C H A P T E R 7
Energy and Chemistry

Opening Essay

It takes energy to launch a spaceship into space. If it takes 1 energy unit to warm 0.25 g of water by 1°C, then it takes over 15,100 energy units to put that 0.25 g of water into earth orbit. The most powerful engines designed to lift rockets into space were part of the Saturn V rocket, that was built by the National Aeronautics and Space Administration (NASA). The rocket had three stages, with the first stage having the capability of launching about 3.5 million kg of mass. About 2.3 million kg was the actual fuel for the first stage; rockets in space have the unpleasant task of having to take their own chemicals with them to provide thrust.

It takes a lot of energy to launch a rocket into space. The Saturn V rocket used five of the most powerful engines ever built to take its initial step into orbit.

© Thinkstock

Having to carry its own fuel puts a lot of mass burden on an engine in space. This is why NASA is developing other types of engines to minimize fuel mass. An ion thruster uses xenon atoms that have had at least one electron removed from their atoms. The resulting ions can be accelerated by electric fields, causing a thrust. Because xenon atoms are very large for atoms, the thrusting efficiency is high even though the actual thrust is low. Because of this, ion engines are useful only in space.

Ion drives have low thrust but high efficiency. They have already been used on several space missions, including NASA's *Deep Space 1* spacecraft and Japan's *Hayabusa* asteroid sampling probe.
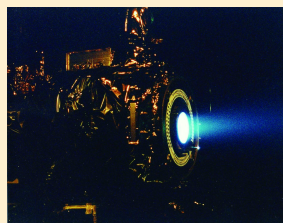
Source: Photo courtesy of NASA, http://commons.wikimedia.org/wiki/File:Ion_Engine_Test_Firing_-_GPN-2000-000482.jpg.

Energy is a very important quantity in science and the world around us. Although most of our energy ultimately comes from the sun, much of the energy we use on a daily basis is rooted in chemical reactions. The gasoline in

your car, the electricity in your house, the food in your diet—all provide substances for chemical reactions to provide energy (gasoline, food) or are produced from chemical reactions (electricity, about 50% of which is generated by burning coal). As such, it is only natural that the study of chemistry involves energy.

1. ENERGY

L E A R N I N G   O B J E C T I V E S

1. **Define *energy*.**
2. **Know the units of energy.**
3. **Understand the law of conservation of energy.**

energy
The ability to do work.

joule
The SI unit of energy.

Energy is the ability to do work. Think about it: when you have a lot of energy, you can do a lot of work; but if you're low on energy, you don't want to do much work. Work (w) itself is defined as a force (F) operating over a distance (Δx):

$$w = F \times \Delta x$$

In SI, force has units of newtons (N), while distance has units of meters. Therefore, work has units of N·m. This compound unit is redefined as a **joule** (J):

$$1 \text{ joule} = 1 \text{ newton·meter}$$

$$1 \text{ J} = 1 \text{ N·m}$$

Because energy is the ability to do work, energy is also measured in joules. This is the primary unit of energy we will use here.

How much is 1 J? It is enough to warm up about one-fourth of a gram of water by 1°C. It takes about 12,000 J to warm a cup of coffee from room temperature to 50°C. So a joule is not a lot of energy. It will not be uncommon to measure energies in thousands of joules, so the kilojoule (kJ) is a common unit of energy, with 1 kJ equal to 1,000 J.

An older—but still common—unit of energy is the *calorie*. The calorie (cal) was originally defined in terms of warming up a given quantity of water. The modern definition of calorie equates it to joules:

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

One area where the calorie is used is in nutrition. Energy contents of foods are often expressed in calories. However, the calorie unit used for foods is actually the kilocalorie (kcal). Most foods indicate this by spelling the word with a capital C—Calorie. Figure 7.1 shows one example. So be careful counting calories when you eat!

E X A M P L E   1

The label in Figure 7.1 states that the serving has 38 Cal. How many joules is this?

Solution

We recognize that with a capital C, the Calories unit is actually kilocalories. To determine the number of joules, we convert first from kilocalories to calories (using the definition of the *kilo-* prefix) and then from calories to joules (using the relationship between calories and joules). So

$$38 \text{ kcal} \times \frac{1,000 \text{ cal}}{1 \text{ kcal}} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 160,000 \text{ J}$$

Test Yourself

A serving of breakfast cereal usually has 110 Cal. How many joules of energy is this?

Answer

460,000 J

FIGURE 7.1
Calories on Food Labels

This label expresses the energy content of the food, but in Calories (which are actually kilocalories).

Nutrition Facts
Serving Size 3 oz. (85g)

Amount Per Serving	As Served
Calories 38	Calories from Fat 0

	% Daily Value
Total Fat 0g	0%
Saturated Fat 0g	0%
Cholesterol 0g	0%
Sodium 0g	2%
Total Carbohydrate 0g	3%
Dietary Fiber 0g	8%
Sugars 0g	
Protein 0g	

Vitamin A 270%	•	**Vitamin C** 10%
Calcium 2%	•	**Iron** 0%

Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs:

		Calories	2,000	2,500
Total Fat	Less than		65g	80g
Sat Fat	Less than		20g	80g
Cholesterol	Less than		300mg	300mg
Sodium	Less than		2,400mg	2,400mg
Total Carbohydrate			300g	375g
Dietary Fiber			25g	30g

© *Thinkstock*

system
The part of the universe under study.

isolated system
A system that does not allow a transfer of energy or matter into or out of the system.

law of conservation of energy
The total energy of an isolated system does not increase or decrease.

In the study of energy, we use the term **system** to describe the part of the universe under study: a beaker, a flask, or a container whose contents are being observed and measured. An **isolated system** is a system that does not allow a transfer of energy or matter into or out of the system. A good approximation of an isolated system is a closed, insulated thermos-type bottle. The fact that the thermos-type bottle is closed keeps matter from moving in or out, and the fact that it is insulated keeps energy from moving in or out.

One of the fundamental ideas about the total energy of an isolated system is that is does not increase or decrease. When this happens to a quantity, we say that the quantity is *conserved*. The statement that the total energy of an isolated system does not change is called the **law of conservation of energy**. As a scientific law, this concept occupies the highest level of understanding we have about the natural universe.

K E Y   T A K E A W A Y S

- Energy is the ability to do work and uses the unit joule.
- The law of conservation of energy states that the total energy of an isolated system does not increase or decrease.

E X E R C I S E S

1. Define *energy*. How is work related to energy?

2. Give two units of energy and indicate which one is preferred.

3. Express the quantity of 422 J in calories.

4. Express the quantity of 3.225 kJ in calories.

5. Express the quantity 55.69 cal in joules.

6. Express the quantity 965.33 kcal in joules.

7. How does a Calorie differ from a calorie?

8. Express the quantity 965.33 Cal in joules.

9. What is the law of conservation of energy?

10. What does the word *conserved* mean as applied to the law of conservation of energy?

---

2. WORK AND HEAT

L E A R N I N G   O B J E C T I V E S

1. **Define a type of work in terms of pressure and volume.**
2. **Define *heat*.**
3. **Relate the amount of heat to a temperature change.**

We have already defined work as a force acting through a distance. It turns out that there are other equivalent definitions of work that are also important in chemistry.

When a certain volume of a gas expands, it works against an external pressure to expand (Figure 7.2). That is, the gas must perform work. Assuming that the external pressure P_{ext} is constant, the amount of work done by the gas is given by the equation

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

where ΔV is the change in volume of the gas. This term is always the final volume minus the initial volume,

$$\Delta V = V_{final} - V_{initial}$$

and can be positive or negative, depending on whether V_{final} is larger (is expanding) or smaller (is contracting) than $V_{initial}$. The negative sign in the equation for work is important and implies that as volume expands (ΔV is positive), the gas in the system is *losing* energy as work. On the other hand, if the gas is contracting, ΔV is negative, and the two negative signs make the work positive, so energy is being added to the system.

FIGURE 7.2 **Volume versus Pressure**

When a gas expands against an external pressure, the gas does work.
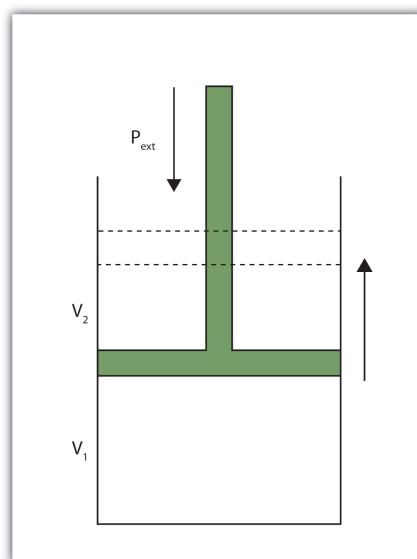
Finally, let us consider units. Volume changes are usually expressed in units like liters, while pressures are usually expressed in atmospheres. When we use the equation to determine work, the unit for work

comes out as liter·atmospheres, or L·atm. This is not a very common unit for work. However, there is a conversion factor between L·atm and the common unit of work, joules:

$$1 \text{ L·atm} = 101.32 \text{ J}$$

Using this conversion factor and the previous equation for work, we can calculate the work performed when a gas expands or contracts.

E X A M P L E   2

What is the work performed by a gas if it expands from 3.44 L to 6.19 L against a constant external pressure of 1.26 atm? Express the final answer in joules.

Solution

First we need to determine the change in volume, ΔV. A change is always the final value minus the initial value:

$$\Delta V = V_{final} - V_{initial} = 6.19 \text{ L} - 3.44 \text{ L} = 2.75 \text{ L}$$

Now we can use the definition of work to determine the work done:

$$w = -P_{ext} \cdot \Delta V = -(1.26 \text{ atm})(2.75 \text{ L}) = -3.47 \text{ L·atm}$$

Now we construct a conversion factor from the relationship between liter·atmospheres and joules:

$$-3.47 \text{ L·atm} \times \frac{101.32 \text{ J}}{1 \text{ L·atm}} = -351 \text{ J}$$

We limit the final answer to three significant figures, as appropriate.

Test Yourself

What is the work performed when a gas expands from 0.66 L to 1.33 L against an external pressure of 0.775 atm?

Answer

−53 J

Heat is another aspect of energy. **Heat** is the transfer of energy from one body to another due to a difference in temperature. For example, when we touch something with our hands, we interpret that object as either hot or cold depending on how energy is transferred: If energy is transferred into your hands, the object feels hot. If energy is transferred from your hands to the object, your hands feel cold. Because heat is a measure of energy transfer, heat is also measured in joules.

For a given object, the amount of heat (q) involved is proportional to two things: the mass of the object (m) and the temperature change (ΔT) evoked by the energy transfer. We can write this mathematically as

$$q \propto m \times \Delta T$$

where $\propto$ means "is proportional to." To make a proportionality an equality, we include a proportionality constant. In this case, the proportionality constant is labeled c and is called the **specific heat capacity**, or, more succinctly, **specific heat**:

$$q = mc\Delta T$$

where the mass, specific heat, and change in temperature are multiplied together. Specific heat is a measure of how much energy is needed to change the temperature of a substance; the larger the specific heat, the more energy is needed to change the temperature. The units for specific heat are $\frac{J}{g \cdot {}^\circ C}$ or $\frac{J}{g \cdot K}$, depending on what the unit of ΔT is. You may note a departure from the insistence that temperature be expressed in Kelvin. That is because a *change* in temperature has the same value whether the temperatures are expressed in degrees Celsius or kelvins.

heat

The transfer of energy from one body to another due to a difference in temperature.

specific heat capacity

The proportionality constant between heat, mass, and temperature change; also called specific heat.

EXAMPLE 3

Calculate the heat involved when 25.0 g of Fe increase temperature from 22°C to 76°C. The specific heat of Fe is 0.449 J/g·°C.

Solution

First we need to determine ΔT. A change is always the final value minus the initial value:

$$\Delta T = 76°C - 22°C = 54°C$$

Now we can use the expression for q, substitute for all variables, and solve for heat:

$$q = (25.0 \, \cancel{g})\left(0.449 \, \frac{J}{\cancel{g} \cdot \cancel{°C}}\right)(54 \, \cancel{°C}) = 610 \, J$$

Note how the g and °C units cancel, leaving J, a unit of heat. Also note that this value of q is inherently positive, meaning that energy is going into the system.

Test Yourself

Calculate the heat involved when 76.5 g of Ag increase temperature from 17.8°C to 144.5°C. The specific heat of Ag is 0.233 J/g·°C.

Answer

2,260 J

As with any equation, when you know all but one variable in the expression for q, you can determine the remaining variable by using algebra.

EXAMPLE 4

It takes 5,408 J of heat to raise the temperature of 373 g of Hg by 104°C. What is the specific heat of Hg?

Solution

We can start with the equation for q, but now different values are given, and we need to solve for specific heat. Note that ΔT is given directly as 104°C. Substituting,

$$5,408 \, J = (373 \, g)c(104°C)$$

We divide both sides of the equation by 373 g and 104°C:

$$c = \frac{5408 \, J}{(373 \, g)(104°C)}$$

Combining the numbers and bringing together all the units, we get

$$c = 0.139 \frac{J}{g \cdot °C}$$

Test Yourself

Gold has a specific heat of 0.129 J/g·°C. If 1,377 J are needed to increase the temperature of a sample of gold by 99.9°C, what is the mass of the gold?

Answer

107 g

Table 7.1 lists the specific heats of some substances. Specific heat is a physical property of substances, so it is a characteristic of the substance. The general idea is that the lower the specific heat, the less energy is required to change the temperature of the substance by a certain amount.

TABLE 7.1 **Specific Heats of Various Substances**

Substance	Specific Heat (J/g·°C)
water	4.184
iron	0.449
gold	0.129
mercury	0.139
aluminum	0.900
ethyl alcohol	2.419
magnesium	1.03
helium	5.171
oxygen	0.918

KEY TAKEAWAYS

- Work can be defined as a gas changing volume against a constant external pressure.
- Heat is the transfer of energy due to temperature differences.
- Heat can be calculated in terms of mass, temperature change, and specific heat.

EXERCISES

1. Give two definitions of work.

2. What is the sign on work when a sample of gas increases its volume? Explain why work has that sign.

3. What is the work when a gas expands from 3.00 L to 12.60 L against an external pressure of 0.888 atm?

4. What is the work when a gas expands from 0.666 L to 2.334 L against an external pressure of 2.07 atm?

5. What is the work when a gas contracts from 3.45 L to 0.97 L under an external pressure of 0.985 atm?

6. What is the work when a gas contracts from 4.66 L to 1.22 L under an external pressure of 3.97 atm?

7. Like work, the sign on heat can be positive or negative. What is happening to the total energy of a system if heat is positive?

8. Like work, the sign on heat can be positive or negative. What is happening to the total energy of a system if heat is negative?

9. What is the heat when 55.6 g of Fe increase temperature from 25.6°C to 177.9°C? The heat capacity of Fe is in Table 7.1.

10. What is the heat when 0.444 g of Au increases temperature from 17.8°C to 222.5°C? The heat capacity of Au is in Table 7.1.

11. What is the heat when 245 g of H_2O cool from 355 K to 298 K? The heat capacity of H_2O is in Table 7.1.

12. What is the heat when 100.0 g of Mg cool from 725 K to 552 K? The heat capacity of Mg is in Table 7.1.

13. It takes 452 J of heat to raise the temperature of a 36.8 g sample of a metal from 22.9°C to 98.2°C. What is the heat capacity of the metal?

14. It takes 2,267 J of heat to raise the temperature of a 44.5 g sample of a metal from 33.9°C to 288.3°C. What is the heat capacity of the metal?

15. An experimenter adds 336 J of heat to a 56.2 g sample of Hg. What is its change in temperature? The heat capacity of Hg is in Table 7.1.

16. To a 0.444 g sample of H_2O, 23.4 J of heat are added. What is its change in temperature? The heat capacity of H_2O is in Table 7.1.

17. An unknown mass of Al absorbs 187.9 J of heat and increases its temperature from 23.5°C to 35.6°C. What is the mass of the aluminum? How many moles of aluminum is this?

18. A sample of He goes from 19.4°C to 55.9°C when 448 J of energy are added. What is the mass of the helium? How many moles of helium is this?

<div>

A N S W E R S

1. Work is a force acting through a distance or a volume changing against some pressure.

3. −864 J

5. 248 J

7. When heat is positive, the total energy of the system is increasing.

9. 3.80×10^3 J

11. −58,400 J

13. 0.163 J/g·°C

15. 43.0°C

17. 17.3 g; 0.640 mol

</div>

3. ENTHALPY AND CHEMICAL REACTIONS

L E A R N I N G   O B J E C T I V E S

1. **Define *enthalpy*.**
2. **Properly express the enthalpy change of chemical reactions.**
3. **Explain how enthalpy changes are measured experimentally.**

Now that we have shown how energy, work, and heat are related, we are ready to consider energy changes in chemical reactions. A fundamental concept is that *every chemical reaction occurs with a concurrent change in energy*. Now we need to learn how to properly express these energy changes.

Our study of gases in Chapter 6 and our definition of work in Section 2 indicate that conditions like pressure, volume, and temperature affect the energy content of a system. What we need is a definition of energy that holds when some of these conditions are specified (somewhat similar to our definition of standard temperature and pressure in our study of gases). We define the **enthalpy change** (ΔH) as the heat of a process when pressure is held constant:

$$\Delta H \equiv q \quad \text{at constant pressure}$$

> **enthalpy change**
>
> The heat of a process at constant pressure; denoted ΔH.

The letter H stands for "enthalpy," a kind of energy, while the Δ implies a change in the quantity. We will always be interested in the change in H, rather than the absolute value of H itself.

When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line. For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \; \Delta H = -570 \text{ kJ}$$

> **thermochemical equation**
>
> A chemical equation that includes an enthalpy change.

A chemical equation that includes an enthalpy change is called a **thermochemical equation**. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

EXAMPLE 5

Write the thermochemical equation for the reaction of $PCl_3(g)$ with $Cl_2(g)$ to make $PCl_5(g)$, which has an enthalpy change of −88 kJ.

Solution

The thermochemical equation is

$$PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g) \; \Delta H = -88 \text{ kJ}$$
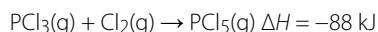
Test Yourself

Write the thermochemical equation for the reaction of $N_2(g)$ with $O_2(g)$ to make $2NO(g)$, which has an enthalpy change of 181 kJ.

Answer

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \; \Delta H = 181 \text{ kJ}$$
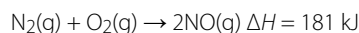
You may have noticed that the ΔH for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be **endothermic**, while a chemical reaction that has a negative ΔH is said to be **exothermic**.

What does it mean if the ΔH of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be diagrammed as in part (a) in Figure 7.3: the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) in Figure 7.3. If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

endothermic

A chemical reaction that has a positive change in enthalpy.

exothermic

A chemical reaction that has a negative change in enthalpy.

FIGURE 7.3 **Reaction Energy**

(a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy). (b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).
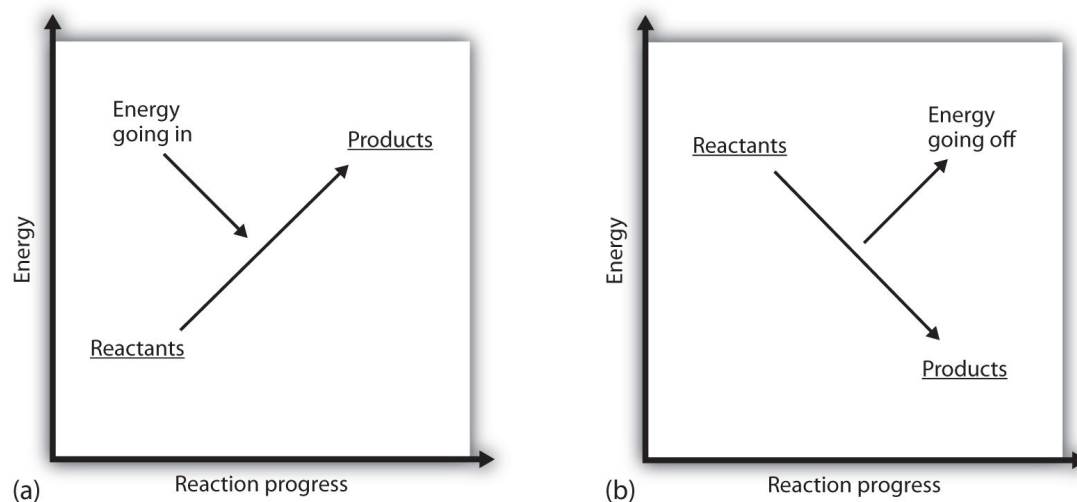
EXAMPLE 6

Consider this thermochemical equation.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)\ \Delta H = -565\ kJ$$
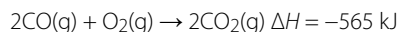
Is it exothermic or endothermic? How much energy is given off or absorbed?

Solution

By definition, a chemical reaction that has a negative ΔH is exothermic, meaning that this much energy—in this case, 565 kJ—is given off by the reaction.

Test Yourself

Consider this thermochemical equation.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)\ \Delta H = 42\ kJ$$

Is it exothermic or endothermic? How much energy is given off or absorbed?

Answer

Endothermic; 42 kJ are absorbed.

How are ΔH values measured experimentally? Actually, ΔH is not measured; q is measured. But the measurements are performed under conditions of constant pressure, so ΔH is equal to the q measured.

Experimentally, q is measured by taking advantage of the equation
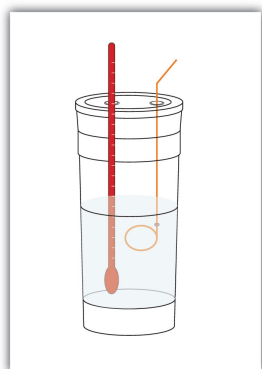
$$q = mc\Delta T$$

calorimeter

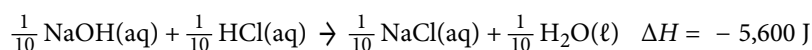A container used to measure the heat of a chemical reaction.

calorimetry

The process of measuring enthalpy changes for chemical reactions.

FIGURE 7.4
Calorimeters

A simple calorimeter can be constructed from some nested foam coffee cups, a cover, a thermometer, and a stirrer.

We premeasure the mass of the chemicals in a system. Then we let the chemical reaction occur and measure the change in temperature (ΔT) of the system. If we know the specific heat of the materials in the system (typically, we do), we can calculate q. That value of q is numerically equal to the ΔH of the process, which we can scale up to a molar scale. The container in which the system resides is typically insulated, so any energy change goes into changing the temperature of the system, rather than being leaked from the system. The container is referred to as a **calorimeter**, and the process of measuring changes in enthalpy is called **calorimetry**.

For example, suppose 4.0 g of NaOH, or 0.10 mol of NaOH, are dissolved to make 100.0 mL of aqueous solution, while 3.65 g of HCl, or 0.10 mol of HCl, are dissolved to make another 100.0 mL of aqueous solution. The two solutions are mixed in an insulated calorimeter, a thermometer is inserted, and the calorimeter is covered (see Figure 7.4 for an example setup). The thermometer measures the temperature change as the following chemical reaction occurs:

$$NaOH\ (aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)$$
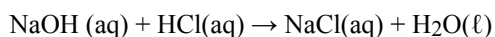
An observer notes that the temperature increases from 22.4°C to 29.1°C. Assuming that the heat capacities and densities of the solutions are the same as those of pure water, we now have the information we need to determine the enthalpy change of the chemical reaction. The total amount of solution is 200.0 mL, and with a density of 1.00 g/mL, we thus have 200.0 g of solution. Using the equation for q, we substitute for our experimental measurements and the specific heat of water (Table 7.1):

$$q = (200.0\ \cancel{g})\left(4.184\ \frac{J}{\cancel{g} \cdot \cancel{°C}}\right)(6.7\ \cancel{°C})$$

Solving for q, we get

$$q = 5{,}600\ J \equiv \Delta H\ \text{for the reaction}$$

The heat q is equal to the ΔH for the reaction because the chemical reaction occurs at constant pressure. However, the reaction is giving off this amount of energy, so the actual sign on ΔH is negative:

$$\Delta H = -5{,}600\ J\ \text{for the reaction}$$

Thus, we have the following thermochemical equation for the chemical reaction that occurred in the calorimeter:

$$\tfrac{1}{10}\,NaOH(aq) + \tfrac{1}{10}\,HCl(aq) \rightarrow \tfrac{1}{10}\,NaCl(aq) + \tfrac{1}{10}\,H_2O(\ell) \quad \Delta H = -5{,}600\ J$$

The 1/10 coefficients are present to remind us that we started with one-tenth of a mole of each reactant, so we make one-tenth of a mole of each product. Typically, however, we report thermochemical equations in terms of moles, not one-tenth of a mole. To scale up to molar quantities, we must multiply the coefficients by 10. However, when we do this, we get 10 times as much energy. Thus, we have

$$NaOH\ (aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)\ \Delta H = -56{,}000\ J$$
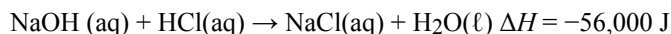
The ΔH can be converted into kJ units, so our final thermochemical equation is

$$NaOH\ (aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)\ \Delta H = -56\ kJ$$

We have just taken our experimental data from calorimetry and determined the enthalpy change of a chemical reaction. Similar measurements on other chemical reactions can determine the ΔH values of any chemical reaction you want to study.

E X A M P L E 7

A 100 mL solution of 0.25 mol of Ca^{2+}(aq) was mixed with 0.50 mol of F^-(aq) ions, and CaF_2 was precipitated:

$$Ca^{2+}(aq) + 2F^-(aq) \rightarrow CaF_2(s)$$
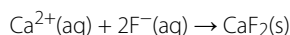
The temperature of the solution increased by 10.5°C. What was the enthalpy change for the chemical reaction? What was the enthalpy change for the production of 1 mol of CaF_2? Assume that the solution has the same density and specific heat as water.

Solution

Because we are given ΔT directly, we can determine the heat of the reaction, which is equal to ΔH:

$$q = (100\ \cancel{g})\left(4.184\ \frac{J}{\cancel{g} \cdot \cancel{°C}}\right)(10.5°\cancel{C})$$

Solving for q, we get

$$q = 4{,}400\ J$$

Therefore, $\Delta H = -4{,}400\ J$.

According to the stoichiometry of the reaction, exactly 0.25 mol of CaF_2 will form, so this quantity of heat is for 0.25 mol. For 1 mol of CaF_2, we need to scale up the heat by a factor of four:

$$q = 4{,}400\ J \times 4 = 17{,}600\ J\ for\ 1\ mol\ CaF_2$$

On a molar basis, the change in enthalpy is

$$\Delta H = -17{,}600\ J = -17.6\ kJ$$

Test Yourself

In a calorimeter at constant pressure, 0.10 mol of CH_4(g) and 0.20 mol of O_2(g) are reacted.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
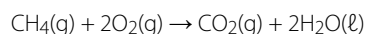
The reaction warms 750.0 g of H_2O by 28.4°C. What is ΔH for the reaction on a molar scale?

Answer

−891 kJ

K E Y   T A K E A W A Y S

- Every chemical reaction occurs with a concurrent change in energy.
- The change in enthalpy equals heat at constant pressure.
- Enthalpy changes can be expressed by using thermochemical equations.
- Enthalpy changes are measured by using calorimetry.

E X E R C I S E S

1. Under what circumstances are q and ΔH the same?

2. Under what circumstances are q and ΔH different?

3. Hydrogen gas and chlorine gas react to make hydrogen chloride gas with an accompanying enthalpy change of −184 kJ. Write a properly balanced thermochemical equation for this process.

4. Propane (C_3H_8) reacts with elemental oxygen gas to produce carbon dioxide and liquid water with an accompanying enthalpy change of −2,220 kJ. Write a properly balanced thermochemical equation for this process.

5. Nitrogen gas reacts with oxygen gas to make NO(g) while absorbing 180 kJ. Write a properly balanced thermochemical equation for this process.

6. Solid sodium reacts with chlorine gas to make solid sodium chloride while giving off 772 kJ. Write a properly balanced thermochemical equation for this process.

7. Hydrogen gas and chlorine gas react to make hydrogen chloride gas with an accompanying enthalpy change of −184 kJ. Is this process endothermic or exothermic?

8. Propane (C_3H_8) reacts with elemental oxygen gas to produce carbon dioxide while giving off 2,220 kJ of energy. Is this process endothermic or exothermic?

9. Nitrogen gas reacts with oxygen gas to make NO(g) while absorbing 180 kJ. Is this process exothermic or endothermic?

10. Sodium metal can react with nitrogen to make sodium azide (NaN_3) with a ΔH of 21.72 kJ. Is this process exothermic or endothermic?

11. Draw an energy level diagram for the chemical reaction in Exercise 8. (See Figure 7.3 for an example.)

12. Draw an energy level diagram for the chemical reaction in Exercise 9. (See Figure 7.3 for an example.)

13. In a 250 mL solution, 0.25 mol of KOH(aq) and 0.25 mol of HNO_3(aq) are combined. The temperature of the solution increases from 22.5°C to 35.9°C. Assume the solution has the same density and heat capacity of water. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?

14. In a 600 mL solution, 0.50 mol of $Ca(OH)_2$(aq) and 0.50 mol of H_2SO_4(aq) are combined. The temperature of the solution increases by 22.3°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis? Assume the solution has the same density and heat capacity of water.

15. To warm 400.0 g of H_2O, 0.050 mol of ethanol (C_2H_5OH) is burned. The water warms from 24.6°C to 65.6°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?

16. To warm 100.0 g of H_2O, 0.066 mol beeswax is burned. The water warms from 21.4°C to 25.5°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?

A N S W E R S

1. under conditions of constant pressure

3. H_2(g) + Cl_2(g) → 2HCl(g) ΔH = −184 kJ

5. N_2(g) + O_2(g) → 2NO(g) ΔH = 180 kJ

7. exothermic

9. endothermic

11.
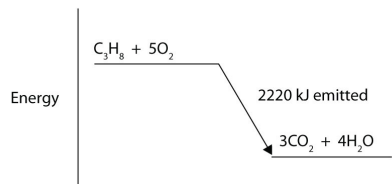
13. heat of reaction = −14.0 kJ; ΔH = −56.0 kJ/mol of reactants

15. heat of reaction = −68.6 kJ; ΔH = −1,370 kJ/mole of ethanol

# 4. STOICHIOMETRY CALCULATIONS USING ENTHALPY

LEARNING OBJECTIVE

1. **Perform stoichiometry calculations using energy changes from thermochemical equations.**

In Chapter 5, we related quantities of one substance to another in a chemical equation by performing calculations that used the balanced chemical equation; the balanced chemical equation provided equivalences that we used to construct conversion factors. For example, in the balanced chemical equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
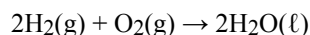
we recognized the equivalences

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$
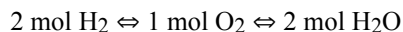
where $\Leftrightarrow$ is the mathematical symbol for "is equivalent to." In our thermochemical equation, however, we have another quantity—energy change:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \ \Delta H = -570 \text{ kJ}$$
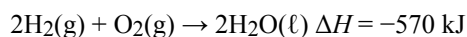
This new quantity allows us to add another equivalence to our list:

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O \Leftrightarrow -570 \text{ kJ}$$

That is, we can now add an energy amount to the equivalences—the enthalpy change of a balanced chemical reaction. This equivalence can also be used to construct conversion factors so that we can relate enthalpy change to amounts of substances reacted or produced.

Note that these equivalences address a concern. When an amount of energy is listed for a balanced chemical reaction, what amount(s) of reactants or products does it refer to? The answer is that relates to the number of moles of the substance as indicated by its coefficient in the balanced chemical reaction. Thus, 2 mol of H_2 are related to −570 kJ, while 1 mol of O_2 is related to −570 kJ. This is why the unit on the energy change is kJ, not kJ/mol.

For example, consider the thermochemical equation

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \ \Delta H = -184.6 \text{ kJ}$$

The equivalences for this thermochemical equation are

$$1 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } Cl_2 \Leftrightarrow 2 \text{ mol } HCl \Leftrightarrow -184.6 \text{ kJ}$$
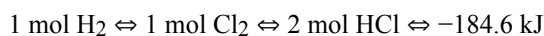
Suppose we asked how much energy is given off when 8.22 mol of H_2 react. We would construct a conversion factor between the number of moles of H_2 and the energy given off, −184.6 kJ:

$$8.22 \ \cancel{\text{mol } H_2} \times \frac{-184.6 \text{ kJ}}{1 \ \cancel{\text{mol } H_2}} = -1,520 \text{ kJ}$$

The negative sign means that this much energy is given off.

EXAMPLE 8

Given the thermochemical equation

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \ \Delta H = -91.8 \text{ kJ}$$

how much energy is given off when 222.4 g of N_2 reacts?

Solution

The balanced thermochemical equation relates the energy change to moles, not grams, so we first convert the amount of N_2 to moles and then use the thermochemical equation to determine the energy change:

$$222.4 \text{ g } N_2 \ \times \ \frac{1 \text{ mol } N_2}{28.00 \text{ g } N_2} \ \times \ \frac{-91.8 \text{ kJ}}{1 \text{ mol } N_2} \ = \ -729 \text{ kJ}$$

Test Yourself

Given the thermochemical equation

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \ \Delta H = -91.8 \text{ kJ}$$
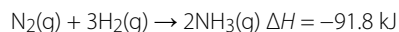
how much heat is given off when 1.00 g of H_2 reacts?

Answer

−15.1 kJ

Like any stoichiometric quantity, we can start with energy and determine an amount, rather than the other way around.

EXAMPLE 9

Given the thermochemical equation

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \ \Delta H = 180.6 \text{ kJ}$$

if 558 kJ of energy are supplied, what mass of NO can be made?

Solution

This time, we start with an amount of energy:

$$558 \text{ kJ } \times \ \frac{2 \text{ mol NO}}{180.6 \text{ kJ}} \ \times \ \frac{30.0 \text{ g NO}}{1 \text{ mol NO}} = 185 \text{ g NO}$$

Test Yourself

How many grams of N_2 will react if 100.0 kJ of energy are supplied?

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \ \Delta H = 180.6 \text{ kJ}$$
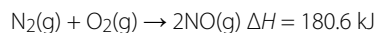
Answer

15.5 g

Chemistry Is Everywhere: Welding with Chemical Reactions

One very energetic reaction is called the *thermite reaction*. Its classic reactants are aluminum metal and iron(III) oxide; the reaction produces iron metal and aluminum oxide:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s) \ \Delta H = -850.2 \text{ kJ}$$
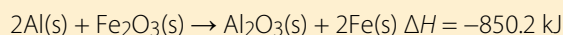
When properly done, the reaction gives off so much energy that the iron product comes off as a *liquid*. (Iron normally melts at 1,536°C.) If carefully directed, the liquid iron can fill spaces between two or more metal parts and, after it quickly cools, can weld the metal parts together.

Thermite reactions are used for this purpose even today. For civilian purposes, they are used to reweld broken locomotive axles that cannot be easily removed for repair. They are used to weld railroad tracks together. Thermite reactions can also be used to separate thin pieces of metal if, for whatever reason, a torch doesn't work.

A small clay pot contains a thermite mixture. It is reacting at high temperature in the photo and will eventually produce molten metal to join the railroad tracks below it.

Source: Photo courtesy of Skatebiker, http://commons.wikimedia.org/wiki/File:Velp-thermitewelding-1.jpg.

Thermite reactions are also used for military purposes. Thermite mixtures are frequently used with additional components as incendiary devices—devices that start fires. Thermite reactions are also useful in disabling enemy weapons: a piece of artillery doesn't work so well when it has a hole melted into its barrel because of a thermite reaction!

KEY TAKEAWAY

- The energy change of a chemical reaction can be used in stoichiometry calculations.

EXERCISES

1. Write the equivalences that this balanced thermochemical equation implies.

    $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ $\Delta H = -87.9$ kJ

2. Write the equivalences that this balanced thermochemical equation implies.

    $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$ $\Delta H = 197.9$ kJ
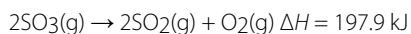
3. How many kilojoules are given off when 17.8 mol of $CH_4(g)$ react?

    $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
    $\Delta H = -890.1$ kJ
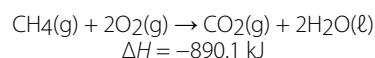
4. How many kilojoules are absorbed when 0.772 mol of $N_2(g)$ reacts?

    $N_2(g) + 2NO(g) \rightarrow 2N_2O(g)$ $\Delta H = 73.8$ kJ
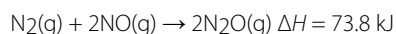
5. How many kilojoules are absorbed when 23.09 mol of $C_6H_6(\ell)$ are formed?

    $6C(s) + 3H_2(g) \rightarrow C_6H_6(\ell)$ $\Delta H = 49.0$ kJ
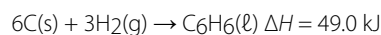
6. How many kilojoules are given off when 8.32 mol of Mg react?

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \; \Delta H = -1{,}213 \text{ kJ}$$

7. Glucose is the main fuel metabolized in animal cells:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$
$$\Delta H = -2{,}799 \text{ kJ}$$
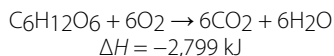
How much energy is given off when 100.0 g of $C_6H_{12}O_6$ react?

8. Given the thermochemical equation

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$$
$$\Delta H = -850.2 \text{ kJ}$$
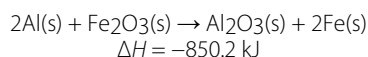
how much energy is given off when 288 g of Fe are produced?

9. Given the thermochemical equation

$$2CO_2(g) \rightarrow 2CO(g) + O_2(g) \; \Delta H = 566 \text{ kJ}$$
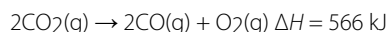
how much energy is absorbed when 85.2 g of CO_2 are reacted?

10. Given the thermochemical equation

$$2Na^+(aq) + SO_4{}^{2-}(aq) \rightarrow Na_2SO_4(s)$$
$$\Delta H = 819.8 \text{ kJ}$$
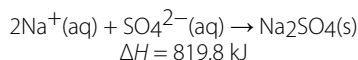
how much energy is absorbed when 55.9 g of $Na^+(aq)$ are reacted?

11. $NaHCO_3$ decomposes when exposed to heat:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g)$$
$$+ H_2O(\ell) \; \Delta H = 91.5 \text{ kJ}$$
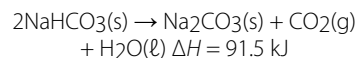
What mass of $NaHCO_3$ is decomposed by 256 kJ?

12. HgO decomposes when exposed to heat:

$$2HgO(s) \rightarrow 2Hg(\ell) + O_2(g) \; \Delta H = 181.6 \text{ kJ}$$
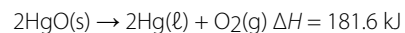
What mass of O_2 can be made with 100.0 kJ?

13. For the thermochemical equation

$$Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3 \text{ (s)}$$
$$\Delta H = -570.2 \text{ kJ}$$
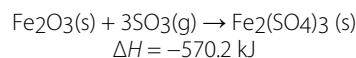
what mass of SO_3 is needed to generate 1,566 kJ?

14. For the thermochemical equation

$$H_2(g) + Br_2(\ell) \rightarrow 2HBr(g) \; \Delta H = -72.6 \text{ kJ}$$
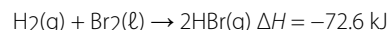
what mass of HBr will be formed when 553 kJ of energy are given off?

ANSWERS

1. 1 mol of PCl_3 ⇔ 1 mol of Cl_2 ⇔ 1 mol of PCl_5 ⇔ −87.9 kJ

3. 15,800 kJ

5. 1,130 kJ

7. 1,554 kJ

9. 548 kJ

11. 470 g

13. 6.60×10^2 g

---

5. HESS'S LAW

LEARNING OBJECTIVE

1. **Learn how to combine chemical equations and their enthalpy changes.**

Now that we understand that chemical reactions occur with a simultaneous change in energy, we can apply the concept more broadly. To start, remember that some chemical reactions are rather difficult to perform. For example, consider the combustion of carbon to make carbon monoxide:

$$2C(s) + O_2(g) \rightarrow 2CO(g) \; \Delta H = \text{?}$$
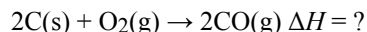
In reality, this is extremely difficult to do; given the opportunity, carbon will react to make another compound, carbon dioxide:

$$2C(s) + O_2(g) \rightarrow 2CO_2(g) \; \Delta H = -393.5 \text{ kJ}$$

Is there a way around this? Yes. It comes from the understanding that chemical equations can be treated like algebraic equations, with the arrow acting like the equals sign. Like algebraic equations, chemical equations can be combined, and if the same substance appears on both sides of the arrow, it can be canceled out (much like a spectator ion in ionic equations). For example, consider these two reactions:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$$

$$2CO_2(g) \rightarrow 2CO(g) + O_2(g)$$
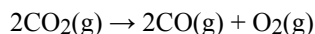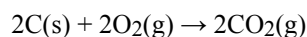
If we added these two equations by combining all the reactants together and all the products together, we would get

$$2C(s) + 2O_2(g) + 2CO_2(g) \rightarrow 2CO_2(g) + 2CO(g) + O_2(g)$$
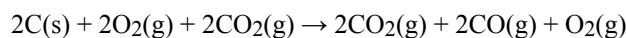
We note that $2CO_2(g)$ appears on both sides of the arrow, so they cancel:

$$2C(s) + 2O_2(g) + \cancel{2CO_2(g)} \rightarrow \cancel{2CO_2(g)} + 2CO(g) + O_2(g)$$
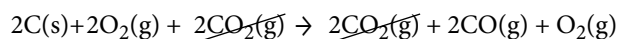
We also note that there are 2 mol of O_2 on the reactant side, and 1 mol of O_2 on the product side. We can cancel 1 mol of O_2 from both sides:

$$2C(s) + \cancel{2}O_2(g) \rightarrow 2CO(g) + \cancel{O_2(g)}$$
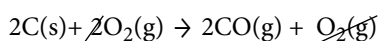
What do we have left?

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
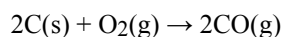
This is the reaction we are looking for! So by algebraically combining chemical equations, we can generate new chemical equations that may not be feasible to perform.

What about the enthalpy changes? **Hess's law** states that when chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way. Two corollaries immediately present themselves:

1. If a chemical reaction is reversed, the sign on ΔH is changed.
2. If a multiple of a chemical reaction is taken, the same multiple of the ΔH is taken as well.

What are the equations being combined? The first chemical equation is the combustion of C, which produces CO_2:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$$
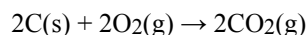
This reaction is two times the reaction to make CO_2 from C(s) and $O_2(g)$, whose enthalpy change is known:

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$
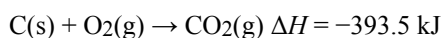
According to the first corollary, the first reaction has an energy change of two times −393.5 kJ, or −787.0 kJ:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = -787.0 \text{ kJ}$$

The second reaction in the combination is related to the combustion of CO(g):

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = -566.0 \text{ kJ}$$

The second reaction in our combination is the *reverse* of the combustion of CO. When we reverse the reaction, we change the sign on the ΔH:

$$2CO_2(g) \rightarrow 2CO(g) + O_2(g) \quad \Delta H = +566.0 \text{ kJ}$$
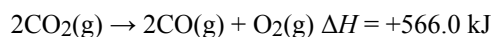
Now that we have identified the enthalpy changes of the two component chemical equations, we can combine the ΔH values and add them:

$$2C(s) + \cancel{2}O_2(g) \rightarrow \cancel{2CO_2(g)} \qquad \Delta H = -787.0 \text{ kJ}$$
$$\underline{\cancel{2CO_2(g)} \rightarrow 2CO(g) + \cancel{O_2(g)} \qquad \Delta H = +566.0 \text{ kJ}}$$
$$2C(s) + O_2(g) \rightarrow 2CO(g) \qquad \Delta H = -787.0 + 566.0 \text{ kJ} = -221.0 \text{ kJ}$$
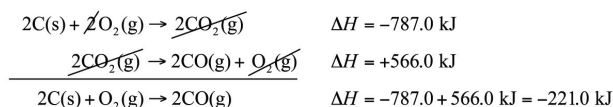
Hess's law

When chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way.
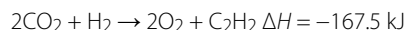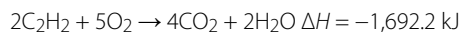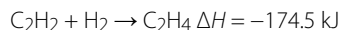
Hess's law is very powerful. It allows us to combine equations to generate new chemical reactions whose enthalpy changes can be calculated, rather than directly measured.

E X A M P L E   1 0

Determine the enthalpy change of

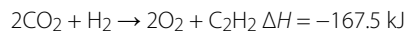$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H = ?$$

from these reactions:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \quad \Delta H = -174.5 \text{ kJ}$$

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O \quad \Delta H = -1{,}692.2 \text{ kJ}$$

$$2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2 \quad \Delta H = -167.5 \text{ kJ}$$

Solution

We will start by writing chemical reactions that put the correct number of moles of the correct substance on the proper side. For example, our desired reaction has C_2H_4 as a reactant, and only one reaction from our data has C_2H_4. However, it has C_2H_4 as a product. To make it a reactant, we need to reverse the reaction, changing the sign on the ΔH:

$$C_2H_4 \rightarrow C_2H_2 + H_2 \quad \Delta H = +174.5 \text{ kJ}$$
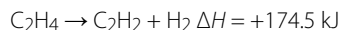
We need CO_2 and H_2O as products. The second reaction has them on the proper side, so let us include one of these reactions (with the hope that the coefficients will work out when all our reactions are added):

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O \quad \Delta H = -1{,}692.2 \text{ kJ}$$
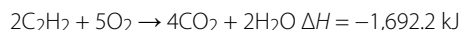
We note that we now have 4 mol of CO_2 as products; we need to get rid of 2 mol of CO_2. The last reaction has $2CO_2$ as a reactant. Let us use it as written:

$$2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2 \quad \Delta H = -167.5 \text{ kJ}$$

We combine these three reactions, modified as stated:

$$
\begin{array}{ll}
C_2H_4 \rightarrow C_2H_2 + H_2 & \Delta H = +174.5 \text{ kJ} \\
2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O & \Delta H = -1{,}692.2 \text{ kJ} \\
\underline{2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2} & \Delta H = -167.5 \text{ kJ} \\
C_2H_4 + 2C_2H_2 + 5O_2 + 2CO_2 + H_2 \rightarrow C_2H_2 + H_2 + 4CO_2 + 2H_2O + 2O_2 + C_2H_2 &
\end{array}
$$
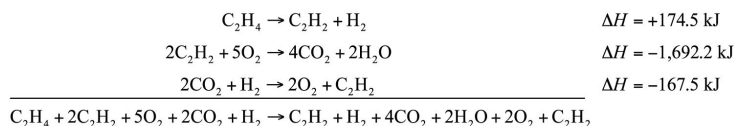
What cancels? $2C_2H_2$, H_2, $2O_2$, and $2CO_2$. What is left is

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
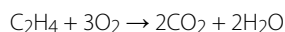
which is the reaction we are looking for. The ΔH of this reaction is the sum of the three ΔH values:

$$\Delta H = +174.5 - 1{,}692.2 - 167.5 = -1{,}685.2 \text{ kJ}$$

Test Yourself

Given the thermochemical equations

$$Pb + Cl_2 \rightarrow PbCl_2 \quad \Delta H = -223 \text{ kJ}$$

$$PbCl_2 + Cl_2 \rightarrow PbCl_4 \quad \Delta H = -87 \text{ kJ}$$

determine ΔH for

$$2PbCl_2 \rightarrow Pb + PbCl_4$$
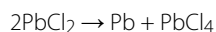
Answer
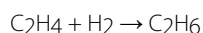
+136 kJ

KEY TAKEAWAY

- Hess's law allows us to combine reactions algebraically and then combine their enthalpy changes the same way.

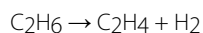### EXERCISES

1. Define *Hess's law*.

2. What does Hess's law require us to do to the ΔH of a thermochemical equation if we reverse the equation?
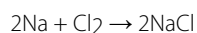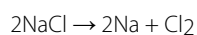
3. If the ΔH for

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

is −65.6 kJ, what is the ΔH for this reaction?

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

4. If the ΔH for

$$2Na + Cl_2 \rightarrow 2NaCl$$

is −772 kJ, what is the ΔH for this reaction:

$$2NaCl \rightarrow 2Na + Cl_2$$

5. If the ΔH for

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

is −65.6 kJ, what is the ΔH for this reaction?

$$2C_2H_4 + 2H_2 \rightarrow 2C_2H_6$$

6. If the ΔH for

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

is −2,650 kJ, what is the ΔH for this reaction?

$$6C_2H_6 + 21O_2 \rightarrow 12CO_2 + 18H_2O$$

7. The ΔH for

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

is −44 kJ. What is the ΔH for this reaction?

$$2C_2H_5OH \rightarrow 2C_2H_4 + 2H_2O$$

8. The ΔH for

$$N_2 + O_2 \rightarrow 2NO$$

is 181 kJ. What is the ΔH for this reaction?

$$NO \rightarrow 1/2N_2 + 1/2O_2$$

9. Determine the ΔH for the reaction

$$Cu + Cl_2 \rightarrow CuCl_2$$

given these data:

$$2Cu + Cl_2 \rightarrow 2CuCl \; \Delta H = -274 \text{ kJ}$$

$$2CuCl + Cl_2 \rightarrow 2CuCl_2 \; \Delta H = -166 \text{ kJ}$$

10. Determine ΔH for the reaction

$$2CH_4 \rightarrow 2H_2 + C_2H_4$$

given these data:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \; \Delta H = -891 \text{ kJ}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \; \Delta H = -1,411 \text{ kJ}$$

$$2H_2 + O_2 \rightarrow 2H_2O \; \Delta H = -571 \text{ kJ}$$

11. Determine ΔH for the reaction

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

given these data:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \; \Delta H = -1,650 \text{ kJ}$$

$$2S + 3O_2 \rightarrow 2SO_3 \; \Delta H = -792 \text{ kJ}$$

$$2Fe + 3S + 6O_2 \rightarrow Fe_2(SO_4)_3 \; \Delta H = -2,583 \text{ kJ}$$

12. Determine ΔH for the reaction

$$CaCO_3 \rightarrow CaO + CO_2$$

given these data:

$$2Ca + 2C + 3O_2 \rightarrow 2CaCO_3 \; \Delta H = -2,414 \text{ kJ}$$

$$C + O_2 \rightarrow CO_2 \; \Delta H = -393.5 \text{ kJ}$$

$$2Ca + O_2 \rightarrow 2CaO \; \Delta H = -1,270 \text{ kJ}$$

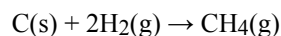# 6. FORMATION REACTIONS

L E A R N I N G   O B J E C T I V E S

1. **Define a *formation reaction* and be able to recognize one.**
2. **Use enthalpies of formation to determine the enthalpy of reaction.**

Hess's law allows us to construct new chemical reactions and predict what their enthalpies of reaction will be. This is a very useful tool because now we don't have to measure the enthalpy changes of every possible reaction. We need measure only the enthalpy changes of certain benchmark reactions and then use these reactions to algebraically construct any possible reaction and combine the enthalpies of the benchmark reactions accordingly.

But what are the benchmark reactions? We need to have some agreed-on sets of reactions that provide the central data for any thermochemical equation.
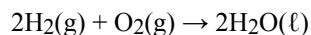
Formation reactions are chemical reactions that form one mole of a substance from its constituent elements in their standard states. By *standard states* we mean as a diatomic molecule if that is how the element exists and the proper phase at normal temperatures (typically room temperature). The product is one mole of substance, which may require that coefficients on the reactant side be fractional (a change from our normal insistence that all coefficients be whole numbers). For example, the formation reaction for methane (CH_4) is

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

The formation reaction for carbon dioxide (CO_2) is

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
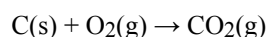
In both cases, one of the elements is a diatomic molecule because that is the standard state for that particular element. The formation reaction for H_2O—

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

—is *not* in a standard state because the coefficient on the product is 2; for a proper formation reaction, only one mole of product is formed. Thus, we have to divide all coefficients by 2:

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(\ell)$$
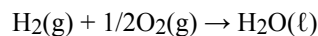
On a molecular scale, we are using half of an oxygen molecule, which may be problematic to visualize. However, on a molar level, it implies that we are reacting only half of a mole of oxygen molecules, which should be an easy concept for us to understand.

formation reaction

A chemical reaction that forms one mole of a substance from its constituent elements in their standard states.

E X A M P L E   1 1

Which of the following are proper formation reactions?

1. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
2. $Si(s) + 2F_2(g) \rightarrow SiF_4(g)$
3. $CaO(s) + CO_2 \rightarrow CaCO_3(s)$

Solution

1. In this reaction, two moles of product are produced, so this is not a proper formation reaction.
2. In this reaction, one mole of a substance is produced from its elements in their standard states, so this is a proper formation reaction.
3. One mole of a substance is produced, but it is produced from two other compounds, not its elements. So this is not a proper formation reaction.

Test Yourself

Is this a proper formation reaction? Explain why or why not.

$$2Fe(s) + 3P(s) + 12O(g) \rightarrow Fe_2(PO_4)_3(s)$$

Answer

This is not a proper formation reaction because oxygen is not written as a diatomic molecule.

Given the formula of any substance, you should be able to write the proper formation reaction for that substance.

E X A M P L E   1 2

Write formation reactions for each of the following.

1. $FeO(s)$
2. $C_2H_6(g)$

Solution

In both cases, there is one mole of the substance as product, and the coefficients of the reactants may have to be fractional to balance the reaction.

1. $Fe(s) + 1/2O_2(g) \rightarrow FeO(s)$
2. $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$

Test Yourself

Write the equation for the formation of $CaCO_3(s)$.

*Answer*

$$Ca(s) + C(s) + 3/2O_2(g) \rightarrow CaCO_3(s)$$

The enthalpy change for a formation reaction is called the **enthalpy of formation** and is given the symbol ΔH_f. The subscript f is the clue that the reaction of interest is a formation reaction. Thus, for the formation of FeO(s),

$$Fe(s) + \tfrac{1}{2}O_2(g) \rightarrow FeO(s) \qquad\qquad \Delta H \equiv \Delta H_f = -272 \text{ kJ/mol}$$

enthalpy of formation

The enthalpy change for a formation reaction; denoted ΔH_f.

Note that now we are using kJ/mol as the unit because it is understood that the enthalpy change is for one mole of substance. Note, too, by definition, that the enthalpy of formation of an element is exactly zero because making an element from an element is no change. For example,

$$H_2(g) \rightarrow H_2(g) \quad \Delta H_f = 0$$
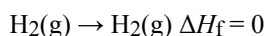
Formation reactions and their enthalpies are important because *these are the thermochemical data that are tabulated* for any chemical reaction. Table 7.2 lists some enthalpies of formation for a variety of substances; in some cases, however, phases can be important (e.g., for H_2O).
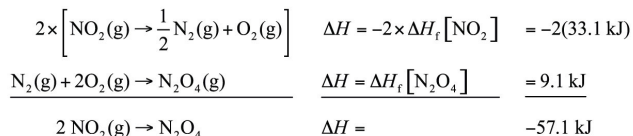
It is easy to show that any general chemical equation can be written in terms of the formation reactions of its reactants and products, some of them reversed (which means the sign must change in accordance with Hess's law). For example, consider

$$2NO_2(g) \rightarrow N_2O_4(g)$$
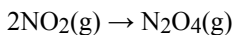
We can write it in terms of the (reverse) formation reaction of NO_2 and the formation reaction of N_2O_4:

$$2 \times \left[NO_2(g) \rightarrow \frac{1}{2}N_2(g) + O_2(g) \right] \quad \Delta H = -2 \times \Delta H_f\left[NO_2\right] \quad = -2(33.1 \text{ kJ})$$

$$\underline{N_2(g) + 2O_2(g) \rightarrow N_2O_4(g) \quad\quad \Delta H = \Delta H_f\left[N_2O_4\right] \quad = 9.1 \text{ kJ}}$$

$$2 NO_2(g) \rightarrow N_2O_4 \quad\quad\quad \Delta H = \quad\quad\quad -57.1 \text{ kJ}$$

We must multiply the first reaction by 2 to get the correct overall balanced equation. We are simply using Hess's law in combining the ΔH_f values of the formation reactions.

TABLE 7.2 **Enthalpies of Formation for Various Substances**

Compound	ΔH_f (kJ/mol)	Compound	ΔH_f (kJ/mol)	Compound	ΔH_f (kJ/mol)	Compound	ΔH_f (kJ/mol)
Ag(s)	0	Ca(s)	0	Hg2Cl2(s)	−265.37	NaHCO3(s)	−950.81
AgBr(s)	−100.37	CaCl2(s)	−795.80	I2(s)	0	NaN3(s)	21.71
AgCl(s)	−127.01	CaCO3(s, arag)	−1,207.1	K(s)	0	Na2CO3(s)	−1,130.77
Al(s)	0	CaCO3(s, calc)	−1,206.9	KBr(s)	−393.8	Na2O(s)	−417.98
Al2O3(s)	−1,675.7	Cl2(g)	0	KCl(s)	−436.5	Na2SO4(s)	−331.64
Ar(g)	0	Cr(s)	0	KF(s)	−567.3	Ne(g)	0
Au(s)	0	Cr2O3(s)	−1,134.70	KI(s)	−327.9	Ni(s)	0
BaSO4(s)	−1,473.19	Cs(s)	0	Li(s)	0	O2(g)	0
Br2(ℓ)	0	Cu(s)	0	LiBr(s)	−351.2	O3(g)	142.67
C(s, dia)	1.897	F2(g)	0	LiCl(s)	−408.27	PH3(g)	22.89
C(s, gra)	0	Fe(s)	0	LiF(s)	−616.0	Pb(s)	0
CCl4(ℓ)	−128.4	Fe2(SO4)3(s)	−2,583.00	LiI(s)	−270.4	PbCl2(s)	−359.41
CH2O(g)	−115.90	Fe2O3(s)	−825.5	Mg(s)	0	PbO2(s)	−274.47
CH3COOH(ℓ)	−483.52	Ga(s)	0	MgO(s)	−601.60	PbSO4(s)	−919.97
CH3OH(ℓ)	−238.4	HBr(g)	−36.29	NH3(g)	−45.94	Pt(s)	0
CH4(g)	−74.87	HCl(g)	−92.31	NO(g)	90.29	S(s)	0
CO(g)	−110.5	HF(g)	−273.30	NO2(g)	33.10	SO2(g)	−296.81
CO2(g)	−393.51	HI(g)	26.5	N2(g)	0	SO3(g)	−395.77
C2H5OH(ℓ)	−277.0	HNO2(g)	−76.73	N2O(g)	82.05	SO3(ℓ)	−438
C2H6(g)	−83.8	HNO3(g)	−134.31	N2O4(g)	9.08	Si(s)	0
C6H12(ℓ)	−157.7	H2(g)	0	N2O5(g)	11.30	U(s)	0
C6H12O6(s)	−1277	H2O(g)	−241.8	Na(s)	0	UF6(s)	−2,197.0
C6H14(ℓ)	−198.7	H2O(ℓ)	−285.83	NaBr(s)	−361.1	UO2(s)	−1,085.0
C6H5CH3(ℓ)	12.0	H2O(s)	−292.72	NaCl(s)	−385.9	Xe(g)	0
C6H6(ℓ)	48.95	He(g)	0	NaF(s)	−576.6	Zn(s)	0
C10H8(s)	77.0	Hg(ℓ)	0	NaI(s)	−287.8	ZnCl2(s)	−415.05
C12H22O11(s)	−2,221.2						

Sources: National Institute of Standards and Technology's Chemistry WebBook, http://webbook.nist.gov/chemistry; D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 89th ed. (Boca Raton, FL: CRC Press, 2008); J. A. Dean, ed., Lange's Handbook of Chemistry, 14th ed. (New York: McGraw-Hill, 1992).
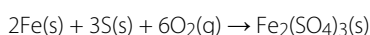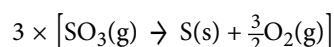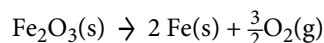
E X A M P L E   1 3

Show that the reaction

$$Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3(s)$$
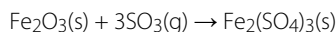
can be written as a combination of formation reactions.
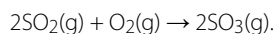
Solution

There will be three formation reactions. The one for the products will be written as a formation reaction, while the ones for the reactants will be written in reverse. Furthermore, the formation reaction for SO_3 will be multiplied by 3 because there are three moles of SO_3 in the balanced chemical equation. The formation reactions are as follows:
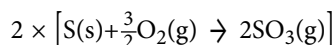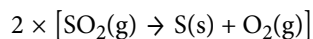
$$Fe_2O_3(s) \rightarrow 2\,Fe(s) + \tfrac{3}{2}O_2(g)$$

$$3 \times \left[SO_3(g) \rightarrow S(s) + \tfrac{3}{2}O_2(g)\right]$$

$$2Fe(s) + 3S(s) + 6O_2(g) \rightarrow Fe_2(SO_4)_3(s)$$

When these three equations are combined and simplified, the overall reaction is

$$Fe_2O_3(s) + 3SO_3(s) \rightarrow Fe_2(SO_4)_3(s)$$
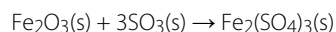
Test Yourself

Write the formation reactions that will yield

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g).$$

Answer

$$2 \times \left[SO_2(g) \rightarrow S(s) + O_2(g)\right]$$

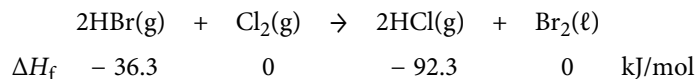$$2 \times \left[S(s) + \tfrac{3}{2}O_2(g) \rightarrow 2SO_3(g)\right]$$

Now that we have established formation reactions as the major type of thermochemical reaction we will be interested in, do we always need to write all the formation reactions when we want to determine the enthalpy change of any random chemical reaction? No. There is an easier way. You may have noticed in all our examples that we change the signs on all the enthalpies of formation of the reactants, and we don't change the signs on the enthalpies of formation of the products. We also multiply the enthalpies of formation of any substance by its coefficient—technically, even when it is just 1. This allows us to make the following statement: *the enthalpy change of any chemical reaction is equal to the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants.* In mathematical terms,

$$\Delta H_{rxn} = \sum n_p \Delta H_{f,p} - \sum n_r \Delta H_{f,r}$$

where n_p and n_r are the number of moles of products and reactants, respectively (even if they are just 1 mol), and $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the enthalpies of formation of the product and reactant species, respectively. This *products-minus-reactants* scheme is very useful in determining the enthalpy change of any chemical reaction, if the enthalpy of formation data are available. Because the mol units cancel when multiplying the amount by the enthalpy of formation, the enthalpy change of the chemical reaction has units of energy (joules or kilojoules) only.

E X A M P L E   1 4

Use the products-minus-reactants approach to determine the enthalpy of reaction for

$$2HBr(g) \quad + \quad Cl_2(g) \quad \rightarrow \quad 2HCl(g) \quad + \quad Br_2(\ell)$$

$\Delta H_f \quad -36.3 \qquad\qquad 0 \qquad\qquad -92.3 \qquad\qquad 0 \qquad kJ/mol$

Solution

The enthalpies of formation are multiplied by the number of moles of each substance in the chemical equation, and the total enthalpy of formation for reactants is subtracted from the total enthalpy of formation of the products:

$$\Delta H_{rxn} = [(2 \text{ mol})(-92.3 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$
$$- [(2 \text{ mol})(-36.3 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

All the mol units cancel. Multiplying and combining all the values, we get

$$\Delta H_{rxn} = -112.0 \text{ kJ}$$

Test Yourself

What is the enthalpy of reaction for this chemical equation?

$$CO(g) \quad + \quad H_2O(\ell) \quad \rightarrow \quad CO_2(g) \quad + \quad H_2(g)$$

$\Delta H_f \quad -110.5 \qquad\qquad -285.8 \qquad\qquad -393.5 \qquad\qquad 0 \qquad kJ/mol$
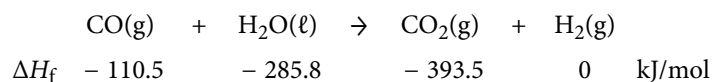
Answer

+2.8 kJ

Food and Drink App: Calories and Nutrition

Section 1 mentioned the connection between the calorie unit and nutrition: the calorie is the common unit of energy used in nutrition, but we really consider the kilocalorie (spelled Calorie with a capital C). A daily diet of 2,000 Cal is actually 2,000,000 cal, or over 8,000,000 J, of energy.

Nutritionists typically generalize the Calorie content of foods by separating it into the three main food types: proteins, carbohydrates, and fats. The general rule of thumb is as follows:

If the food is	It has this energy content
protein	4 Cal/g
carbohydrate	4 Cal/g
fat	9 Cal/g

This table is very useful. Assuming a 2,000 Cal daily diet, if our diet consists solely of proteins and carbohydrates, we need only about 500 g of food for sustenance—a little more than a pound. If our diet consists solely of fats, we need only about 220 g of food—less than a half pound. Of course, most of us have a mixture of proteins, carbohydrates, and fats in our diets. Water has no caloric value in the diet, so any water in the diet is calorically useless. (However, it is important for hydration; also, many forms of water in our diet are highly flavored and sweetened, which bring other nutritional issues to bear.)

When your body works, it uses calories provided by the diet as its energy source. If we eat more calories than our body uses, we gain weight—about 1 lb of weight for every additional 3,500 Cal we ingest. Similarly, if we want to lose weight, we need to expend an extra 3,500 Cal than we ingest to lose 1 lb of weight. No fancy or fad diets are needed; maintaining an ideal body weight is a straightforward matter of thermochemistry—pure and simple.

KEY TAKEAWAYS

- A formation reaction is the formation of one mole of a substance from its constituent elements.
- Enthalpies of formation are used to determine the enthalpy change of any given reaction.

EXERCISES

1. Define *formation reaction* and give an example.

2. Explain the importance of formation reactions in thermochemical equations.

3. Which of the following reactions is a formation reaction? If it is not a formation reaction, explain why.
   a. $H_2(g) + S(s) \rightarrow H_2S(g)$
   b. $2HBr(g) + Cl_2(g) \rightarrow 2HCl(g) + Br_2(\ell)$

4. Which of the following reactions is a formation reaction? If it is not a formation reaction, explain why.
   a. $Fe(g) + 1/2O_2(g) \rightarrow FeO(s)$
   b. $Hg(\ell) + 1/2O_2(g) \rightarrow HgO(s)$

5. Which of the following reactions is a formation reaction? If it is not a formation reaction, explain why.
   a. $H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(\ell)$
   b. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$

6. Which of the following reactions is a formation reaction? If it is not a formation reaction, explain why.
   a. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
   b. $2Na(s) + C(s) + 3/2O_2(g) \rightarrow Na_2CO_3(s)$

7. Write a proper formation reaction for each substance.
   a. $H_3PO_4(s)$
   b. $Na_2O(s)$
   c. $C_3H_7OH(\ell)$

8. Write a proper formation reaction for each substance.
   a. $N_2O_5(g)$
   b. $BaSO_4(s)$
   c. $Fe(OH)_3(s)$

9. Write a proper formation reaction for each substance.
   a. $C_{12}H_{22}O_{11}(s)$
   b. $Zn(NO_3)_2(s)$
   c. $Al(OH)_3(s)$

10. Write a proper formation reaction for each substance.
    a. $O_3(g)$
    b. $Na_2O_2(s)$
    c. $PCl_5(g)$

11. Write this reaction in terms of formation reactions.

    $$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

12. Write this reaction in terms of formation reactions.

    $$2NO + 4NO_2 \rightarrow 2N_2O_5 + N_2$$

13. Write this reaction in terms of formation reactions.

    $$2CuCl(s) \rightarrow Cu(s) + CuCl_2(s)$$

14. Write this reaction in terms of formation reactions.

    $$SiH_4 + 4F_2 \rightarrow SiF_4 + 4HF$$

15. Determine the enthalpy change of this reaction. Data can be found in Table 7.2.

    $$CH_2O(g) + O_2 \rightarrow CO_2(g) + H_2O(\ell)$$

16. Determine the enthalpy change of this reaction. Data can be found in Table 7.2.

    $$2AgBr(s) + Cl_2(g) \rightarrow 2AgCl(s) + Br_2(\ell)$$

17. Determine the enthalpy change of this reaction. Data can be found in Table 7.2.

    $$Mg(s) + N_2O_5(g) \rightarrow MgO(s) + 2NO_2(g)$$

18. Determine the enthalpy change of this reaction. Data can be found in Table 7.2.

    $$2C_6H_6(\ell) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(\ell)$$

ANSWERS

1. A formation reaction is a reaction that produces one mole of a substance from its elements. Example: $C(s) + O_2(g) \rightarrow CO_2(g)$

3. a. formation reaction
   b. It is not the formation of a single substance, so it is not a formation reaction.

5. a. formation reaction

   b. It is not the formation of a single substance, so it is not a formation reaction.

7. a. $3/2H_2(g) + P(s) + 2O_2(g) \rightarrow H_3PO_4(s)$

   b. $2Na(s) + 1/2O_2(g) \rightarrow Na_2O(s)$

   c. $3C(s) + 1/2O_2(g) + 4H_2(g)$ $\rightarrow C_3H_7OH(\ell)$

9. a. $12C(s) + 11H_2(g) + 11/2O_2(g)$ $\rightarrow C_{12}H_{22}O_{11}(s)$

   b. $Zn(s) + N_2(g) + 3O_2(g) \rightarrow Zn(NO_3)_2$

   c. $Al(s) + 3/2O_2(g) + 3/2H_2(g)$ $\rightarrow Al(OH)_3(s)$

11. $MgCO_3(s) \rightarrow Mg(s) + C(s) + 3/2O_2(g)$

    $Mg(s) + 1/2O_2(g) \rightarrow MgO(s)$

    $C(s) + O_2(g) \rightarrow CO_2(g)$

13. $2 \times [CuCl(s) \rightarrow Cu(s) + 1/2Cl_2(g)]$

    $Cu(s) \rightarrow Cu(s)$

    $Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$

15. $\Delta H = -563.44$ kJ

17. $\Delta H = -546.7$ kJ

# 7. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

1. What is the work when 124 mL of gas contract to 72.0 mL under an external pressure of 822 torr?

2. What is the work when 2,345 mL of gas contract to 887 mL under an external pressure of 348 torr?

3. A 3.77 L volume of gas is exposed to an external pressure of 1.67 atm. As the gas contracts, 156 J of work are added to the gas. What is the final volume of the gas?

4. A 457 mL volume of gas contracts when 773 torr of external pressure act on it. If 27.4 J of work are added to the gas, what is its final volume?

5. What is the heat when 1,744 g of Hg increase in temperature by 334°C? Express your final answer in kJ.

6. What is the heat when 13.66 kg of Fe cool by 622°C? Express your final answer in kJ.

7. What is final temperature when a 45.6 g sample of Al at 87.3°C gains 188 J of heat?

8. What is final temperature when 967 g of Au at 557°C lose 559 J of heat?

9. Plants take CO_2 and H_2O and make glucose ($C_6H_{12}O_6$) and O_2. Write a balanced thermochemical equation for this process. Use data in Table 7.2.

10. Exercise 9 described the formation of glucose in plants, which take in CO_2 and H_2O and give off O_2. Is this process exothermic or endothermic? If exothermic, where does the energy go? If endothermic, where does the energy come from?

11. The basic reaction in the refining of aluminum is to take $Al_2O_3(s)$ and turn it into $Al(s)$ and $O_2(g)$. Write the balanced thermochemical equation for this process. Use data in Table 7.2.

12. Is the enthalpy change of the reaction

$$H_2O(\ell) \rightarrow H_2O(g)$$

zero or nonzero? Use data in Table 7.2 to determine the answer.

13. What mass of H_2O can be heated from 22°C to 80°C in the combustion of 1 mol of CH_4? You will need the balanced thermochemical equation for the combustion of CH_4. Use data in Table 7.2.

14. What mass of H_2O can be heated from 22°C to 80°C in the combustion of 1 mol of C_2H_6? You will need the balanced thermochemical equation for the combustion of C_2H_6. Use data in Table 7.2. Compare your answer to Exercise 13.

15. What is the enthalpy change for the unknown reaction?

$$Pb(s) + Cl_2(g) \rightarrow PbCl_2(s) \; \Delta H = -359 \text{ kJ}$$

$$PbCl_2(s) + Cl_2(g) \rightarrow PbCl_4(\ell) \; \Delta H = ?$$

$$Pb(s) + 2Cl_2(g) \rightarrow PbCl_4(\ell) \; \Delta H = -329 \text{ kJ}$$

16. What is the enthalpy change for the unknown reaction?

$$P(s) + 3/2Br_2(\ell) \rightarrow PBr_3(\ell) \; \Delta H = -185 \text{ kJ}$$

$$PI_3(s) \rightarrow P(s) + 3/2I_2(s) \; \Delta H = ?$$

$$PI_3(s) + 3/2Br_2(\ell) \rightarrow PBr_3(\ell) + 3/2I_2(s)$$
$$\Delta H = -139 \text{ kJ}$$

17. What is the ΔH for this reaction? The label *gra* means graphite, and the label *dia* means diamond. What does your answer mean?

$$C(s, gra) \rightarrow C(s, dia)$$
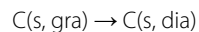
18. Without consulting any tables, determine the ΔH for this reaction. Explain your answer.

$$H_2O(\ell, 25°C) \rightarrow H_2O(\ell, 25°C)$$
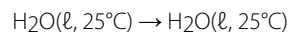
ANSWERS

1. 5.70 J

3. 4.69 L

5. 80.97 kJ

7. 91.9°C

9. $6CO_2(g) + 6H_2O(\ell) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$ $\Delta H = 2,799$ kJ

11. $2Al_2O_3(s) \rightarrow 4Al(s) + 3O_2(g)$ $\Delta H = 3351.4$ kJ

13. 3,668 g

15. $\Delta H = 30$ kJ

17. $\Delta H = 1.897$ kJ; the reaction is endothermic.