UNIT 3

Energy Changes and Rates of Reaction

UNIT 3 CONTENTS

UNIT 3 OVERALL EXPECTATIONS

- What energy transformations and mechanisms are involved in chemical change?
- What skills are involved in determining energy changes for physical and chemical processes and rates of reaction?
- How do chemical technologies and processes depend on the energetics of chemical reactions?

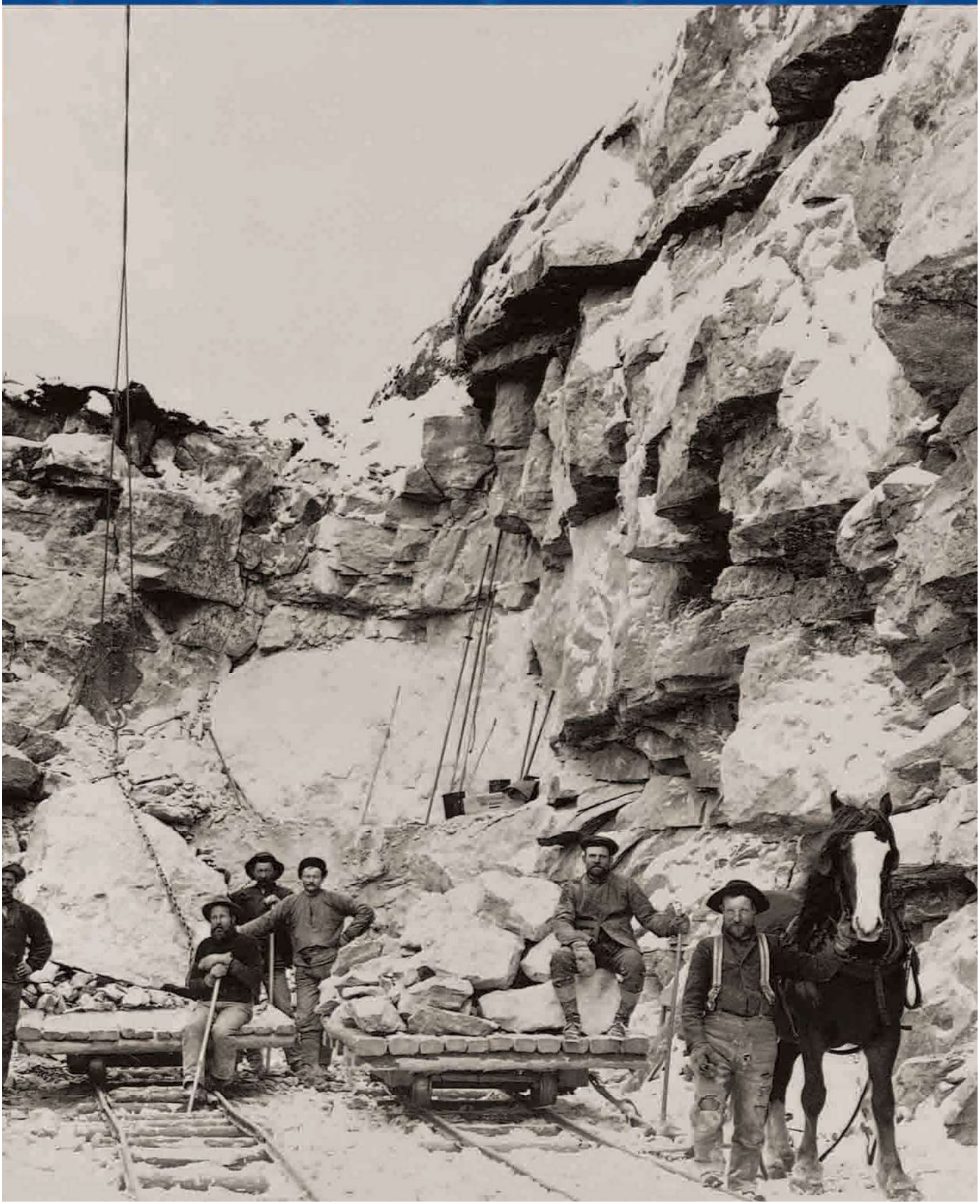
Unit Project Prep

Look ahead to the project at the end of Unit 3. Start preparing for the project now by listing what you already know about catalysts and enzymes. Think about how catalysts and enzymes affect chemical reactions. As you work through the unit, plan how you will investigate and present a bulletin about the uses of catalysts and enzymes in Canadian industries.

In the nineteenth century, railway tunnels were blasted through the Rocky Mountains to connect British Columbia with the rest of Canada. Workers used nitroglycerin to blast through the rock. This compound is so unstable, however, that accidents were frequent and many workers died. Alfred B. Nobel found a way to stabilize nitroglycerin, and make it safer to use, when he invented dynamite.

What makes nitroglycerin such a dangerous substance? First, nitroglycerin, $C_3H_5(NO_3)_{3(\ell)}$, gives off a large amount of energy when it decomposes. In fact, about 1500 kJ of energy is released for every mole of nitroglycerin that reacts. Second, the decomposition of nitroglycerin occurs very quickly—in a fraction of a second. This fast, exothermic reaction is accompanied by a tremendous shock wave, which is caused by the expansion of the gaseous products. Finally, nitroglycerin is highly shock-sensitive. Simply shaking or jarring it can cause it to react.

Thus, nitroglycerin's explosive properties are caused by three factors: the energy that is given off by its decomposition, the rate at which the reaction occurs, and the small amount of energy that is needed to initiate the reaction. In this unit, you will learn about the energy and rates of various chemical reactions.



CHAPTER 5

Energy and Change

Chapter Preview

Prerequisite Concepts and Skills

Before you begin this chapter, review the following concepts and skills:

- writing balanced chemical equations (Concepts and Skills Review)
- performing stoichiometric calculations (Concepts and Skills Review)

Think about a prehistoric family group building a fire. It may seem as though this fire does not have much in common with a nuclear power plant. Both the fire and the nuclear power plant, however, are technologies that harness energy-producing processes.

As you learned in Unit 2, humans continually devise new technologies that use chemical reactions to produce materials with useful properties. Since the invention of fire, humans have also worked to devise technologies that harness energy. These technologies depend on the fact that every chemical, physical, and nuclear process is accompanied by a characteristic energy change. Consider the melting of an ice cube to cool a drink, the combustion of natural gas to cook a meal, and the large-scale production of electricity via a nuclear power plant. All societies depend on the energy changes that are associated with these physical, chemical, and nuclear processes.

In this chapter, you will study the causes and magnitude of the energy changes that accompany physical changes, chemical reactions, and nuclear reactions. You will see that different processes involve vastly different amounts of energy. You will learn how to calculate the amount of energy that is absorbed or released by many simple physical changes and chemical reactions. This will allow you to predict energy changes without having to carry out the reaction—an important skill to have when dealing with dangerous reactions. Finally, you will examine the efficiency and environmental impact of traditional and alternative energy sources.

Enough radiant energy reaches Earth every day to meet the world's energy needs many times over. Since this is the case, why do fossil fuels provide most of Canada's energy, while solar power supplies only a tiny fraction?

The Energy of Physical, Chemical, and Nuclear Processes

5.1

Most physical changes, chemical reactions, and nuclear reactions are accompanied by changes in energy. These energy changes are crucial to life on Earth. For example, chemical reactions in your body generate the heat that helps to regulate your body temperature. Physical changes, such as evaporation, help to keep your body cool. On a much larger scale, there would be no life on Earth without the energy from the nuclear reactions that take place in the Sun.

The study of energy and energy transfer is known as **thermodynamics**. Chemists are interested in the branch of thermodynamics known as **thermochemistry:** the study of energy involved in chemical reactions. In order to discuss energy and its interconversions, thermochemists have agreed on a number of terms and definitions. You will learn about these terms and definitions over the next few pages. Then you will examine the energy changes that accompany chemical reactions, physical changes, and nuclear reactions.

Section Preview/ Specific Expectations

In this section, you will

- **write** thermochemical equations, expressing the energy change as a heat term in the equation or as ΔH
- **represent** energy changes using diagrams
- **compare** energy changes that result from physical changes, chemical reactions, and nuclear reactions
- **communicate** your understanding of the following terms: *thermodynamics, thermochemistry, law of conservation of energy, system, surroundings, heat (Q), temperature (T), enthalpy (H), enthalpy change (ΔH), endothermic reaction, exothermic reaction, enthalpy of reaction (ΔH_{rxn}), standard enthalpy of reaction (ΔH°_{rxn}), thermochemical equation, mass defect, nuclear binding energy, nuclear fission, nuclear fusion*

Studying Energy Changes

The **law of conservation of energy** states that the total energy of the universe is constant. In other words, energy can be neither destroyed nor created. This idea can be expressed by the following equation:

$$\Delta E_{\text{universe}} = 0$$

Energy can, however, be transferred from one substance to another. It can also be converted into various forms. In order to interpret energy changes, scientists must clearly define what part of the universe they are dealing with. The **system** is defined as the part of the universe that is being studied and observed. In a chemical reaction, the system is usually made up of the reactants and products. By contrast, the **surroundings** are everything else in the universe. The two equations below show the relationship between the universe, a system, and the system's surroundings.

$$\text{Universe} = \text{System} + \text{Surroundings}$$

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

From the relationship, we know that any change in the system is accompanied by an equal and opposite change in the surroundings.

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

Look at the chemical reaction that is taking place in the flask in Figure 5.1. A chemist would probably define the system as the contents of the flask—the reactants and products. Technically, the rest of the universe is the surroundings. In reality, however, the entire universe changes very little when the system changes. Therefore, the surroundings are considered to be only the part of the universe that is likely to be affected by the energy changes of the system. In Figure 5.1, the flask, the lab bench, the air in the room, and the student who is carrying out the reaction all make up the surroundings. The system is more likely to significantly influence its immediate surroundings than, say, a mountaintop in Japan (also, technically, part of the surroundings).

Figure 5.1 **The solution in the flask is the system. The flask, the laboratory, and the student are the surroundings.**

Heat and Temperature

Heat, ***Q***, refers to the transfer of kinetic energy. Heat is expressed in the same units as energy—joules (J). Heat is transferred spontaneously from a warmer object to a cooler object. When you close the door of your home on a cold day to "prevent the cold from getting in," you are actually preventing the heat from escaping. You are preventing the kinetic energy in your warm home from transferring to colder objects, including the cold air, outside.

Temperature, ***T***, is a measure of the average kinetic energy of the particles that make up a substance or system. You can think of temperature as a way of quantifying how hot or cold a substance is, relative to another substance.

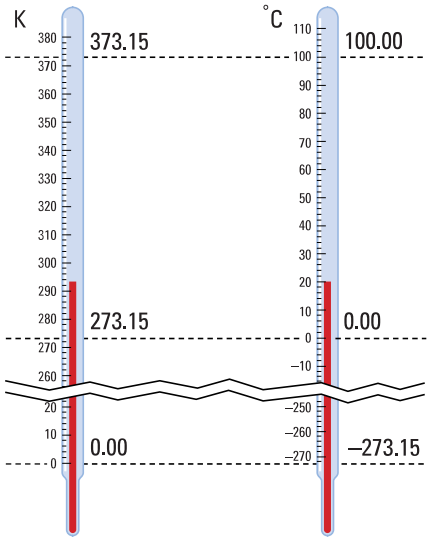


Figure 5.2 **Celsius degrees and Kelvin degrees are the same size. The Kelvin scale begins at absolute zero. This is the temperature at which the particles in a substance have no kinetic energy. Therefore, Kelvin temperatures are never negative. By contrast, 0°C is set at the melting point of water. Celsius temperatures can be positive or negative.**

Temperature is measured in either Celsius degrees (°C) or kelvins (K). The Celsius scale is a relative scale. It was designed so that water's boiling point is at 100°C and water's melting point is at 0°C. The Kelvin scale, on the other hand, is an absolute scale. It was designed so that 0 K is the temperature at which a substance possesses no kinetic energy. The relationship between the Kelvin and Celsius scales is shown in Figure 5.2, and by the following equation.

Temperature in Kelvin degrees = Temperature in Celsius degrees + 273.15

Enthalpy and Enthalpy Change

Chemists define the total internal energy of a substance at a constant pressure as its **enthalpy**, ***H***. Chemists do not work with the *absolute* enthalpy of the reactants and products in a physical or chemical process. Instead, they study the **enthalpy change**, ΔH, that accompanies a process. That is, they study the *relative* enthalpy of the reactants and products in a system. This is like saying that the distance between your home and your school is 2 km. You do not usually talk about the *absolute* position of your home and school in terms of their latitude, longitude, and elevation. You talk about their *relative* position, in relation to each other.

The enthalpy change of a process is equivalent to its heat change at constant pressure.

Enthalpy Changes in Chemical Reactions

In chemical reactions, enthalpy changes result from chemical bonds being broken and formed. Chemical bonds are sources of stored energy. *Breaking a bond is a process that requires energy. Creating a bond is a process that releases energy.* For example, consider the combustion reaction that takes place when nitrogen reacts with oxygen.

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$$

In this reaction, one mole of nitrogen-nitrogen triple bonds and one mole of oxygen-oxygen double bonds are broken. Two moles of nitrogen-oxygen bonds are formed. This reaction absorbs energy. In other words, more energy is released to form two nitrogen-oxygen bonds than is used to break one nitrogen-nitrogen bond and one oxygen-oxygen bond. When a reaction results in a net *absorption* of energy, it is called an **endothermic reaction**.

On the other hand, when a reaction results in a net *release* of energy, it is called an **exothermic reaction**. In an exothermic reaction, more energy is released to form bonds than is used to break bonds. Therefore, energy is released. Figure 5.3 shows the relationship between bond breaking, bond formation, and endothermic and exothermic reactions.

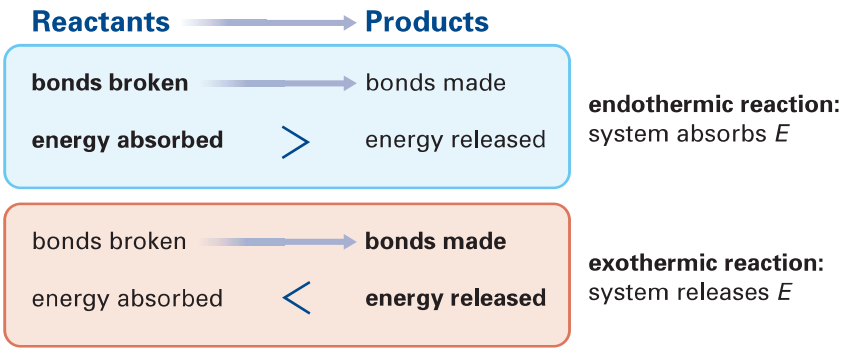


Figure 5.3 **The energy changes that result from bonds breaking and forming determine whether a reaction is exothermic or endothermic.**

Representing Enthalpy Changes

The enthalpy change of a chemical reaction is known as the **enthalpy of reaction**, ΔH_{rxn}. The enthalpy of reaction is dependent on conditions such as temperature and pressure. Therefore, chemists often talk about the **standard enthalpy of reaction**, ΔH°_{rxn}: the enthalpy change of a chemical reaction that occurs at SATP (25°C and 100 kPa). Often, ΔH°_{rxn} is written simply as ΔH°. The ° symbol is called "nought." It refers to a property of a substance at a standard state or under standard conditions. You may see the enthalpy of reaction referred to as the *heat of reaction* in other chemistry books.

CHEM FACT

Chemists use different subscripts to represent enthalpy changes for specific kinds of reactions. For example, ΔH_{comb} represents the enthalpy change of a combustion reaction.

Representing Exothermic Reactions

There are three different ways to represent the enthalpy change of an exothermic reaction. The simplest way is to use a **thermochemical equation**: a balanced chemical equation that indicates the amount of heat that is absorbed or released by the reaction it represents. For example, consider the exothermic reaction of one mole of hydrogen gas with half a mole of oxygen gas to produce liquid water. For each mole of hydrogen gas that reacts, 285.8 kJ of heat is produced. Notice that the heat term is included with the products because heat is produced.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} + 285.8\ kJ$$

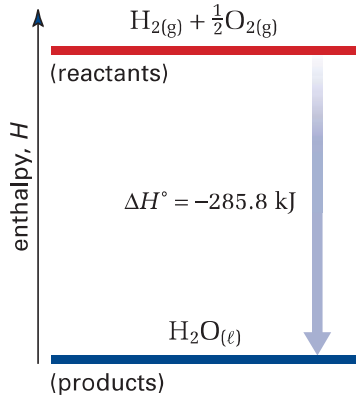


Figure 5.4 **In an exothermic reaction, the enthalpy of the system decreases as energy is released to the surroundings.**

You can also indicate the enthalpy of reaction as a separate expression beside the chemical equation. For exothermic reactions, ΔH° is always negative.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ_{rxn} = -285.8 \text{ kJ}$$

A third way to represent the enthalpy of reaction is to use an enthalpy diagram. Examine Figure 5.4 to see how this is done.

Representing Endothermic Reactions

The endothermic decomposition of solid magnesium carbonate produces solid magnesium oxide and carbon dioxide gas. For each mole of magnesium carbonate that decomposes, 117.3 kJ of energy is absorbed. As for an exothermic reaction, there are three different ways to represent the enthalpy change of an endothermic reaction.

You can include the enthalpy of reaction as a heat term in the chemical equation. Because heat is absorbed in an endothermic reaction, the heat term is included on the reactant side of the equation.

$$117.3 \text{ kJ} + MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$$

You can also indicate the enthalpy of reaction as a separate expression beside the chemical reaction. For endothermic reactions, the enthalpy of reaction is always positive.

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)} \quad \Delta H^\circ_{rxn} = 117.3 \text{ kJ}$$

Finally, you can use a diagram to show the enthalpy of reaction. Figure 5.5 shows how the decomposition of solid magnesium carbonate can be represented graphically.

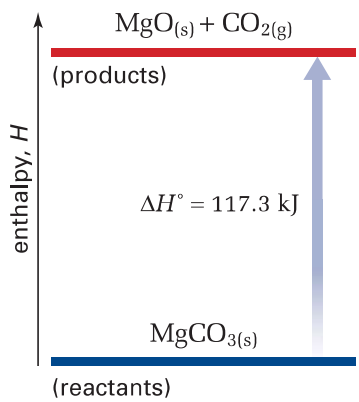


Figure 5.5 **In an endothermic reaction, the enthalpy of the system increases as heat energy is absorbed from the surroundings.**

Stoichiometry and Thermochemical Equations

The thermochemical equation for the decomposition of magnesium carbonate, shown above, indicates that 117.3 kJ of energy is absorbed when one mole, or 84.32 g, of magnesium carbonate decomposes. The decomposition of two moles of magnesium carbonate absorbs twice as much energy, or 234.6 kJ.

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)} \quad \Delta H^\circ_{rxn} = 117.3 \text{ kJ}$$
$$2MgCO_{3(s)} \rightarrow 2MgO_{(s)} + 2CO_{2(g)} \quad \Delta H^\circ_{rxn} = 234.6 \text{ kJ}$$

Enthalpy of reaction is *linearly dependent* on the quantity of products. That is, if the amount of products formed doubles, the enthalpy change also doubles. Figure 5.6 shows the relationship between the stoichiometry of a reaction and its enthalpy change. Because of this relationship, an exothermic reaction that is relatively safe on a small scale may be extremely dangerous on a large scale. One of the jobs of a chemical engineer is to design systems that allow exothermic reactions to be carried out safely on a large scale. For example, the blast furnaces used in steel making must withstand temperatures of up to 2000°C, produced by the exothermic combustion reaction of coal with oxygen.

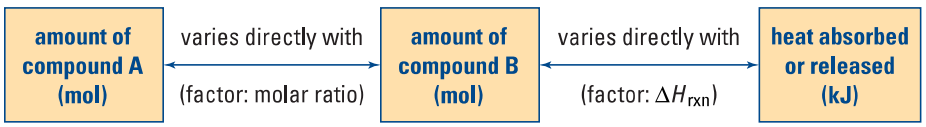


Figure 5.6 **This diagram summarizes the relationship between the stoichiometry of a reaction and ΔH.**

Sample Problem

Stoichiometry and Thermochemical Reactions

Problem

Aluminum reacts readily with chlorine gas to produce aluminum chloride. The reaction is highly exothermic.

$2Al_{(s)} + 3Cl_{2(g)} \rightarrow 2AlCl_{3(s)} \quad \Delta H^{\circ}_{rxn} = -1408\ kJ$

What is the enthalpy change when 1.0 kg of Al reacts completely with excess Cl_2?

What Is Required?

You need to calculate the enthalpy change, ΔH, when the given amount of Al reacts.

What Is Given?

You know the enthalpy change for the reaction of two moles of Al with one mole of Cl_2. From the periodic table, you know the molar mass of Al.

$2Al_{(s)} + 3Cl_{2(g)} \rightarrow 2AlCl_{3(s)} \quad \Delta H^{\circ}_{rxn} = -1408\ kJ$

$M_{Al} = 26.98\ g/mol$

Plan Your Strategy

Convert the given mass of Al to moles. The enthalpy change is linearly dependent on the quantity of reactants. Therefore, you can use a ratio to determine the enthalpy change for 1.0 kg of Al reacting with Cl_2.

Act on Your Strategy

Determine the number of moles of Al in 1 kg. Remember to convert to grams.

$$n\ \text{mol Al} = \frac{m_{Al}}{M_{Al}}$$

$$= \frac{1.0 \times 10^3\ g}{26.98\ g/mol}$$

$$= 37\ \text{mol}$$

Use ratios to compare the reference reaction with the known enthalpy change (ΔH_1) to the reaction with the unknown enthalpy change (ΔH_2).

$$\frac{\Delta H_2}{\Delta H_1} = \frac{n_2\ \text{mol Al}}{n_1\ \text{mol Al}}$$

$$\frac{\Delta H_2}{-1408\ kJ} = \frac{37\ \text{mol Al}}{2\ \text{mol Al}}$$

$$\Delta H_2 = -2.6 \times 10^4\ kJ$$

Check Your Solution

The sign of the answer is negative, which corresponds to an exothermic reaction. The 1 kg sample contained about 20 times more moles of Al. Therefore, the enthalpy change for the reaction should be about 20 times greater, and it is.

Practice Problems

1. Consider the following reaction.
   $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} \quad \Delta H^{\circ}_{rxn} = +180.6\ kJ$
   - **(a)** Rewrite the thermochemical equation, including the standard enthalpy of reaction as either a reactant or a product.
   - **(b)** Draw an enthalpy diagram for the reaction.
   - **(c)** What is the enthalpy change for the formation of one mole of nitrogen monoxide?
   - **(d)** What is the enthalpy change for the reaction of 1.000×10^2 g of nitrogen with sufficient oxygen?
2. The reaction of iron with oxygen is very familiar. You can see the resulting rust on buildings, vehicles, and bridges. You may be surprised, however, at the large amount of heat that is produced by this reaction.
   $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 1.65 \times 10^3\ kJ$
   - **(a)** What is the enthalpy change for this reaction?
   - **(b)** Draw an enthalpy diagram that corresponds to the thermochemical equation.
   - **(c)** What is the enthalpy change for the formation of 23.6 g of iron(III) oxide?
3. Consider the following thermochemical equation.
   $25.9\ kJ + \frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightarrow HI_{(g)}$
   - **(a)** What is the enthalpy change for this reaction?
   - **(b)** How much energy is needed for the reaction of 4.57×10^{24} molecules of iodine, I_2, with excess hydrogen, H_2?
   - **(c)** Draw and label an enthalpy diagram that corresponds to the given thermochemical equation.
4. Tetraphosphorus decoxide, P_4O_{10}, is an acidic oxide. It reacts with water to produce phosphoric acid, H_3PO_4, in an exothermic reaction.
   $P_4O_{10(s)} + 6H_2O_{(\ell)} \rightarrow 4H_3PO_{4(aq)} \quad \Delta H^{\circ}_{rxn} = -257.2\ kJ$
   - **(a)** Rewrite the thermochemical equation, including the enthalpy change as a heat term in the equation.
   - **(b)** How much energy is released when 5.00 mol of P_4O_{10} reacts with excess water?
   - **(c)** How much energy is released when 235 g of $H_3PO_{4(aq)}$ is formed?

Heat Changes and Physical Changes

Enthalpy changes are associated with physical changes as well as with chemical reactions. You have observed examples of these enthalpy changes in your daily life. Suppose that you want to prepare some pasta. You put an uncovered pot of water on a stove element. The heat from the element causes the water to become steadily hotter, until it reaches 100°C (the boiling point of water at 100 kPa). At this temperature, heat is still being added to the water. The average kinetic energy of the liquid water molecules does not increase, however. Instead, the energy is used to break the intermolecular bonds between the water molecules as they change from liquid to vapour. The temperature of the liquid water remains at

100°C until all the water has been vaporized. If you add heat to the vapour, the temperature of the vapour will increase steadily.

When you heat ice that is colder than 0°C, a similar process occurs. The temperature of the ice increases until it is 0°C (the melting point of water). If you continue to add heat, the ice remains at 0°C but begins to melt, as the bonds between the water molecules in the solid state begin to break.

Figure 5.7 shows the relationship between temperature and heat for a solid substance that melts and then vaporizes as heat is added to it.

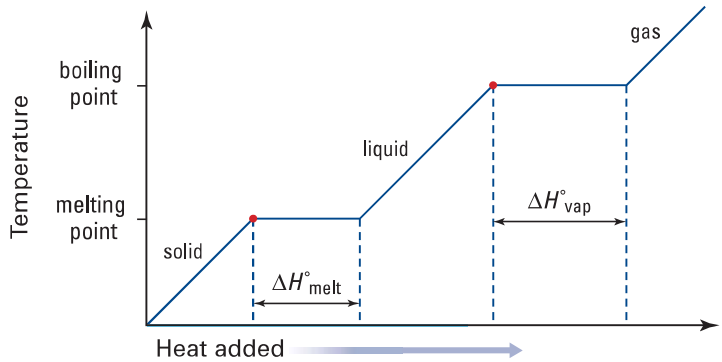


Figure 5.7 **As heat is added to a substance, the temperature of the substance steadily increases until it reaches its melting point or boiling point. The temperature then remains steady as the substance undergoes a phase change.**

You can represent the enthalpy change that accompanies a phase change—from liquid to solid, for example—just like you represented the enthalpy change of a chemical reaction. You can include a heat term in the equation, or you can use a separate expression of enthalpy change. For example, when one mole of water melts, it absorbs 6.02 kJ of energy.

$$H_2O_{(s)} + 6.02\ \text{kJ} \rightarrow H_2O_{(\ell)}$$

$$H_2O_{(s)} \rightarrow H_2O_{(\ell)} \quad \Delta H = 6.02\ \text{kJ}$$

Normally, however, chemists represent enthalpy changes associated with phase changes using modified ΔH symbols. These symbols are described below.

- *enthalpy of vaporization*, ΔH_{vap}: the enthalpy change for the phase change from liquid to gas
- *enthalpy of condensation*, ΔH_{cond}: the enthalpy change for the phase change of a substance from gas to liquid
- *enthalpy of melting*, ΔH_{melt}: the enthalpy change for the phase change of a substance from solid to liquid
- *enthalpy of freezing*, ΔH_{fre}: the enthalpy change for the phase change of a substance from liquid to solid

Vaporization and condensation are opposite processes. Thus, the enthalpy changes for these processes have the same value but opposite signs. For example, 6.02 kJ is needed to vaporize one mole of water. Therefore, 6.02 kJ of energy is released when one mole of water freezes.

$$\Delta H_{vap} = -\Delta H_{cond}$$

Similarly, melting and freezing are opposite processes.

$$\Delta H_{melt} = -\Delta H_{fre}$$

Several enthalpies of melting and vaporization are shown in Table 5.1. Notice that the same units (kJ/mol) are used for the enthalpies of melting, vaporization, condensation, and freezing. Also notice that energy changes associated with phase changes can vary widely.

CHEM FACT

The process of melting is also known as *fusion*. Therefore, you will sometimes see the enthalpy of melting referred to as the *enthalpy of fusion*.

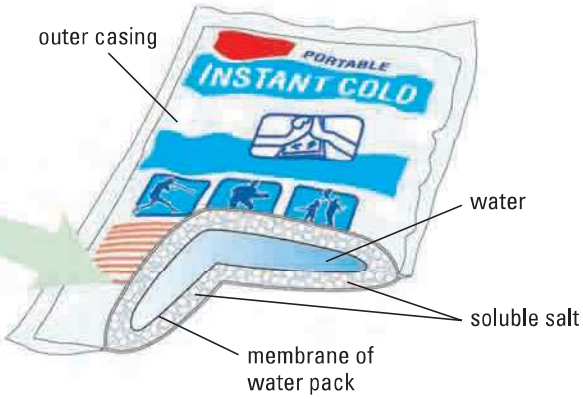
Table 5.1 Enthalpies of Melting and Vaporization for Several Substances

Substance	Enthalpy of melting, ΔH_{melt} (kJ/mol)	Enthalpy of vaporization, ΔH_{vap} (kJ/mol)
argon	1.3	6.3
diethyl ether	7.3	29
ethanol	5.0	40.5
mercury	23.4	59
methane	8.9	0.94
sodium chloride	27.2	207
water	6.02	40.7

Hot Packs and Cold Packs: Using the Energy of Physical Changes

You just learned about the enthalpy changes that are associated with phase changes. Another type of physical change that involves a heat transfer is dissolution. When a solute dissolves in a solvent, the enthalpy change that occurs is called the *enthalpy of solution*, ΔH_{soln}. Dissolution can be either endothermic or exothermic.

Manufacturers take advantage of endothermic dissolution to produce cold packs that athletes can use to treat injuries. One type of cold pack contains water and a salt, such as ammonium nitrate, in separate compartments. When you crush the pack, the membrane that divides the compartments breaks, and the salt dissolves. This dissolution process is endothermic. It absorbs heat for a short period of time, so the cold pack feels cold. Figure 5.8 shows how a cold pack works.



A typical cold pack has two separate chambers. One chamber contains a salt. The other chamber contains water. Crushing the pack allows the salt to dissolve in the water—an endothermic process.

Figure 5.8 **This person's shoulder was injured. Using a cold pack helps to reduce the inflammation of the joint.**

Some types of hot packs are constructed in much the same way as the cold packs described above. They have two compartments. One compartment contains a salt, such as calcium chloride. The other compartment contains water. In hot packs, however, the dissolution process is exothermic. It releases heat to the surroundings.

Energy and Nuclear Reactions

The energy that is released by a physical change, such as the dissolution of calcium chloride, can warm your hands. The energy that is released by a chemical reaction, such as the formation of water, can power a rocket. The energy that is released by a nuclear reaction, such as the nuclear reactions in the Sun, however, can provide enough heat to fry an egg on a sidewalk that is 150 000 000 km away from the surface of the Sun.

From previous science courses, you will recall that nuclear reactions involve changes in the nuclei of atoms. Often nuclear reactions result in the transformation of one or more elements into one or more different elements.

Like physical changes and chemical reactions, nuclear reactions are accompanied by energy changes. Nuclear reactions, however, produce significantly more energy than physical and chemical processes. *In nuclear reactions, a significant amount of the mass of the reactants is actually converted into energy.*

Ever since Albert Einstein devised his famous equation, $E = mc^2$, we have known that mass and energy are interconvertible. In Einstein's equation, E is energy in $kg \cdot m^2/s^2$ (J), m is the mass in kg, and c^2 is the square of the speed of light.

$$\begin{aligned} c^2 &= (3.0 \times 10^8 \text{ m/s})^2 \\ &= 9.0 \times 10^{16} \text{ m}^2/\text{s}^2 \end{aligned}$$

As you can see, c^2 is an enormous number. Therefore, even a very tiny amount of matter is equivalent to a significant amount of energy.

For example, compare the mass of 1 mol of carbon-12 atoms with the mass of the individual nucleons in 1 mol of carbon-12 atoms. The mass of 6 mol of hydrogen-1 atoms (one proton and one electron each) and 6 mol of neutrons is 12.098 940 g. The mass of 1 mol of carbon-12 atoms is exactly 12 g. Note that the mass of the electrons does not change in a nuclear reaction.

$$\begin{array}{r} 12.098\ 940 \text{ g/mol} \\ -\ 12.000\ 000 \text{ g/mol} \\ \hline 0.098\ 940 \text{ g/mol} \end{array}$$

The difference in mass is significant. It would show up on any reasonably precise balance. Thus, the mass of the nucleus of carbon-12 is significantly less than the mass of its component nucleons. The difference in mass between a nucleus and its nucleons is known as the **mass defect**. What causes this mass defect? It is caused by the **nuclear binding energy**: the energy associated with the strong force that holds a nucleus together.

$$\text{Nucleus} + \text{Nuclear binding energy} \rightarrow \text{Nucleons}$$

You can use Einstein's equation to calculate the nuclear binding energy for carbon-12.

$$\begin{aligned} \Delta E &= \Delta mc^2 \\ &= (9.89 \times 10^{-5} \text{ kg/mol})(9.0 \times 10^{16} \text{ m}^2/\text{s}^2) \\ &= 8.9 \times 10^{12} \text{ J/mol} \\ &= 8.9 \times 10^{9} \text{ kJ/mol} \end{aligned}$$

Clearly, the energy associated with the bonds that hold a nucleus together is much greater than the energy associated with chemical bonds, which are usually only a few hundred kJ/mol.

The higher the binding energy of a nucleus, the more stable the nucleus is. Nuclei with mass numbers (A) that are close to 60 are the most stable. Nuclear reactions, in which nuclei break apart or fuse, tend to form nuclei that are more stable than the reactant nuclei. Figure 5.9 illustrates the relative stability of various nuclei.

Web LINK

www.mcgrawhill.ca/links/chemistry12

Not all hot packs use dissolution processes. For example, one kind of hot pack exploits the crystallization of sodium thiosulfate or sodium acetate. Another kind uses the oxidation of iron (rusting). On the Internet, investigate different kinds of hot packs. Are they all used for the same purpose? What are the pros and cons of their designs? To start your search, go to the web site above and click on **Web Links**.

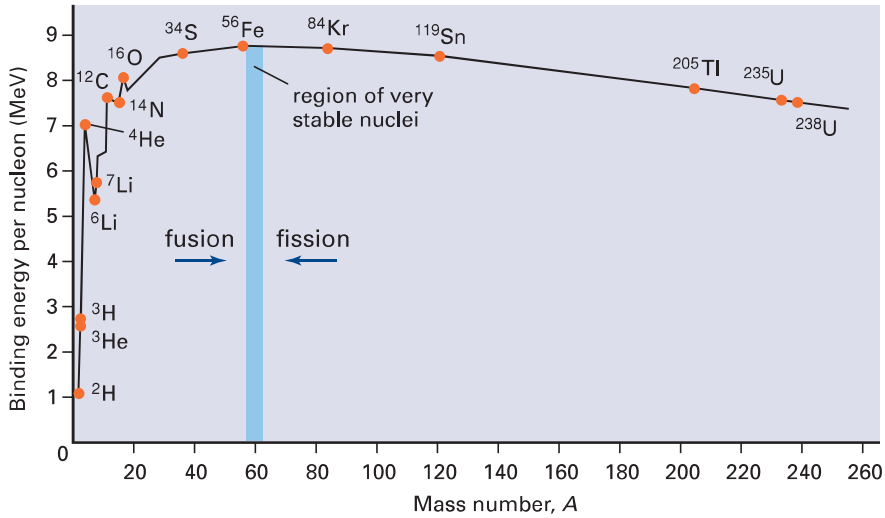


Figure 5.9 This graph shows the relative stability of nuclei. It indicates whether nuclei are more likely to split or fuse in a nuclear reaction. Notice that the helium-4 nucleus is unusually stable.

The difference between the nuclear binding energy of the reactant nuclei and the product nuclei represents the energy change of the nuclear reaction.

Nuclear Fission

A heavy nucleus can split into lighter nuclei by undergoing **nuclear fission**. Nuclear power plants use controlled nuclear fission to provide energy. Uncontrolled nuclear fission is responsible for the massive destructiveness of an atomic bomb.

The most familiar fission reactions involve the splitting of uranium atoms. In these reactions, a uranium-235 atom is bombarded with neutrons. The uranium nucleus then splits apart into various product nuclei. Two examples of fission reactions that involve uranium-235 are shown in Figure 5.10.

Electronic Learning Partner

To learn more about nuclear fission, go to the Chemistry 12 Electronic Learning Partner.

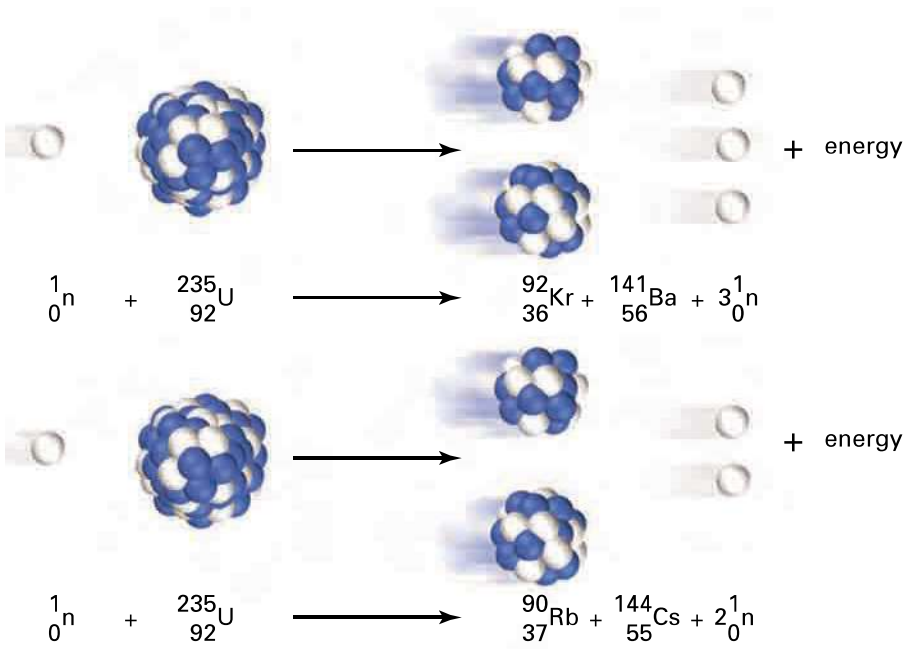


Figure 5.10 Uranium can undergo fission in numerous different ways, producing various product nuclei. Two examples are shown here.

Fission reactions produce vast quantities of energy. For example, when one mole of uranium-235 splits, it releases 2.1×10^{13} J. By contrast, when one mole of coal burns, it releases about 3.9×10^{6} J. Thus, the combustion of coal releases about five million times fewer joules of energy per mole than the fission of uranium-235.

Math LINK

The fission of one mole of uranium-235 produces more energy than the fusion of one mole of deuterium with one mole of tritium. What if you compare the energy that is produced in terms of *mass* of reactants? Calculate a ratio to compare the energy that is produced from fusion and fission, per gram of fuel. What practical consequences arise from your result?

Nuclear Fusion

Two smaller nuclei can fuse to form a larger nucleus, in what is called a **nuclear fusion** reaction. You and all other life on Earth would not exist without nuclear fusion reactions. These reactions are the source of the energy produced in the Sun.

One example of a fusion reaction is the fusion of deuterium and tritium.

$$^{2}_{1}\text{H} + ^{3}_{1}\text{H} \rightarrow ^{4}_{2}\text{He} + ^{1}_{0}\text{n}$$

The seemingly simple reaction between deuterium and tritium produces 1.7×10^{12} J of energy for each mole of deuterium. This is about 10 times fewer joules of energy than are produced by the fission of one mole of uranium. It is still, however, 500 000 times more energy than is produced by burning one mole of coal.

Scientists are searching for a way to harness the energy from fusion reactions. Fusion is a more desirable way to produce energy than fission. The main product of fusion, helium, is relatively harmless compared with the radioactive products of fission. Unfortunately, fusion is proving more difficult than fission to harness. Fusion will not proceed at a reasonable rate without an enormous initial input of energy. This is not a problem in the core of the Sun, where the temperature ranges from 7 500 000°C to 15 000 000°C. It is a problem in industry. Scientists are working on safe and economical ways to provide the high-temperature conditions that are needed to make fusion a workable energy source.

Comparing the Energy of Physical, Chemical, and Nuclear Processes

In this section, you learned that physical changes, chemical reactions, and nuclear reactions all involve energy changes. You also learned that the energy changes have some striking differences in magnitude. Figure 5.11 shows energy changes for some physical, chemical, and nuclear processes. Some other interesting energy statistics are included for reference.

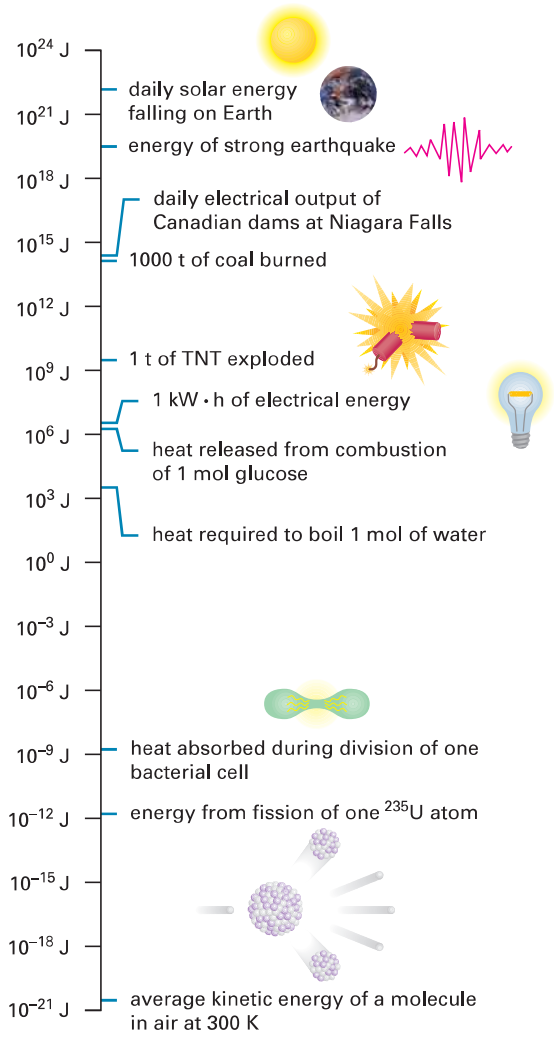
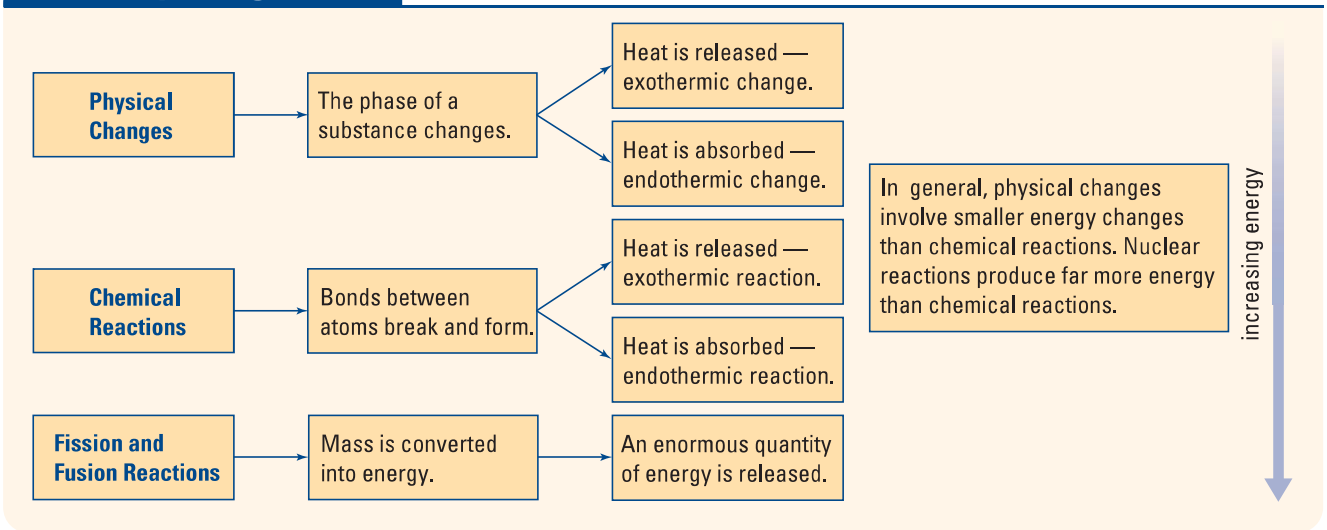


Figure 5.11 **The energy changes of physical, nuclear, and chemical processes vary widely. In general, however, chemical reactions are associated with greater energy changes than physical changes. Nuclear reactions are associated with far greater energy changes than chemical reactions.**

The following Concept Organizer summarizes what you learned about the energy changes associated with physical changes, chemical reactions, and nuclear reactions.

Concept Organizer — Energy Changes



Section Summary

In section 5.1, you learned about the energy changes that accompany physical changes, chemical reactions, and nuclear reactions. You learned how to represent energy changes using thermochemical equations and diagrams. In the next section, you will determine the enthalpy of a reaction by experiment.

Section Review

1. K/U In your own words, explain why exothermic reactions have $\Delta H < 0$.

2. K/U Label each thermochemical equation with the most specific form(s) of ΔH. Remember to pay attention to the *sign* of ΔH.
   - **(a)** $Ag_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow AgCl_{(s)} + 127.0\ kJ$ (at 25°C and 100 kPa)
   - **(b)** $44.0\ kJ + H_2O_{(\ell)} \rightarrow H_2O_{(g)}$ (at 25°C and 100 kPa)
   - **(c)** $C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)} + \text{energy}$

3. C Suppose that one of your friends was absent on the day that you learned about labelling ΔH. To help your friend, create a table that summarizes the different ways to label ΔH, and their meanings.

4. I Calcium oxide, CaO, reacts with carbon in the form of graphite. Calcium carbide, CaC_2, and carbon monoxide, CO, are produced in an endothermic reaction.

   $CaO_{(s)} + 3C_{(s)} + 462.3\ kJ \rightarrow CaC_{2(s)} + CO_{(g)}$

   (a) 246.7 kJ of energy is available to react. What mass of calcium carbide is produced, assuming sufficient reactants?

(b) What is the enthalpy change for the reaction of 46.7 g of graphite with excess calcium oxide?

(c) 1.38×10^{24} formula units of calcium oxide react with excess graphite. How much energy is needed?

5 I Acetylene, C_2H_2, undergoes complete combustion in oxygen. Carbon dioxide and water are formed. When one mole of acetylene undergoes complete combustion, 1.3×10^3 kJ of energy is released.

(a) Write a thermochemical equation for this reaction.

(b) Draw a diagram to represent the thermochemical equation.

(c) How much energy is released when the complete combustion of acetylene produces 1.50 g of water?

6 C Write an equation to represent each phase change in Table 5.1 on page 228. Include the enthalpy change as a heat term in the equation.

7 MC When one mole of gaseous water forms from its elements, 241.8 kJ of energy is released. In other words, when hydrogen burns in oxygen or air, it produces a great deal of energy. Since the nineteenth century, scientists have been researching the potential of hydrogen as a fuel. One way in which the energy of the combustion of hydrogen has been successfully harnessed is as rocket fuel for aircraft.

(a) Write a thermodynamic equation for the combustion of hydrogen.

(b) Describe three reasons why hydrogen gas is a desirable rocket fuel.

(c) Suggest challenges that engineers might have had to overcome in order to make hydrogen a workable rocket fuel for aircraft.

(d) Use print and electronic resources to find out about research into hydrogen as a fuel. Create a time line that shows significant events and discoveries in this research.

8 MC A healthy human body maintains a temperature of about 37.0°C. Explain how physical, chemical, and nuclear processes all contribute, directly or indirectly, to keeping the human body at a constant temperature.

5.2 Determining Enthalpy of Reaction by Experiment

Section Preview/ Specific Expectations

In this section, you will

- **determine** the heat that is produced by a reaction using a calorimeter, and use the data obtained to calculate the enthalpy change for the reaction
- **communicate** your understanding of the following terms: *specific heat capacity (c), heat capacity (C), calorimeter, coffee-cup calorimeter, constant-pressure calorimeter*

Chemical and physical processes, such as the ones you studied in section 5.1, are associated with characteristic enthalpy changes. How do chemists measure these enthalpy changes?

To measure the enthalpy of a chemical or physical process, chemists insulate the system from the surroundings. They can then determine the heat change by measuring the temperature change of the system. What is the relationship between the heat change and the temperature change? As you learned in previous science courses, each substance has a characteristic property that dictates how its temperature will change when heat is lost or gained.

Specific Heat Capacity

The amount of energy that is needed to raise the temperature of one gram of a substance 1°C (or 1 K) is the **specific heat capacity**, ***c***, of the substance. Specific heat capacity is usually expressed in units of J/g • °C. The specific heat capacities of several substances are given in Table 5.2. Figure 5.12 shows that you can often predict the relative specific heat capacities of familiar substances.

Figure 5.12 On a sunny day, you would probably prefer to sit on a bench made of wood rather than a bench made of aluminum. Wood has a higher heat capacity than aluminum. Therefore, more heat is needed to increase its temperature.

Table 5.2 Specific Heat Capacities of Selected Substances

Substance	Specific heat capacity (J/g • °C at 25°C)
Element	
aluminum	0.900
carbon (graphite)	0.711
hydrogen	14.267
iron	0.444
Compound	
ammonia (liquid)	4.70
ethanol	2.46
ethylene glycol	2.42
water (liquid)	4.184
Other material	
air	1.02
concrete	0.88
glass	0.84
wood	1.76

You can use the specific heat capacity of a substance to calculate the amount of energy that is needed to heat a given mass a certain number of degrees. You can also use the specific heat capacity to determine the amount of heat that is released when the temperature of a given mass decreases. The specific heat capacity of liquid water, as shown in Table 5.2, is 4.184 J/g • °C. This relatively large value indicates that a considerable amount of energy is needed to raise or lower the temperature of water.

CONCEPT CHECK

Explain why water is sometimes used as a coolant for automobile engines.

All samples of the same substance have the same specific heat capacity. In contrast, **heat capacity**, ***C***, relates the heat of a sample, object, or system to its change in temperature. Heat capacity is usually expressed in units of kJ/°C.

Consider a bathtub full of water and a teacup full of water at room temperature. All the water has the same specific heat capacity, but the two samples have different heat capacities. It would take a great deal more heat to raise the temperature of the water in the bathtub by 10°C than it would take to raise the temperature of the water in the teacup by 10°C. Therefore, the water in the bathtub has a higher heat capacity.

Specific Heat Capacity and Heat Transfer

You can use the following equation to calculate the heat change of a substance, based on the mass of the substance. You can also use this equation to calculate the specific heat capacity of the substance and the change in its temperature.

$$Q = m \bullet c \bullet \Delta T$$

where Q = heat (J)

m = mass (g)

c = specific heat capacity (J/g • °C)

$\Delta T = T_f$(final temperature) $- T_i$(initial temperature)(°C or K)

Water is often used in controlled surroundings to measure the heat of a reaction. For example, you can use the equation above to determine the amount of energy that is needed to heat 1.00×10^2 g of water from 20.0°C to 45.0°C.

$$Q = m \bullet c \bullet \Delta T$$

The mass of the water is 1.00×10^2 g. The specific heat capacity of water is 4.184 J/g • °C. The temperature of the water increases by 25.0°C.

$$\therefore Q = (1.00 \times 10^2\ \cancel{g})(4.184\ \text{J}/\cancel{g} \bullet \cancel{°C})(25.0\ \cancel{°C})$$
$$= 1.05 \times 10^4\ \text{J}$$

To raise the temperature of 1.00×10^2 g of water by 25°C, 1.05×10^4 J of heat is needed.

Try the following problems to practise working with specific heat capacity and temperature change.

Practice Problems

5. A sample of ethylene glycol, used in car radiators, has a mass of 34.8 g. The sample liberates 783 J of heat. The initial temperature of the sample is 22.1°C. What is the final temperature?
6. A sample of ethanol, C_2H_5OH, absorbs 23.4 kJ of energy. The temperature of the sample increases from 5.6°C to 19.8°C. What is the mass of the ethanol sample? The specific heat capacity of ethanol is 2.46 J/g • °C.
7. A child's swimming pool contains 1000 L of water. When the water is warmed by solar energy, its temperature increases from 15.3°C to 21.8°C. How much heat does the water absorb?
8. What temperature change results from the loss of 255 kJ from a 10.0 kg sample of water?

Measuring Heat Transfer in a Laboratory

From previous science courses, you will probably remember that a **calorimeter** is used to measure enthalpy changes for chemical and physical reactions. A calorimeter works by insulating a system from its surroundings. By measuring the temperature change of the system, you can determine the amount of heat that is released or absorbed by the reaction. For example, the heat that is released by an exothermic reaction raises the temperature of the system.

$$Q_{\text{reaction}} = -Q_{\text{insulated system}}$$

In your previous chemistry course, you learned about various types of calorimeters. For instance, you learned about a *bomb calorimeter*, which allows chemists to determine energy changes under conditions of constant volume.

In section 5.1, however, you learned that an enthalpy change represents the heat change between products and reactants *at a constant pressure*. Therefore, the calorimeter you use to determine an enthalpy change should allow the reaction to be carried out at a constant pressure. In other words, it should be open to the atmosphere.

To determine enthalpy changes in high school laboratories, a **coffee-cup calorimeter** provides fairly accurate results. A coffee-cup calorimeter is composed of two nested polystyrene cups ("coffee cups"). They can be placed in a 250 mL beaker for added stability. Since a coffee-cup calorimeter is open to the atmosphere, it is also called a **constant-pressure calorimeter**.

As with any calorimeter, each part of the coffee-cup calori-meter has an associated heat capacity. Because these heat capacities are very small, however, and because a coffee-cup calorimeter is not as accurate as other calorimeters, the heat capacity of a coffee-cup calorimeter is usually assumed to be negligible. It is assumed to have a value of 0 J/°C.

Web LINK

www.mcgrawhill.ca/links/chemistry12

The famous French scientist Antoine Laviosier (1743-1794) is considered by many to be the first modern chemist. Lavoisier created a calorimeter to study the energy that is released by the metabolism of a guinea pig. To learn about Lavoisier's experiment, go to the web site above and click on **Web Links**. What do you think about using animals in experiments? Write an essay to explain why you agree or disagree with this practice.

Using a Calorimeter to Determine the Enthalpy of a Reaction

A coffee-cup calorimeter is well-suited to determining the enthalpy changes of reactions in dilute aqueous solutions. The water in the calorimeter absorbs (or provides) the energy that is released (or absorbed) by a chemical reaction. When carrying out an experiment in a dilute solution, the solution itself absorbs or releases the energy. You can calculate the amount of energy that is absorbed or released by the solution using the equation mentioned earlier.

$$Q = m \cdot c \cdot \Delta T$$

The mass, m, is the mass of the *solution*, because the solution absorbs the heat. When a dilute aqueous solution is used in a calorimeter, you can assume that the solution has the same density and specific heat capacity as pure water. As you saw above, you can also assume that the heat capacity of the calorimeter is negligible. In other words, you can assume that all the heat that is released or absorbed by the reaction is absorbed or released by the solution.

The following Sample Problem illustrates how calorimetry can be used to determine ΔH of a chemical reaction.

Sample Problem

Determining the Enthalpy of a Chemical Reaction

Problem

Copper(II) sulfate, $CuSO_4$, reacts with sodium hydroxide, NaOH, in a double displacement reaction. A precipitate of copper(II) hydroxide, $Cu(OH)_2$, and aqueous sodium sulfate, Na_2SO_4, is produced.

$$CuSO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Cu(OH)_{2(s)} + Na_2SO_{4(aq)}$$

50.0 mL of 0.300 mol/L $CuSO_4$ solution is mixed with an equal volume of 0.600 mol/L NaOH. The initial temperature of both solutions is 21.4°C. After mixing the solutions in the coffee-cup calorimeter, the highest temperature that is reached is 24.6°C. Determine the enthalpy change of the reaction. Then write the thermochemical equation.

What Is Required?

You need to calculate ΔH of the given reaction.

What Is Given?

You know the volume of each solution. You also know the initial temperature of each solution and the final temperature of the reaction mixture.

Volume of $CuSO_4$ solution, $V_{CuSO_4} = 50.0$ mL

Volume of NaOH solution, $V_{NaOH} = 50.0$ mL

Initial temperature, $T_i = 21.4°C$

Final temperature, $T_f = 24.6°C$

Plan Your Strategy

Step 1 Determine the total volume by adding the volumes of the two solutions. Determine the total mass of the reaction mixture, assuming a density of 1.00 g/mL (the density of water).

Step 2 Use the equation $Q = m \cdot c \cdot \Delta T$ to calculate the amount of heat that is absorbed by the solution (in J). Assume that the reaction mixture has the same specific heat capacity as water ($c = 4.184$ J/g • °C).

Step 3 Use the equation $Q_{reaction} = -Q_{solution}$ to determine the amount of heat that is released by the reaction.

Step 4 Determine the number of moles of $CuSO_4$ and NaOH that reacted. If necessary, determine the limiting reactant. Use the amount of limiting reactant to get ΔH of the reaction (in kJ/mol).

Step 5 Use your ΔH to write the thermochemical equation for the reaction.

Act on Your Strategy

Step 1 The total volume of the reaction mixture is
50.0 mL + 50.0 mL = 100.0 mL

The mass of the reaction mixture, assuming a density of 1.00 g/mL, is

$$\begin{aligned} m &= DV \\ &= (1.00\ \text{g/m}\cancel{\text{L}})(100.0\ \text{m}\cancel{\text{L}}) \\ &= 1.00 \times 10^2\ \text{g} \end{aligned}$$

Continued ...

Continued ...

Step 2 The amount of heat, Q, that is absorbed by the solution is

$$Q_{solution} = m_{solution} \cdot c_{solution} \cdot \Delta T_{solution}$$
$$= (100\ \cancel{g})(4.184\ J/\cancel{g} \cdot \cancel{°C})(24.6\cancel{°C} - 21.4\cancel{°C})$$
$$= 1.3 \times 10^3\ J$$

Step 3 Based on the value of Q in step 2, the heat change for the reaction is -1.3×10^3 J.

Step 4 Calculate the number of moles of $CuSO_4$ as follows.

$$n = c \cdot V$$
$$= (0.300\ mol/\cancel{L})(50.0 \times 10^{-3}\cancel{L})$$
$$= 0.0150\ mol$$

Calculate the number of moles of NaOH.

$$n\ mol\ NaOH = (0.600\ mol/\cancel{L})(50.0 \times 10^{-3}\cancel{L})$$
$$= 0.300\ mol$$

The reactants are present in stoichiometric amounts. (There is no limiting reactant.)

ΔH of the reaction, in kJ/mol $CuSO_4$, is

$$\Delta H = \frac{-1.3 \times 10^3\ J}{0.0150\ mol\ CuSO_4}$$
$$= -8.9 \times 10^3\ J/mol\ CuSO_4$$
$$= -89\ kJ/mol\ CuSO_4$$

The enthalpy change of the reaction is -89 kJ/mol $CuSO_4$.

Step 5 The thermochemical equation is

$$CuSO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Cu(OH)_{2(s)} + Na_2SO_{4(aq)} \quad \Delta H = -89\ kJ$$

Check Your Solution

The solution has the correct number of significant digits. The units are correct. You know that the reaction was exothermic, because the temperature of the solution increased. The calculated ΔH is negative, which is correct for an exothermic reaction.

Practice Problems

9. A chemist wants to determine the enthalpy of neutralization for the following reaction.

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}$$

The chemist uses a coffee-cup calorimeter to neutralize completely 61.1 mL of 0.543 mol/L $HCl_{(aq)}$ with 42.6 mL of $NaOH_{(aq)}$. The initial temperature of both solutions is 17.8°C. After neutralization, the highest recorded temperature is 21.6°C. Calculate the enthalpy of neutralization, in units of kJ/mol of HCl. Assume that the density of both solutions is 1.00 g/mL. Also assume that the specific heat capacity of both solutions is the same as the specific heat capacity of water.

10. A chemist wants to determine empirically the enthalpy change for the following reaction.

$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

The chemist uses a coffee-cup calorimeter to react 0.50 g of Mg ribbon with 100 mL of 1.00 mol/L $HCl_{(aq)}$. The initial temperature of the $HCl_{(aq)}$ is 20.4°C. After neutralization, the highest recorded temperature is 40.7°C.

(a) Calculate the enthalpy change, in kJ/mol of Mg, for the reaction.

(b) State any assumptions that you made in order to determine the enthalpy change.

11. Nitric acid is neutralized with potassium hydroxide in the following reaction.

$HNO_{3(aq)} + KOH_{(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(\ell)} \quad \Delta H = -53.4$ kJ/mol

55.0 mL of 1.30 mol/L solutions of both reactants, at 21.4°C, are mixed in a calorimeter. What is the final temperature of the mixture? Assume that the density of both solutions is 1.00 g/mL. Also assume that the specific heat capacity of both solutions is the same as the specific heat capacity of water. No heat is lost to the calorimeter itself.

12. A student uses a coffee-cup calorimeter to determine the enthalpy of reaction for hydrobromic acid and potassium hydroxide. The student mixes 100.0 mL of 0.50 mol/L $HBr_{(aq)}$ at 21.0°C with 100.0 mL of 0.50 mol/L $KOH_{(aq)}$, also at 21.0°C. The highest temperature that is reached is 24.4°C. Write a thermochemical equation for the reaction.

In Practice Problems 9, 11, and 12, you used experimental data to determine the enthalpy of reaction for neutralization reactions. Neutralization reactions are particularly well suited to analysis involving the use of a coffee-cup calorimeter for a number of reasons:

- When using dilute solutions of acids and bases, you can assume their density is close to the density of water. Therefore, you can easily measure the volume of the solutions and calculate their mass.
- Neutralization reactions between dilute strong acids and dilute strong bases tend to cause temperature changes in the reaction mixture that are large enough to be measurable using a standard thermometer, but small enough for safety.
- Neutralization reactions take place very quickly. Therefore, the peak temperature change also occurs very quickly. There is little time for heat transfer between the insulated system and the surroundings to take place.

In the following investigation, you will construct a coffee-cup calorimeter and use it to determine the enthalpy of a neutralization reaction.

Investigation 5-A

SKILL FOCUS
Predicting
Performing and recording
Analyzing and interpreting

Determining the Enthalpy of a Neutralization Reaction

The neutralization of hydrochloric acid with sodium hydroxide solution is represented by the following equation.

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}$

Using a coffee-cup calorimeter, you will determine the enthalpy change for this reaction.

Question

What is the heat of neutralization for hydrochloric acid and sodium hydroxide solution?

Prediction

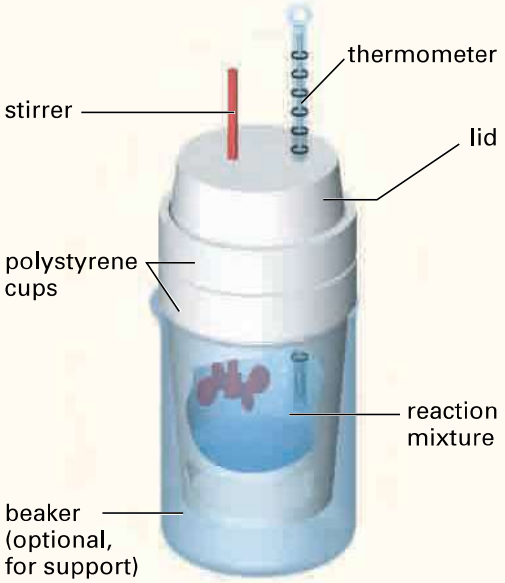
Will the neutralization reaction be endothermic or exothermic? Record your prediction, and give reasons.

Safety Precautions

If you get any hydrochloric acid or sodium hydroxide solution on your skin, flush your skin with plenty of cold water.

Materials

100 mL graduated cylinder
400 mL beaker
2 polystyrene cups that are the same size
polystyrene lid
thermometer
stirring rod
1.00 mol/L $HCl_{(aq)}$
1.00 mol/L $NaOH_{(aq)}$



Procedure

1. Your teacher will allow the hydrochloric acid and sodium hydroxide solution to come to room temperature overnight.
2. Read the rest of this Procedure carefully before you continue. Set up a graph to record your temperature observations.
3. Build a coffee-cup calorimeter, using the diagram above as a guide. You will need to make two holes in the polystyrene lid—one for the thermometer and one for the stirring rod. The holes should be as small as possible to minimize heat loss to the surroundings.
4. Rinse the graduated cylinder with a small quantity of 1.00 mol/L $NaOH_{(aq)}$. Use the cylinder to add 50.0 mL of 1.00 mol/L $NaOH_{(aq)}$ to the calorimeter. Record the initial temperature of the $NaOH_{(aq)}$. (This will also represent the initial temperature of the $HCl_{(aq)}$.) CAUTION The $NaOH_{(aq)}$ can burn your skin.

5. Rinse the graduated cylinder with tap water. Then rinse it with a small quantity of 1.00 mol/L $HCl_{(aq)}$. Quickly and carefully, add 50.0 mL of 1.00 mol/L $HCl_{(aq)}$ to the $NaOH_{(aq)}$ in the calorimeter. **CAUTION** The $HCl_{(aq)}$ can burn your skin.

6. Cover the calorimeter. Record the temperature every 30 s, stirring gently and continuously.

7. When the temperature levels off, record the final temperature, T_f.

8. If time permits, repeat steps 4 to 7.

Analysis

1. Determine the amount of heat that is absorbed by the solution in the calorimeter.

2. Use the following equation to determine the amount of heat that is released by the reaction:

$$-Q_{reaction} = Q_{solution}$$

3. Determine the number of moles of $HCl_{(aq)}$ and $NaOH_{(aq)}$ that were involved in the reaction.

4. Use your knowledge of solutions to explain what happens during a neutralization reaction. Use equations in your answer. Was heat released or absorbed during the neutralization reaction? Explain your answer.

Conclusion

5. Use your results to determine the enthalpy change of the neutralization reaction, in kJ/mol of NaOH. Write the thermochemical equation for the neutralization reaction.

Applications

6. When an acid gets on your skin, why must you flush the area with plenty of water rather than neutralizing the acid with a base?

7. Suppose that you had added solid sodium hydroxide pellets to hydrochloric acid, instead of adding hydrochloric acid to sodium hydroxide solution?

   (a) Do you think you would have obtained a different enthalpy change?

   (b) Would the enthalpy change have been higher or lower?

   (c) How can you test your answer? Design an investigation, and carry it out with the permission of your teacher.

   (d) What change do you need to make to the thermochemical equation if you perform the investigation using solid sodium hydroxide?

8. In Investigation 5-A, you assumed that the heat capacity of your calorimeter was 0 J/°C.

   (a) Design an investigation to determine the actual heat capacity of your coffee-cup calorimeter, $C_{calorimeter}$. Include equations for any calculations you will need to do. If time permits, have your teacher approve your procedure and carry out the investigation. **Hint:** If you mix hot and cold water together and no heat is absorbed by the calorimeter itself, then the amount of heat absorbed by the cold water should equal the amount of heat released by the hot water. If more heat is released by the hot water than is absorbed by the cold water, the difference must be absorbed by the calorimeter.

   (b) Include the heat capacity of your calorimeter in your calculations for $\Delta H_{neutralization}$. Use the following equation:

$$-Q_{reaction} = (m_{solution} \cdot c_{solution} \cdot \Delta T) + (C_{calorimeter} \cdot \Delta T)$$

PROBEWARE

If you have access to probeware, do Probeware Investigation 5-A, or a similar investigation from a probeware company.

Section Summary

In this section, you measured the enthalpy change of a reaction by calorimetry. You may have noticed that the reactions you studied in this section involved relatively small energy changes. How do chemists work quantitatively with some of the large energy changes you examined in section 5.1? In the next section, you will learn how to calculate the heat of reaction for virtually any chemical reaction or physical change. This powerful skill will allow you to find heats of reaction without carrying out experiments.

Section Review

1. K/U Distinguish between heat capacity and specific heat capacity.
2. K/U What properties of polystyrene make it a suitable material for a constant-pressure calorimeter? Why are polystyrene coffee cups not suitable for a constant-volume calorimeter?
3. K/U Suppose that you use concentrated reactant solutions in an experiment with a coffee-cup calorimeter. Will you make the same assumptions that you did when you used dilute solutions? Explain.
4. I Concentrated sulfuric acid can be diluted by adding it to water. The reaction is extremely exothermic. In this question, you will design an experiment to measure the enthalpy change (in kJ/mol) for the dilution of concentrated sulfuric acid. Assume that you have access to any equipment in your school's chemistry laboratory. Do not carry out this experiment.
   - (a) State the equipment and chemicals that you need.
   - (b) Write a step-by-step procedure.
   - (c) Set up an appropriate data table.
   - (d) State any information that you need.
   - (e) State any simplifying assumptions that you will make.
5. I A chemist mixes 100.0 mL of 0.050 mol/L potassium hydroxide with 100.0 mL of 0.050 mol/L nitric acid in a constant-pressure calorimeter. The temperature of the reactants is 21.01°C. The temperature of the products is 21.34°C.
   - (a) Write a thermochemical equation for the reaction.
   - (b) If you performed this investigation, would you change the procedure? If so, how?
6. C Explain why a bomb calorimeter may not provide accurate results for determining the enthalpy of a reaction.
7. MC From experience, you know that you produce significantly more heat when you are exercising than when you are resting. Scientists can study the heat that is produced by human metabolism reactions using a "human calorimeter." Based on what you know about calorimetry, how would you design a human calorimeter? What variables would you control and study in an investigation using your calorimeter? Write a brief proposal outlining the design of your human calorimeter and the experimental approach you would take.

Hess's Law of Heat Summation

5.3

In section 5.2, you used a coffee-cup calorimeter to determine the quantity of heat that was released or absorbed in a chemical reaction. Coffee-cup calorimeters are generally used only for dilute aqueous solutions. There are many non-aqueous chemical reactions, however. There are also many reactions that release so much energy they are not safe to perform using a coffee-cup calorimeter. Imagine trying to determine the enthalpy of reaction for the detonation of nitroglycerin, an unstable and powerfully explosive compound. Furthermore, there are reactions that occur too slowly for the calorimetric method to be practical. (You will learn more about rates of reactions in the next chapter.)

Chemists can determine the enthalpy change of any reaction using an important law, known as **Hess's law of heat summation**. This law states that *the enthalpy change of a physical or chemical process depends only on the beginning conditions (reactants) and the end conditions (products). The enthalpy change is independent of the pathway of the process and the number of intermediate steps in the process.* It is the sum of the enthalpy changes of all the individual steps that make up the process.

For example, carbon and oxygen can form carbon dioxide via two pathways.

1. Carbon can react with oxygen to form carbon monoxide. The carbon monoxide then reacts with oxygen to produce carbon dioxide. The two equations below represent this pathway.

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H^\circ = -110.5\ \text{kJ}$$
$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -283.0\ \text{kJ}$$

2. Carbon can also react with oxygen to produce carbon dioxide directly.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -393.5\ \text{kJ}$$

In both cases, the net result is that one mole of carbon reacts with one mole of oxygen to produce one mole of carbon dioxide. (In the first pathway, all the carbon monoxide that is produced reacts with oxygen to form carbon dioxide.) Notice that the sum of the enthalpy changes for the first pathway is the same as the enthalpy change for the second pathway.

Examine Figure 5.13 to see how to represent the two pathways using one enthalpy diagram.

Section Preview/ Specific Expectations

In this section, you will

- **explain** Hess's law of heat summation, using examples
- **apply** Hess's law to solve problems, including problems that involve data obtained through experimentation
- **calculate** heat of reaction using given enthalpies of formation
- **communicate** your understanding of the following terms: *Hess's law of heat summation, formation reactions, standard molar enthalpy of formation (ΔH°_f)*

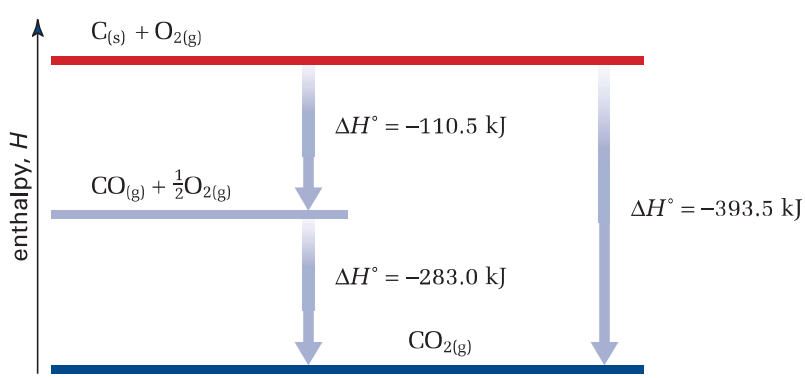


Figure 5.13 **Carbon dioxide can be formed by the reaction of oxygen with carbon to form carbon monoxide, followed by the reaction of carbon monoxide with oxygen. Carbon dioxide can also be formed directly from carbon and oxygen. No matter which pathway is used, the enthalpy change of the reaction is the same.**

One way to think about Hess's law is to compare the energy changes that occur in a chemical reaction with the changes in the potential energy of a cyclist on hilly terrain. This comparison is shown in Figure 5.14.

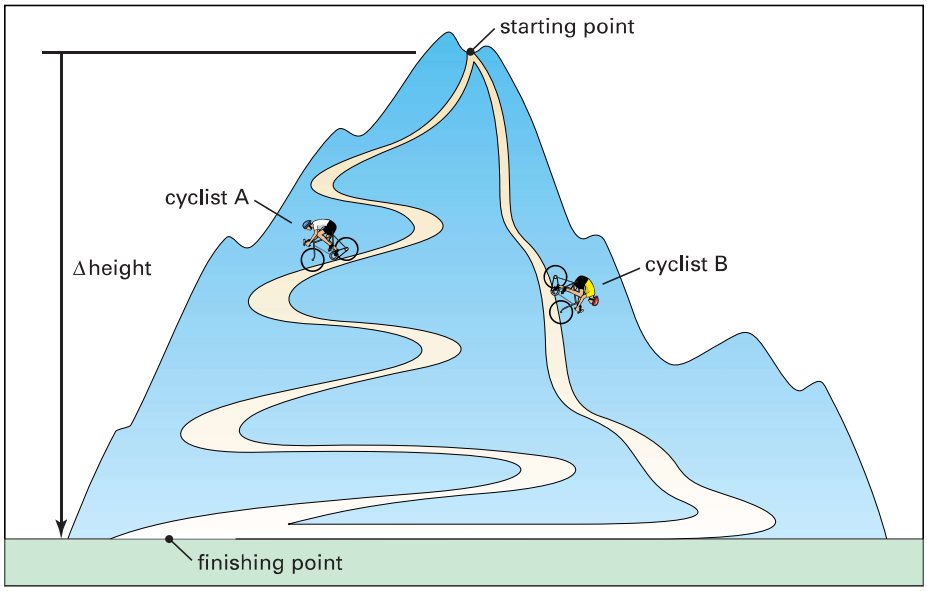


Figure 5.14 **The routes that cyclists take to get from the starting point to the finishing point has no effect on the *net* change in the cyclists' gravitational potential energy.**

Hess's law allows you to determine the energy of a chemical reaction without directly measuring it. In this section, you will examine two ways in which you can use Hess's law to calculate the enthalpy change of a chemical reaction:

1. by combining chemical equations algebraically
2. by using the enthalpy of a special class of reactions called formation reactions

Combining Chemical Equations Algebraically

According to Hess's law, the pathway that is taken in a chemical reaction has no effect on the enthalpy change of the reaction. How can you use Hess's law to calculate the enthalpy change of a reaction? One way is to add equations for reactions with known enthalpy changes, so that their net result is the reaction you are interested in.

For example, you can combine thermochemical equations (1) and (2) below to find the enthalpy change for the decomposition of hydrogen peroxide, equation (3).

$$\textbf{(1)} \quad H_2O_{2(\ell)} \rightarrow H_{2(g)} + O_{2(g)} \qquad \Delta H^\circ = +188\ \text{kJ}$$

$$\textbf{(2)} \quad H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \qquad \Delta H^\circ = -286\ \text{kJ}$$

$$\textbf{(3)} \quad H_2O_{2(\ell)} \rightarrow H_2O_{(\ell)} + \tfrac{1}{2}O_{2(g)} \qquad \Delta H^\circ = ?$$

Carefully examine equation (3), the *target* equation. Notice that H_2O_2 is on the left (reactant) side, while H_2O and $\frac{1}{2}O_2$ are on the right (product) side. Now examine equations (1) and (2). Notice which sides of the equations H_2O_2 and H_2O are on. They are on the correct sides, based on equation (3). Also notice that hydrogen does not appear in equation (3). Therefore, it must cancel out when equations (1) and (2) are added. Since there is one mole of $H_{2(g)}$ on the product side of equation (1) and one mole of $H_{2(g)}$ on the reactant side of equation (2), these two terms cancel. Set up equations (1) and (2) as shown on the next page. Add the products and the reactants. Then cancel any substances that appear on opposite sides.

(1)	$H_2O_{2(\ell)} \rightarrow H_{2(g)} + O_{2(g)}$	$\Delta H^\circ = +188$ kJ
(2)	$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$	$\Delta H^\circ = -286$ kJ

$$H_2O_{2(\ell)} + \cancel{H_{2(g)}} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} + O_{2(g)} + \cancel{H_{2(g)}} \qquad \Delta H^\circ = ?$$

or

(3) $H_2O_{2(\ell)} \rightarrow H_2O_{(\ell)} + \frac{1}{2}O_{2(g)}$ $\qquad \Delta H^\circ = ?$

Equations (1) and (2) add to give equation (3). Therefore, you know that the enthalpy change for the decomposition of hydrogen peroxide is the sum of the enthalpy changes of equations (1) and (2).

$$H_2O_{2(\ell)} \rightarrow H_2O_{(\ell)} + \frac{1}{2}O_{2(g)} \qquad \Delta H^\circ = 188 \text{ kJ} - 286 \text{ kJ} = -98 \text{ kJ}$$

Figure 5.15 illustrates this combination of chemical equations in an enthalpy diagram.

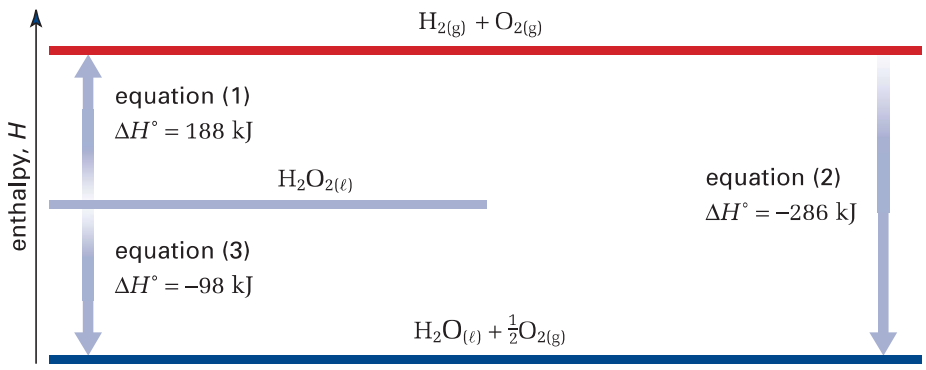


Figure 5.15 **The algebraic combination of chemical reactions can be represented in an enthalpy diagram.**

In the previous example, you did not need to manipulate the two equations with known enthalpy changes. They added to the target equation as they were written. In many cases, however, you will need to manipulate the equations before adding them. There are two key ways in which you can manipulate an equation:

1. *Reverse an equation* so that the products become reactants and the reactants become products. When you reverse an equation, you need to change the sign of ΔH°(multiply by –1).
2. *Multiply each coefficient in an equation* by the same integer or fraction. When you multiply an equation, you need to multiply ΔH° by the same number.

Examine the following Sample Problem to see how to manipulate equations so that they add to the target equation. Try the problems that follow to practise finding the enthalpy change by adding equations.

Sample Problem

Using Hess's Law to Determine Enthalpy Change

Problem

One of the methods that the steel industry uses to obtain metallic iron is to react iron(III) oxide, Fe_2O_3, with carbon monoxide, CO.

$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)}$

Continued ...

PROBLEM TIP

Before adding chemical equations, be sure to line up the equation arrows.

Electronic Learning Partner

Go to the Chemistry 12 Electronic Learning Partner for more information about aspects of material covered in this section of the chapter.

Continued ...

Determine the enthalpy change of this reaction, given the following equations and their enthalpy changes.

(1) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^\circ = -283.0\ kJ$

(2) $2Fe_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Fe_2O_3 \quad \Delta H^\circ = -822.3\ kJ$

What Is Required?

You need to find ΔH° of the target reaction.

$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)}$

What Is Given?

You know the chemical equations for reactions (1) and (2), and their corresponding enthalpy changes.

Plan Your Strategy

Step 1 Examine equations (1) and (2) to see how they compare with the target equation. Decide how you need to manipulate equations (1) and (2) so that they add to the target equation. (Reverse the equation, multiply the equation, do both, or do neither). Remember to adjust ΔH° accordingly for each equation.

Step 2 Write the manipulated equations so that their equation arrows line up. Add the reactants and products on each side, and cancel substances that appear on both sides.

Step 3 Ensure that you have obtained the target equation. Add ΔH° for the combined equations.

Act on Your Strategy

Step 1 Equation (1) has CO as a reactant and CO_2 as a product, as does the target reaction. The stoichiometric coefficients do not match the coefficients in the target equation, however. To achieve the same coefficients, you must multiply equation (1) by 3. Equation (2) has the required stoichiometric coefficients, but Fe and Fe_2O_3 are on the wrong sides of the equation. You need to reverse equation (2) and change the sign of ΔH°.

Step 2 Multiply each equation as required, and add them.

$$\begin{array}{lll} \mathbf{3 \times (1)} & 3CO_{(g)} + \frac{3}{2}O_{2(g)} \rightarrow 3CO_{2(g)} & \Delta H^\circ = 3(-283.0\ kJ) \\ \mathbf{-1 \times (2)} & Fe_2O_{3(s)} \rightarrow 2Fe_{(s)} + \frac{3}{2}O_{2(g)} & \Delta H^\circ = -1(-824.2\ kJ) \\ \hline \end{array}$$

$$Fe_2O_{3(s)} + \cancel{\tfrac{3}{2}O_{2(g)}} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)} + \cancel{\tfrac{3}{2}O_{2(g)}}$$

or

$$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)}$$

Step 3 The desired equation is achieved. Therefore, you can calculate the enthalpy change of the target reaction by adding the heats of reaction for the manipulated equations.

$\Delta H^\circ = 3(-283.0\ kJ) + 824.2\ kJ = -24.8\ kJ$

$\therefore Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)} \quad \Delta H^\circ = -24.8\ kJ$

Check Your Solution

Because the equations added correctly to the target equation, you know you manipulated the equations with known enthalpy changes correctly. Check to ensure that you adjusted ΔH° accordingly for each equation.

Practice Problems

13. Ethene, C_2H_4, reacts with water to form ethanol, $CH_3CH_2OH_{(\ell)}$.

$C_2H_{4(g)} + H_2O_{(\ell)} \rightarrow CH_3CH_2OH_{(\ell)}$

Determine the enthalpy change of this reaction, given the following thermochemical equations.

(1) $CH_3CH_2OH_{(\ell)} + 3O_{2(g)} \rightarrow 3H_2O_{(\ell)} + 2CO_{2(g)} \quad \Delta H^\circ = -1367\ \text{kJ}$

(2) $C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2H_2O_{(\ell)} + 2CO_{2(g)} \quad \Delta H^\circ = -1411\ \text{kJ}$

14. A typical automobile engine uses a lead-acid battery. During discharge, the following chemical reaction takes place.

$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(\ell)} \rightarrow 2PbSO_{4(aq)} + 2H_2O_{(\ell)}$

Determine the enthalpy change of this reaction, given the following equations.

(1) $Pb_{(s)} + PbO_{2(s)} + 2SO_{3(g)} \rightarrow 2PbSO_{4(s)} \quad \Delta H^\circ = -775\ \text{kJ}$

(2) $SO_{3(g)} + H_2O_{(\ell)} \rightarrow H_2SO_{4(\ell)} \quad \Delta H^\circ = -133\ \text{kJ}$

15. Mixing household cleansers can result in the production of hydrogen chloride gas, $HCl_{(g)}$. Not only is this gas dangerous in its own right, but it also reacts with oxygen to form chlorine gas and water vapour.

$4HCl_{(g)} + O_{2(g)} \rightarrow 2Cl_{2(g)} + 2H_2O_{(g)}$

Determine the enthalpy change of this reaction, given the following equations.

(1) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)} \quad \Delta H^\circ = -185\ \text{kJ}$

(2) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ = -285.8\ \text{kJ}$

(3) $H_2O_{(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ = -40.7\ \text{kJ}$

16. Calculate the enthalpy change of the following reaction between nitrogen gas and oxygen gas, given thermochemical equations (1), (2), and (3).

$2N_{2(g)} + 5O_{2(g)} \rightarrow 2N_2O_{5(g)}$

(1) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \quad \Delta H^\circ = -572\ \text{kJ}$

(2) $N_2O_{5(g)} + H_2O_{(\ell)} \rightarrow 2HNO_{3(\ell)} \quad \Delta H^\circ = -77\ \text{kJ}$

(3) $\frac{1}{2}N_{2(g)} + \frac{3}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \rightarrow HNO_{3(\ell)} \quad \Delta H^\circ = -174\ \text{kJ}$

Sometimes it is impractical to use a coffee-cup calorimeter to find the enthalpy change of a reaction. You can, however, use the calorimeter to find the enthalpy changes of other reactions, which you can combine to arrive at the desired reaction. In the following investigation, you will determine the enthalpy changes of two reactions. Then you will apply Hess's law to determine the enthalpy change of a third reaction.

Investigation 5-B

SKILL FOCUS
- Performing and recording
- Analyzing and interpreting
- Communicating results

Hess's Law and the Enthalpy of Combustion of Magnesium

Magnesium ribbon burns in air in a highly exothermic combustion reaction. (See equation (1).) A very bright flame accompanies the production of magnesium oxide, as shown in the photograph below. It is impractical and dangerous to use a coffee-cup calorimeter to determine the enthalpy change for this reaction.

(1) $Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)}$

Instead, you will determine the enthalpy changes for two other reactions (equations (2) and (3) below). You will use these enthalpy changes, along with the known enthalpy change for another reaction (equation (4) below), to determine the enthalpy change for the combustion of magnesium.

(2) $MgO_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{(\ell)}$

(3) $Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

(4) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$ $\Delta H^\circ = -285.8$ kJ/mol

Notice that equations (2) and (3) occur in aqueous solution. You can use a coffee-cup calorimeter to determine the enthalpy changes for these reactions. Equation (4) represents the formation of water directly from its elements in their standard state.

Question

How can you use equations (2), (3), and (4) to determine the enthalpy change of equation (1)?

Prediction

Predict whether reactions (2) and (3) will be exothermic or endothermic.

Materials

coffee cup calorimeter (2 nested coffee cups sitting in a 250 mL beaker)
thermometer
100 mL graduated cylinder
scoopula
electronic balance
MgO powder
Mg ribbon (or Mg turnings)
sandpaper or emery paper
1.00 mol/L $HCl_{(aq)}$

Safety Precautions

- Hydrochloric acid is corrosive. Use care when handling it.
- Be careful not to inhale the magnesium oxide powder.

Procedure

Part 1 Determining ΔH of Equation (2)

1. Read the Procedure for Part 1. Prepare a fully-labelled set of axes to graph your temperature observations.
2. Set up the coffee-cup calorimeter. (Refer to Investigation 5-A) Using a graduated cylinder, add 100 mL of 1.00 mol/L $HCl_{(aq)}$ to the calorimeter. **CAUTION** $HCl_{(aq)}$ can burn your skin.

3. Record the initial temperature, T_i, of the $HCl_{(aq)}$, to the nearest tenth of a degree.
4. Find the mass of no more than 0.80 g of MgO. Record the exact mass.
5. Add the MgO powder to the calorimeter containing the $HCl_{(aq)}$. Swirl the solution gently, recording the temperature every 30 s until the highest temperature, T_f, is reached.
6. Dispose of the reaction solution as directed by your teacher.

Part 2 Determining ΔH of Equation (3)

1. Read the Procedure for Part 2. Prepare a fully-labelled set of axes to graph your temperature observations.
2. Using a graduated cylinder, add 100 mL of 1.00 mol/L $HCl_{(aq)}$ to the calorimeter.
3. Record the initial temperature, T_i, of the $HCl_{(aq)}$, to the nearest tenth of a degree.
4. If you are using magnesium ribbon (as opposed to turnings), sand the ribbon. Accurately determine the mass of no more than 0.50 g of magnesium. Record the exact mass.
5. Add the Mg to the calorimeter containing the $HCl_{(aq)}$. Swirl the solution gently, recording the temperature every 30 s until the highest temperature, T_f, is reached.
6. Dispose of the solution as directed by your teacher.

Analysis

1. Use the equation $Q = m \cdot c \cdot \Delta T$ to determine the amount of heat that is released or absorbed by reactions (2) and (3). List any assumptions you make.
2. Convert the mass of MgO and Mg to moles. Calculate ΔH of each reaction in units of kJ/mol of MgO or Mg. Remember to put the proper sign (+ or –) in front of each ΔH value.
3. Algebraically combine equations (2), (3), and (4), and their corresponding ΔH values, to get equation (1) and ΔH of the combustion of magnesium.
4. (a) Your teacher will tell you the accepted value of ΔH of the combustion of magnesium. Based on the accepted value, calculate your percent error.
   (b) Suggest some sources of error in the investigation. In what ways could you improve the procedure?
5. What assumption did you make about the amount of heat that was lost to the calorimeter? Do you think that this is a fair assumption? Explain.
6. Why was it fair to assume that the hydrochloric acid solution has the same density and specific heat capacity as water?

Conclusion

7. Explain how you used Hess's law of heat summation to determine ΔH of the combustion of magnesium. State the result you obtained for the thermochemical equation that corresponds to chemical equation (1).

Extension

8. Design an investigation to verify Hess's law, using the following equations.

   (1) $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

   (2) $NaOH_{(s)} + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(\ell)}$

   (3) $Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(\ell)}$

   Assume that you have a coffee-cup calorimeter, solid NaOH, 1.00 mol/L $HCl_{(aq)}$, 1.00 mol/L $NaOH_{(aq)}$, and standard laboratory equipment. Write a step-by-step procedure for the investigation. Then outline a plan for analyzing your data. Be sure to include appropriate safety precautions. If time permits, obtain your teacher's approval and carry out the investigation.

Using Standard Molar Enthalpies of Formation

You have learned how to add equations with known enthalpy changes to obtain the enthalpy change for another equation. This method can be time-consuming and difficult, however, because you need to find reactions with known enthalpy changes that will add to give your target equation. There is another way to use Hess's law to find the enthalpy of an equation.

Formation Reactions

In Investigation 5-B, you used the reaction of oxygen with hydrogen to form water. Reactions like this one are known as **formation reactions**. In a formation reaction, a substance is formed from elements in their standard states. The enthalpy change of a formation reaction is called the **standard molar enthalpy of formation**, ΔH°_f. *The standard molar enthalpy of formation is the quantity of energy that is absorbed or released when one mole of a compound is formed directly from its elements in their standard states.*

Some standard molar enthalpies of formation are listed in Table 5.3. Notice that the standard enthalpies of formation of most compounds are negative. Thus, most compounds are more stable than the elements they are made from.

Table 5.3 Selected Standard Molar Enthalpies of Formation

Compound	ΔH°_f	Formation equations
$CO_{(g)}$	−110.5	$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$
$CO_{2(g)}$	−393.5	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
$CH_{4(g)}$	−74.6	$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$
$CH_3OH_{(\ell)}$	−238.6	$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(\ell)}$
$C_2H_5OH_{(\ell)}$	−277.6	$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow C_2H_5OH_{(\ell)}$
$C_6H_{6(\ell)}$	+49.0	$6C_{(s)} + 3H_{2(g)} \rightarrow C_6H_{6(\ell)}$
$C_6H_{12}O_{6(s)}$	−1274.5	$6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \rightarrow C_6H_{12}O_{6(s)}$
$H_2O_{(\ell)}$	−285.8	$H_{2(s)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)}$
$H_2O_{(g)}$	−241.8	$H_{2(s)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$
$CaCl_{2(s)}$	−795.4	$Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)}$
$CaCO_{3(s)}$	−1206.9	$Ca_{(s)} + C_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow CaCO_{3(s)}$
$NaCl_{(s)}$	−411.1	$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(g)}$
$HCl_{(g)}$	−92.3	$\frac{1}{2}H_{2(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}$
$HCl_{(aq)}$	−167.5	$\frac{1}{2}H_{2(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(ag)}$

By definition, the enthalpy of formation of an element in its standard state is zero. The standard state of an element is usually its most stable form under standard conditions. Recall, from section 5.1, that standard conditions are 25°C and 100 kPa (close to room temperature and pressure). Therefore, the standard state of nitrogen is $N_{2(g)}$. The standard state of magnesium is $Mg_{(s)}$.

Some elements exist in more than one form under standard conditions. For example, carbon can exist as either graphite or diamond, as shown in Figure 5.16. Graphite is defined as the standard state of carbon. Therefore, the standard enthalpy of formation of graphite carbon is 0 kJ/mol. The standard enthalpy of formation of diamond is 1.9 kJ/mol. Another example is oxygen, $O_{2(g)}$. Oxygen also exists in the form of ozone,

$O_{3(g)}$, under standard conditions. The diatomic molecule is defined as the standard state of oxygen, however, because it is far more stable than ozone. Therefore, the standard enthalpy of formation of oxygen gas, $O_{2(g)}$, is 0 kJ/mol. The standard enthalpy of formation of ozone is 143 kJ/mol.

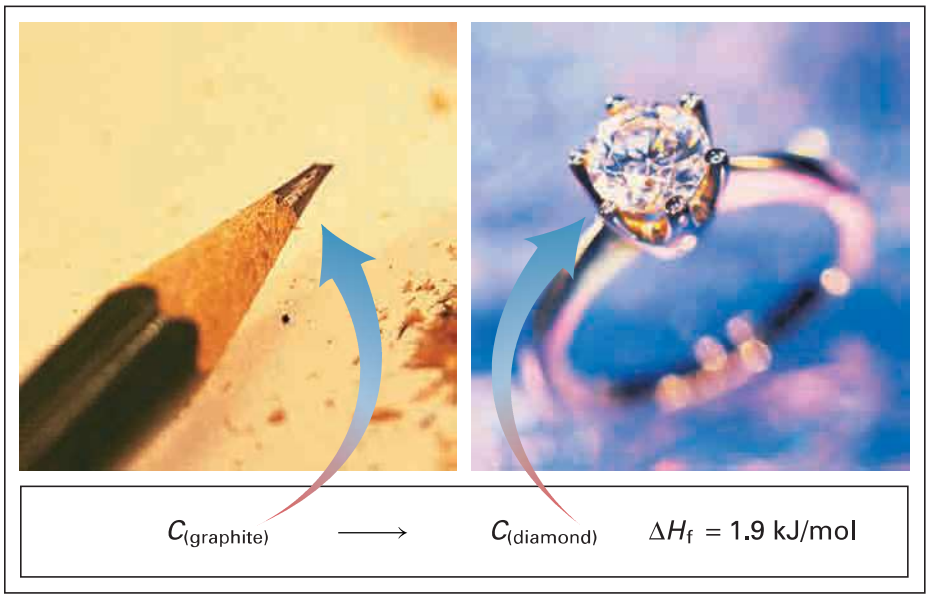


Figure 5.16 **Carbon can exist as graphite or diamond under standard conditions. It can, however, have only one standard state. Carbon's standard state is graphite.**

When writing a formation equation, always write the elements in their standard states. For example, examine the equation for the formation of water directly from its elements under standard conditions.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ_f = -285.8 \text{ kJ}$$

A formation equation should show the formation of exactly one mole of the compound of interest. The following equation shows the formation of benzene, C_6H_6 under standard conditions.

$$6C_{(graphite)} + 3H_{2(g)} \rightarrow C_6H_{6(\ell)} \quad \Delta H^\circ_f = 49.1 \text{ kJ}$$

Practice Problems

17. Write a thermochemical equation for the formation of each substance. Be sure to include the physical state of all the elements and compounds in the equation. You can find the standard enthalpy of formation of each substance in Appendix E.

(a) CH_4 **(b)** NaCl **(c)** MgO **(d)** $CaCO_3$

18. Liquid sulfuric acid has a very large negative standard enthalpy of formation (−814.0 kJ/mol). Write an equation to show the formation of liquid sulfuric acid. The standard state of sulfur is rhombic sulfur ($S_{(s)}$).

19. Write a thermochemical equation for the formation of gaseous cesium. The standard enthalpy of formation of $Cs_{(g)}$ is 76.7 kJ/mol.

20. Solid phosphorus is found in two forms: white phosphorus (P_4) and red phosphorus (P). White phosphorus is the standard state.

(a) The enthalpy of formation of red phosphorus is −17.6 kJ/mol. Write a thermochemical equation for the formation of red phosphorus.

(b) 32.6 g of white phosphorus reacts to form red phosphorus. What is the enthalpy change?

Calculating Enthalpy Changes

You can calculate the enthalpy change of a chemical reaction by adding the heats of formation of the products and subtracting the heats of formation of the reactants. The following equation can be used to determine the enthalpy change of a chemical reaction.

$$\Delta H^\circ = \Sigma(n\Delta H^\circ_f \text{ products}) - \Sigma(n\Delta H^\circ_f \text{ reactants})$$

In this equation, n represents the molar coefficient of each compound in the balanced chemical equation and Σ means "the sum of."

As usual, you need to begin with a balanced chemical equation. If a given reactant or product has a molar coefficient that is not 1, you need to multiply its ΔH°_f by the same molar coefficient. This makes sense because the units of ΔH°_f are kJ/mol. Consider, for example, the complete combustion of methane, $CH_{4(g)}$.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Using the equation for the enthalpy change, and the standard enthalpies of formation in Appendix E, you can calculate the enthalpy change of this reaction.

$$\Delta H^\circ = [(\Delta H^\circ_f \text{ of } CO_{2(g)}) + 2(\Delta H^\circ_f \text{ of } H_2O_{(g)})] - [1(\Delta H^\circ_f \text{ of } CH_{4(g)}) + 2(\Delta H^\circ_f \text{ of } O_{2(g)})]$$

Substitute the standard enthalpies of formation from Appendix E to get the following calculation.

$$\begin{aligned}\Delta H^\circ &= [(-393.5 \text{ kJ/mol}) + 2(-241.8 \text{ kJ/mol})] - [(-74.8 \text{ kJ/mol}) + 2(0 \text{ kJ/mol})]\\ &= -802.3 \text{ kJ/mol of } CH_4\end{aligned}$$

How does this method of adding heats of formation relate to Hess's law? Consider the equations for the formation of each compound that is involved in the reaction of methane with oxygen.

$$\begin{aligned}&\textbf{(1)} \quad H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H^\circ_f = -241.8 \text{ kJ}\\ &\textbf{(2)} \quad C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H^\circ_f = -393.5 \text{ kJ}\\ &\textbf{(3)} \quad C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H^\circ_f = -74.6 \text{ kJ}\end{aligned}$$

CONCEPT CHECK

"Using enthalpies of formation is like a shortcut for adding equations to obtain ΔH°." Do you agree with this statement? Explain your answer.

There is no equation for the formation of oxygen, because oxygen is an element in its standard state.

By adding the formation equations, you can obtain the target equation. Notice that you need to reverse equation (3) and multiply equation (1) by 2.

$$\begin{array}{rrcll}
\textbf{2 × (1)} & 2H_{2(g)} + O_{2(g)} & \rightarrow & 2H_2O_{(g)} & \Delta H^\circ_f = 2(-241.8) \text{ kJ}\\
\textbf{(2)} & C_{(s)} + O_{2(g)} & \rightarrow & CO_{2(g)} & \Delta H^\circ_f = -393.5 \text{ kJ}\\
\textbf{−1 × (3)} & CH_{4(g)} & \rightarrow & C_{(s)} + 2H_{2(g)} & \Delta H^\circ_f = -1(-74.6) \text{ kJ}\\
\hline
\end{array}$$

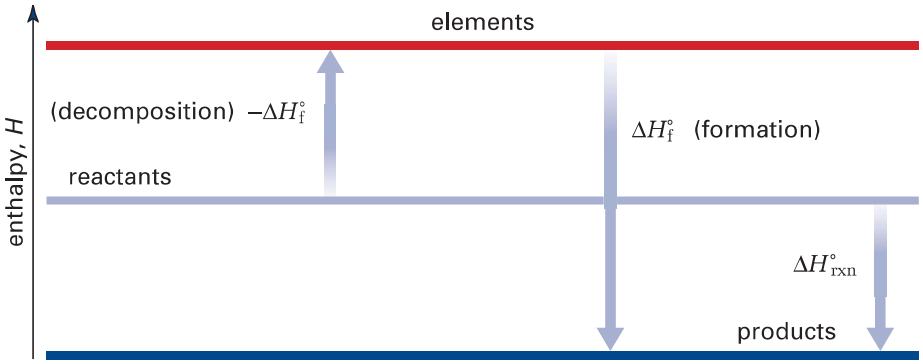
$$CH_{4(g)} + 2O_{2(g)} + \cancel{C}_{(s)} + 2\cancel{H}_{2(g)} \rightarrow 2H_2O_{(g)} + CO_{2(g)} + \cancel{C}_{(s)} + 2\cancel{H}_{2(g)}$$

or

$$CH_{4(g)} + 2O_{2(g)} \rightarrow 2H_2O_{(g)} + CO_{2(g)}$$

Add the manipulated ΔH°_f values: $\Delta H^\circ = 2(-241.8) \text{ kJ} - 393.5 \text{ kJ} + 74.6 \text{ kJ}$.
$= -802.3 \text{ kJ}$

This value of ΔH° is the same as the value you obtained using ΔH°_f data. When you used the addition method, you performed the same operations on the enthalpies of formation before adding them. Therefore, using enthalpies of formation to determine the enthalpy of a reaction is consistent with Hess's law. Figure 5.17 shows the general process for determining the enthalpy of a reaction from enthalpies of formation.



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

Figure 5.17 **The overall enthalpy change of any reaction is the sum of the enthalpy change of the decomposition of the reactants to their elements and the enthalpy change of the formation of the products from their elements.**

It is important to realize that, in most reactions, *the reactants do not actually break down into their elements and then react to form products.* Since there is extensive data about enthalpies of formation, however, it is useful to calculate the overall enthalpy change this way. Moreover, according to Hess's law, the enthalpy change is the same, regardless of the pathway. (In Chapter 6, you will learn more about the mechanisms by which compounds and elements react to form different elements and compounds.) Examine the following Sample Problem to see how to use enthalpies of formation to determine the enthalpy change of a reaction. Then try the Practice Problems that follow.

Sample Problem

Using Enthalpies of Formation

Problem

Iron(III) oxide reacts with carbon monoxide to produce elemental iron and carbon dioxide. Determine the enthalpy change of this reaction, using known enthalpies of formation.

$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)}$

What Is Required?

You need to find ΔH° of the given chemical equation, using ΔH°_f data.

What Is Given?

From Appendix E, you can obtain the enthalpies of formation.

ΔH°_f of $Fe_2O_{3(s)} = -824.2$ kJ/mol

ΔH°_f of $CO_{(g)} = -110.5$ kJ/mol

ΔH°_f of $CO_{2(g)} = -393.5$ kJ/mol

ΔH°_f of $Fe_{(s)} = 0$ kJ/mol (by definition)

Plan Your Strategy

Multiply each ΔH°_f value by its molar coefficient from the balanced chemical equation. Substitute into the following equation, and then solve.

$\Delta H^\circ = \Sigma(n\Delta H^\circ_f \text{ products}) - \Sigma(n\Delta H^\circ_f \text{ reactants})$

Continued ...

CONCEPT CHECK

You saw the reaction between iron(III) oxide and carbon monoxide in the Sample Problem on page 245. Which method for determining the enthalpy of reaction do you prefer? Explain your answer.

Continued ...

Act on Your Strategy

$\Delta H^\circ = \Sigma(n\Delta H^\circ_f \text{ products}) - \Sigma(n\Delta H^\circ_f \text{ reactants})$

$= [3(\Delta H^\circ_f\, CO_{2(g)}) + 2(\Delta H^\circ_f\, Fe_{(s)})] - [(\Delta H^\circ_f\, Fe_2O_{3(s)}) + 3(\Delta H^\circ_f\, CO_{(g)})]$

$= [(-393.5 \text{ kJ/mol}) + 2(0 \text{ kJ/mol})] - [(-824.2 \text{ kJ/mol}) + 3(-110.5 \text{ kJ/mol})]$

$= -24.8 \text{ kJ/mol}$

$\therefore Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 3CO_{2(g)} + 2Fe_{(s)} \quad \Delta H^\circ = -24.8 \text{ kJ/mol}$

Check Your Solution

A balanced chemical equation was used in the calculation. The number of significant digits is correct. The units are also correct.

Practice Problems

21. Hydrogen can be added to ethene, C_2H_4, to obtain ethane, C_2H_6.

$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$

Show that the equations for the formation of ethene and ethane from their elements can be algebraically combined to obtain the equation for the addition of hydrogen to ethene.

22. Zinc sulfide reacts with oxygen gas to produce zinc oxide and sulfur dioxide.

$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$

Write the chemical equation for the formation of the indicated number of moles of each compound from its elements. Algebraically combine these equations to obtain the given equation.

23. Small amounts of oxygen gas can be produced in a laboratory by heating potassium chlorate, $KClO_3$.

$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$

Calculate the enthalpy change of this reaction, using enthalpies of formation from Appendix E.

24. Use the following equation to answer the questions below.

$CH_3OH_{(\ell)} + 1.5O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

(a) Calculate the enthalpy change of the complete combustion of one mole of methanol, using enthalpies of formation.

(b) How much energy is released when 125 g of methanol undergoes complete combustion?

Section Summary

In this section, you learned how to calculate the enthalpy change of a chemical reaction using Hess's law of heat summation. Enthalpies of reaction can be calculated by combining chemical equations algebraically or by using enthalpies of formation. Hess's law allows chemists to determine enthalpies of reaction without having to take calorimetric measurements. In the next section, you will see how the use of energy affects your lifestyle and your environment.

Section Review

1. K/U Explain why you need to reverse the sign of ΔH° when you reverse an equation. Use an example in your answer.

2. C In section 5.3, you learned two methods for calculating enthalpy changes using Hess's law. If you had only this textbook as a reference, which method would allow you to calculate enthalpy changes for the largest number of reactions? Explain your answer.

3. I In the early 1960s, Neil Bartlett, at the University of British Columbia, was the first person to synthesize compounds of the noble gas xenon. A number of noble gas compounds (such as XeF_2, XeF_4, XeF_6, and XeO_3) have since been synthesized. Consider the reaction of xenon difluoride with fluorine gas to produce xenon tetrafluoride.

   $XeF_{2(g)} + F_{2(g)} \rightarrow XeF_{4(s)}$

   Use the following standard molar enthalpies of formation to calculate the enthalpy change for this reaction.

Compound	ΔH°_f (kJ/mol)
$XeF_{2(g)}$	−108
$XeF_{4(s)}$	−251

4. I Calculate the enthalpy change of the following reaction, given equations (1), (2), and (3).

   $2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(\ell)}$

   (1) $H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(\ell)}$ $\Delta H^\circ = -0.02$ kJ

   (2) $H_2B_4O_{7(s)} + H_2O_{(\ell)} \rightarrow 4HBO_{2(aq)}$ $\Delta H^\circ = -11.3$ kJ

   (3) $H_2B_4O_{7(s)} \rightarrow 2B_2O_{3(s)} + H_2O_{(\ell)}$ $\Delta H^\circ = 17.5$ kJ

5. I The standard molar enthalpy of formation of calcium carbonate is −1207.6 kJ/mol. Calculate the enthalpy of formation of calcium oxide, given the following equation.

   $CaO_{(g)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$ $\Delta H^\circ = -178.1$ kJ

6. C A classmate is having difficulty understanding Hess's law. Write a few paragraphs to explain the law. Include examples, diagrams, and an original analogy.

7. C In your own words, explain why using enthalpies of formation to determine enthalpy of reaction depends on Hess's law. Include an example.

5.4 Energy Sources

Section Preview/ Specific Expectations

In this section, you will

- **compare** the efficiency and environmental impact of conventional and alternative sources of energy
- **communicate** your understanding of the following terms: *non-renewable, renewable*

Canadians depend on energy sources, such as those listed in Figure 5.18, to power vehicles, light and heat buildings, and manufacture products that support our lives and lifestyles. As society's needs for energy and energy-using products grow, scientists and technologists search for more economical and environmentally responsible ways to meet these needs. In this section, you will compare energy sources based on their efficiency and environmental impact.

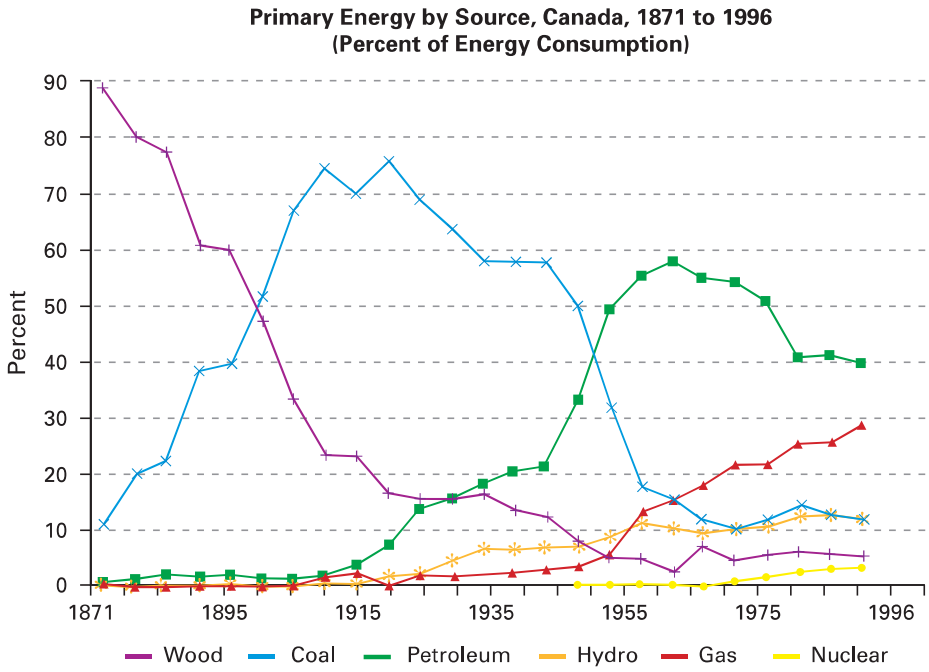


Figure 5.18 **The energy that Canadians use comes from a variety of sources. What factors account for the changes you can see in this graph? How do you think energy use has changed since 1996?**

Energy and Efficiency

When you think about energy efficiency, what comes to mind? You may think about taking the stairs instead of the elevator, choosing to drive a small car instead of a sport utility vehicle, or turning off lights when you are not using them. What, however, does efficiency really mean? How do you quantify it?

There are several ways to define efficiency. One general definition says that energy efficiency is the ability to produce a desired effect with minimum energy expenditure. For example, suppose that you want to bake a potato. You can use a microwave oven or a conventional oven. Both options achieve the same effect (baking the potato), but the first option uses less energy. According to the general definition above, using the microwave oven is more energy-efficient than using the conventional oven. The general definition is useful, but it is not quantitative.

Another definition of efficiency suggests that it is *the ratio of useful energy produced to energy used in its production, expressed as a percent.* This definition quantitatively compares input and output of energy. When you use it, however, you need to be clear about what you mean by "energy used." Figure 5.19 shows factors to consider when calculating efficiency or analyzing efficiency data.

"Useful energy" is
- energy delivered to consumer in usable form
- actual work done

$$\text{Efficiency} = \frac{\text{Useful energy produced}}{\text{Energy used}} \times 100\%$$

"Energy used" could include
- ideal energy content of fuel
- energy used to extract and transport fuel
- solar energy used to create fuel (e.g. biomass)
- energy used to build and maintain power plant

Figure 5.19 **Efficiency is expressed as a percent. Always specify what is included in the "energy used" part of the ratio.**

It is often difficult to determine how much energy is used to produce useful energy. Often an efficiency percent only takes into account the "ideal" energy output of a system, based on the energy content of the fuel.

Efficiency and Natural Gas

When discussing the efficiency of a fuel such as natural gas, you need to specify how that fuel is being used. Consider, for example, natural gas. Natural gas is primarily methane. Therefore, you can estimate an ideal value for energy production using the enthalpy of combustion of methane.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \quad \Delta H^\circ = -802 \text{ kJ}$$

In other words, 16 g of methane produces 802 kJ of heat (under constant pressure conditions).

When natural gas is used directly in cooking devices, its efficiency can be as high as 90%. Thus, for every 16 g of gas burned, you get about 720 kJ (0.90 × 802 kJ) of usable energy as heat for cooking. This is a much higher fuel efficiency than you can get with appliances that use electrical energy produced in a power plant that runs on a fuel such as coal.

If natural gas is used to produce electricity in a power plant, however, the efficiency is much lower—around 37%. Why? The heat from the burning natural gas is used to boil water. The kinetic energy of the resulting steam is transformed to mechanical energy for turning a turbine. The turbine generates the electrical energy. Each of these steps has an associated efficiency that is less than 100%. Thus, at each step, the overall efficiency of the fuel decreases.

Thinking About the Environment

Efficiency is not the only criterion for selecting an energy source. Since the 1970s, society has become increasingly conscious of the impact of energy technologies on the environment.

Suppose that you want to analyze the environmental impact of an energy source. You can ask the following questions:

- Are any waste products or by-products of the energy production process harmful to the environment? For example, any process in which a hydrocarbon is burned produces carbon dioxide. Carbon dioxide is a known greenhouse gas, which contributes to global warming. Any combustion process provides the heat required to form oxides of nitrogen from nitrogen gas. Nitrogen oxides contribute to acid precipitation.
- Is obtaining or harnessing the fuel harmful to the environment? For example, oil wells and strip coal mines destroy habitat. Natural gas pipelines, shown in Figure 5.20, are visually unappealing. They also split up habitat, which harms the ecosystem.

Figure 5.20 **This gas pipeline harms the ecosystem by splitting up habitat.**

- Will using the energy source permanently remove the fuel from the environment? A **non-renewable** energy source (such as coal, oil, or natural gas) is effectively gone once we have used it up. Non-renewable energy sources take millions of years to form. We use them up at a much faster rate than they can be replenished. An energy source that is clearly **renewable** is solar energy. The Sun will continue to radiate energy toward Earth over its lifetime—many millions of years. A somewhat renewable energy source is wood. Trees can be grown to replace those cut down. It takes trees a long time to grow, however, and habitat is often destroyed in the meantime.

Comparing Energy Sources

Both efficiency and environmental impact are important factors to consider when comparing energy sources. In the following ThoughtLab, you will research and compare alternative and conventional energy sources.

ThoughtLab Comparing Energy Sources

In this ThoughtLab, you will work as a class to compare two different energy sources.

Procedure

1. On your own, or with a group, choose an energy source from the following list. Other energy sources may be discussed and added in class.

solar (radiant) energy	wood
petroleum	biomass
hydrogen fuel cell	nuclear fission
natural gas fuel cell	natural gas
wind energy	coal
hydroelectric power	tar sands
geothermal energy	

2. Before beginning your research, record your current ideas about the efficiency and environmental impact of your chosen energy source.
3. Research the efficiency and environmental impact of your energy source. If possible, determine what the efficiency data means. For example, suppose that a source tells you that natural gas is 90% efficient. Is the source referring to natural gas burned directly for heat or for cooking? Is the energy being converted from heat to electricity in a power plant? Be as specific as possible.
4. Ensure that you use a variety of sources to find your data. Be aware of any bias that might be present in your sources.
5. Trace the energy source as far back as you can. For example, you can trace the energy in fossil fuels back to solar energy that powered the photosynthesis in the plants that eventually became the fossil fuel. Write a brief outline of your findings.
6. Your teacher will pair you (or your group) with another student (or group) that has researched a different energy source. Work together to analyze the comparative merits and drawbacks of the two energy sources, based on your research.
7. Write a conclusion that summarizes the benefits and risks of both energy sources, in terms of their efficiency and environmental impact.
8. Present your findings to the class.

Analysis

1. Discuss the presentations as a class.
   (a) Decide which energy sources are most efficient. Also decide which energy sources are least damaging to the environment.
   (b) Decide which energy source is best overall in terms of both efficiency and environmental impact.
2. Could the "best overall" energy source be used to provide a significant portion of Canada's energy needs? What obstacles would need to be overcome for this to happen?
3. Besides efficiency and environmental impact, what other factors are involved in developing and delivering an energy source to consumers?

Careers in Chemistry

Nuclear Safety Supervisor

Jennifer Noronha

In some ways, nuclear power is an appealing power source. Nuclear reactions create large amounts of energy from minimal material, and they generate none of the carbon dioxide and other emissions that cause acid rain and global warming. The products and reactants of nuclear reactions, however, are dangerously radioactive. Therefore, special measures are needed to protect nuclear power station employees from daily exposure to radiation. That is where Jennifer Noronha comes in. Noronha is the supervisor of Radiological Services at Darlington. Employee safety—especially from high radiation doses—is her first priority.

The Darlington Nuclear Generating Station is located 70 km east of Toronto. It uses a fuel of natural uranium to produce enough electricity to provide power for a city the size of Toronto. Noronha and her radiation protection team plan and implement safety programs that minimize dose rates, or the amount of radiation that station employees are exposed to.

Station employees must undergo four weeks of radiation protection training. This training was designed by Noronha's department, based on an extensive investigation of radiation fields within the station, as well as a thorough evaluation of past safety programs and approaches. Through this training, employees learn how to measure existing dose rates with survey equipment, assess what kinds of tools and protective clothing are needed, and take appropriate action to lower radiation doses. For example:

- Airborne hazards, such as tritium (present in radiated water vapour), can be reduced by running the station's dryer system. The dryer system catches the radiated vapour and dries it out of the air.
- Non-airborne radiation can be countered by shielding the affected area with lead blankets or sheeting material.

Noronha's strong mathematics skills were evident from an early age. When she moved to Canada from Kenya at age 11, she was immediately put ahead a grade. Her mathematics skills and her father's engineering profession were what propelled her toward engineering. Noronha earned her engineering physics degree from McMaster University. Her courses included general chemistry, biomedical theory, and nuclear theory. She worked as a commissioning engineer at Darlington during its start-up. She tested the station's safety shut-down systems and helped to bring the station's first reactor on-line. "It was pretty amazing," Noronha says. "At the time, it was still relatively new technology, and it was Canadian technology."

Noronha got her MBA from the University of Toronto in 1998. Soon after, she moved to her current position, which allows her to combine her people skills and technical expertise.

Making Career Connections

1. Are you interested in the different safety concerns related to Canadian nuclear reactors, and the steps that are being taken to counter these concerns? Contact the Canadian Nuclear Safety Commission (CNSC) or explore their web site. (The CNSC is the Ottawa-based government watchdog for the use of nuclear energy in Canada.)
2. To learn more about the wide variety of careers in nuclear power generation, Ontario Power Generation is a good place to start. Their web site has a helpful career page that lists opportunities for students and recent graduates, as well as experienced professionals.

Chemistry Bulletin

Science | Technology | Society | Environment

Hot Ice

When engineers first began extending natural gas pipelines through regions of bitter cold, they noticed that their lines plugged with a dangerous slush of ice and gas. The intense pressure of the lines, combined with the cold, led to the formation of *methane hydrates*, a kind of gas-permeated ice. More than a mere nuisance, methane hydrate plugs were a potential threat to pipelines. The build-up of gas pressure behind a methane hydrate plug could lead to an explosion. Now, however, this same substance may hold the key to a vast fuel supply.

Methane hydrates form when methane molecules become trapped within an ice lattice as water freezes. They can form in very cold conditions or under high-pressure conditions. Both of these conditions are met in deep oceans and in permafrost. In Canada, hydrates have already been found in large quantities in the Canadian Arctic. Methane hydrate has a number of remarkable properties. For example, when brought into an oxygen atmosphere, the methane fumes can be ignited, making it appear that the ice is burning!

Methane releases 25% less carbon dioxide per gram than coal, and it emits none of the oxides of nitrogen and sulfur that contribute to acid precipitation. Therefore, using methane in place of other fossil fuels is very desirable. Methane hydrates seem to be an ideal and plentiful "pre-packaged" source of natural gas. Estimates of the exact amount of methane stored in hydrates suggest there could be enough to serve our energy needs anywhere from 350 years to 3500 years, based on current levels of energy consumption. This would constitute a significant source of fossil fuels, if we can find a way to extract the gas safely and economically.

Unfortunately, hydrates become unstable when the pressure or temperature changes. Even small changes in these conditions can cause hydrates to degrade rapidly. Methane hydrates are stable at ocean depths greater than 300 m, but offshore drilling at these depths has been known to disturb the hydrate formations, causing large, uncontrolled releases of flammable methane gas. Also, methane hydrates often hold sediment layers together. Therefore, in addition to the danger of a gas explosion, there is the danger of the sea floor collapsing where drilling occurs.

Methane is a significant greenhouse gas. A massive release of methane could cause catastrophic global climate change. Some researchers believe that the drastic climate change that occurred during the Pleistocene era was due to methane hydrate destabilization and widespread methane release.

Nonetheless, Canada, Japan, the United States, and Russia all have active research and exploration programs in this area. As global oil supplies dwindle, using methane hydrates might increasingly be seen as worth the risk and cost.

Making Connections

1. Compare using methane from natural gas with using methane from methane hydrates in terms of environmental impact and efficiency. You will need to do some research to find out extraction methods for each source of methane.
2. On the Internet, research one possible structure of methane hydrate. Create a physical model or a three-dimensional computer model to represent it. Use your model to explain why methane hydrates are unstable at temperatures that are warmer than 0°C.

Emerging Energy Sources

In the ThoughtLab on page 258, you probably noticed that all energy sources have drawbacks as well as benefits. Scientists and engineers are striving to find and develop new and better energy sources. One energy source that engineers are trying to harness is nuclear fusion. As you learned in section 5.1, nuclear fusion provides a great deal of energy from readily available fuel (isotopes of hydrogen). In addition, nuclear fusion produces a more benign waste product than nuclear fission (helium). Unfortunately, fusion is not yet practical and controllable on a large scale because of the enormous temperatures involved.

Chemists are also striving to find new sources for existing fuels that work well. The Chemistry Bulletin on the facing page discusses a new potential source of methane.

Section Summary

In this section, you learned about efficiency. You learned how it can be defined in different ways for different purposes. You used your understanding of processes that produce energy to investigate the efficiency and environmental impact of different energy sources.

In Chapter 5, you learned about the energy that is associated with chemical reactions. You used a calorimeter to measure heat changes, and you used these heat changes to write thermochemical equations. You probably already realize that adding heat to reactants often speeds up a reaction. In other words, raising the temperature of a system consisting of a chemical reaction often increases the speed of the reaction. A familiar example is cooking. You increase the temperature of a heating element to speed up the reactions that are taking place in the food as it cooks. How does increasing temperature speed up a reaction? Is the enthalpy of a reaction related to its speed? Chapter 6 addresses these questions.

Section Review

1. C Your friend tells you about an energy source that is supposed to be 46% efficient. What questions do you need to ask your friend in order to clarify this claim?

2. C Efficiency and environmental concerns are not always separate. In fact, they are often closely linked. Give three examples of energy sources in which changes in efficiency affect environmental impact, or vice versa.

3. I Design an experiment to determine the efficiency of a laboratory burner. You will first need to decide how to define the efficiency, and you will also need to find out what fuel your burner uses. Include a complete procedure and safety precautions.

4. MC Some high-efficiency gas furnaces can heat with an efficiency of up to 97%. These gas furnaces work by allowing the water vapour produced during combustion to condense. Condensation is an exothermic reaction that releases further energy for heating. Use the information in this section to demonstrate the increased heat output, using Hess's law. The enthalpy of condensation of water is 44 kJ/mol.

5 MC "Nuclear energy is an energy source that is less hazardous to the environment than energy derived from burning coal." Write a brief essay, explaining why you agree or disagree with this statement.

6 MC The label on an electric kettle claims that the kettle is 95% efficient.

(a) What definition of efficiency is the manufacturer using?

(b) Write an expression that shows how the manufacturer might have arrived at an efficiency of 95% for the kettle.

(c) Design a detailed experiment to test the manufacturers' claim. Include safety precautions.

7 K/U Read the Chemistry Bulletin on page 260. How does the efficiency of using methane as a fuel source compare to using methane hydrates? Justify your answer.

8 I Hydrogen is a very appealing fuel, in part because burning it produces only non-polluting water. One of the challenges that researchers face in making hydrogen fuel a reality is how to produce hydrogen economically. Researchers are investigating methods of producing hydrogen indirectly. The following series of equations represent one such method.

$$3FeCl_{2(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 6HCl_{(g)} + H_{2(g)} \qquad \Delta H^\circ = 318\ kJ$$

$$Fe_3O_{4(s)} + \frac{3}{2}Cl_{2(g)} + 6HCl_{(g)} \rightarrow 3FeCl_{3(s)} + 3H_2O_{(g)} + \frac{1}{2}O_{2(g)} \qquad \Delta H^\circ = -249\ kJ$$

$$3FeCl_{3(s)} \rightarrow 3FeCl_{2(s)} + \frac{3}{2}Cl_{2(g)} \qquad \Delta H^\circ = 173\ kJ$$

(a) Show that the net result of the three reactions is the decomposition of water to produce hydrogen and oxygen.

(b) Use Hess's law and the enthalpy changes for the reactions to determine the enthalpy change for the decomposition of one mole of water. Check your answer, using the enthalpy of formation of water.

CHAPTER 5 Review

Reflecting on Chapter 5

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

- Compare the magnitude of energy changes resulting from physical changes, chemical reactions, and nuclear reactions.
- Compare the processes that are responsible for the energy changes resulting from physical changes, chemical reactions, and nuclear reactions.
- Explain the different ways to represent the energy changes of physical and chemical processes.
- Give examples of important exothermic and endothermic processes.
- Explain how a calorimeter is used to determine enthalpy of reaction.
- Use examples and analogies to explain Hess's law.
- Show how to use Hess's law and experimentally determined enthalpies of reaction to calculate unknown enthalpies of reaction.
- Show how to calculate enthalpy of reaction using known enthalpies of formation, and explain how this calculation relates to Hess's law.
- Explain the concept of efficiency, and discuss the efficiency and environmental impact of conventional and alternative energy sources.

Reviewing Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

thermodynamics	thermochemistry
law of conservation of energy	system
surroundings	heat (Q)
temperature (T)	enthalpy (H)
enthalpy change (ΔH)	endothermic reaction
exothermic reaction	enthalpy of reaction
standard enthalpy of reaction (ΔH°)	thermochemical equation
mass defect	nuclear binding energy
nuclear fission	nuclear fusion
specific heat capacity (c)	heat capacity (C)
calorimeter	coffee-cup calorimeter
constant-pressure calorimeter	Hess's law of heat summation
formation reactions	standard molar enthalpy of formation (ΔH°_f)
non-renewable	renewable

Knowledge/Understanding

1. In your own words, describe the relationship between a system and its surroundings. Use an example to illustrate your description.
2. The vaporization of liquid carbon disulfide, CS_2, requires an energy input of 29 kJ/mol.
   (a) Is this reaction exothermic or endothermic? What is the enthalpy change of this reaction?
   (b) Write a thermochemical equation of this reaction. Include 29 kJ as either a reactant or a product.
   (c) Draw and label an enthalpy diagram for the vaporization of liquid carbon disulfide.
3. A given chemical equation is tripled and then reversed. What effect, if any, will there be on the enthalpy change of the reaction?
4. Explain why two nested polystyrene coffee cups, with a lid, make a good constant-pressure calorimeter.
5. Write the balanced equation for the formation of each substance.
   (a) $LiCl_{(s)}$ **(b)** $C_2H_5OH_{(\ell)}$ **(c)** $NH_4NO_{3(s)}$
6. If the enthalpy of formation of an element in its standard state is equal to zero, explain why the heat of formation of iodine gas, $I_{2(g)}$, is 21 kJ/mol.

Inquiry

7. In an oxygen-rich atmosphere, carbon burns to produce carbon dioxide, CO_2. Both carbon monoxide, CO, and carbon dioxide are produced when carbon is burned in an oxygen-deficient atmosphere. This makes the direct measurement of the enthalpy of formation of CO difficult. CO, however, also burns in oxygen, O_2, to produce pure carbon dioxide. Explain how you would experimentally determine the enthalpy of formation of carbon monoxide.
8. Two 30.0 g pieces of aluminium, Al, are placed in an insulated container.
   (a) One piece of Al has an initial temperature of 100.0°C. The other piece has an initial temperature of 20.0°C. What is the temperature inside the container after the system has equilibrated? Assume that no heat is lost to the container or the surroundings.

(b) Repeat the calculation in part (a) with the following change: The piece of Al at 20.0°C has a mass of 50.0 g.

9. The complete combustion of 1.00 mol of sucrose, $C_{12}H_{22}O_{11}$, releases –5641 kJ of energy (at 25°C and 100 kPa).

$C_{12}H_{22}O_{11(s)} + 12O_{2(g)} \rightarrow 12CO_{2(g)} + 11H_2O_{(\ell)}$

(a) Use the enthalpy change of this reaction, and enthalpies of formation from Appendix E, to determine the enthalpy of formation of sucrose.

(b) Draw and label an enthalpy diagram for this reaction.

10. A 10.0 g sample of pure acetic acid, CH_3CO_2H, is completely burned. The heat released warms 2.00 L of water from 22.3°C to 39.6°C. Assuming that no heat was lost to the calorimeter, what is the enthalpy change of the complete combustion of acetic acid? Express your answer in units of kJ/g and kJ/mol.

11. Use equations (1), (2), and (3) to find the enthalpy change of the formation of methane, CH_4, from chloroform, $CHCl_3$.

$CHCl_{3(\ell)} + 3HCl_{(g)} \rightarrow CH_{4(g)} + 3Cl_{2(g)}$

(1) $\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)} \quad \Delta H^\circ = -92.3$ kJ

(2) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H^\circ = -74.8$ kJ

(3) $C_{(s)} + \frac{1}{2}H_{2(g)} + \frac{3}{2}Cl_{2(g)} \rightarrow CHCl_{3(\ell)} \quad \Delta H^\circ = -134.5$ kJ

12. The following equation represents the combustion of ethylene glycol, $(CH_2OH)_2$.

$(CH_2OH)_{2(\ell)} + \frac{5}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \quad \Delta H^\circ = -1178$ kJ

Use known enthalpies of formation and the given enthalpy change to determine the enthalpy of formation of ethylene glycol.

13. Most of us associate the foul smell of hydrogen sulfide gas, $H_2S_{(g)}$, with the smell of rotten eggs.

$H_2S_{(g)} + \frac{3}{2}O_{2(g)} \rightarrow SO_{2(g)} + H_2O_{(g)} \quad \Delta H = -519$ kJ

How much energy is released when 15.0 g of $H_2S_{(g)}$ burns?

14. Hydrogen peroxide, H_2O_2, is a strong oxidizing agent. It is used as an antiseptic in a 3.0% aqueous solution. Some chlorine-free bleaches contain 6.0% hydrogen peroxide.

(a) Write the balanced chemical equation for the formation of one mole of $H_2O_{2(\ell)}$.

(b) Using the following equations, determine the enthalpy of formation of H_2O_2.

(1) $2H_2O_{2(\ell)} \rightarrow 2H_2O_{(\ell)} + O_{2(g)} \quad \Delta H^\circ = -196$ kJ

(2) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} \quad \Delta H^\circ = -286$ kJ

15. Hydrogen cyanide is a highly poisonous gas. It is produced from methane and ammonia.

$CH_{4(g)} + NH_{3(g)} \rightarrow HCN_{(g)} + 3H_{2(g)}$

Find the enthalpy change of this reaction, using the following thermochemical equations.

(1) $H_{2(g)} + 2C_{(graphite)} + N_{2(g)} \rightarrow 2HCN_{(g)} \quad \Delta H^\circ = 270$ kJ

(2) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \quad \Delta H^\circ = -92$ kJ

(3) $C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)} \quad \Delta H^\circ = -75$ kJ

16. The following equation represents the complete combustion of butane, C_4H_{10}.

$C_4H_{10(g)} + 6.5O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(g)}$

(a) Using known enthalpies of formation, calculate the enthalpy change of the complete combustion of C_4H_{10}. (The enthalpy of formation of C_4H_{10} is –126 kJ/mol.)

(b) Using known enthalpies of formation, calculate the enthalpy change of the complete combustion of ethane, C_2H_6, to produce carbon dioxide and water vapour. Express your answer in units of kJ/mol and kJ/g.

(c) A 10.0 g sample that is 30% C_2H_6 and 70% C_4H_{10}, by mass, is burned in excess oxygen. How much energy is released?

17. The caloric content (energy content) of foods is measured using a bomb calorimeter. A sample of food is burned in oxygen, O_2, inside the calorimeter. You can make a simple food calorimeter using an empty food can or pop can. Design an investigation in which you make your own calorimeter and then use your calorimeter to measure the energy content of a piece of cheese or a cracker. Include a diagram of your proposed calorimeter. List the data, and other observations, that you plan to record. Get your teacher's approval before carrying out your investigation. **Note:** Some students have a severe nut allergy. Do not use peanuts, or any other nuts, in your investigation.

18. Design an investigation to determine the enthalpy change of the combustion of ethanol using a wick-type burner, similar to that in a kerosene lamp.

(a) Draw and label a diagram of the apparatus.

(b) Write a step-by-step procedure.
(c) Prepare a table to record your data and other observations.
(d) State any assumptions that you will make when carrying out the calculations.

Communication

19. Suppose that you need to find the enthalpy change of a chemical reaction. Unfortunately, you are unable to carry out the reaction in your school laboratory. Does this mean that you cannot find the enthalpy change of the reaction? Explain.

20. Acetylene, C_2H_2, and ethylene, C_2H_4, are both used as fuels. They combine with oxygen gas to produce carbon dioxide and water in an exothermic reaction. Acetylene also reacts with hydrogen to produce ethylene, as shown.

$C_2H_{2(g)} + H_{2(g)} \rightarrow C_2H_{4(g)} \quad \Delta H^\circ = -175.1$ kJ

(a) Without referring to any tables or doing any calculations, explain why C_2H_2 has a more positive enthalpy of formation than C_2H_4.
(b) Do you think C_2H_2 or C_2H_4 is a more energetic fuel? Explain.

Making Connections

21. When a vehicle is parked in the sunlight on a hot summer day, the temperature inside can approach 55°C. One company has patented a non-CFC propelled aerosol that can be sprayed inside a vehicle to reduce the temperature to 25°C within seconds. The spray contains a mixture of two liquids: 10% ethanol, C_2H_5OH, and 90% water by mass.

(a) Use thermochemical equations, and the corresponding enthalpy changes, to explain how the spray works.
(b) 1.0 g of the aerosol is sprayed into a hot vehicle. How much heat (in kJ) can be absorbed due to vaporization of the aerosol? **Note:** ΔH_{vap} of water = 44.0 kJ/mol and ΔH_{vap} of ethanol = 38.56 kJ/mol
(c) Do you think there are any risks associated with using a spray like the one described above? Explain your answer.

22. Consider methane, CH_4, and hydrogen, H_2, as possible fuel sources.

(a) Write the chemical equation for the complete combustion of each fuel. Then find the enthalpy of combustion, ΔH_{comb}, of each fuel. Express your answers in kJ/mol and kJ/g. Assume that water *vapour*, rather than liquid water, is formed in both reactions.
(b) Which is the more energetic fuel, per unit mass?
(c) Consider a fixed mass of each fuel. Which fuel would allow you to drive a greater distance? Explain briefly.
(d) Describe how methane and hydrogen could be obtained. Which of these methods do you think is less expensive? Explain.
(e) Which fuel do you think is more environmentally friendly? Explain.

Answers to Practice Problems and Short Answers to Section Review Questions

Practice Problems: **1.(a)** $N_{2(g)} + O_{2(g)} + 180.6$ kJ $\rightarrow 2NO_{(g)}$ **(b)** Reactants have lower energy than products. **(c)** +90.3 kJ **(d)** +644.5 kJ **2.(a)** -1.65×10^3 kJ **(b)** Reactants have higher energy than products. **(c)** -1.22×10^2 kJ **3.(a)** +25.9 kJ **(b)** +393 kJ **(c)** Reactants have lower energy than products. **4.(a)** $P_4O_{10(s)} + 6H_2O_{(\ell)} \rightarrow 4H_3PO_{4(aq)} + 257.2$ kJ **(b)** -1.29×10^3 kJ **(c)** -1.54×10^2 kJ **5.** 12.8°C **6.** 6.70×10^2 g **7.** 2.7×10^4 kJ **8.** 6.09°C **9.** −50 kJ/mol **10.(a)** -4.1×10^2 kJ/mol Mg **(b)** The density and heat capacity of the solutions are the same as the density and heat capacity of water. No heat is lost to the calorimeter. **11.** 29.7°C **12.** $HBr_{(aq)} + KOH_{(aq)} \rightarrow H_2O_{(\ell)} + KBr_{(aq)} + 57$ kJ **13.** −44 kJ **14.** −509 kJ **15.** −120 kJ **16.** +30 kJ **17.(a)** $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} + 74.6$ kJ **(b)** $Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(s)} + 411.2$ kJ **(c)** $Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} + 601.2$ kJ **(d)** $Ca_{(s)} + C_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow CaCO_{3(s)} + 1207.6$ kJ **18.** $H_{2(g)} + S_{(s)} + 2O_{2(g)} \rightarrow H_2SO_{4(\ell)} + 814.0$ kJ **19.** $Cs_{(s)} + 76.7$ kJ $\rightarrow Cs_{(g)}$ **20.(a)** $\frac{1}{4}P_{4(s)} \rightarrow P_{(s)} + 17.6$ kJ **(b)** −18.5 kJ **21.** Get the target equation from the two formation equations. **22.** Get the target equation from the formation equations. **23.** −77.6 kJ/mol **24.(a)** −637.9 kJ **(b)** 2.49×10^3 kJ

Section Review: 5.1: **2.(a)** $\Delta H^\circ_{rxn} = -127.0$ kJ **(b)** $\Delta H^\circ_{vap} = +44.0$ kJ **(c)** $\Delta H^\circ_{rxn} = \Delta H^\circ_{comb} < 0$ **4.(a)** 34.21 g **(b)** 599 kJ **(c)** 1.06×10^3 kJ **5.(a)** $C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \rightarrow H_2O_{(\ell)} + 2CO_{2(g)} + 1.3 \times 10^3$ kJ **(c)** 108 kJ **7.(a)** $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} + 241.8$ kJ **5.2:** **5.(a)** $KOH_{(aq)} + HNO_{3(aq)} \rightarrow H_2O_{(\ell)} + KNO_{3(aq)} + 55$ kJ **5.3:** **3.** −143 kJ **4.** 14.3 kJ **5.** −636.0 kJ