m/s. Assume the first billiard ball is the system. Calculate w , q , and ΔE for the process.

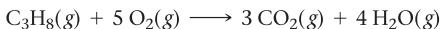
- 98.** A 100-W lightbulb is placed in a cylinder equipped with a movable piston. The lightbulb is turned on for 0.015 hour, and the assembly expands from an initial volume of 0.85 L to a final volume of 5.88 L against an external pressure of 1.0 atm. Use the wattage of the lightbulb and the time it is on to calculate ΔE in joules (assume that the cylinder and lightbulb assembly is the system and assume two significant figures). Calculate w and q .

- 99.** Evaporating sweat cools the body because evaporation is an endothermic process:



Estimate the mass of water that must evaporate from the skin to cool the body by 0.50°C . Assume a body mass of 95 kg and assume that the specific heat capacity of the body is $4.0 \text{ J/g} \cdot ^\circ\text{C}$.

- 100.** LP gas burns according to the exothermic reaction:



$$\Delta H_{\text{rxn}}^\circ = -2044 \text{ kJ}$$

What mass of LP gas is necessary to heat 1.5 L of water from room temperature (25.0°C) to boiling (100.0°C)? Assume that during heating, 15% of the heat emitted by the LP gas combustion goes to heat the water. The rest is lost as heat to the surroundings.

- 101.** Use standard enthalpies of formation to calculate the standard change in enthalpy for the melting of ice. (The ΔH_f° for $\text{H}_2\text{O}(s)$ is -291.8 kJ/mol .) Use this value to calculate the mass of ice required to cool 355 mL of a beverage from room temperature (25.0°C) to 0.0°C . Assume that the specific heat capacity and density of the beverage are the same as those of water.

- 102.** Dry ice is solid carbon dioxide. Instead of melting, solid carbon dioxide sublimes according to the equation:



When dry ice is added to warm water, heat from the water causes the dry ice to sublime more quickly. The evaporating carbon dioxide produces a dense fog often used to create special



▲ When carbon dioxide sublimes, the gaseous CO_2 is cold enough to cause water vapor in the air to condense, forming fog.

effects. In a simple dry ice fog machine, dry ice is added to warm water in a Styrofoam cooler. The dry ice produces fog until it evaporates away, or until the water gets too cold to sublime the dry ice quickly enough. Suppose that a small Styrofoam cooler holds 15.0 L of water heated to 85°C . Use standard enthalpies of formation to calculate the change in enthalpy for dry ice sublimation, and calculate the mass of dry ice that should be added to the water so that the dry ice completely sublimes away when the water reaches 25°C . Assume no heat loss to the surroundings. (The ΔH_f° for $\text{CO}_2(s)$ is -427.4 kJ/mol .)

- 103.** A 25.5-g aluminum block is warmed to 65.4°C and plunged into an insulated beaker containing 55.2 g water initially at 22.2°C . The aluminum and the water are allowed to come to thermal equilibrium. Assuming that no heat is lost, what is the final temperature of the water and aluminum?

- 104.** If 50.0 mL of ethanol (density = 0.789 g/mL) initially at 7.0°C is mixed with 50.0 mL of water (density = 1.0 g/mL) initially at 28.4°C in an insulated beaker, and assuming that no heat is lost, what is the final temperature of the mixture?

- 105.** Palmitic acid ($C_{16}H_{32}O_2$) is a dietary fat found in beef and butter. The caloric content of palmitic acid is typical of fats in general. Write a balanced equation for the complete combustion of palmitic acid and calculate the standard enthalpy of combustion. What is the caloric content of palmitic acid in Cal/g? Do the same calculation for table sugar (sucrose, $C_{12}H_{22}O_{11}$). Which dietary substance (sugar or fat) contains more Calories per gram? The standard enthalpy of formation of palmitic acid is -208 kJ/mol and that of sucrose is -2226.1 kJ/mol . [Use $H_2O(l)$ in the balanced chemical equations because the metabolism of these compounds produces liquid water.]
- 106.** Hydrogen and methanol have both been proposed as alternatives to hydrocarbon fuels. Write balanced reactions for the complete combustion of hydrogen and methanol and use standard enthalpies of formation to calculate the amount of heat released per kilogram of the fuel. Which fuel contains the most energy in the least mass? How does the energy of these fuels compare to that of octane (C_8H_{18})?
- 107.** Derive a relationship between ΔH and ΔE for a process in which the temperature of a fixed amount of an ideal gas changes.
- 108.** Under certain nonstandard conditions, oxidation by $O_2(g)$ of 1 mol of $SO_2(g)$ to $SO_3(g)$ absorbs 89.5 kJ. The enthalpy of formation of $SO_3(g)$ is -204.2 kJ under these conditions. Find the enthalpy of formation of $SO_2(g)$.
- 109.** One tablespoon of peanut butter has a mass of 16 g. It is combusted in a calorimeter whose heat capacity is $120.0\text{ kJ}/^\circ\text{C}$. The temperature of the calorimeter rises from $22.2\text{ }^\circ\text{C}$ to $25.4\text{ }^\circ\text{C}$. Find the food caloric content of peanut butter.
- 110.** A mixture of 2.0 mol of $H_2(g)$ and 1.0 mol of $O_2(g)$ is placed in a sealed evacuated container made of a perfect insulating material at $25\text{ }^\circ\text{C}$. The mixture is ignited with a spark and reacts to form liquid water. Determine the temperature of the water.
- 111.** A 20.0-L volume of an ideal gas in a cylinder with a piston is at a pressure of 3.0 atm. Enough weight is suddenly removed from the piston to lower the external pressure to 1.5 atm. The gas then expands at constant temperature until its pressure is 1.5 atm. Find ΔE , ΔH , q , and w for this change in state.
- 112.** When 10.00 g of phosphorus is burned in $O_2(g)$ to form $P_4O_{10}(s)$, enough heat is generated to raise the temperature of 2950 g of water from $18.0\text{ }^\circ\text{C}$ to $38.0\text{ }^\circ\text{C}$. Calculate the enthalpy of formation of $P_4O_{10}(s)$ under these conditions.
- 113.** The ΔH for the oxidation of sulfur in the gas phase to SO_3 is -204 kJ/mol and for the oxidation of SO_2 to SO_3 is 89.5 kJ/mol . Find the enthalpy of formation of SO_2 under these conditions.
- 114.** The ΔH_f° of $TiI_3(s)$ is -328 kJ/mol and the ΔH° for the reaction $2\text{ Ti}(s) + 3\text{ I}_2(g) \longrightarrow 2\text{ TiI}_3(s)$ is -839 kJ . Calculate the ΔH of sublimation of $I_2(s)$, which is a solid at $25\text{ }^\circ\text{C}$.
- 115.** A gaseous fuel mixture contains 25.3% methane (CH_4), 38.2% ethane (C_2H_6), and the rest propane (C_3H_8) by volume. When the fuel mixture contained in a 1.55 L tank, stored at 755 mmHg and 298 K, undergoes complete combustion, how much heat is emitted? (Assume that the water produced by the combustion is in the gaseous state.)
- 116.** A gaseous fuel mixture stored at 745 mmHg and 298 K contains only methane (CH_4) and propane (C_3H_8). When 11.7 L of this fuel mixture is burned, it produces 769 kJ of heat. What is the mole fraction of methane in the mixture? (Assume that the water produced by the combustion is in the gaseous state.)
- 117.** A copper cube with an edge measuring 1.55 cm and an aluminum cube with an edge measuring 1.62 cm are both heated to $55.0\text{ }^\circ\text{C}$ and submerged in 100.0 mL of water at $22.2\text{ }^\circ\text{C}$. What is the final temperature of the water when equilibrium is reached? (Assume a density of 0.998 g/mL for water.)
- 118.** A pure gold ring and a pure silver ring have a total mass of 14.9 g. The two rings are heated to $62.0\text{ }^\circ\text{C}$ and dropped into 15.0 mL of water at $23.5\text{ }^\circ\text{C}$. When equilibrium is reached, the temperature of the water is $25.0\text{ }^\circ\text{C}$. What is the mass of each ring? (Assume a density of 0.998 g/mL for water.)

CHALLENGE PROBLEMS

- 119.** A typical frostless refrigerator uses 655 kWh of energy per year in the form of electricity. Suppose that all of this electricity is generated at a power plant that burns coal containing 3.2% sulfur by mass and that all of the sulfur is emitted as SO_2 when the coal is burned. If all of the SO_2 goes on to react with rainwater to form H_2SO_4 , what mass of H_2SO_4 does the annual operation of the refrigerator produce? (Hint: Assume that the remaining percentage of the coal is carbon and begin by calculating ΔH_{rxn}° for the combustion of carbon.)
- 120.** A large sport utility vehicle has a mass of $2.5 \times 10^3\text{ kg}$. Calculate the mass of CO_2 emitted into the atmosphere upon accelerating the SUV from 0.0 mph to 65.0 mph. Assume that the required energy comes from the combustion of octane with 30% efficiency. (Hint: Use $KE = \frac{1}{2}mv^2$ to calculate the kinetic energy required for the acceleration.)
- 121.** Combustion of natural gas (primarily methane) occurs in most household heaters. The heat given off in this reaction is used to raise the temperature of the air in the house. Assuming that all the energy given off in the reaction goes to heating up only the air in the house, determine the mass of methane required to heat the air in a house by $10.0\text{ }^\circ\text{C}$. Assume that the house dimensions are $30.0\text{ m} \times 30.0\text{ m} \times 3.0\text{ m}$, specific heat capacity of air is $30\text{ J/K} \cdot \text{mol}$, and 1.00 mol of air occupies 22.4 L for all temperatures concerned.
- 122.** When backpacking in the wilderness, hikers often boil water to sterilize it for drinking. Suppose that you are planning a backpacking trip and will need to boil 35 L of water for your group. What volume of fuel should you bring? Assume that the fuel has an average formula of C_7H_{16} , 15% of the heat generated from combustion goes to heat the water (the rest is lost to the surroundings), the density of the fuel is 0.78 g/mL, the initial temperature of the water is $25.0\text{ }^\circ\text{C}$, and the standard enthalpy of formation of C_7H_{16} is -224.4 kJ/mol .
- 123.** An ice cube of mass 9.0 g is added to a cup of coffee. The coffee's initial temperature is $90.0\text{ }^\circ\text{C}$ and the cup contains 120.0 g of liquid. Assume the specific heat capacity of the coffee is the same as that of water. The heat of fusion of ice (the heat associated with ice melting) is 6.0 kJ/mol . Find the temperature of the coffee after the ice melts.
- 124.** Find ΔH , ΔE , q , and w for the freezing of water at $-10.0\text{ }^\circ\text{C}$. The specific heat capacity of ice is $2.04\text{ J/g} \cdot {^\circ\text{C}}$ and its heat of fusion (the quantity of heat associated with melting) is -332 J/g .
- 125.** Starting from the relationship between temperature and kinetic energy for an ideal gas, find the value of the molar heat capacity of an ideal gas when its temperature is changed at constant volume. Find its molar heat capacity when its temperature is changed at constant pressure.

- 126.** An amount of an ideal gas expands from 12.0 L to 24.0 L at a constant pressure of 1.0 atm. Then the gas is cooled at a constant volume of 24.0 L back to its original temperature. Then it contracts back to its original volume. Find the total heat flow for the entire process.
- 127.** The heat of vaporization of water at 373 K is 40.7 kJ/mol. Find q , w , ΔE , and ΔH for the evaporation of 454 g of water at this temperature at 1 atm.
- 128.** Find ΔE , ΔH , q , and w for the change in state of 1.0 mol $\text{H}_2\text{O}(l)$ at 80 °C to $\text{H}_2\text{O}(g)$ at 110 °C. The heat capacity of $\text{H}_2\text{O}(l)$

= 75.3 J/mol K, the heat capacity of $\text{H}_2\text{O}(g)$ = 25.0 J/mol K, and the heat of vaporization of H_2O is 40.7×10^3 J/mol at 100 °C.

- 129.** The heat of combustion of liquid octane (C_8H_{18}) to carbon dioxide and liquid water at 298 K is -1303 kJ/mol. Find ΔE for this reaction.
- 130.** Find ΔH for the combustion of ethanol ($\text{C}_2\text{H}_6\text{O}$) to carbon dioxide and liquid water from the following data. The heat capacity of the bomb calorimeter is 34.65 kJ/K, and the combustion of 1.765 g of ethanol raises the temperature of the calorimeter from 294.33 K to 295.84 K.

CONCEPTUAL PROBLEMS

- 131.** Which statement is true of the internal energy of the system and its surroundings following a process in which $\Delta E_{\text{sys}} = +65$ kJ? Explain.
- The system and the surroundings both lose 65 kJ of energy.
 - The system and the surroundings both gain 65 kJ of energy.
 - The system loses 65 kJ of energy and the surroundings gain 65 kJ of energy.
 - The system gains 65 kJ of energy and the surroundings lose 65 kJ of energy.
- 132.** The internal energy of an ideal gas depends only on its temperature. Which statement is true of an isothermal (constant-temperature) expansion of an ideal gas against a constant external pressure? Explain.
- ΔE is positive.
 - w is positive.
 - q is positive.
 - ΔE is negative.
- 133.** Which expression describes the heat evolved in a chemical reaction when the reaction is carried out at constant pressure? Explain.
- $\Delta E - w$
 - ΔE
 - $\Delta E - q$
- 134.** Two identical new refrigerators are plugged in for the first time. Refrigerator A is empty (except for air) and refrigerator B is filled with jugs of water. The compressors of both refrigerators immediately turn on and begin cooling the interiors of the refrigerators. After two hours, the compressor of refrigerator A turns off, while the compressor of refrigerator B continues to run. The next day, the compressor of refrigerator A can be heard turning on and off every few minutes, while the compressor of refrigerator B turns off and on every hour or so (and stays on longer each time). Explain these observations.
- 135.** A 1-kg cylinder of aluminum and 1-kg jug of water, both at room temperature, are put into a refrigerator. After 1 hour, the temperature of each object is measured. One of the objects is much cooler than the other. Which one is cooler and why?
- 136.** Two substances A and B, initially at different temperatures, are thermally isolated from their surroundings and allowed to come into thermal contact. The mass of substance A is twice the mass of substance B, but the specific heat capacity of substance B is four times the specific heat capacity of substance A. Which substance will undergo a larger change in temperature?
- 137.** When 1 mol of a gas burns at constant pressure, it produces 2418 J of heat and does 5 J of work. Determine ΔE , ΔH , q , and w for the process.
- 138.** In an exothermic reaction, the reactants lose energy, and the reaction feels hot to the touch. Explain why the reaction feels hot even though the reactants are losing energy. Where does the energy come from?
- 139.** Which statement is true of a reaction in which ΔV is positive? Explain.
- $\Delta H = \Delta E$
 - $\Delta H > \Delta E$
 - $\Delta H < \Delta E$

QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 140.** Have each group member write a problem involving the transfer of heat from one material in Table 7.4 to another material in the table. Working as a group, solve each problem. The group member who wrote each problem may act as the group facilitator when the group is working on his or her problem. What do all of your problems have in common? How do they differ?
- 141.** Classify each process as endothermic or exothermic. What is the sign of ΔH for each process? Explain your answers.
- gasoline burning in an engine
 - steam condensing on a mirror
 - water boiling in a pot
- Provide at least two additional examples of exothermic processes and two additional examples of endothermic processes. Have each member of your group provide an example.
- 142.** A propane tank on a home barbecue contains 10.4×10^3 g of propane.
- Write the balanced chemical reaction for the combustion of gaseous propane (C_3H_8) to form water vapor and gaseous carbon dioxide.

Active Classroom Learning

- Use the value for ΔH_{rxn} provided in the text to calculate the total amount of heat produced when the entire contents of the tank of propane is burned.
 - What mass of water could be warmed from 25 °C to 100 °C with this much heat?
- 143.** Consider the decomposition of liquid hydrogen peroxide (H_2O_2) to form water and oxygen.
- What is the heat of formation for hydrogen peroxide?
 - What is the heat of formation for liquid water?
 - What is the heat of formation for gaseous oxygen? Why?
 - Write the balanced chemical equations that correspond to the ΔH values you looked up for parts a, b, and c.
 - Write the balanced chemical equation for the decomposition of hydrogen peroxide to form water and oxygen. (Write the equation such that the coefficient on oxygen is 1.)
 - What is the heat of reaction for the process in part e?
 - Draw a scale diagram of this reaction (1 cm = 100 kJ) that shows the relative energies of reactants (on the left), products (on the right), and the elements in their most stable states (in the middle). Label all the energies you know.



DATA INTERPRETATION AND ANALYSIS

Heat Content of Fuels

- 144.** The heating value of combustible fuels is evaluated based on the quantities known as the higher heating value (HHV) and the lower heating value (LHV). The HHV has a higher absolute value and assumes that the water produced in the combustion reaction is formed in the liquid state. The LHV has a lower absolute value and assumes that the water produced in the combustion reaction is formed in the gaseous state. The LHV is therefore the sum of the HHV (which is negative) and the heat of vaporization of water for the number of moles of water formed in the reaction (which is positive). The table lists the enthalpy of combustion—which is equivalent to the HHV—for several closely related hydrocarbons.

| Hydrocarbon | ΔH_{comb} (kJ/mol) |
|------------------------------|-----------------------------------|
| $\text{CH}_4(g)$ | -890 |
| $\text{C}_2\text{H}_6(g)$ | -1560 |
| $\text{C}_3\text{H}_8(g)$ | -2219 |
| $\text{C}_4\text{H}_{10}(g)$ | -2877 |
| $\text{C}_5\text{H}_{12}(l)$ | -3509 |
| $\text{C}_6\text{H}_{14}(l)$ | -4163 |
| $\text{C}_7\text{H}_{16}(l)$ | -4817 |
| $\text{C}_8\text{H}_{18}(l)$ | -5470 |

Use the information in the table to answer the following questions.

- Write two balanced equations for the combustion of C_3H_8 ; one assuming the formation of liquid water and the other assuming the formation of gaseous water.
- Given that the heat of vaporization of water is 44.0 kJ/mol, what is ΔH_{rxn} for each reaction in part a? Which quantity is the HHV? The LHV?
- When propane is used to cook in an outdoor grill, is the amount of heat released the HHV or the LHV? What amount of heat is released upon combustion of 1.00 kg of propane in an outdoor grill?
- For each CH_2 unit added to a hydrocarbon, what is the average increase in the absolute value of ΔH_{comb} ?

Cc

ANSWERS TO CONCEPTUAL CONNECTIONS

System and Surroundings

- 7.1 (a)** When ΔE_{sys} is negative, energy flows out of the system and into the surroundings. The energy increase in the surroundings must exactly match the decrease in the system.

Heat and Work

- 7.2 (b)** Rolling a metal cylinder up a ramp requires that a force be applied to the cylinder over a distance and is therefore work.

The Heat Capacity of Water

- 7.3 (a)** Bring the water into your sleeping bag; it has the higher heat capacity and will therefore release more heat as it cools.

Thermal Energy Transfer

- 7.4 (c)** The specific heat capacity of substance B is twice that of A, but since the mass of B is half that of A, the quantity $m \times C_s$ is identical for both substances so that the final temperature is exactly midway between the two initial temperatures.

Pressure–Volume Work

- 7.5 (d)** The work done is given by $w = -P_{\text{ext}} \cdot \Delta V$, which is equal to $-1.00 \text{ atm} (2.00 \text{ L} - 1.00 \text{ L}) = -1.00 \text{ L} \cdot \text{atm}$. Since $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$, the work done (rounded to the correct number of significant figures) is -101 J .

The Difference between ΔH and ΔE

- 7.6 (c)** ΔH represents only the heat exchanged; therefore, $\Delta H = -2658 \text{ kJ}$. ΔE represents the heat *and work* exchanged; therefore, $\Delta E = -2661 \text{ kJ}$. The signs of both ΔH and ΔE are

negative because heat and work are flowing out of the system and into the surroundings. Notice that the values of ΔH and ΔE are similar in magnitude, as is the case in many chemical reactions.

Exothermic and Endothermic Reactions

- 7.7 (b)** The temperature falls. An endothermic reaction absorbs heat from the surroundings. Since the flask is part of the immediate surroundings, the temperature of the flask falls.

Thermochemical Equations

- 7.8 (c)** From the thermochemical equation, you can get the ratio $2 \text{ mol A} : -51.0 \text{ J} \quad 6 \text{ mol A} \left(\frac{-51.0 \text{ J}}{2 \text{ mol A}} \right) = -153 \text{ J}$

Constant-Pressure versus Constant-Volume Calorimetry

- 7.9 (a)** The value of q_{rxn} with the greater magnitude (-12.5 kJ) must have come from the bomb calorimeter. Recall that $\Delta E_{\text{rxn}} = q_{\text{rxn}} + w_{\text{rxn}}$. In a bomb calorimeter, the energy change that occurs in the course of the reaction all takes the form of heat (q). In a coffee-cup calorimeter, the amount of energy released as heat may be smaller because some of the energy may be used to do work (w).

Relationships Involving ΔH_{rxn}

- 7.10 (d)** When a chemical equation is multiplied by some factor, ΔH_{rxn} must be multiplied by the same factor and when a chemical equation is reversed, ΔH_{rxn} changes sign. So $\Delta H_{\text{rxn}} = -2(122 \text{ J}) = -144 \text{ J}$.