Unit 6
Chemical Energy
In your life you encounter many different kinds of energy: radiant energy from our sun warms you on a spring day; electrical energy provides the energy to run your computer; chemical energy from food keeps your body functioning. In each of these cases energy is transformed from one form to another.

Energy transformations are the basis for all change, everywhere. Photosynthesis is a chemical process that takes radiant energy from the sun and stores it within molecules of glucose. This stored chemical energy provides the energy for life. Fossil fuels also contain stored chemical energy that can be transformed into other forms of energy. Energy links together all components of the universe as it is emitted, captured, stored, and used. All physical, chemical, and nuclear changes involve changes in energy, but this unit will focus on chemical changes involving energy: thermochemical changes, or thermochemistry.

Consider the Alberta photo on the right. Solar energy from the nuclear reactions in our sun is being used through photosynthesis by the barley plants. Carbohydrates are being chemically produced, which may be used to fuel us as human beings. The pumpjack is removing conventional crude oil from below the surface. The oil, we believe, was produced from the decay of plants. The oil is then processed by chemical technologies to, for example, run our cars and trucks. Solar energy, directly or indirectly, is the source of most energy available to us on Earth.

Everything humans do requires energy. It is a major factor in social change on our planet. Technologies, which inevitably consume energy, are developed for a social purpose. These technologies, however, often have drawbacks related to their use of energy. The control and use of our present sources of energy, as well as the development of new sources, will continue to have far-reaching environmental, economic, social, technological, and political implications for many years.

As you progress through the unit, think about these focusing questions:

- How does our society use the energy of chemical changes?
- How do chemists determine how much energy will be produced or absorbed for a given chemical reaction?
GENERAL OUTCOMES

In this unit, you will
• determine and interpret energy changes in chemical reactions
• explain and communicate energy changes in chemical reactions
**Unit 6 Chemical Energy**

**ARE YOU READY?**

These questions will help you find out what you already know, and what you need to review, before you continue with this unit.

**Knowledge**

1. Most of the energy available on Earth comes from our sun. For each of the Alberta-based technological devices in Figure 1, briefly trace the energy produced back to its source, our sun, Sol.

![Figure 1](a) photovoltaic (solar) cells: Students and teachers have installed photovoltaic technology at Cochrane High School, Alberta.

![Figure 1](b) wind turbine: The Castle River Wind Farm is one of many in Alberta, which (along with Quebec) leads Canada in wind-generated electricity.

![Figure 1](c) hydroelectric power plant: Belly River Hydroelectric Plant is a low-impact generating station near Glenwood, Alberta.

![Figure 1](d) coal-fired power plant: Sundance Powerplant is on the south shore of Lake Wabamun, Alberta.

2. Write balanced chemical equations for the complete combustion of the following fuels:
   (a) coal (assume C(s))
   (b) propane (C₃H₈(g))
   (c) gasoline (assume C₈H₁₈(l))

3. List five energy sources that do not directly produce carbon dioxide.

4. The overall reaction for photosynthesis can be written as
   \[ 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) + \text{sunlight} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(aq) + 6 \text{O}_2(g) \]
   (a) What additional substance must be present for this reaction to occur?
   (b) Is photosynthesis an endothermic or exothermic process?
   (c) What industries depend heavily on the chemistry of photosynthesis?

5. The overall reaction for cellular respiration can be written as
   \[ \text{C}_6\text{H}_{12}\text{O}_6(aq) + 6 \text{O}_2(g) \rightarrow 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) \]
   (a) Cellular respiration is similar to what common type of reaction?
   (b) If energy were to be included as a term in this reaction equation, should it be written on the right or left side of the arrow?
(c) Is cellular respiration an endothermic or exothermic process?
(d) Give two examples of cellular respiration.

6. Explain why fossil fuel energy can be considered as stored solar energy.

7. The carbon cycle involves the interrelationship of living things with the environment and with technologies that use fossil fuels. Draw a diagram of the carbon cycle using examples from the natural world, agriculture, forestry, transportation, and electricity generation. Use arrows to illustrate the relationships (by the processes of cellular respiration, photosynthesis, or combustion) among these aspects of life in Alberta.

8. From a theoretical perspective, kinetic energy is related to the motion of an entity. The *temperature* of an object is a measure of the average kinetic energy of its entities, while the *thermal energy* of an object is the total kinetic energy of its entities. *Heat* is energy being transferred between two objects or materials. 

   (Figure 2).

   What happens to the average kinetic energy of water molecules when the water is
   (a) heated       (c) maintained at a constant temperature
   (b) cooled       (d) boiled

9. Potential energy is a stored form of energy. Chemical potential energy involves the energy stored in the bonds between atoms and molecules. State what happens to the potential energy of water molecules when the water is
   (a) heated       (b) boiled       (c) frozen

10. The motion of molecules can be translational (straight-line), rotational, and/or vibrational. Describe the dominant types of motion of water molecules in
   (a) ice           (b) liquid water   (c) water vapour

11. A pot of water at room temperature is placed on the burner of a gas stove and heated until 15% of the water has evaporated due to boiling.
   (a) Copy Figure 3, and complete it to show a temperature–time graph for the heating (including boiling) of the water.
   (b) Describe the changes that take place in the kinetic and potential energy of the water molecules as the water is heated, and then when it boils.
   (c) Describe the changes that take place in the kinetic and potential energy of the gas molecules as they undergo combustion in the stove.
   (d) Use the law of conservation of energy to explain the graph that you have drawn.

**STS Connections**

12. List three energy sources that are renewable and three that are nonrenewable.

13. What is your reasoned response to someone trying to sell you shares in a corporation that is manufacturing a perpetual motion machine?

**Skills**

14. Laboratory thermometers are usually read to ±0.2 °C.
   (a) Interpret a thermometer reading of 22.4 °C on this thermometer.
   (b) Critique the communication when someone interprets a reading of 22.0 °C as “exactly twenty-two degrees Celsius” and records the temperature as 22 °C.
We have invented many technologies to use energy: campfires and wood stoves use energy stored in wood; stoves, heaters, and cars use energy stored in liquid hydrocarbons; industries use energy stored in natural gas; and power plants convert the chemical energy stored in natural gas, oil, and coal into electrical energy. Trucks, trains, and airplanes use energy stored in fuels refined from crude oil, heavy oil, and oil sands.

The future could look quite different from the present. Transportation technologies may derive their energy from the combustion of alternative fuels such as hydrogen, ethanol, and methanol. Hybrid cars, operating on both gasoline and batteries, are already becoming more common. Science and technology work in parallel with one another—although sometimes one is ahead of the other—often driven by social pressures. Sometimes a scientific concept is applied by technology; other times science is used to explain a technology after it is invented (independent of the science).

Consumers will have many choices to make about energy technologies. Knowing the science and technology of energy is advantageous. Energy-related issues are important from many perspectives. Will you support politicians who advocate further development of Alberta’s oil sands? Will your next car be gasoline powered? This chapter will help you make these decisions in a more informed manner.

**STARTING Points**

**Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.**

1. Consider the following changes: photosynthesis, cellular respiration, and combustion of gasoline. Classify each of these changes as exothermic or endothermic.
2. How is electrical energy produced in Alberta? What are the sources of energy that produce this electricity?
3. Select one energy source for producing electrical energy, and list three benefits and three risks.
4. Trace the transformations of energy from solar radiation through to using an incandescent light bulb at home.
5. (a) How can we measure how much energy is released or absorbed by a chemical reaction?
   (b) How can we communicate how much energy is released or absorbed by a chemical reaction?
Enthalpy Change

Exploration

Burning Oil

Engineers who design furnaces to heat homes and nutritionists who calculate the energy value of different foods need to analyze the energy supplied by different fuels. In experiments in which thermal energy is absorbed by water, they use the equation

\[ Q = mc\Delta t \]

(thermal energy = mass × specific heat capacity × temperature change)

(c = 4.19 J/(g°C) for water)

The general concept of what these technology experts do is illustrated by the following low-technology experiment.

Materials: eye protection; centigram balance; unshelled pecan or other nut; paper clip; small tin can, open at one end and punctured under the rim on opposite sides; pencil; thermometer; beaker; matches; laboratory stand with ring

- Measure the mass of the nut or assume that an average pecan has a mass of about 0.5 g.
- Bend a paper clip so that it forms a stand that will support a nut above the lab bench (Figure 2).
- Place 50 mL of tap water in the tin can. Measure the temperature of the water.
- Suspend the can of water inside the ring and above the nut by putting the pencil through the holes and under the rim of the can.
- Using a match, light the nut. When it has finished burning, measure the final temperature of the water.

(a) Calculate how much energy was absorbed by the water.
(b) Where did this energy come from?
(c) Calculate the quantity of energy produced per gram of fuel (nut) burned.
(d) Compare this combustion reaction to the reaction that would happen if you were to eat the nut instead of burning it.
(e) This experiment uses low-tech equipment. How can you improve on the technology and, therefore, improve on the certainty of the experimental results?

Students with sensitivity to nuts or nut products should not perform this activity.

Figure 1
Our lives depend on energy transformations: from solar energy to wind energy to electrical energy; and from solar energy to chemical energy (food for cattle and ourselves).

Figure 2
Experimental set-up
11.1 Energy Demands and Sources

Photosynthesis is a major natural contributor to stored chemical energy on Earth. Research has indicated that photosynthesis takes energy from our sun, Sol, and converts this radiant (electromagnetic) energy into chemical energy (Figure 1). Carbon dioxide and water react in plants, in the presence of sunlight, to produce glucose and oxygen. This chemical (potential) energy is consumed by animals, such as ourselves, and is stored or used to fuel life. The chemical energy stored by photosynthesis is accessed through cellular respiration, in which glucose and oxygen react to produce carbon dioxide and water and to supply energy. (This reaction is the reverse of photosynthesis.)

As presented in the carbon cycle in Chapter 9, the most accepted hypothesis for the origin of fossil fuels is the biogenic hypothesis. This hypothesis suggests that fossil fuels had their origins in deposits of plant and animal material. Solar energy was captured and stored by photosynthesis. The plant matter was either eaten by animals and stored as chemical potential energy (in carbohydrates, protein, and fat) in the body of the animal before the animal died, or the plant itself died. In certain geological areas, time, temperature, and pressure converted the dead animal and plant material, with its stored chemical potential energy, into hydrocarbons. This line of reasoning is used to support the claim that fossil-fuel energy has its origins in solar energy from our sun.

Fossil fuels are a major source of stored chemical energy. Humans have invented technologies to extract and process fossil fuels (Figure 1). In Alberta, huge technological advances have been made for recovering chemical energy from, in chronological order, coal, natural gas, crude oil, heavy oil, oil sands, and coal-bed methane. The demand for energy has challenged the technological inventiveness of engineers, scientists, and others in the energy workplace. In Alberta, for example, nearly 20% of all jobs are in the energy sector.

DID YOU KNOW?

Energy Production and Consumption
In the 1960s Canada moved from being a net consumer of energy to a net producer of energy. By 2002 Canada was producing 45% more energy than it consumed. In the same year, according to Statistics Canada, Canadian energy consumption per capita reached a record high. More recent statistics may, however, rewrite that record.

CAREER CONNECTION

Chemical Engineering Technologist
This career requires problem-solving skills and creativity, and there are many different options for jobs. Chemical engineering technologists may work in production facilities, where they operate process control equipment and supervise construction activity, or they may work in engineering offices, where they redesign process equipment and perform computer-based simulations. Explore the variety of tasks performed in this career, and learn what training is needed.

Figure 1
Crude oil, pumped near Longview, Alberta, is an indirect source of solar energy.
Transportation and building designers have to use just as much ingenuity as the engineers and scientists working in the energy sector. On the production side, the processes have been made more efficient and economical. On the consumption side, the technologies (such as cars and homes) also need to be more efficient and economical. Of course, there are other perspectives, such as environmental, legal, ethical, and social, that also need to be considered when designing a technology for converting and using energy.

Chemists have created some concepts that help us explain chemical technologies and the transformation of energy to and from chemical energy. These concepts are conveyed using chemical energy terms, some of which are presented in the Summary on page 493. These definitions are simplified. If you take more in-depth chemistry courses you will learn more elaborate definitions, but these will suit us very nicely for now.

There are four major demands for energy from fossil fuels—heating, transportation, industry, and commercial and institutional. What are some alternatives to using fossil fuels? Options include both the use of different fuels and more economical management of fossil fuels (Table 1).

### Table 1 Alternatives to Current Fossil Fuel Uses

<table>
<thead>
<tr>
<th>Energy demands</th>
<th>Alternative energy sources and practices</th>
</tr>
</thead>
<tbody>
<tr>
<td>heating</td>
<td>• solar heating (Figure 2), heat pumps, geothermal energy, biomass gas, and electricity from hydroelectric and nuclear plants</td>
</tr>
<tr>
<td>residential (~15%)</td>
<td>• improved building insulation and design</td>
</tr>
<tr>
<td>transportation (~30%)</td>
<td>• alcohol/gasohol and hydrogen fuels (Figure 3), and electric and hybrid (electric and gasoline) vehicles</td>
</tr>
<tr>
<td>industry (~40%)</td>
<td>• solar energy, nuclear energy, and hydroelectricity</td>
</tr>
<tr>
<td>commercial</td>
<td>• solar water pre-heating and heat pumps, including geothermal</td>
</tr>
<tr>
<td>and institutional</td>
<td>• water and heat conservation</td>
</tr>
<tr>
<td>(~15%)</td>
<td></td>
</tr>
</tbody>
</table>

**DID YOU KNOW?**

### Electric Cars

Although electric cars are making a comeback in popularity, at one time they were more prevalent than gasoline-powered cars. For example, in 1900, in the cities of New York, New York, Chicago, Illinois, and Boston, Massachusetts, there was a total of 2370 automobiles: 400 gasoline-powered, 800 battery-powered, and 1170 steam-driven.

**DID YOU KNOW?**

### Living Lightly on the Earth

Many Aboriginal lifestyle philosophies embrace the idea of taking as little as possible from the environment and leaving more for future generations. In the 21st century, we are using energy at an accelerating rate, especially nonrenewable energy in the form of fossil fuels. To live more lightly on the Earth should we be looking for a technological fix or personal lifestyle changes?
Personal Use of Chemical Energy

We rely on chemical energy for our very lives, as well as to heat our homes, cook our food, and move us around. Chemical energy for personal use comes from two main sources: combustion reactions and electrochemical reactions. The most personal use of chemical energy is eating food. The human body converts the chemical energy in food into mechanical energy and body heat through the process of cellular respiration, a form of combustion. A typical high-calorie fast-food meal (burger, fries, and drink) provides about 6 MJ of energy. (Research indicates that daily intakes would be around 9 to 12 MJ for a normally active young adult, and up to 29 MJ for an extreme high-performance athlete.) When you buy food, you are buying energy to keep your body running.

First Nations peoples of Alberta traditionally consumed much less energy in their balanced, self-sustaining mode of life. It has been generally noted by anthropologists that earlier lifestyles, barring accidents and foreign disease, were much more healthful for individuals than current lifestyles, which too often include diets high in fat and sugar.

In Alberta, nearly all the energy for home heating and cooking comes from the combustion of fossil fuels, either directly or indirectly. For example, many homes are heated directly by burning methane or propane on-site, or by electricity, which may be produced by burning fossil fuels off-site. Propane and butane are convenient fuels for motor homes and campers because these hydrocarbons can easily be compressed, stored, and transported. A century ago in Alberta, firewood and coal were important fuels for heating and cooking, but now firewood is used mainly by wilderness campers and people living in remote areas.

Our transportation needs are also supplied by chemical energy (Figures 5 and 6). The family car and motorcycle use gasoline, which stores a large quantity of energy in a small volume. The combustion of a litre of gasoline produces about 34 MJ of energy.

Case Study

Gasohol is a mixture of gasoline and methanol/ethanol, designed to reduce pollution and our reliance on fossil fuels. Renewable fuels derived from biomass (such as wood pulp, grain, and crop by-products) are used together with fossil fuels. The technology for using hydrogen gas to run automobiles has been developed but its use is not widespread. Chemical energy stored in batteries is used to power golf carts, passenger cars, and delivery vans. A battery-powered vehicle can travel only a relatively short distance before the battery needs to be recharged. Hybrid automobiles combine a gasoline engine with a battery-powered electric motor that becomes a generator and recharges as you drive. Hybrid vehicles are also able to use gravitational potential energy when going downhill, and kinetic energy when braking, to help recharge the battery.

The portability of small batteries makes them valuable for radios, cameras, music players, phones, and personal computers.

Most of our personal use of chemical energy, however, comes from burning fossil fuels—even the energy used to recharge batteries likely comes from an electrical energy plant that burns coal or natural gas. Our dependence on fossil fuels raises concerns about depleting our energy reserves and increasing greenhouse gas emissions. On a personal level, a simple solution is to drive a car less and walk, bike, or ride a bus more often. The chemical energy for self-propulsion comes from food, and the carbon dioxide produced by cellular respiration is significantly less than that produced by a car.

Case Study Questions

1. What are the two main sources of chemical energy for personal use?
2. When 1 mol of glucose is burned, 2803.1 kJ of energy is released. Calculate the quantity of energy released to a person by eating 5.00 g of glucose in a candy.
3. How could technology help us meet our need for energy? Suggest at least four ways.
4. Technological solutions (fixes) are often chosen over changing personal habits or behaviour. Some people argue that saving fossil-fuel energy for future generations is important. Provide three examples of technological fixes versus changes in personal behaviour for reducing chemical energy consumption. Briefly evaluate, for each example, which would be the better solution.
5. Identify and list the perspectives represented in this Case Study. See Appendix D1.
### Section 11.1 Questions

Use Table 2 to answer questions 1 and 2. Alternatively, go to the Statistics Canada Web site and obtain the latest data.

#### Table 2 Canadian Energy Production by Fuel Type (Source) in 2003 (in terajoules (TJ), or $10^{12}$ J)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Production (TJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>1 326 114</td>
</tr>
<tr>
<td>Crude oil</td>
<td>5 679 573</td>
</tr>
<tr>
<td>Natural gas</td>
<td>7 024 602</td>
</tr>
<tr>
<td>Natural gas liquids (NGLs)</td>
<td>642 897</td>
</tr>
<tr>
<td>Primary electricity, hydro and nuclear</td>
<td>1 457 467</td>
</tr>
<tr>
<td><strong>Total production</strong></td>
<td><strong>16 130 653</strong></td>
</tr>
</tbody>
</table>

Source: Statistics Canada

1. (a) Convert the Canadian energy production into a percentage of the total for each fuel type for the latest year provided.
   
   (b) Display these percentages as a pie chart. Use graphing software if available.

2. (a) Go to the Statistics Canada Web site and calculate the percentage of the production of each fuel type that is exported from Canada.
   
   (b) Display these percentages as a bar graph. Use graphing software if available.

Use Table 3 to answer questions 3 to 6. Alternatively, go to the Statistics Canada Web site and obtain the latest data.

#### Table 3 Canadian Energy Use/Demand (in terajoules (TJ), or $10^{12}$ J)

<table>
<thead>
<tr>
<th>Energy Use/Demand by Year</th>
<th>1999</th>
<th>2000</th>
<th>2001</th>
<th>2002</th>
<th>2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total industrial (TJ)</td>
<td>2 177 297</td>
<td>2 268 624</td>
<td>2 166 287</td>
<td>2 229 541</td>
<td>2 313 106</td>
</tr>
<tr>
<td>Total transportation (TJ)</td>
<td>2 307 283</td>
<td>2 279 845</td>
<td>2 240 367</td>
<td>2 250 130</td>
<td>2 242 042</td>
</tr>
<tr>
<td>Agriculture (TJ)</td>
<td>229 865</td>
<td>231 927</td>
<td>218 075</td>
<td>206 753</td>
<td>211 866</td>
</tr>
<tr>
<td>Residential (TJ)</td>
<td>1 232 263</td>
<td>1 287 825</td>
<td>1 239 970</td>
<td>1 286 677</td>
<td>1 348 041</td>
</tr>
<tr>
<td>Public administration (TJ)</td>
<td>124 522</td>
<td>131 288</td>
<td>126 813</td>
<td>125 164</td>
<td>127 678</td>
</tr>
<tr>
<td>Commercial and other institutional (TJ)</td>
<td>1 061 446</td>
<td>1 176 423</td>
<td>1 184 065</td>
<td>1 286 657</td>
<td>1 362 441</td>
</tr>
<tr>
<td><strong>Total energy use (TJ)</strong></td>
<td><strong>7 132 504</strong></td>
<td><strong>7 375 967</strong></td>
<td><strong>7 175 442</strong></td>
<td><strong>7 384 682</strong></td>
<td><strong>7 604 948</strong></td>
</tr>
</tbody>
</table>

Source: Statistics Canada

3. For the latest year listed, what are the percentages of use by the sectors listed?

4. Create a line graph for the total energy use over the years for which data are provided. Use graphing software if available.

5. Create a line graph for residential use over the years for which data are provided. Use graphing software if available.

6. Go to the Statistics Canada Web site and obtain the breakdown of residential use by fuel type.
   
   (a) What percentage of residential energy use is from natural gas?
   
   (b) Quote three other statistics that you can extract from the data. Be sure to cite your sources.

7. There is an increasing number of energy choices for operating a car. List at least four of these choices.

8. Homes in Alberta are heated by a variety of energy sources. List at least four of these sources.

9. The Drake Landing Solar Community in Okotoks, Alberta, is an experimental housing project that uses solar energy to heat the homes. Run the animation through the Nelson Web site, and write a short description of the project from a technological perspective.
10. Energy consumption for keeping our homes warm (and supplied with hot water) varies fairly predictably during the year (Table 4).

Table 4 Average Monthly Energy Use in Alberta per Household

<table>
<thead>
<tr>
<th>Month</th>
<th>Energy (GJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>5</td>
</tr>
<tr>
<td>June</td>
<td>3</td>
</tr>
<tr>
<td>July</td>
<td>3</td>
</tr>
<tr>
<td>August</td>
<td>4</td>
</tr>
<tr>
<td>September</td>
<td>5</td>
</tr>
<tr>
<td>October</td>
<td>9</td>
</tr>
<tr>
<td>November</td>
<td>18</td>
</tr>
<tr>
<td>December</td>
<td>22</td>
</tr>
<tr>
<td>January</td>
<td>23</td>
</tr>
<tr>
<td>February</td>
<td>18</td>
</tr>
<tr>
<td>March</td>
<td>16</td>
</tr>
<tr>
<td>April</td>
<td>9</td>
</tr>
<tr>
<td><strong>Annual total</strong></td>
<td><strong>135</strong></td>
</tr>
</tbody>
</table>

(a) Prepare a bar graph to express this data. Use graphing software if available.
(b) From energy bills, how does your household energy use compare with these values?

11. Several energy sources are available for heating: oil, gas, coal, wood, solar, geothermal, and nuclear. These sources produce heat directly. Indirect sources of heat include electric motors and lights.

(a) Which of the direct energy sources originated in our sun, and which originated from the formation of our planet?
(b) Which two energy sources are currently, in your area, most commonly used for heating?
(c) Which two energy sources do you think will be the most widely used for heating by the year 2030?

12. Engineers and scientists have invented technologies for using locally available sources of energy to produce electricity. In Figure 7, the kinetic energy of falling water or of steam is used to turn a turbine attached to an electric generator.

(a) What fuels can be burned to produce the steam?
(b) What other sources of energy (other than hydro and fossil fuels) are available to produce electricity?

13. Some retailers have advertised titanium necklaces as an energy source. As evidence to support their claim, they ask customers to lift a bag containing a brick. They then drape the necklace over the customer’s arm and have the person lift the bag again. Customers find that lifting the bag with the necklace present is easier, and they often buy the necklace as a result. Critique this experimental design.

Extension

14. Energy consumers were briefly excited when successful “cold fusion” was announced by two scientists in 1989. Successful cold fusion would represent an inexpensive, clean, readily available source of energy. Do some library research or search the Internet to learn more about the cold fusion experiments.

(a) Were the two scientists empiricists or theoreticians?
(b) Were they qualified to make theoretical interpretations of their experimental work?
(c) Are there cold-fusion research programs still being funded? If so, where?
(d) Evaluate your research strategies.

15. The caption for Figure 3 (page 481) says that these cars are “true zero-emission vehicles.” Consider this claim. Research the environmental effects of water vapour. Think about the research and production involved in developing such vehicles. Write or present a brief rebuttal or supporting statement for the “zero-emissions” claim.
According to the law of conservation of energy, energy is neither created nor destroyed in any physical or chemical change. In other words, energy is only converted from one form to another. The study of energy changes (that is, energy produced or absorbed) by a chemical system during a chemical reaction is called **thermochemistry**. To study energy changes chemists require an **isolated system**, that is, one in which neither matter nor energy can move in or out. They also need carefully designed experiments and precise measurements. **Calorimetry** is the technological process of measuring energy changes of an isolated system called a **calorimeter** (Figure 1). Within this isolated system the chemical system (reactants and products) being studied is surrounded by a known quantity of liquid (generally water) inside the calorimeter. Energy, as **heat**, is transferred between the chemical system and the water. (Note that heat as a form of energy can only be transferred between substances; heat is never possessed by them.) The energy gained by the chemical system is equal to the energy lost by the calorimeter and its contents, as long as both the chemical system and the calorimeter (the surroundings) are part of an isolated system. In other words, for the measurement to be accurate, no energy may be transferred between the inside of the calorimeter and the environment outside the calorimeter.

The main assumption is that no heat is transferred between the calorimeter and the outside environment. Although chemists know this to be a false assumption, it provides a close approximation. The better the calorimeter technology, the closer the assumption is to being valid. A simplifying assumption is that any heat absorbed or released by the calorimeter materials, such as the container, is negligible. Another assumption is that a dilute aqueous solution in a calorimeter has the same physical properties as pure water (for example, the same volume and specific heat capacity).

**Analyzing Energy Changes**

When methane reacts with oxygen in a laboratory burner, enough energy is transferred to the surroundings to increase the temperature (Figure 2). How is this energy quantified? Calorimetry requires careful measurements of masses and temperature changes. When a fuel such as methane burns, energy is released and heat is transferred from the chemical system to the surroundings (which include the water in the beaker). Given the same quantity of heat, a small quantity of water will undergo a greater increase in temperature than a large quantity of water. In addition, different substances vary in their ability to absorb quantities of thermal energy (Figure 3). Finally, if more heat is transferred, the observed temperature rise in the water is greater.

Calorimetry work in the laboratory has shown that, keeping the type of substance constant (for example, using only water in the calorimeter), the quantity of energy transferred is directly proportional to the mass of the substance and its change in temperature. The chemical energy lost by the chemical system is calculated from the thermal energy gained by the surroundings. **Thermal energy** is the total kinetic energy of the entities of a substance (for example, the molecules of water in a calorimeter).

These three factors—mass \((m)\), type of substance, and temperature change \((\Delta t)\)—are combined in an equation to represent the quantity of thermal energy \((Q)\) transferred:

\[ Q = mc\Delta t \]

where \(c\) is the **specific heat capacity**, the quantity of energy required to raise the temperature of a unit mass (for example, one gram) of a substance by one degree Celsius or one kelvin. For example, an average specific heat capacity of water around room temperature is 4.19 J/(g•°C). (Recall that the SI unit for energy is the **joule**, J.)
Specific heat capacities vary from substance to substance, and even for different states of the same substance (Table 1). The specific and volumetric heat capacities listed in Appendix I were determined by means of calorimetry.

Figure 3
The chemical system inside the calorimeter undergoes either a phase change, such as fusion, or a chemical change, such as a double replacement reaction. Energy is either absorbed from the water or released to the water. An increase in the temperature of the water indicates an exothermic change of the system; a decrease in the temperature of the water indicates an endothermic change of the chemical system.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Specific Heat Capacities of Substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>Specific heat capacity, c (J/(g•°C))</td>
</tr>
<tr>
<td>ice</td>
<td>2.00</td>
</tr>
<tr>
<td>water</td>
<td>4.19</td>
</tr>
<tr>
<td>steam</td>
<td>2.02</td>
</tr>
<tr>
<td>aluminium</td>
<td>0.897</td>
</tr>
<tr>
<td>iron</td>
<td>0.449</td>
</tr>
</tbody>
</table>

Determine the change in thermal energy when 115 mL of water is heated from 19.6 °C to 98.8 °C.

Solution

\[ Q = mc\Delta t \]

\[ = 115 \text{ g} \times \frac{4.19 \text{ J}}{\text{g} \cdot ^\circ \text{C}} \times (98.8 - 19.6) ^\circ \text{C} \]

\[ = 38.2 \text{ kJ} \]

Based upon the assumption that the temperature change is a complete measure of the change in thermal energy, the change in thermal energy of the water is 38.2 kJ.

Some of the assumptions that may be made when using the technique of calorimetry are that:

- all the energy lost or gained by the chemical system is gained or lost (respectively) by the calorimeter; that is, the total system is isolated.
- all the material of the system is conserved; that is, the total system is isolated.
- the specific heat capacity of water over the temperature range is 4.19 J/(g•°C).
- the specific heat capacity of dilute solutions is 4.19 J/(g•°C).
- the density of a dilute solution is the same as that of water; that is, 1.00 g/mL.
- the thermal energy gained or lost by the rest of the calorimeter (other than water) is negligible; that is, the container, lid, thermometer, and stirrer do not gain or lose thermal energy.

### COMMUNICATION example 1

**A Kilojoule of Energy**

Completely burning a wooden match releases about 1 kJ of energy. This quantity of energy could heat \( \frac{1}{4} \) cup of water by about 1 °C, and is equivalent to about a quarter of a calorie of food energy. There are two definitions of calorie but only one for kilojoule: 1000 J.

**DID YOU KNOW?**

Some of the assumptions that may be made when using the technique of calorimetry are that:

- all the energy lost or gained by the chemical system is gained or lost (respectively) by the calorimeter; that is, the total system is isolated.
- all the material of the system is conserved; that is, the total system is isolated.
- the specific heat capacity of water over the temperature range is 4.19 J/(g•°C).
- the specific heat capacity of dilute solutions is 4.19 J/(g•°C).
- the density of a dilute solution is the same as that of water; that is, 1.00 g/mL.
- the thermal energy gained or lost by the rest of the calorimeter (other than water) is negligible; that is, the container, lid, thermometer, and stirrer do not gain or lose thermal energy.
Chemical systems have many different forms of energy, both kinetic and potential. These include the kinetic energies (energy of motions) of
- moving electrons within atoms
- the vibration of atoms connected by chemical bonds
- the rotation and translation of molecules that are made up of these atoms.

The chemical potential energy of a chemical system includes energy stored in
- covalent and/or ionic bonds between the entities
- intermolecular forces between entities

## Heat Transfer and Enthalpy Change

### Purpose
The purpose of this investigation is to create a calorimeter that is improved (based upon your own scientific and technological criteria) over the simplest calorimeter.

### Problem
What is the best design for a simple calorimeter?
The total of the kinetic and potential energy within a chemical system is called its enthalpy. The enthalpy of a chemical system is an expression of the chemical energy possessed by the chemical system. However, if the reactants and products are at the same initial and final temperature, then the kinetic energy of the system does not change.

Just as electrical and gravitational potential difference are most often communicated as a difference from a reference point, enthalpy is most often communicated as a difference in enthalpy between reactants and products for a particular chemical system. An enthalpy change, \( \Delta H \), communicates the difference between the enthalpy (assume the difference in chemical potential energy) of the products and the enthalpy of the reactants.

\[
\Delta H = H_{\text{products}} - H_{\text{reactants}} \quad \text{or} \quad \Delta H = H_p - H_r \quad \text{(IUPAC definition)}
\]

Analysis of calorimetric evidence is based on the law of conservation of energy and on several assumptions. The law of conservation of energy may be expressed in several ways, for example, “The total energy change of the chemical system is equal to the total energy change of the calorimeter surroundings.” Using this method, both the enthalpy change, \( \Delta H \), and the quantity of thermal energy, \( Q \), are calculated as absolute values, without a positive or negative sign.

\[
\Delta H = \frac{Q}{(\text{system})} - \frac{Q}{(\text{calorimeter})}
\]

Energy loss by the chemical system is equal to energy gain by the surroundings. Consider the reaction that occurs when zinc metal is added to hydrochloric acid in an open flask:

\[
\text{Zn(s)} + 2 \text{HCl(aq)} \rightarrow \text{H}_2(g) + \text{ZnCl}_2(\text{aq})
\]

Research on this reaction indicates that the solution increases in temperature. In other words, there is an increase in thermal energy of the surroundings. Chemists infer from the temperature increase that the chemical system (in this case, Zn(s) and HCl(aq)) must have lost chemical energy to the surroundings (Figure 5).

Figure 5
In this example of an exothermic change, the change in potential energy of the chemical system (\( \Delta E_p \) or \( \Delta H \)) equals the change in kinetic energy of the surroundings (\( \Delta E_k \) or \( Q \)). This is consistent with the law of conservation of energy. At this stage in your understanding, you can make the assumptions that \( \Delta E_p = \Delta H \) and \( \Delta E_k = Q \).
The value for the enthalpy change in Sample Problem 11.1 is given as a negative value \( \Delta H = -3.69 \text{ kJ} \) because the change is a decrease. If the surroundings gained energy (i.e., \( Q > 0 \)), then, according to the law of conservation of energy, the chemical system must have decreased in energy (i.e., \( \Delta H < 0 \)). Use this reasoning to add the sign after doing the calculation.

Sample Problem 11.1 illustrates how we can infer the size of an enthalpy change from the size of a thermal energy change. Even though we cannot measure the value of an enthalpy change directly, we can determine it indirectly.

Chemists call a chemical change that produces energy an **exothermic reaction**. The enthalpy change \( \Delta H \) is negative. A reaction that absorbs energy is called an **endothermic reaction**. The enthalpy change \( \Delta H \) is positive.

### COMMUNICATION example 2

When 50 mL of 1.0 mol/L hydrochloric acid is neutralized completely by 75 mL of 1.0 mol/L sodium hydroxide in a polystyrene cup calorimeter, the temperature of the solution changes from 20.2 °C to 25.6 °C. Determine the enthalpy change that occurs in the chemical system.

**Solution**

\[
\Delta H = Q \\
= mc\Delta t \\
= 125 \text{ g} \times \frac{4.19 \text{ J}}{\text{g} \cdot \text{°C}} \times (25.6 - 20.2) \text{ °C} \\
= 2.83 \text{ kJ}
\]

Based upon the evidence available, the enthalpy change for the neutralization of hydrochloric acid in this context is recorded as \(-2.83 \text{ kJ}\).
Molar Enthalpies and Calorimetry

Enthalpy of reaction (change in enthalpy) refers to the energy change for a whole chemical system when reactants change to products. At this stage in your study of thermochemistry you are looking only at energy change as a result of a chemical change in the chemical system. (You are not, for example, investigating energy changes due to phase changes, nuclear changes, or the dissolving of ionic compounds.) For all chemical changes a stated enthalpy change is for the total quantity of chemical involved in the reaction as specified by the reaction equation coefficients. Chemists sometimes want to know the enthalpy change per unit chemical amount (per mole) because they want to relate the enthalpy change to a chemical reaction equation that is balanced in moles.

Theoretically, molar enthalpy of reaction is the enthalpy change in a chemical system per unit chemical amount (per mole) of a specified chemical undergoing change in the system at constant pressure. Although enthalpy changes can be for any amount or mass of chemical undergoing a chemical change, molar enthalpy is the energy lost or gained expressed in units of, for example, kilojoules per mole (kJ/mol). The IUPAC symbol for molar enthalpy for a specified reaction is \( \Delta H_m \).

In order to calculate enthalpy change from their respective molar quantities (Table 3), we have the following equation:

\[
\Delta H = n \Delta H_m
\]

for example, \( \Delta H = n \Delta H_m \) (c for combustion)

The latter equation is read as “the enthalpy of combustion is equal to the chemical amount of the fuel times the molar enthalpy of combustion of the fuel.”

Molar quantities are often referenced (looked up in a table) or memorized: atomic molar masses are obtained from a periodic table; the molar volume of any gas at STP is memorized or referenced as 22.4 L/mol. We can use these molar quantities to predict, for example, the enthalpy of combustion (\( \Delta H \)) of an organic compound (as in Sample Problem 11.2).

Table 3 Quantities and Molar Quantities

<table>
<thead>
<tr>
<th>Quantity (unit)</th>
<th>Molar quantity (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass, ( m ) (g)</td>
<td>molar mass, ( M ) (g/mol)</td>
</tr>
<tr>
<td>volume, ( V ) (L)</td>
<td>molar volume, ( V_m ) (L/mol)</td>
</tr>
<tr>
<td>enthalpy change, ( \Delta H ) (kJ)</td>
<td>molar enthalpy, ( \Delta H_m ) (kJ/mol)</td>
</tr>
</tbody>
</table>

We can see that the equations are correct because the units work out.

**Learning Tip**

Note the logically consistent pattern for calculating quantities from their chemical amount (\( n \)) and molar quantity (Table 3). For example,

\[
\begin{align*}
  m &= n M \\
  &= \text{mol} \times \text{g/mol} \\
  \Delta H &= n \Delta H_m \\
  &= \text{mol} \times \text{kJ/mol}
\end{align*}
\]

DID YOU KNOW?

Measuring Enthalpy Change

Chemists and chemical engineers object to talking about measuring a change in enthalpy. They agree that we can measure a change in temperature (\( \Delta T \)) with a thermometer. Then we can calculate the change in thermal energy from \( Q = mc\Delta T \). However, we must then use the law of conservation of energy to infer the molar enthalpy from the calculated thermal energy. In doing so, we assume that the change in enthalpy of the chemicals involved in a reaction is equal to the change in thermal energy of the surroundings.

**WEB Activity**

Case Study—Thermal Insulation

Living in Alberta in the winter involves dressing for the weather. Investigate what technological “advances” have been made by chemists creating synthetic materials. Compare these modern materials with traditional materials, such as animal skins, used for footwear and warm clothing.

www.science.nelson.com
Predict the change in enthalpy due to the combustion of 10.0 g of propane used in a camp stove (Figure 6).

First, you have to determine the change in enthalpy for the combustion, $\Delta_H$, using the equation

$$\Delta_H = n \Delta_H_m$$

To calculate $\Delta_H$, you need to know the chemical amount ($n$) and the molar enthalpy of combustion ($\Delta_H_m$). You can calculate the chemical amount from the mass and molar mass. The molar enthalpy of combustion of propane (producing water vapour) is $-2043.9 \text{ kJ/mol}$.

$$\Delta_H = 10.0 \text{ g} \times \frac{1 \text{ mol}}{44.11 \text{ g}} \times \frac{-2043.9 \text{ kJ}}{1 \text{ mol}}$$

$$= -463 \text{ kJ}$$

Based on the concept of molar enthalpy, the change in enthalpy due to the combustion of 10.0 g of propane is $-463 \text{ kJ}$.

Predict the enthalpy change due to the combustion of 10.0 g of butane in a camp heater. The molar enthalpy of combustion to produce water vapour is $-2657.3 \text{ kJ/mol}$.

**Solution**

$$\Delta_H = 10.0 \text{ g} \times \frac{1 \text{ mol}}{58.14 \text{ g}} \times \frac{-2657.3 \text{ kJ}}{1 \text{ mol}}$$

$$= -457 \text{ kJ}$$

Based upon the concept of molar enthalpy, the enthalpy change for the combustion of 10.0 g of butane is recorded as $-457 \text{ kJ}$.

The molar enthalpy of reaction can be calculated from or used in calorimetry investigations. Again, the law of conservation of energy is used to produce an equality. The change in enthalpy ($\Delta H$) of the chemical system is equal to the change in thermal energy ($Q$) of the calorimeter.

$$\Delta H = Q$$

$$n \Delta H_m = mc\Delta t$$

From this equation, any one of the five variables can be determined as an unknown. See Communication Example 4.

The IUPAC symbols used in the calorimetry equation need to be interpreted carefully.
9. Write the symbols for the following terms.
(a) enthalpy of formation
(b) enthalpy of decomposition
(c) molar enthalpy of formation
(d) molar enthalpy of decomposition

10. In your own words, describe the similarities and differences between the enthalpy change and molar enthalpy symbols and meanings.

11. What is the significance of a positive or negative sign for an enthalpy change or molar enthalpy value?

12. Predict the enthalpy change for the combustion of every 100 g of methane in a natural gas water heater. (\( \Delta H_{\text{m}} (\text{CH}_4) = 802.5 \text{ kJ/mol} \) (to produce water vapour))

13. Methanol is one type of fuel that is used in fondue heaters. In an experiment using a simple tin can calorimeter, 2.98 g of methanol was burned to raise the temperature of 650 g of water by 20.9 °C. Using this evidence, calculate the molar enthalpy of combustion of methanol (to produce water as a vapour).

- **Communication Example 4**

Ethanol is often added to gasoline as a renewable component that reduces harmful emissions. The mixture is known as gasohol. In a research laboratory, the combustion of 3.50 g of ethanol in a sophisticated calorimeter causes the temperature of 3.63 L of water to increase from 19.88 °C to 26.18 °C. Use this evidence to determine the molar enthalpy of combustion of ethanol.

**Solution**

\[ Q = mc\Delta t \]
\[ = 3.63 \text{ kg} \times \frac{4.19 \text{ J}}{\text{g} \cdot \text{°C}} \times (26.18 - 19.88)^\circ \text{C} \]
\[ = 95.8 \text{ kJ} \]
\[ \Delta H_{\text{m}} = \frac{95.8 \text{ kJ}}{3.50 \text{ g} \times \frac{1 \text{ mol}}{46.08 \text{ g}}} \]
\[ = 1.26 \text{ MJ/mol} \]

Based upon the evidence gathered, the molar enthalpy of combustion of ethanol is recorded as \(-1.26 \text{ MJ/mol}\).
Section 11.2

**Simulation—Calorimetry**

The purpose of this activity is to use a calorimetry computer model to investigate the quantity of heat produced by combustion of various masses of different compounds in excess oxygen. Keep all variables constant, other than changing a reactant.

[www.science.nelson.com](http://www.science.nelson.com)

**INVESTIGATION 11.2 Introduction**

**Molar Enthalpy of Reaction**

The accuracy (percent difference) of the value for molar enthalpy obtained in this investigation is used to evaluate the calorimeter and the assumptions made in the analysis, rather than to evaluate the prediction and its authority. The ultimate authority in this experiment is considered to be the reference value used in the prediction.

**Purpose**

The purpose of this investigation is to test the calorimeter design and calorimetry procedure by comparing experimental evidence with a widely accepted value for the molar enthalpy of a neutralization reaction.

To perform this investigation, turn to page 516.

**Report Checklist**

- Purpose
- Problem
- Hypothesis
- Prediction
- Design
- Materials
- Procedure
- Evidence
- Analysis
- Evaluation (1, 2, 3)

**Problem**

What is the molar enthalpy of neutralization for sodium hydroxide when 50 mL of aqueous 1.0 mol/L sodium hydroxide reacts with an excess quantity of 1.0 mol/L sulfuric acid?

**Prediction**

The molar enthalpy of neutralization for sodium hydroxide is \(-57 \text{ kJ/mol}\), as per *The CRC Handbook of Chemistry and Physics*.

**SUMMARY**

- Thermal energy—the kinetic energy of entities (e.g., molecules of the surroundings, around a chemical system). Thermal energy increases with temperature.
- Change in thermal energy (\(Q\) in kJ)—measured by a temperature change and calculated using the relationship (equation) \(Q = mc\Delta t\)
- Heat—thermal energy transferred between systems. Heat is not possessed by a system. Heat is energy in transition (flowing) between systems.
- Kinetic energy (\(E_k\) in kJ)—a form of energy related to the motion of a chemical entity; measured as an average kinetic energy by the temperature of a chemical system
- Chemical potential energy (\(E_p\) in kJ)—the energy present in the chemical bonds of a substance
- Enthalpy change (\(\Delta H\) in kJ)—a change in the enthalpy of a chemical system under constant pressure; also loosely called heat of reaction
- Molar enthalpy (\(\Delta H_m\) in kJ/mol)—the change in enthalpy expressed per mole of a substance undergoing a specified reaction
- Endothermic change—a change in chemical energy where energy/heat enters (is absorbed by) the chemical system under consideration; results in an increase in chemical potential energy (and enthalpy); the \(\Delta H\) is a positive value
- Exothermic change—a change in chemical energy where energy/heat exits (is released by) the chemical system under consideration; results in a decrease in chemical potential energy (and enthalpy); the \(\Delta H\) is a negative value

Enthalpy Change
Section 11.2 Questions

1. Record whether each of these statements is true or false. Provide your reasoning.
   (a) Heat is possessed by a chemical system.
   (b) For an exothermic change, energy exits from the surroundings and enters the chemical system.
   (c) The change in enthalpy of a chemical system is measured in kilojoules per mole (kJ/mol).
   (d) The change in thermal energy of the surroundings can be calculated using \( Q = mc\Delta t \).
   (e) Temperature is the measure of the average kinetic energy of the entities in a chemical system.

2. It is commonly assumed in calorimetry labs with polystyrene calorimeters that a negligible quantity of heat is absorbed or released by the solid calorimeter materials such as the cup, stirring rod, and thermometer. Use the empirical data in Table 4 to evaluate this assumption.
   (a) For a temperature change of 5.0 °C, calculate the energy change of the water only.
   (b) For a temperature change of 5.0 °C, calculate the total energy change of the water, polystyrene cups, stirring rod, and thermometer.
   (c) Calculate the percent error introduced by using only the energy change of the water.
   (d) Evaluate the assumption of negligible heat transfer to the solid calorimeter materials.

Table 4 Typical Quantities for Materials in a Simple Calorimeter

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat capacity (J/(g°C))</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>4.19</td>
<td>100.00</td>
</tr>
<tr>
<td>polystyrene cups</td>
<td>0.30</td>
<td>3.58</td>
</tr>
<tr>
<td>glass stirring rod</td>
<td>0.84</td>
<td>9.45</td>
</tr>
<tr>
<td>thermometer</td>
<td>0.87</td>
<td>7.67</td>
</tr>
</tbody>
</table>

3. Ethane is a component of natural gas. If the molar enthalpy of combustion of ethane is \(-1.56 \text{ MJ/mol}\), calculate the quantity of heat transferred in the burning of
   (a) 5.0 mol of ethane
   (b) 40.0 g of ethane

4. Decane is one of the hundreds of compounds in gasoline. The molar enthalpy of combustion of decane \((\text{C}_{10}\text{H}_{22})\) is \(-6.78 \text{ MJ/mol}\). What mass of decane would have to be burned in order to raise the temperature of 5.00 L of water from 20.0 °C to 55.0 °C?

5. During sunny days, chemicals can store solar energy in homes for later release. Certain hydrated salts dissolve endothermically in their water of hydration when heated to decomposition and release heat when they solidify. For example, Glauber’s salt, \(\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}\), solidifies at 32 °C, releasing 78.0 kJ/mol of salt. What is the enthalpy change for the solidification of 1.00 kg of Glauber’s salt used to supply energy to a home?

6. In a laboratory investigation into the neutralization reaction \(\text{HNO}_3(\text{aq}) + \text{KOH}(s) \rightarrow \text{KNO}_3(\text{aq}) + \text{H}_2\text{O}(l)\)
   a researcher adds solid potassium hydroxide to nitric acid solution in a polystyrene calorimeter. Complete the Analysis section of the lab report, including a calculation of the molar enthalpy of neutralization of potassium hydroxide.
   **Evidence**
   mass KOH = 5.2 g
   volume of nitric acid solution = 200 mL
   \(t_1 = 21.0 \text{ °C}\)
   \(t_2 = 28.1 \text{ °C}\)

7. In a laboratory investigation into the reaction
   \(\text{Ba(NO}_3)_2(\text{s}) + \text{K}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2 \text{KNO}_3(\text{aq})\)
   a researcher adds a 261 g sample of barium nitrate to 2.0 L of potassium sulfate solution in a polystyrene calorimeter. Complete the Analysis section of the lab report, including a calculation of the molar enthalpy of reaction of barium nitrate.
   **Evidence**
   As the barium nitrate dissolves, a precipitate is immediately formed.
   \(t_1 = 26.0 \text{ °C}\)
   \(t_2 = 29.1 \text{ °C}\)

8. A student noticed that chewing fast-energy dextrose tablets made her mouth feel cold. Write the Purpose, Problem, Hypothesis, and Design for an investigation to find out whether there really is a temperature change.

9. Plan an investigation to compare the molar enthalpies of combustion for butane and propane. Include a Problem statement, a Design, and a list of materials. In your Design, identify major variables and how you will control them, as well as any necessary precautions.

10. Describe the features of a calorimeter that make it appropriate for its purpose. What drawbacks does it have?

11. The molar enthalpy of neutralization, \(\Delta H_m\), for a reactant in an aqueous acid–base reaction can be determined by calorimetry. Write the Problem, Procedure, and Analysis for the lab report.

   **Purpose**
   The purpose of this exercise is to use calorimetry to determine the molar enthalpy of neutralization for nitrous acid or for aqueous potassium hydroxide.

   **Design**
   1.00 L of 0.400 mol/L nitrous acid and 1.00 L of 0.400 mol/L aqueous potassium hydroxide are combined in a calorimeter.

   **Evidence**
   initial temperature of solutions = 22.08 °C
   final temperature of mixture = 24.06 °C

12. Research the technological applications of propane and butane. Identify the chemical properties of each that make these appropriate technologies for each of these hydrocarbons.
Scientists and engineers have a variety of methods for communicating the energy change for chemical reactions. It is not uncommon to find different communication systems in different contexts. Each of these systems has pros and cons, but understanding all of them provides a deeper understanding of the topic of reaction enthalpies.

Most information about energy changes comes from the experimental method of calorimetry (page 485). These studies yield molar enthalpies that can be communicated in at least four ways:

1. by stating the molar enthalpy of a specific reactant in a reaction
2. by stating the enthalpy change for a balanced reaction equation
3. by including an energy value as a term in a balanced reaction equation
4. by drawing a chemical potential energy diagram

All four of these methods of expressing energy changes are equivalent. The first three are closer to empirical descriptions, and the fourth method is a theoretical description. Each of these methods of communicating energy changes in chemical reactions is described in the following sub-sections.

**Method 1: Molar Enthalpies of Reaction, \( \Delta H_m \)**

The molar enthalpy of reaction for a substance is determined empirically from the measurement of the energy released or absorbed per unit chemical amount to or from the surroundings of the chemical system at constant pressure. The energy measurements usually involve calorimetry. To communicate a molar enthalpy, both the substance and the reaction must be specified. The substance is conveniently specified by its chemical formula. Some chemical reactions are well known and specific enough to be identified by name only. For instance, reference books often list standard molar enthalpies of formation (\( \Delta_f H_m^\circ \)) and combustion (\( \Delta_c H_m^\circ \)).

Standard enthalpy values are expressed with a \( ^\circ \) superscript, as in \( \Delta_f H_m^\circ \). The reactants and products are in their standard state: a pressure of 100 kPa, an aqueous concentration of 1 mol/L, and liquids and solids in their pure state. For liquid and solid elements the pure state must be at 25 °C. Liquid and solid compounds must only have the same initial and final temperature (most often 25 °C). For our purposes we often refer to SATP as the standard conditions for both elements and compounds.

For some well-known reactions, such as formation and combustion, no chemical equation is necessary, since formation and combustion refer to specific, unambiguous chemical reactions indicated by the subscript letter after the delta symbol. For example, the molar enthalpy of formation for methanol at standard conditions is communicated internationally as

\[
\Delta_f H_m^\circ \text{CH}_3\text{OH} = -239.2 \text{ kJ/mol}
\]

This means that 239.2 kJ of energy is released to the surroundings when 1 mol of methanol is formed from its elements when they are in their standard states at SATP. The following chemical equation communicates the formation reaction assumed to occur:

\[
\text{C(s)} + 2 \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH(l)}
\]
As you know, we can find molar enthalpies from measurements involving systems at various conditions of temperature and pressure. If, however, chemists determine a molar enthalpy when the initial and final conditions of the chemical system are standard conditions, they call it a standard molar enthalpy of reaction. The symbol $\Delta_r H_m^\circ$ distinguishes standard molar enthalpies from molar enthalpies, $\Delta_r H_m$ (Figure 1). Standard molar enthalpies allow chemists to create tables to compare enthalpy values and to increase the precision of frequently used values by careful experimentation. For an exothermic reaction, the standard molar enthalpy is calculated by taking into account all the energy required to change the reaction system from standard conditions in order to initiate the reaction and all the energy released following the reaction, as the products are cooled to standard conditions. For example, the standard molar enthalpy of combustion of methanol is

$$\Delta_r H_m^\circ = -725.9 \text{ kJ/mol}$$

This means that the complete combustion of 1 mol of methanol (Figure 2) releases 725.9 kJ of energy according to the following balanced equation:

$$\text{CH}_3\text{OH}(1) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$$

For a standard value, the initial and final conditions of the chemical system must be standard state. In this case, the carbon dioxide and liquid water are produced at a high temperature. They would be allowed to cool in a special calorimeter to standard conditions before experimenters take the final measurement in order to calculate the energy produced.

If a chemical reaction is not well known or if the equation for the reaction is not obvious, then the chemical equation must be stated along with the molar enthalpy. For example, methanol is produced industrially by the high-pressure reaction of carbon monoxide and hydrogen gases.

$$\text{CO}(g) + 2 \text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l)$$

Chemists have determined that, in this reaction, the standard molar enthalpy of reaction for methanol, $\Delta_r H_m^\circ$, is $-128 \text{ kJ/mol}$. Note that this is not a formation reaction since the reactants are not all elements. Note also that you must always state which substance you are considering for this method of communication.

$$\Delta_r H_m^\circ = -128 \text{ kJ/mol}$$

**Method 2: Enthalpy Changes, $\Delta_r H$**

A second method for communicating an energy change is to write an enthalpy change ($\Delta_r H$) beside the chemical equations. For example,

$$\text{CO}(g) + 2 \text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l) \quad \Delta_r H = -725.9 \text{ kJ}$$

Molar enthalpies of reaction can be used to calculate the enthalpy change during a chemical reaction; a molar enthalpy and a balanced chemical equation are required for the calculation. The enthalpy change is calculated using the empirical definition,

$$\Delta_r H^\circ = n \Delta_r H_m^\circ$$

where $n$ is the chemical amount (in moles) of the substance whose molar enthalpy is known. The enthalpy change for the equation as written equals the chemical amount (from the coefficient in the equation) times the molar enthalpy of reaction (for a specific chemical). See Sample Problem 11.3.
Sulfur dioxide and oxygen react to form sulfur trioxide (Figure 3). The standard molar enthalpy of combustion of sulfur dioxide, in this reaction, is \(-98.9 \text{ kJ/mol}\). What is the enthalpy change for this reaction? First write the balanced chemical equation.

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g)
\]

Then obtain the chemical amount of sulfur dioxide from its coefficient in the balanced equation and use \(\Delta H^\circ = n \Delta H_m^\circ\).

\[
\Delta H^\circ = n \Delta H_m^\circ = 2 \text{ mol} \times \frac{-98.9 \text{ kJ}}{1 \text{ mol}} = -197.8 \text{ kJ}
\]

Report the enthalpy change for the reaction by writing it next to the balanced equation, as follows:

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad \Delta H^\circ = -197.8 \text{ kJ}
\]

Note that the 2 in 2 mol is an exact number; it does not affect the certainty of the answer.

Note that the enthalpy change is not, in this method, a molar value, so does not require the "m" subscript and is not in kJ/mol. Also, it is not necessary to state which substance is under consideration because the quantity refers to the reaction equation as written.

The enthalpy change depends on the actual chemical amount of reactants and products in the chemical reaction. Therefore, if the balanced equation for the reaction is written differently, the enthalpy change should be reported differently. For example,

\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \quad \Delta H^\circ = -98.9 \text{ kJ}
\]

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \quad \Delta H^\circ = -197.8 \text{ kJ}
\]

Both chemical equations agree with the empirically determined molar enthalpy of combustion for sulfur dioxide in this reaction.

\[
\Delta H_m^\circ = \frac{-197.8 \text{ kJ}}{2 \text{ mol}} = \frac{-98.9 \text{ kJ}}{1 \text{ mol}} = -98.9 \text{ kJ/mol}
\]

Unlike molar enthalpies of formation or combustion, the enthalpy changes for most reactions must be accompanied by a balanced chemical equation so that we know what reaction is being described.

Wild natural gas wells are sometimes lit on fire to eliminate the very toxic hydrogen sulfide gas. The standard molar enthalpy of combustion of hydrogen sulfide is \(-518.0 \text{ kJ/mol}\). Express this value as a standard enthalpy change for the following reaction equation:

\[
2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) + 2 \text{SO}_2(g) \quad \Delta H^\circ = ?
\]

**Solution**

\[
\Delta H = 2 \text{ mol} \times (-518.0 \text{ kJ/mol})
\]

\[
= -1036.0 \text{ kJ}.
\]

\[
2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g) + 2 \text{SO}_2(g) \quad \Delta H^\circ = -1036.0 \text{ kJ}
\]
Method 3: Energy Terms in Balanced Equations

Another way to report the enthalpy change in a chemical reaction is to include it as a term in a balanced equation. If a reaction is endothermic, it requires a certain quantity of additional energy for the reactants to continuously react. This energy (like the reactants) is transformed as the reaction progresses and is listed along with the reactants. For example,

\[ \text{H}_2\text{O}(l) + 285.8 \text{ kJ} \rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \]

If a reaction is exothermic, energy is released as the reaction proceeds (Figure 4) and is listed along with the products. For example,

\[ \text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s) + 601.6 \text{ kJ} \]

In order to specify the initial and final conditions for measuring the enthalpy change of the reaction, the temperature and pressure may be specified at the end of the equation.

\[ \text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s) + 601.6 \text{ kJ} \text{ (under standard conditions)} \]

**Method 4: Chemical Potential Energy Diagrams**

Chemists use the law of conservation of energy to describe what happens during a chemical reaction. They explain their observations theoretically: observed energy changes are due to changes in chemical potential energy that occur during a reaction. This energy is a stored form of energy that is related to the relative positions of particles and the strengths of the bonds between them. As bonds break and re-form and the positions of atoms are altered, changes in potential energy occur. Evidence of a change in enthalpy of a chemical system is provided by a temperature change of its surroundings.

A chemical potential energy diagram shows the potential energy of both the reactants and the products of a chemical reaction (Figures 5 and 6). The difference between the initial and final energies in a chemical potential energy diagram is the enthalpy change, obtained from calorimetry by measuring the temperature change of the calorimeter. A temperature change is caused by a flow of heat into or out of the chemical system.

The vertical axis on the diagram represents the potential energy of the system, \( E_p \). The reactants are written on the left and the products on the right, and the horizontal axis is called the reaction coordinate or reaction progress. In an exothermic change (Figure 5), the products have less potential energy than the reactants: energy is released to the surroundings as the products form. In an endothermic change (Figure 6), the

**Example 2**

Ethane is cracked into ethene in world-scale quantities in Alberta. Communicate the enthalpy of reaction as a term in the equation representing the cracking reaction.

\[ \text{C}_2\text{H}_6(g) \rightarrow \text{C}_2\text{H}_4(g) + \text{H}_2(g) \quad \Delta_f H = +136.4 \text{ kJ} \]

**Solution**

\[ \text{C}_2\text{H}_6(g) + 136.4 \text{ kJ} \rightarrow \text{C}_2\text{H}_4(g) + \text{H}_2(g) \]

Note that, in the first reaction equation, the enthalpy change has a positive value. This tells us that the reaction is endothermic, so the energy term is written with the reactants.
products have more potential energy than the reactants: energy is absorbed from the surroundings. Neither of the axes is numbered; only the numerical change in potential energy (enthalpy change, $\Delta H$) of the system is shown in the diagrams.

> **COMMUNICATION example 3**

Communicate the following enthalpies of reaction as chemical potential energy diagrams.
(a) The burning of magnesium to produce a very bright emergency flare.

$$\text{Mg}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{MgO}(s) \quad \Delta H = -601.6 \text{ kJ}$$

(b) The decomposition of water by electrical energy from a solar cell.

$$\Delta H_m = +285.8 \text{ kJ/mol}$$

**Solution**

(a) **Combustion of Magnesium**

Exothermic Reaction

Surroundings are warmed as chemical system releases energy.

(b) **Decomposition of Water**

Endothermic Reaction

Surroundings are cooled as chemical system absorbs energy.

**Figure 7**

According to the law of conservation of energy, energy is neither created nor destroyed, only transformed. The diagrams above convey the notion that energy exits from an exothermic reaction system and enters into an endothermic reaction system.

### SUMMARY

**Four Ways of Communicating Energy Changes**

<table>
<thead>
<tr>
<th>Method</th>
<th>Exothermic Changes</th>
<th>Endothermic Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Molar Enthalpy</td>
<td>$\Delta H_m &lt; 0$</td>
<td>$\Delta H_m &gt; 0$</td>
</tr>
<tr>
<td>2. Enthalpy Change</td>
<td>reactants $\rightarrow$ products; $\Delta H &lt; 0$</td>
<td>reactants $\rightarrow$ products; $\Delta H &gt; 0$</td>
</tr>
<tr>
<td>3. Term in a Balanced Equation</td>
<td>reactants $\rightarrow$ products $+\text{energy}$</td>
<td>reactants $+\text{energy} \rightarrow$ products</td>
</tr>
</tbody>
</table>
Energy is transformed in cellular respiration and in photosynthesis (Figure 8). Cellular respiration, a series of exothermic reactions, is the breakdown of foodstuffs, such as glucose, that takes place within cells. Photosynthesis, a series of endothermic reactions, is the process by which green plants use light energy to make glucose from carbon dioxide and water.

Express the enthalpy changes for cellular respiration and for photosynthesis by using the four different methods of communication.

(a) One mole of glucose is consumed, during cellular respiration, to release 2803.1 kJ of energy.
(b) Glucose is produced during photosynthesis.

**Solution**

(a) Molar enthalpy for cellular respiration of glucose:

$$\Delta H^\circ = -2803.1 \text{ kJ/mol}$$

$$\text{C}_6\text{H}_{12}\text{O}_6(g) + 6 \text{ O}_2(g) \rightarrow 6 \text{ CO}_2(g) + 6 \text{ H}_2\text{O}(l) \quad \Delta H^\circ = -2803.1 \text{ kJ}$$

(b) Molar enthalpy for photosynthesis of glucose:

$$\Delta H^\circ = +2803.1 \text{ kJ/mol}$$

$$6 \text{ CO}_2(g) + 6 \text{ H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{ O}_2(g) \quad \Delta H^\circ = +2803.1 \text{ kJ}$$

Potential energy diagram for photosynthesis:

> **Cellular Respiration**

\[ \text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{ O}_2(g) \rightarrow 6 \text{ CO}_2(g) + 6 \text{ H}_2\text{O}(l) \quad \Delta H^\circ = -2803.1 \text{ kJ} \]

**Reaction coordinate**

**Potential energy diagram for cellular respiration:**

(b) Potential energy diagram for photosynthesis:

> **Photosynthesis**

\[ 6 \text{ CO}_2(g) + 6 \text{ H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{ O}_2(g) \quad \Delta H^\circ = +2803.1 \text{ kJ} \]

**Reaction coordinate**

**Learning Tip**

Remember that the unit of $\Delta H$ is the kJ and the unit of $\Delta H^\circ$ is the kJ/mol, and that when multiplying by an exact number, you use the precision rule. For example, $2 \times 40.65 \text{ kJ} = 81.30 \text{ kJ}$, retaining the same precision as the measured value.

Figure 8
Energy can be captured by and from grain. The energy may be obtained from the grain in the form of, for example, foodstuffs, ethanol, and/or biodiesel. Grain grows well during the long summer days in Alberta, when the photosynthesis process exceeds the cellular respiration process. A grain field is an example of an open system, in which mass and energy flow freely into and out of the system.
Section 11.3 Questions

1. Translate into words all parts of the following symbols:
   (a) \( \Delta H^\circ_{\text{m}} \)
   \( \text{CH}_4 \)
   (b) \( n \Delta H^\circ_{\text{m}} \)
   \( \text{C}_3\text{H}_8 \)
   (c) \( Q \)
   water

2. Communicate the enthalpy change by using the four methods described in this section for each of the following chemical reactions. Assume standard conditions for the measurements of initial and final states.
   (a) The formation of acetylene (ethyne, \( \text{C}_2\text{H}_2 \)) fuel from solid carbon and gaseous hydrogen
      \( (\Delta H^\circ_{\text{m}} = +227.4 \text{ kJ/mol acetylene}) \)
   (b) The simple decomposition of aluminium oxide powder
      \( (\Delta H^\circ_{\text{m}} = +1675.7 \text{ kJ/mol aluminium oxide}) \)
   (c) The complete combustion of pure carbon fuel
      \( (\Delta H^\circ_{\text{m}} = -393.5 \text{ kJ/mol CO}_2) \)

3. For each of the following balanced chemical equations and enthalpy changes, write the symbol and calculate the molar enthalpy of combustion for the substance that reacts with oxygen.
   (a) \( 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \quad \Delta H^\circ = -483.6 \text{ kJ} \)
   (b) \( 4\text{NH}_3(g) + 7\text{O}_2(g) \rightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O}(g) + 1272.1 \text{ kJ} \)
   (c) \( 2\text{N}_2(g) + \text{O}_2(g) + 163.2 \text{ kJ} \rightarrow 2\text{N}_2\text{O}(g) \)
   (d) \( 3\text{Fe}(s) + 2\text{O}_2(g) \rightarrow \text{Fe}_3\text{O}_4(s) \quad \Delta H^\circ = -1118.4 \text{ kJ} \)

4. The neutralization of a strong acid and a strong base is an exothermic process.
   \( \text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(l) + 114 \text{ kJ} \)
   (a) What is the enthalpy change for this reaction?
   (b) Write this chemical equation, using the \( \Delta H \) notation, under standard conditions.
   (c) Calculate the molar enthalpy of neutralization for sulfuric acid.
   (d) Calculate the molar enthalpy of neutralization for sodium hydroxide.

5. Translate the empirical molar enthalpies given below into a balanced chemical equation, including the enthalpy change; for example,
   \( \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H = -802.5 \text{ kJ} \)
   (a) The standard molar enthalpy of combustion for methanol to produce water vapour is \(-725.9 \text{ kJ/mol.} \)
   (b) The standard molar enthalpy of formation for liquid carbon disulfide is \(89.0 \text{ kJ/mol.} \)
   (c) The standard molar enthalpy of roasting (combustion) for zinc sulfide is \(-441.3 \text{ kJ/mol.} \)
   (d) The standard molar enthalpy of simple decomposition, \( \Delta \text{H}^\circ_{\text{m}} \), for iron(III) oxide is \(824.2 \text{ kJ/mol.} \)

6. For each of the following reactions, translate the given molar enthalpy into a balanced chemical equation using the \( \Delta H \) notation, and then rewrite the equation including the energy as a term in the equation. Use Appendix I to obtain the molar enthalpies of combustion and formation required.
   (a) Propane obtained from natural gas is used as a fuel in barbecues and vehicles (Figure 9).
   (b) Nitrogen monoxide forms at the high temperatures inside an automobile engine.
   (c) Some advocates of alternative fuels have suggested that cars could run on ethanol.

7. The standard molar enthalpy of combustion for hydrogen to produce liquid water is \(-285.8 \text{ kJ/mol.} \) The standard molar enthalpy of decomposition for liquid water is \(+285.8 \text{ kJ/mol.} \)
   (a) Write both chemical equations using the \( \Delta H \) notation.
   (b) How does the enthalpy change for the combustion of hydrogen compare with the enthalpy change for the simple decomposition of liquid water? Suggest a generalization to include all pairs of chemical equations that are the reverse of one another.

8. Combustion reactions are very useful to society, but also have some drawbacks. Create a list of possible drawbacks. Create a list of possible drawbacks of our reliance on combustion reactions, and suggest some possible solutions.

Figure 9
Propane-fuelled vehicles are not allowed to park in underground parking lots. Propane is denser than air, and a dangerous quantity of propane could accumulate in the event of a leak.
11.4 Hess’ Law

Calorimetry is the basis for most information about chemical energy changes. However, not every reaction of interest to scientists and engineers can be studied by means of a calorimetric experiment. For example, the rusting of iron is extremely slow and, therefore, results in temperature changes too small to be measured using a conventional calorimeter. It is impossible to measure, with a calorimeter, the temperature change involved in the energy of formation of carbon monoxide because the combustion of carbon produces carbon dioxide and carbon monoxide simultaneously. Chemists have devised a number of methods to predict an enthalpy change for reactions that are inconvenient to study experimentally. All the methods are based on the law of conservation of energy and the experimentally established principle that net changes in all properties of a system are independent of the way the system changes from the initial state to the final state.

A temperature change is an example of a property that satisfies this principle. A net (overall) temperature change ($t_f - t_i$) does not depend on whether the temperature changed slowly, quickly, or rose and fell several times between the initial temperature and the final temperature. This same principle applies to enthalpy changes. If several reactions occur in different ways but the initial reactants and final products are the same, the net enthalpy change is the same as long as the reactions have the same initial and final conditions.

Predicting $\Delta_r H$: Hess’ Law

Based on experimental measurements and calculations of enthalpy changes, Swiss chemist G.H. Hess suggested in 1840 that the addition of chemical equations yields a net chemical equation whose enthalpy change is the sum of the individual enthalpy changes. This generalization has been tested in many experiments and is now accepted as the law of additivity of enthalpies of reaction, also known as Hess’ law. Hess’ law can be written as an equation using the uppercase Greek letter $\Sigma$ (pronounced “sigma”) to mean “the sum of.”

$$\Delta_r H = \Delta_1 H + \Delta_2 H + \Delta_3 H + \ldots$$

or

$$\Delta_r H = \Sigma \Delta_i H$$

or, in standard conditions,

$$\Delta_r H^\circ = \Sigma \Delta_i H^\circ$$

An analogy for this concept is shown in Figure 1. The net vertical distance that the bricks rise is the same whether they go up in one stage or in two stages. The same principle applies to enthalpy changes: If a set of reactions occurs in different steps but the initial reactants and final products are the same, the overall enthalpy change is the same.

Hess’ discovery allowed the determination of the enthalpy change of a reaction without direct calorimetry (see Sample Problem 11.4), using two rules for chemical equations and enthalpy changes that you already know:

- If a chemical equation is reversed, then the sign of $\Delta_r H$ changes.
- If the coefficients of a chemical equation are altered by multiplying or dividing by a constant factor, then the $\Delta_r H$ is altered by the same factor.
Use Hess’ law to determine the enthalpy change for the formation of carbon monoxide.

\[ \text{C(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta_f H^\circ = ? \]

This reaction cannot be studied calorimetrically since the combustion of carbon produces carbon dioxide as well as carbon monoxide. However, the enthalpy of complete combustion for carbon and for carbon monoxide can be calculated by calorimetric measurements, and the enthalpy of formation for carbon monoxide can be determined using Hess law as follows:

1. \[ \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta_f H^\circ = -393.5 \text{ kJ} \]
2. \[ 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \quad \Delta_f H^\circ = -566.0 \text{ kJ} \]

Rearrange these two equations, and then add them together to obtain the chemical equation for the formation of carbon monoxide. The first term in the formation equation for carbon monoxide is 1 mol of solid carbon. Therefore, leave equation (1) unaltered so that C(s) will appear on the reactant side when we add the equations. However, we want 1 mol of CO(g) to appear as a product, so reverse equation (2) and divide each of its terms (including the enthalpy change) by 2.

\[ \text{C(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta_f H^\circ = -393.5 \text{ kJ} \]
\[ \text{CO}(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta_f H^\circ = +283.0 \text{ kJ} \]

Note that the sign of the enthalpy change in equation (2) has changed, since the equation has been reversed. Now add the reactants, products, and enthalpy changes to get a net reaction equation. Note that CO$_2$(g) can be cancelled because it appears on both sides of the net equation. Similarly, \( \frac{1}{2} \text{O}_2(g) \) can be cancelled from each side of the equation, resulting in:

\[ \text{C(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta_f H^\circ = -110.5 \text{ kJ} \]

While manipulating equations (1) and (2), you should check the desired equation and plan ahead to ensure that the substances end up on the correct sides and in the correct chemical amounts.

Sketching a chemical potential energy diagram (Figure 2) might help you ensure that you have made the appropriate additions and subtractions.

**Figure 2**
Carbon and oxygen react, forming carbon dioxide (\( \Delta_f H^\circ = -393.5 \text{ kJ} \)), which theoretically could react to form carbon monoxide and oxygen (\( \Delta_f H^\circ = +283.0 \text{ kJ} \)). The net enthalpy change of the two-step reaction is

\[ -393.5 \text{ kJ} + 283.0 \text{ kJ} = -110.5 \text{ kJ} \].

Note that the label on the y-axis must be “standard enthalpy of formation, \( \Delta_f H^\circ \).”
To determine an enthalpy change of a reaction by using Hess' law, follow these steps:

1. Write the net reaction equation, if it is not given.
2. Manipulate the given equations so they will add to yield the net equation.
3. Multiply, divide, and/or reverse the sign of the enthalpy of reaction.
4. Cancel and add the remaining reactants and products to yield the net equation.
5. Add the component enthalpy changes to obtain the net enthalpy change.
6. Determine the molar enthalpy for a reactant or product, if required.

### Summary

**Enthalpy of Reaction and Hess’ Law**

To determine an enthalpy change of a reaction by using Hess’ law, follow these steps:

1. Write the net reaction equation, if it is not given.
2. Manipulate the given equations so they will add to yield the net equation.
3. Multiply, divide, and/or reverse the sign of the enthalpy of reaction.
4. Cancel and add the remaining reactants and products to yield the net equation.
5. Add the component enthalpy changes to obtain the net enthalpy change.
6. Determine the molar enthalpy for a reactant or product, if required.

### Practice

1. The standard enthalpy changes for the formation of aluminium oxide and iron(III) oxide (Figure 4) are

   \[ 2 \text{Al(s)} + \frac{3}{2} \text{O}_2(g) \rightarrow \text{Al}_2\text{O}_3(s) \quad \Delta H_r^o = -1675.7 \text{kJ} \]
   \[ 2 \text{Fe(s)} + \frac{3}{2} \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s) \quad \Delta H_r^o = -824.2 \text{kJ} \]

   Calculate the standard enthalpy change for the following reaction:

   \[ \text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \rightarrow 2\text{Al}_2\text{O}_3(s) + 2\text{Fe(s)} \quad \Delta H_r^o = ? \]
Figure 5
Electric power-generating stations that use coal as a fuel are 30% to 40% efficient. Coal gasification and combustion of the coal gas provide one alternative to burning coal. Efficiency is improved by about 10% by using both a combustion turbine and a steam turbine to produce electricity.
The following data are from a test of Hess’ law using a calorimeter. Use these data in your prediction, assuming that combustion produces carbon dioxide gas and liquid water.

5 C(s) + 6 H_2(g) → C_5H_{12}(l)  \quad \Delta_r H^o = -173.5 \text{ kJ}

C(s) + O_2(g) → CO_2(g)  \quad \Delta_r H^o = -393.5 \text{ kJ}

H_2(g) + \frac{1}{2} O_2(g) → H_2O(g)  \quad \Delta_r H^o = -241.8 \text{ kJ}

H_2O(l) → H_2O(g)  \quad \Delta_{vap} H^o = +40.65 \text{ kJ}

Then complete the Prediction, Analysis, and Evaluation of the investigation report.

**Purpose**
The purpose of this investigation is to test Hess’ law.

**Problem**
What is the standard molar enthalpy of combustion of pentane?

**Design**
Hess’ law is used to predict the standard molar enthalpy of combustion of pentane. To test the prediction and the acceptability of the law, the standard molar enthalpy of combustion of pentane is determined calorimetrically.

**Evidence**
- mass of pentane reacted = 2.15 g
- mass of water equivalent to calorimeter = 1.24 kg
- initial temperature of calorimeter and contents = 18.4 °C
- final temperature of calorimeter and contents = 37.6 °C

(Note that the calorimeter has the same thermal energy gain or loss as the water equivalent stated.)

---

**LAB EXERCISE 11.C**

**Analysis Using Hess’ Law**

Most natural gas is burned as fuel to provide heat. However, natural gas is also a source of hydrogen gas for producing ammonia-based fertilizers. Complete one possible Analysis for the investigation report. Not all the evidence need be used for a particular analysis.

**Purpose**
The purpose of this exercise is to use Hess’ law to determine an enthalpy change.

**Problem**
What is the standard enthalpy change for the production of hydrogen from methane and steam?

\[
\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3 \text{H}_2(g) \quad \Delta_r H^o = ?
\]
INVESTIGATION 11.3 Introduction

Applying Hess’ Law

Magnesium burns rapidly, releasing heat and light. The enthalpy change of this reaction can be calculated from measurements involving a highly sophisticated calorimeter, but not a polystyrene cup calorimeter. The enthalpy change for the combustion of magnesium can, however, be determined by applying Hess’ law to a series of chemical reaction equations.

Purpose
The purpose of this investigation is to use Hess’ law to determine a molar enthalpy of combustion.

Problem
What is the molar enthalpy of combustion for magnesium?

Prediction
The standard molar enthalpy of combustion for magnesium is $-601.6 \text{ kJ/mol}$, as per the table of standard molar enthalpies of formation (Appendix I). (The molar enthalpy of combustion of magnesium is the same as the molar enthalpy of formation of magnesium oxide because both processes have the same chemical reaction equation.)

Design
The enthalpy changes for the first two reactions in the series are determined empirically using a polystyrene calorimeter, and the third enthalpy change is obtained from Appendix I. The three $\Delta H^\circ$ values are used, along with Hess’ law, to obtain the molar enthalpy of combustion for magnesium.

To perform this investigation, turn to page 517.

EXPLORE an issue

Alternative Energy Sources and Technologies

Photosynthesis is the key to life on Earth. For millions of years green plants have used sunlight, water, and carbon dioxide to produce biomass. When prehistoric plants and the tiny animals that ate them died, the organic materials they contained settled on the bottom of swamps, lakes, and seas, where rocky sediments eventually buried them. Fossil fuels (coal, oil, and natural gas) are the remains of these ancient organisms, transformed by a combination of heat and pressure. While living organisms are composed mainly of carbon, hydrogen, and oxygen, the process of being converted into fossil fuels removed the oxygen from the organic matter so the remaining compounds are referred to as hydrocarbons. Although Alberta’s hydrocarbon reserves are very large, they are also finite because of the time and conditions necessary to produce fossil fuels (Figure 6).

For several decades researchers have been looking for alternatives to fossil fuels. One promising alternative involves using “renewable” plant material from managed forests or farms, which takes a few months or years to grow, rather than using fossil fuels, which take about 300 million years to form. Another option takes waste agricultural or industrial material.

A bio-based economy uses renewable energy and renewable materials instead of fossil fuels to provide the energy, chemicals, and material for society. Proponents of a bio-based economy see a fuel source in the waste carbon compounds produced by agriculture and forestry (Figure 7). These waste plant and animal materials could supply the biomass to produce ethanol or biodiesel, or even hydrogen gas.

Figure 6
A Suncor Energy Inc. shovel fills the bed of a heavy hauler truck in the oil sands region near Fort McMurray.

Figure 7
The new Grande Prairie EcoPower™ Centre uses wood waste to co-generate both electricity and steam for use in two nearby sawmills. The Government of Alberta and the City of Grande Prairie have committed to a long-term purchase of electricity from the EcoPower™ Centre.
for use in fuel cells. This is not a new concept. Wood has been and is being used for heating and cooking. When wood biomass was unavailable, people made use of other biomass sources. For example, prairie First Nations people used buffalo dung for heating, and the Inuit have made efficient use of seal oil for heating and light.

Biomass could also produce the feedstock chemicals used to make the wide array of synthetic materials, including plastics, that are currently synthesized from petrochemicals. Proponents insist that such an economy has the potential to be both renewable and sustainable.

Many of the processes needed to utilize the biomass from agriculture and forestry are already in place, but would need to be adapted and expanded. For example, ethanol is now made largely from starch, which could be used as a food source for people or animals. It may be more efficient to convert the waste parts of crop plants, or the waste from sawmills, into useable fuels.

Many people in the energy industry are skeptical about the practicability of a bio-based economy. They argue that the technology for finding and using fossil fuels is already well established, while the technologies of a bio-based economy will take considerable time and money to develop. In their view, research would be better directed at finding cleaner and more efficient ways of extracting and using traditional fossil fuels. For example, three projects aimed at developing cleaner fossil fuels are

- enhanced coal bed methane
- heavy oil recovery using vapour extraction
- paste technology for oil sands tailings treatment

Energy issues have pros and cons from many perspectives (see Appendix D). Your minimum task is to write an energy issue with a technology emphasis and complete the Resolution and Design. (An example is provided.) Your teacher may also give you instructions to complete the Evidence, Analysis, and Evaluation components of this issue resolution process.

**Issue**

What is the most effective use of government funding for research in energy technology?

**Resolution**

The provincial and federal governments should direct all their research funding to bio-based energy technology.

**Design**

Within small groups, research the pros and cons of using public money to fund bio-based versus fossil-fuel-based energy technology.

www.science.nelson.com

---

### Section 11.4 Questions

Use the following information to answer questions 1 to 5.

Energy may be produced or consumed by the production and synthesis of fuels such as alcohols. Use Hess’ law to determine the quantity of energy required or released during the production of various alcohol fuels.

1. Ethanol (grain alcohol) is a renewable energy gasoline additive that can be made from glucose obtained from the fermentation of grain. Determine the enthalpy of reaction for C₆H₁₂O₆(s) → 2 C₂H₅OH(l) + 2 CO₂(g) \( \Delta H = ? \) from the following reaction equations.

   \[
   \begin{align*}
   C₂H₄O₂(s) &\rightarrow 2 C₂H₅OH(l) + 2 CO₂(g) \quad \Delta H = ? \\
   C₆H₁₂O₆(s) + 6 O₂(g) &\rightarrow 6 CO₂(g) + 6 H₂O(l) + 2 803.1 \text{ kJ} \\
   C₂H₅OH(l) + 3 O₂(g) &\rightarrow 2 CO₂(g) + 3 H₂O(l) + 1 366.8 \text{ kJ}
   \end{align*}
   \]

2. Ethanol can also be made from the nonrenewable resource ethene. First, ethene from natural gas is cracked to produce ethene, as is done in several ethene plants in Alberta. C₆H₁₂O₂(l) → C₂H₄(g) \( \Delta H = ? \)

   The second step is the production (synthesis) of ethanol from ethene by an addition reaction with water.

   C₂H₄(g) + H₂O(l) → C₂H₅OH(l) \( \Delta H = ? \)

   (a) Using the following standard enthalpies of reaction, predict the enthalpy of reaction for the ethane cracking reaction equation given.

   \[
   \begin{align*}
   2 C₂H₆(g) + 7 O₂(g) &\rightarrow 4 CO₂(g) + 6 H₂O(l) + 3 120.8 \text{ kJ} \\
   C₂H₄(g) + 3 O₂(g) &\rightarrow 2 CO₂(g) + 2 H₂O(l) \quad \Delta H = -1 411.0 \text{ kJ} \\
   H₂(g) + \frac{1}{2} O₂(g) &\rightarrow H₂O(l) \quad \Delta H = -285.8 \text{ kJ}
   \end{align*}
   \]

   (b) Using the following standard enthalpies of reaction, predict the enthalpy of reaction for the addition reaction of ethene to water to produce ethanol.

   \[
   \begin{align*}
   C₂H₄(g) + 3 O₂(g) &\rightarrow 2 CO₂(g) + 2 H₂O(l) \quad \Delta H = -1 411.0 \text{ kJ} \\
   C₂H₅OH(l) + 3 O₂(g) &\rightarrow 2 CO₂(g) + 3 H₂O(l) + 1 366.8 \text{ kJ}
   \end{align*}
   \]

   (c) If the reaction equations that you just used (to determine the enthalpies of reaction for the cracking of ethane and for the addition of water to ethene) are not the actual steps used in these chemical processes, then why does this Hess’ law technique work?
3. Methanol (wood alcohol) is a fuel that can be made from biomass (such as cellulose obtained from aspen trees). Methanol can also be made from natural gas. The overall synthesis reaction for the latter case is
\[ \text{CH}_4(g) + 3 \text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(g) \]
Use the reactions below and Hess’ law to predict the molar enthalpy of synthesis of methanol by this chemical process.
\[ \text{CO}(g) + 3 \text{H}_2(g) \rightarrow \text{CH}_3\text{OH}(l) \quad \Delta H = -249.9 \text{ kJ} \]
\[ \text{CO}(g) + 2 \text{H}_2(g) \rightarrow \text{CH}_2\text{O}(l) \quad \Delta H = -128.7 \text{ kJ} \]
4. Consider each of the net reactions in questions 1, 2, and 3 for the synthesis of ethanol and methanol fuels: ethanol from glucose, ethanol from ethane, and methanol from methane. Create a summary, such as a table, in which to present your answers to the following questions.
(a) Is each net synthesis reaction endothermic or exothermic?
(b) Reference (look up) and record the molar enthalpies of combustion of each fuel.
(c) Compare the molar enthalpy of synthesis of each fuel (ethanol and methanol) to the molar enthalpy of combustion of the fuel. Is the net chemical process, considering the synthesis and the combustion of the fuel, endothermic or exothermic?
(d) Quantitatively, what is the net molar enthalpy of reaction for the combined chemical process of synthesis and combustion for each fuel in each of the synthesis processes?
(e) What implications does this have for the production of these alcohols as fuels?
5. Of course, the net energy is less than that calculated in the previous question. What other kinds of energy costs might be associated with the manufacture of fuels such as ethanol and methanol?
6. Describe some other technological solutions to the problem of our growing per-capita and per-country demand for energy.
7. Ethyne may react with hydrogen gas to form ethane gas in the following reaction:
\[ \text{C}_2\text{H}_2(g) + 2 \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) \]
Predict the enthalpy change for the reaction of 200 g of ethyne, using the following information.
\[ \text{C}_2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{CO}(g) + \text{H}_2\text{O}(l) \quad \Delta H^\circ = -1299 \text{ kJ} \]
\[ \text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H^\circ = -286 \text{ kJ} \]
\[ \text{C}_2\text{H}_6(g) + \text{O}_2(g) \rightarrow 2 \text{CO}(g) + 3 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -1560 \text{ kJ} \]
8. As an alternative to combustion, coal gas can undergo a process called methanation.
\[ 3 \text{H}_2(g) + \text{CO}(g) \rightarrow \text{CH}_4(g) + \text{H}_2\text{O}(g) \quad \Delta H^\circ = ? \]
Determine the enthalpy change involved in the reaction of 300 g of carbon monoxide in this methanation reaction.
9. C(s) + O_2(g) → CO_2(g) \quad \Delta_f H = -393.5 \text{ kJ}
2 H_2(g) + O_2(g) → 2 H_2O(g) + 483.6 kJ
\[ \Delta_{\text{H}_\text{m}} = -5074.1 \text{ kJ/mol} \]
\[ \text{C}_8\text{H}_{18} \]
Use Hess’ law and combustion reaction information above to predict the enthalpy change for the formation of octane from its elements.
\[ 8 \text{C(s)} + 9 \text{H}_2(g) \rightarrow \text{C}_8\text{H}_{18}(l) \quad \Delta H = ? \]
10. Bacteria sour wines and beers by converting ethanol, \( \text{C}_2\text{H}_5\text{OH} \), into acetic acid, \( \text{CH}_3\text{COOH} \). Assume that the reaction is
\[ \text{C}_2\text{H}_5\text{OH}(l) + \text{O}_2(g) \rightarrow \text{CH}_3\text{COOH}(l) + \text{H}_2\text{O}(l) \]
The molar enthalpies of combustion of ethanol and acetic acid to produce liquid water are, respectively, \(-1367 \text{ kJ/mol} \) and \(-875 \text{ kJ/mol} \). Write chemical equations for the combustions, and use Hess’ law to determine the enthalpy change for the conversion of ethanol to acetic acid.
11. A series of calorimetric experiments is performed to test Hess’ law. Complete the Purpose, Prediction, Analysis, and Evaluation (1, 2, 3) sections of the investigation report. Evaluation should include a calculation of a percent difference in the experiment, given that the \( \Delta H \) for equation (1) should equal the sum of the \( \Delta H \)’s for equations (2) and (3).

### Table 1: Reaction of KOH(aq) and HBr(aq)

<table>
<thead>
<tr>
<th>Observation</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>quantity of reactant 1</td>
<td>100.0 mL of 1.00 mol/L HBr(aq)</td>
<td>5.61 g KOH(s) in 200.0 mL of solution</td>
<td>5.61 g KOH(s)</td>
</tr>
<tr>
<td>quantity of reactant 2</td>
<td>100.0 mL of 1.00 mol/L KOH(aq)</td>
<td>N/A</td>
<td>200.0 mL of 0.50 mol/L HBr(aq)</td>
</tr>
<tr>
<td>initial temperature</td>
<td>20.0 °C</td>
<td>20.0 °C</td>
<td>20.0 °C</td>
</tr>
<tr>
<td>final temperature</td>
<td>22.5 °C</td>
<td>24.1 °C</td>
<td>26.7 °C</td>
</tr>
</tbody>
</table>
Chemists rely on conventions to simplify explanations and communication. For example, SATP is a set of internationally accepted conditions that define a standard state for formation reactions. It is convenient to set at zero the value for the enthalpies of elements in their most stable form at SATP (the standard conditions for elements). This convention, defining elements as the reference point at which the potential energy is zero, is the reference energy state. This does not mean that the enthalpy of an element is always considered to be zero; in another situation, a different convention might be more convenient. (Similarly, the Celsius temperature scale sets 0 °C at the freezing point of pure water. This is a convenient reference point but it does not mean that water molecules have zero thermal or kinetic energy at that temperature.)

A formation reaction is a reaction in which a compound is formed from its constituent elements. The enthalpy change calculated from measurements of a formation reaction under standard conditions is called the standard enthalpy of formation, $\Delta H^\circ$. We can now describe $\Delta H^\circ$ theoretically: as a change in enthalpy from zero (the reference enthalpy of formation of the elements) to some final value determined by the enthalpy change. For example,

$$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H^\circ = -285.8 \text{ kJ}$$

The potential energy decreases from 0 kJ for the reactants to –285.8 kJ for the product. In other words, the reactants are at a higher chemical potential energy than the product. This potential energy is transferred to the surroundings and appears as thermal energy or other forms of energy. Suppose you were seated on a bicycle at the top of a hill and coasted downhill. Your potential energy at the top of the hill is converted into kinetic energy as you move from a point of higher potential energy (top) to one of lower potential energy (bottom) (Figure 1). Of course, to return to the top of the hill you must supply the energy to move to a higher potential energy. Similarly, to convert the water back into hydrogen and oxygen requires that energy be added, specifically 285.8 kJ/mol of water.

We can use tables of standard molar enthalpies of formation (Appendix I) to compare the stabilities of compounds. Most compounds are formed exothermically from their constituent elements, and the molar enthalpies of formation are negative. This means that the compounds are more stable than their elements (defined at 0 kJ/mol). Thermal stability is the tendency of a compound to resist decomposition when heated. The standard molar enthalpies of formation give an indication of thermal stability. The lower the value, the greater the thermal stability. By analogy, you are physically more stable when you are at a lower gravitational potential energy—closer to the ground. Another example is a comparison of the standard molar enthalpies of formation for tin(II) oxide and tin(IV) oxide, which can be obtained in Appendix I.

$$\Delta H_m^\circ = -280.7 \text{ kJ/mol} \quad \text{SnO} \quad \Delta H_m^\circ = -577.6 \text{ kJ/mol} \quad \text{SnO}_2$$

Chemists explain that tin(IV) oxide has more thermal stability than tin(II) oxide because tin(IV) oxide has a more negative molar enthalpy of formation. The lower the energy, the greater the stability.

Enthalpies of reaction and molar enthalpies of reaction for many chemical reactions can be predicted from the molar enthalpies of formation of elements and compounds. Sample Problem 11.5 illustrates the derivation of the molar enthalpies of formation method from the Hess’ law method.
How can molar enthalpies of formation be used to calculate enthalpies of reaction? Consider the slaking of lime, calcium oxide, represented by the following chemical reaction equation (Figure 2).

\[
\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta_H^o = ?
\]

What is the standard enthalpy of reaction for this reaction?

First, write the formation equation and corresponding standard enthalpy of formation (Appendix I) for each compound in the given equation. To find the enthalpy of formation, \( \Delta_H^o \), multiply the chemical amount by the molar enthalpy of formation, \( \Delta_H^o \), of each respective compound:

\[
\begin{align*}
\text{Ca}(s) + \frac{1}{2} \text{O}_2(g) &\rightarrow \text{CaO}(s) \quad \Delta_H^o = 1 \text{ mol} \times -634.9 \text{ kJ/mol} \\
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) &\rightarrow \text{H}_2\text{O}(l) \quad \Delta_H^o = 1 \text{ mol} \times -285.8 \text{ kJ/mol} \\
\text{Ca}(s) + \text{O}_2(g) + \text{H}_2(g) &\rightarrow \text{Ca(OH)}_2(s) \quad \Delta_H^o = 1 \text{ mol} \times -986.1 \text{ kJ/mol}
\end{align*}
\]

By adding the third equation to the reverse of the first two equations, the chemical equation required for the slaking of lime is obtained.

\[
\begin{align*}
\text{CaO}(s) &\rightarrow \text{Ca}(s) + \frac{1}{2} \text{O}_2(g) \\
\text{H}_2\text{O}(l) &\rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \\
\text{Ca(OH)}_2(s) &\rightarrow \text{Ca}(s) + \text{O}_2(g) + \text{H}_2(g)
\end{align*}
\]

Net: \( \text{CaO}(s) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta_H^o = ? \)

Applying Hess’ law gives the following equation:

\[
\Delta_H^o = \Delta_H^o + (-\Delta_H^o) + (-\Delta_H^o)
\]

Notice that the net enthalpy change is equal to the enthalpy of formation for the product minus the enthalpies of formation of the reactants.

\[
\Delta_H^o = \Delta_H^o - (\Delta_H^o + \Delta_H^o)
\]

Substituting the definition \( \Delta_H^o = n \Delta_H^o \) (Section 11.1) and combining terms results in the following formula, where \( \sum n \Delta_H^o \) is the standard enthalpy change of all the products (P), and \( \sum n \Delta_H^o \) is the standard enthalpy change of all the reactants (R).

\[
\Delta_H^o = \sum n \Delta_H^o - \sum n \Delta_H^o
\]

\[
\begin{align*}
\text{Ca(OH)}_2 &\rightarrow \text{Ca}(s) + \text{H}_2\text{O}(l) \\
\text{Ca}(s) &\rightarrow \text{Ca}(s) + \frac{1}{2} \text{O}_2(g) \\
\text{H}_2\text{O}(l) &\rightarrow \text{H}_2(g) + \frac{1}{2} \text{O}_2(g)
\end{align*}
\]

[...]

According to Hess’ law and empirically determined molar enthalpies of formation, the standard enthalpy change for the slaking of lime is reported as follows:

\[
\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta_H^o = -65.4 \text{ kJ}
\]
The enthalpy change of the reaction in Sample Problem 11.5 can be theoretically described by an enthalpy change diagram similar to a chemical potential energy diagram (Figure 3). Note that the derived formula provides a negative enthalpy change for an exothermic reaction, consistent with the accepted convention. Also note that the value of $\sum n f_P H^\circ_m$ appears on the diagram as the enthalpy of formation of the product, and the value of $\sum n f_R H^\circ_m$ is the enthalpy of formation of the reactants. The label on the y-axis must be "standard enthalpy of formation, $H^\circ_f$."

**Figure 3**
Enthalpy change diagram for the slaking of lime. The two summation ($\Sigma$) terms in the mathematical formula become the positions of the reactants and the products on the potential energy scale.

**The Slaking of Lime**

\[
\begin{align*}
\text{CaO}(s) + \text{H}_2\text{O}(l) & \rightarrow \text{Ca}(\text{OH})_2(s) \\
\Delta H^\circ & = -920.7 \text{ kJ} \\
\text{H}_2\text{O}(l) & \rightarrow \text{H}_2\text{O}(g)
\end{align*}
\]

**SUMMARY**
Using Enthalpies of Formation to Predict Standard Enthalpy Changes, $\Delta_r H^\circ$

According to Hess’ law, the net enthalpy change for a chemical reaction is equal to the sum of the chemical amounts times the molar enthalpies of formation of the products minus the sum of the chemical amounts times the molar enthalpies of formation of the reactants (Figure 4).

\[
\Delta_r H^\circ = \sum n f_P H^\circ_m - \sum n f_R H^\circ_m
\]

**Example**

Methane is burned in furnaces and in some power plants (Figure 5). What is the standard molar enthalpy of combustion of methane? Assume that water vapour is a product.

**Solution**

\[
\begin{align*}
\text{CH}_4(g) + 2 \text{O}_2(g) & \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \\
\Delta_r H^\circ & = \left( 1 \text{ mol } \text{CO}_2 \times \frac{-393.5 \text{ kJ}}{1 \text{ mol } \text{CO}_2} + 2 \text{ mol } \text{H}_2\text{O} \times \frac{-241.8 \text{ kJ}}{1 \text{ mol } \text{H}_2\text{O}} \right) \\
& - \left( 1 \text{ mol } \text{CH}_4 \times \frac{-74.6 \text{ kJ}}{1 \text{ mol } \text{CH}_4} + 2 \text{ mol } \text{O}_2 \times \frac{0 \text{ kJ}}{1 \text{ mol } \text{O}_2} \right) \\
& = -877.1 \text{ kJ} - (-74.6 \text{ kJ}) \\
& = -802.5 \text{ kJ}
\end{align*}
\]

According to the molar enthalpy of formation method, the standard molar enthalpy of combustion of methane to produce water vapour is $-802.5 \text{ kJ/mol}$. 

**Learning Tip**

Think of the fairly complicated equation for calculating the enthalpy of reaction $\Delta_r H^\circ = \sum n f_P H^\circ_m - \sum n f_R H^\circ_m$ as communicating a necessary concept. Basically, the equation communicates the idea that the change in enthalpy for a reaction is the total chemical potential energy of the products minus that of the reactants. The order of “products minus reactants” makes the sign for the enthalpy change come out correctly.
The combustion of methane is communicated as an enthalpy change diagram in Figure 6. Note that the labelling of the y-axis is different from that in a chemical potential energy diagram.

![Figure 6](image)

The enthalpy change diagram for the combustion of methane conveys the same information as the equation in the Communication Example.

\[
\text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \]

\[
\Delta_r H^\circ = -877.1 \text{ kJ} \]

\[
\Delta_r H^\circ = -74.6 \text{ kJ} \]

**Reaction coordinate**

**Figure 5** A blue flame in a home furnace indicates that the gas is burning completely, and no carbon monoxide gas is being produced.

---

**LAB EXERCISE 11.D**

**Testing \( \Delta_r H^\circ \) from Formation Data**

The molar enthalpies of formation method was created earlier in this section from Hess' law. Both problem-solving methods are consistent with the law of conservation of energy. This lab exercise tests this new method against evidence gathered from calorimetry.

**Purpose**

The purpose of this problem is to test the use of molar enthalpies of formation as a method of predicting the enthalpy change of a reaction.

**Problem**

What is the standard molar enthalpy of combustion of methanol?

**Design**

Methanol is burned in excess oxygen in a special calorimeter. Assume that liquid water is produced.

**Evidence**

- mass of methanol reacted = 4.38 g
- mass of water equivalent to calorimeter = 2.60 kg
- initial temperature of calorimeter = 20.4 °C
- final temperature of calorimeter = 27.9 °C

(Note that the calorimeter has the same thermal energy gain or loss as the water equivalent stated.)

---

**WEB Activity**

**Web Quest—Rocket Fuel Thermochemistry**

This Web Quest allows you to work as part of a research team, exploring the differences between types of rocket fuels. You can use your results to support a competitor for the latest $10 million Ansari X Prize, given for inventions that promote space travel. You can look at the properties of reactants and products as well as the energy changes involved in the rocket fuel reactions. You and your team can create and deliver a PowerPoint™ presentation about your findings.

[www.science.nelson.com](http://www.science.nelson.com)
Section 11.5 Questions

1. Which of the following fuels has the greater thermal stability: methanol or ethanol? Provide your reasoning.

2. Methane, the major component of natural gas, is used as a source of hydrogen gas to produce ammonia. Ammonia is used as a fertilizer and a refrigerant, and is used to manufacture fertilizers, plastics, cleaning agents, and prescription drugs. The following questions refer to some of the chemicals involved.
   (a) The first step in the production of ammonia is the reaction of methane with steam using a nickel catalyst. Use the molar enthalpies of formation method to predict the $\Delta H^\circ$ for the following reaction:
      $$\text{CH}_4(g) + H_2O(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g)$$
   (b) Another step of this process is the further reaction of carbon monoxide to produce more hydrogen. Iron and zinc–copper catalysts are used. Predict the $\Delta H^\circ$.
      $$\text{CO}(g) + H_2O(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g)$$
   (c) After the carbon dioxide gas is removed, the hydrogen reacts with nitrogen obtained from the air. Predict the $\Delta f H^\circ$ to form 2 mol of ammonia.
      $$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$$

3. Nitric acid, required in the production of nitrate fertilizers, is produced from ammonia by the Ostwald process (Figure 7). Predict the standard enthalpy change for each reaction in the process, as written, and then predict the standard molar enthalpy of reaction for the first reactant listed in each equation.
   (a) $4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$
   (b) $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$
   (c) $3\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(l) + \text{NO}(g)$

4. Ammonium nitrate fertilizer is produced by the reaction of ammonia with the nitric acid resulting from the series of reactions given in question 3. Ammonium nitrate is one of the most important fertilizers for increasing crop yields.
   (a) Predict the standard enthalpy change of the reaction used to produce ammonium nitrate.
      $$\text{NH}_3(g) + \text{HNO}_3(l) \rightarrow \text{NH}_4\text{NO}_3(s)$$
      $\Delta H^\circ = ?$
   (b) Sketch an enthalpy change diagram for the reaction of ammonia and nitric acid.

5. During World War II an oil embargo on Germany left that country short of fuels. Germany responded by producing and burning ammonia as a fuel for cars, trucks, and tanks.
   (a) What is the standard molar enthalpy of combustion of ammonia gas? Assume that nitrogen dioxide and liquid water are the products of combustion.
   (b) Draw an enthalpy change diagram for the burning of 4 mol of ammonia, including labelling the y-axis with the energy involved.
   (c) Evaluate this technological solution from two perspectives.

6. The refining of sour natural gas removes toxic hydrogen sulfide from the natural gas at many of the gas plants in Alberta. One of the reactions during the conversion of the hydrogen sulfide to sulfur is the combustion of some of this gas.
   (a) What is the standard molar enthalpy of combustion of hydrogen sulfide to produce sulfur dioxide gas and liquid water?
   (b) Communicate the enthalpy of combustion of hydrogen sulfide in the four ways described earlier in this chapter.
   (c) Should the products of the combustion of hydrogen sulfide be released into the atmosphere? Provide your reasoning.

7. You now have several ways of knowing the enthalpy of a chemical reaction. The simplest are to be given, to reference, or to memorize the enthalpy change for selected chemical reactions. The law of conservation of energy has so far provided you with three other methods for calculating an enthalpy change. How would you recognize when you are supposed to use each of these methods, listed below, in a question? That is, what would the question look like? What information would you be given in the question?
   (a) calorimetry
   (b) Hess’ law
   (c) molar enthalpies of formation

---

**Figure 7**

An Ostwald process plant converts ammonia to nitric acid cleanly and efficiently. Unreacted gases and energy from the exothermic reactions are recycled. Catalytic combustors burn noxious fumes to minimize environmental effects and to supply additional energy to operate the plant.

Use this information to answer questions 8 and 9.

There is a whitish-grey mountain near Exshaw, Alberta from which limestone is mined (Figure 2, page 511). This limestone is then thermally decomposed into lime and carbon dioxide. Some of the lime is then slaked: the lime reacts with water to produce slaked lime.
8. (a) Use standard molar enthalpies of formation to predict the standard reaction enthalpy for the first step of the chemical process to produce slaked lime.

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \quad \Delta H^\circ = ? \]

(b) Now predict the \( \Delta H^\circ \) for the second step.

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta H^\circ = ? \]

(c) Write the overall (net) reaction equation for the two steps, and use Hess’ law to predict the net standard enthalpy of reaction.

(d) Use the net reaction equation and molar enthalpies of formation to predict the net standard reaction enthalpy.

(e) Compare your answers in (c) and (d).

(f) List some further technological applications of lime and slaked lime.

9. Slaked lime is used in mortar, for building brick walls (Figure 8). As the wall “cures,” the mortar is strengthened by the reaction of slaked lime with carbon dioxide from the air to produce calcium carbonate and water. Look back at your answers for the previous question to determine the standard enthalpy of reaction without having to use Hess’ law or standard molar enthalpies of reaction.

10. The prediction of enthalpy changes using standard molar enthalpies of formation depends entirely on the availability of tables of standard molar enthalpies of formation. Many of these \( \Delta H^\circ_m \) values can be initially determined from \( \Delta H^\circ_c \) values by using the formation method equation. In this problem you will use a known \( \Delta H^\circ_m \) value to calculate a corresponding \( \Delta H^\circ_c \) value. Complete the Analysis of the investigation report. Work out your own problem-solving approach here.

**Problem**

What is the standard molar enthalpy of formation for hexane, \( \text{C}_6\text{H}_{14}(l) \)?

**Design**

The standard molar enthalpy of formation for hexane is determined using the concept

\[ \Delta H^\circ = \sum n \Delta H^\circ_m - \sum \text{n} \Delta H^\circ_c \]

to describe the hexane combustion reaction. The standard molar enthalpy of combustion of hexane is obtained from a reference source.

**Evidence**

The CRC Handbook of Chemistry and Physics lists the calorimetric value for the standard molar enthalpy of combustion for hexane as \(-4162.9 \text{ kJ/mol}\). Carbon dioxide gas and liquid water are the only products of the combustion.

11. Besides specific heat capacity (e.g., 4.19 J/(g•°C) for water (on the average)), there are other energy descriptions for chemical substances. Based upon the units used for these quantities, describe as best you can what the quantity is about and where it might be of importance or of use.

(a) Volumetric heat capacity (e.g., 1.2 kJ/(m³•°C) for air at SATP)

(b) Molar heat capacity (e.g., 75.5 kJ/(mol•°C) for water)

(c) Heat capacity (e.g., 9.12 kJ/°C for a particular bomb calorimeter)

(d) Specific heat (e.g., 13.4 kJ/g of water for the formation of water vapour from hydrogen and oxygen)

12. The bomb calorimeter and flow calorimeter are high-tech calorimeters used to determine, for example, the energy value of foodstuffs. In a test of the molar enthalpies of formation method, a prediction is made of the molar enthalpy of respiration of glucose. Use calorimetry in the analysis to obtain an empirical test value. Complete the evaluation (2 and 3). (Assume liquid water is produced.)

**Problem**

What is the molar enthalpy of respiration of glucose?

**Evidence**

- Mass of glucose: 3.00 g
- Heat capacity of calorimeter: 8.52 kJ/°C
- Initial temperature: 25.02 °C
- Final temperature: 30.49 °C

13. There are many commercial products sold in automotive parts and service centres that claim to increase gas mileage, for example, oil and gasoline additives. Your company has been chosen to test one of these claims. Design an investigation to determine the validity of the claim.

14. Research an R-2000 (energy-efficient) home on the Internet, and write a brief description.
Chapter 11 INVESTIGATIONS

INVESTIGATION 11.1

Designing and Evaluating a Calorimeter

A calorimeter can be as simple as an uninsulated beaker or can. Literature research indicates that very sophisticated calorimeters, such as bomb and flow calorimeters, are also available. There are many laboratory calorimeters between these extremes. In this investigation you will create your own calorimeter. Use modern materials and/or consider what Aboriginal peoples might have used for insulating a calorimeter-like vessel.

Purpose
The purpose of this investigation is to create a calorimeter that is improved (based upon your own scientific and technological criteria) over the simplest calorimeter.

Problem
What is the best design for a simple calorimeter?

Materials
- lab apron
- eye protection
- small soup can
- insulation
- aluminium foil
- duct tape
- thermometer or temperature probe
- centigram balance
- stirring rod
- ring and stand
- paraffin candle
- matches
- watch glass
- 100 mL graduated cylinder
- timer

Take care around lit matches and candles. Tie back loose hair and clothing. Never leave a flame unattended.

INVESTIGATION 11.2

Molar Enthalpy of Reaction

Evaluating evidence (dependent upon an experimental design, materials, procedure, and skill) and estimating the certainty of empirically determined values are important skills in interpreting scientific statements. The accuracy (percent difference) of the value for molar enthalpy obtained in this investigation is used to evaluate the calorimeter and the assumptions made in the analysis, rather than to evaluate the prediction and its authority. The ultimate authority in this experiment is considered to be the reference value used in the prediction.

Problem
What is the molar enthalpy of neutralization for sodium hydroxide when 50 mL of aqueous 1.0 mol/L sodium hydroxide reacts with an excess quantity of 1.0 mol/L sulfuric acid?

Prediction
The molar enthalpy of neutralization for sodium hydroxide is $-57$ kJ/mol, as per The CRC Handbook of Chemistry and Physics.

Wear eye protection. Both sodium hydroxide and sulfuric acid are corrosive chemicals. Rinse with lots of cold water if these chemicals contact your skin.
Applying Hess’ Law

Magnesium burns rapidly, releasing heat and light.

\[
\text{Mg(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO(s)} \quad \Delta H = ?
\]

The enthalpy change of this reaction can be calculated from measurements involving a highly sophisticated calorimeter, but not a polystyrene cup calorimeter. The enthalpy change for the combustion of magnesium can, however, be determined by applying Hess’ law to the following three chemical equations.

\[
\text{MgO(s)} + 2 \text{HCl(aq)} \rightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O(l)} \quad \Delta H = ?
\]
\[
\text{Mg(s)} + 2 \text{HCl(aq)} \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g) \quad \Delta H = ?
\]
\[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O(l)} \quad \Delta f H^\circ = -285.8 \text{ kJ}
\]

Purpose

The purpose of this investigation is to use Hess’ law to determine a molar enthalpy of combustion.

Problem

What is the molar enthalpy of combustion for magnesium?

Prediction

The standard molar enthalpy of combustion for magnesium is \(-601.6 \text{ kJ/mol}\), as per the table of standard molar enthalpies of formation (Appendix I). (The molar enthalpy of combustion of magnesium is the same as the molar enthalpy of formation of magnesium oxide because both processes have the same chemical reaction equation.)

\[
\Delta_{f} H^\circ_{\text{Mg}} = \Delta_{f} H^\circ_{\text{MgO}} = -601.6 \text{ kJ/mol}
\]

\[
\text{Mg(s)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO(s)} \quad \Delta f H^\circ = -601.6 \text{ kJ}
\]

Design

The enthalpy changes for the first two reactions in the series are determined empirically using a polystyrene calorimeter (Figure 1), and the third enthalpy change is obtained from Appendix I. The three \(\Delta f H^\circ\) values are used, along with Hess’ law, to obtain the molar enthalpy of combustion for magnesium.
**Outcomes**

**Knowledge**
- explain how the sun is a major source of stored chemical energy on Earth (11.1)
- apply the equation \( Q = mc\Delta t \) to the analysis of energy transfer (11.2)
- define enthalpy and molar enthalpy for chemical reactions (11.2)
- use calorimetry evidence to determine enthalpy changes in chemical reactions (11.2, 11.3, 11.4, 11.5)
- describe photosynthesis, cellular respiration, and hydrocarbon combustion reactions, and understand that combustion and cellular respiration are similar and the reverse of photosynthesis (11.3)
- write and interpret balanced chemical equations incorporating \( \Delta H^\circ \) notation (11.3)
- classify chemical reactions as endothermic or exothermic (11.3, 11.4, 11.5)
- explain and use Hess’ law to calculate energy changes for a net reaction from a series of reactions (11.4)
- predict the enthalpy change for chemical equations using standard molar enthalpies of formation (11.5)

**STS**
- state that a goal of technology is to solve practical problems (11.1, 11.2)
- recognize that solving technological problems may require various solutions and have both intended and unintended consequences (11.1, 11.3, 11.4)

**Skills**
- initiating and planning: design a method to compare molar enthalpy changes when burning fuels (11.2); describe procedures for safe handling, storage, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (11.2, 11.4)
- performing and recording: perform calorimetry experiments to determine molar enthalpy changes and use thermometers appropriately (11.2, 11.4)
- analyzing and interpreting: compare energy changes by analyzing data and energy diagrams (11.3, 11.4, 11.5)
- communication and teamwork: work collaboratively using appropriate notation and units for enthalpy changes and molar enthalpies (11.2, 11.3, 11.4, 11.5)

**Key Terms**
- thermochemistry
- isolated system
- calorimetry
- calorimeter
- heat
- thermal energy, \( Q \)
- specific heat capacity, \( c \)
- joule (J)
- enthalpy change, \( \Delta H \) or \( \Delta H^\circ \)
- exothermic reaction
- endothermic reaction

**Key Equations**
- \( Q = mc\Delta t \)
- \( \Delta H = n\Delta H_m \)
- \( n\Delta H = mc\Delta t \) (calorimetry)
- \( \Delta H = \Sigma \Delta H \) (Hess’ law)
- \( \Delta H^\circ = \Sigma n\Delta H_m^\circ - \Sigma n\Delta H_m^\circ \) (enthalpies of formation)

**MAKE a summary**

1. Prepare a table to summarize the four methods for communicating enthalpies of reaction, the quantities and symbols used, the units used. Prepare a second table showing the three methods for determining enthalpy changes. Use the adjectives “molar” and “standard” (and symbols) where appropriate.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

**Go To**
- The following components are available on the Nelson Web site. Follow the links for Nelson Chemistry Alberta 20–30.
  - an interactive Self Quiz for Chapter 11
  - additional Diploma Exam-style Review questions
  - Illustrated Glossary
  - additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

**EXTENSION**
- A New Kind of Rocket Science

Scientists are looking beyond chemical reactions for rocket propulsion systems. They are investigating nuclear thermal rockets, nuclear electricity, and even solar sailing.

www.science.nelson.com
Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

1. A source of energy that is an alternative to fossil fuels is
   A. coal C. kerosene
   B. solar D. natural gas

2. Over 95% of the electricity in Alberta is generated by burning fossil fuels. In thermal electric generating stations, energy moves through several forms. List these forms in order.
   1 chemical 3 mechanical
   2 electrical 4 thermal

3. The quantity of thermal energy required to raise the temperature of a unit mass of a substance by one degree Celsius is referred to as
   A. specific heat
   B. heat capacity
   C. specific heat capacity
   D. volumetric heat capacity

4. A propane camp stove is used to heat 1.50 L of water for making tea. If the water is heated from 5.5 °C to 98.6 °C, the energy absorbed by the water is ____________________ kJ.

5. Enthalpy change (ΔH) is defined as the change in the
   A. thermal energy in a system
   B. property of a substance or system that relates to its ability to do work
   C. state of a closed system in which all measurable properties are constant
   D. chemical energy of a system when the pressure of the system is held constant

6. Some coal deposits contain significant quantities of sulfur, which forms sulfur dioxide when the coal is burned. Sulfur dioxide reacts with oxygen in the atmosphere to produce sulfur trioxide, which in turn reacts with rainwater to produce sulfurous acid. Use the following equation to determine the molar enthalpy of reaction for sulfur dioxide.
   \( 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g) + 197.8 \text{ kJ} \)
   ____________________ \text{kJ/mol}

7. The correct reaction equation for the formation of water vapour is
   A. \( 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 120.9 \text{ kJ} \)
   B. \( 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 241.9 \text{ kJ} \)
   C. \( 2\text{H}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 483.6 \text{ kJ} \)
   D. \( 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 571.6 \text{ kJ} \)

8. The equation that correctly represents the enthalpy change involved in the simple decomposition of dinitrogen tetroxide, \( \text{N}_2\text{O}_4(g) \), is
   A. \( \text{N}_2(g) + 2\text{O}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \quad \Delta H^\circ = +11.1 \text{ kJ} \)
   B. \( \text{N}_2(g) + 2\text{O}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \quad \Delta H^\circ = -11.1 \text{ kJ} \)
   C. \( \text{N}_2\text{O}_4(g) \rightarrow \text{N}_2(g) + 2\text{O}_2(g) \quad \Delta H^\circ = +11.1 \text{ kJ} \)
   D. \( \text{N}_2\text{O}_4(g) \rightarrow \text{N}_2(g) + 2\text{O}_2(g) \quad \Delta H^\circ = -11.1 \text{ kJ} \)

Part 2

15. Explain, in general terms, how stored energy in the bonds of hydrocarbons originated from the sun.

16. Distinguish between an enthalpy change and a molar enthalpy including general symbols and word descriptions.
17. The energy content of foods can be determined by combustion analysis using a calorimeter. The combustion of 1.25 g of peanut oil caused the temperature of 2.0 kg of water to increase by 5.3 °C.
(a) **Determine** the increase in thermal energy of the water.
(b) **Determine** the energy content of peanut oil in kilojoules per gram.

18. Methylpropane, \( \text{C}_4\text{H}_{10}(g) \), is used as a lighter fluid. When 1.52 g of methylpropane is burned in a calorimeter, the temperature of 2.23 kg of water changed by 8.04 °C.
(a) Calculate the change in thermal energy of the water.
(b) **Determine** the enthalpy change for the combustion of 1.52 g of methylpropane.
(c) If you were using this evidence to report the molar enthalpy of combustion for methylpropane, what symbol, value, and sign would you use? **Justify** your answer.

19. The enthalpy of neutralization of an acid–base reaction can be determined using a graduated cylinder, a thermometer, and a simple polystyrene calorimeter. Complete the Analysis of the investigation report.

**Problem**
What is the molar enthalpy of neutralization for ethanoic acid?

**Design**
Measured volumes of ethanoic acid and sodium hydroxide are mixed in a polystyrene calorimeter. The temperatures of the solutions are measured before and after mixing.

**Evidence**
- Volume of 1.00 mol/L ethanoic acid = 50.0 mL
- Volume of 1.00 mol/L sodium hydroxide = 50.0 mL
- Initial temperature of ethanoic acid = 22.5 °C
- Initial temperature of sodium hydroxide = 22.5 °C
- Final temperature of mixture = 27.8 °C

20. As an alternative to chemical energy, heating water is one of the most cost-effective uses of solar energy, providing hot water for showers, dishwashers, and washing machines.
(a) **Determine** the thermal energy acquired (and chemical energy saved) when the temperature of 100 L of water is raised from 6.5 °C to 58.5 °C.
(b) What mass of natural gas (methane) would have to be burned to heat the same volume of water by the same temperature change?
(c) A domestic solar water heater saves 32.5 MJ of chemical (combustion) energy while increasing the thermal energy of some water from 12.3 °C to 45.5 °C. What mass and volume of water did the water heater contain?

21. Prepare a general comparison of photosynthesis, cellular respiration, and hydrocarbon combustion. Your response, which could be a paper or electronic graphic or table, should include:
- reactants
- products
- endothermic/exothermic description
- sign of the enthalpy change

22. The flame of an oxyacetylene torch is hot enough to melt most metals. Communicate the energy changes for the combustion of acetylene (ethyne) in four different ways.

23. Although calorimetry is the basic method of obtaining enthalpy changes, this method cannot always be directly used for many reactions. **Describe** two other methods commonly used to obtain an enthalpy change for a reaction. Include what information is required, where this information is obtained, and any mathematical formulas.

24. Vinyl chloride monomer is produced at Fort Saskatchewan, Alberta, to produce, in turn, polyvinyl chloride (PVC). Use Hess’ law to **determine** the enthalpy of reaction for the conversion of ethene into chloroethene (vinyl chloride).

\[
\begin{align*}
\text{C}_2\text{H}_4(g) + \text{Cl}_2(g) & \rightarrow \text{C}_2\text{H}_3\text{Cl}(g) + \text{HCl}(g) \quad \Delta H = ? \\
\text{C}_2\text{H}_4(g) + \text{Cl}_2(g) & \rightarrow \text{CH}_2\text{ClCH}_2\text{Cl}(l) \quad \Delta H = -179.3 \text{ kJ} \\
\text{C}_2\text{H}_4\text{Cl}(g) + \text{HCl}(g) & \rightarrow \text{CH}_2\text{ClCH}_2\text{Cl}(l) \quad \Delta H = -71.9 \text{ kJ}
\end{align*}
\]

25. To meet the demand for gasoline, hydrocarbons of large molar mass are broken into smaller fragments in a process called **cracking**. An overall reaction equation for producing octane from hexadecane is

\[
\text{C}_{16}\text{H}_{34}(l) + \text{H}_2(g) \rightarrow 2 \text{C}_8\text{H}_{18}(l) \quad \Delta H^\circ = ?
\]

Use the following reaction equations to **determine** the enthalpy change for the above reaction.

\[
\begin{align*}
2 \text{C}_2\text{H}_2\text{O}(l) + 49 \text{O}_2(g) & \rightarrow 32 \text{CO}_2(g) + 34 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -21,446 \text{ kJ} \\
2 \text{C}_8\text{H}_{18}(l) + 25 \text{O}_2(g) & \rightarrow 16 \text{CO}_2(g) + 18 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -10,940 \text{ kJ} \\
2 \text{H}_2(g) + \text{O}_2(g) & \rightarrow 2 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -572 \text{ kJ}
\end{align*}
\]

26. In the metal refining industry, sulfide ores are usually roasted in air to produce metal oxides and sulfur dioxide. For example, copper(II) sulfide is converted to copper(II) oxide as part of the refining of copper.
(a) Use referenced data to **determine** the molar enthalpy of roasting for copper(II) sulfide.
(b) Draw a chemical potential energy diagram for this roasting reaction.

27. Calculate the enthalpy of reaction for the following organic reactions in the Alberta chemical industry studied in Unit 5.
(a) octane reacts with hydrogen (i.e., undergoes hydrocracking) to produce pentane and propane
(b) ethene reacts with benzene to produce phenylethene (polystyrene monomer) and hydrogen
28. The following investigation was carried out to find the enthalpy of formation, $\Delta_fH^\circ$, for calcium oxide. Complete the Prediction and the Analysis of the investigation report.

**Problem**
What is the enthalpy change for the reaction?

$$\text{Ca(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO(s)}$$

**Design**
Calcium metal reacts with hydrochloric acid in a calorimeter and the enthalpy change is determined. Similarly, the enthalpy change for the reaction of calcium oxide with hydrochloric acid is determined. These two chemical equations are combined with the formation equation for water to determine the required enthalpy change.

**Evidence**
- Concentration of HCl(aq) = 1.0 mol/L
- Volume of HCl(aq) = 100 mL

**Table 1**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Mass (g)</th>
<th>Initial temperature (°C)</th>
<th>Final temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(s)</td>
<td>0.52</td>
<td>21.3</td>
<td>34.5</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>1.47</td>
<td>21.1</td>
<td>28.0</td>
</tr>
</tbody>
</table>

29. Cars and furnaces often do not run at their highest energy efficiency.
(a) Calculate the molar enthalpy of complete combustion of propane (to produce liquid water).
(b) Calculate the molar enthalpy of complete combustion of propane (to produce water vapour).
(c) Calculate the molar enthalpy of incomplete combustion for propane. Use the following chemical equation for the incomplete combustion of propane.

$$2\text{C}_3\text{H}_8(\text{g}) + 8 \text{O}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{g}) + 2 \text{CO}(\text{g}) + 3 \text{CO}_2(\text{g}) + 8 \text{H}_2\text{O}(\text{g})$$
(d) List the above molar enthalpies of combustion of propane from lowest to highest.

(e) Research the features of a high-efficiency (condensing) furnace, and relate these features to your calculations above.

30. According to an Inuit Elder, the refrigerator has damaged the Inuit community and lifestyle because families do not have to share in the same way that they used to. Suggest possible community interactions before and after the arrival of refrigerators. What does this imply about our notion of technological progress?

**Extension**

31. Choose an “alternative” fuel to research. Select and integrate information (including graphs, tables, and graphics) from several sources. Your information should illustrate at least three perspectives on the use of this fuel. Decide on the target audience, and present your findings attractively and persuasively.

32. Thermal-electric power stations burn coal (various types), fuel oil (heavy and light), natural gas, or wood to produce steam to drive a turbine and generator. The efficiency of converting the available chemical energy into electrical energy can be expressed as a percentage. The Statistics Canada publication *Human Activity and the Environment* provides this kind of data shown in Table 2.

(a) Analyze the data in Table 2 (or obtain more recent data) to find any trends or other insights.
(b) Identify other non-combustible energy sources that can be used to produce steam in a power station.

**Table 2** Percent Efficiency of Thermal-Electric Power Stations by Fuel Type (%)

<table>
<thead>
<tr>
<th>Year</th>
<th>CB</th>
<th>IB</th>
<th>CSB</th>
<th>ISB</th>
<th>Lig</th>
<th>HFO</th>
<th>LFO</th>
<th>NG</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>34.01</td>
<td>37.21</td>
<td>32.51</td>
<td>34.91</td>
<td>29.71</td>
<td>33.01</td>
<td>32.21</td>
<td>34.71</td>
<td>40.01</td>
</tr>
<tr>
<td>1999</td>
<td>33.91</td>
<td>35.61</td>
<td>32.71</td>
<td>35.11</td>
<td>29.11</td>
<td>33.21</td>
<td>30.41</td>
<td>35.41</td>
<td>35.41</td>
</tr>
<tr>
<td>2000</td>
<td>31.31</td>
<td>34.81</td>
<td>32.81</td>
<td>32.81</td>
<td>32.81</td>
<td>30.11</td>
<td>30.11</td>
<td>35.11</td>
<td>31.31</td>
</tr>
<tr>
<td>2001</td>
<td>32.41</td>
<td>32.81</td>
<td>32.41</td>
<td>28.51</td>
<td>30.11</td>
<td>33.01</td>
<td>29.31</td>
<td>34.41</td>
<td>26.81</td>
</tr>
<tr>
<td>2002</td>
<td>30.21</td>
<td>33.91</td>
<td>32.81</td>
<td>33.01</td>
<td>30.21</td>
<td>33.51</td>
<td>29.41</td>
<td>35.91</td>
<td>27.11</td>
</tr>
</tbody>
</table>

CB: Canadian bituminous; IB: imported bituminous; CSB: Canadian sub-bituminous; ISB: imported sub-bituminous; Lig: lignite; HFO: heavy fuel oil; LFO: light fuel oil and diesel; NG: natural gas; W: wood
Explaining Chemical Changes

It is part of human nature to try to make sense of the world around us and to develop technologies to solve practical problems, especially problems involving survival in a harsh environment. Fire is one of the earliest technologies, and a good example of the many energy changes that are an important part of the natural world. What is fire, and how can it be used? Almost every culture has had its stories or explanations about the origin and use of fire. From the Greek culture we have the story of Prometheus, and from North American Aboriginal peoples there is the story of the coyote stealing fire from the fire beings to give to the humans. Western science also has its “fire story” in the form of theories of chemical reactions, such as combustion. Scientists have considerable empirical knowledge of fire, or combustion. They can take measurements and calculate the energy changes, and represent them quantitatively in various forms as shown in the previous chapter. How does fire, or any other reaction, get started? How does it progress? And how can it be manipulated to alter its rate? The answers to these questions form part of Western science’s story or theory of fire and other reactions. This chapter will start to answer these questions.

Not surprisingly, the empirical and theoretical descriptions about the nature of chemical energy changes are interwoven with the technologies of energy changes. Technologies that are researched and developed lead to advances in science, and scientific research leads to improved technologies. An important example is the study and application of catalysts—substances used extensively to increase the rate of chemical reactions. Industries that use catalysts include oil refining (catalytic cracking), petrochemical production (for polymerization), and chemical technologies (such as automobile catalytic converters, Figure 1). The story or theory of chemical energy changes in this chapter will also include numerous important technological applications.

**Starting Points**

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. What is necessary for a successful collision to occur between reacting entities?
2. How do bond energies affect the rate and enthalpy of reaction?
3. (a) What is the purpose of using a catalyst in a chemical process?
   (b) Why does a catalyst have this effect?
4. List some technological products and processes that employ catalysts.

**Career Connection:**
Field Production Operator
Starting, Comparing, and Altering Reactions

We have seen many chemical reactions and know that they can be classified into different categories (reaction types). We can use this knowledge for predicting reaction equations and analyzing the stoichiometry of reactions. Although this is an important starting point, it leaves many questions unanswered. How do reactions start, and why do they keep going? Why do apparently similar reactions proceed at very different rates? How can the rate of a reaction be altered? The three parts of this Exploration will help you think about answers to these three questions.

Materials: eye protection; lab apron; 5 small test tubes; test tube rack; tweezers; distilled water wash bottle; 1 mol/L HCl(aq); 3% H₂O₂(aq); pieces of Mg(s), Zn(s), Fe(s), and fruits such as bananas and apples; some flakes of rust; cut open D cell

Hydrochloric acid is corrosive; hydrogen peroxide is both corrosive and a strong oxidizer. The chemicals in an open dry cell are likely to be corrosive and possibly toxic. Handle all substances with care. If they contact the skin, wash thoroughly with cool water. If they contact the eyes, flush with cool water for at least 15 min and inform your teacher.

Part A: Starting Reactions
Baking generally starts with measuring and mixing the ingredients, which include some potential reactants.
(a) Is mixing the ingredients all that you need to do? What is the usual next step in the baking procedure?
(b) List some observations that would indicate that a chemical reaction is occurring or has occurred.

When using a laboratory burner, natural gas and air are mixed together at the bottom of the tube and emerge out the top.
(c) Does the combustion start when the two reactants mix? What needs to be done next?
(d) List some observations that would indicate that a chemical reaction is occurring.

Part B: Comparing Reactions
One of the empirical properties of acids is that they react with active metals to produce hydrogen gas.
(e) When comparing the reactions of different metals with an acid, what variables need to be kept constant?
• Set up three test tubes containing about 1 cm depth of hydrochloric acid. Add a piece of Mg(s) to the first test tube, Zn(s) to the second, and Fe(s) to the third. Observe for a few minutes, and remove the metal with tweezers.
(f) List the similarities and differences in the evidence for the reactions of the three metals.

Part C: Altering Reactions
Hydrogen peroxide is produced in both natural and technological systems. When hydrogen peroxide decomposes it produces oxygen gas and water.
• Set up several clean test tubes with equal volumes (about 1 cm depth) of hydrogen peroxide.
• To all but one of the test tubes containing the hydrogen peroxide, add a small quantity of MnO₂(s) from the inside of a dry cell, some rust particles, and some small pieces of fruit. Leave one test tube containing only hydrogen peroxide.
(g) Record the evidence of reaction including comparisons of different test tubes.
(h) Why was one test tube set up with only hydrogen peroxide?

Figure 1
A catalytic converter in a car exhaust reduces the toxic emissions by converting the harmful exhaust by-products into relatively harmless by-products. Oxidation catalysts convert hydrocarbons into carbon dioxide and water. Three-way catalysts also convert oxides of nitrogen back into nitrogen.
12.1 Activation Energy

Chemical technologies, like most technologies, are evaluated on the basis of whether they are simple, economical, reliable, and efficient. Chemists, chemical engineers, and chemical technologists work on chemical processes for years—sometimes even decades—to perfect a technology that meets these criteria. Each chemical process, past and present, has its own story of people and technologies. For example, the refining of crude oil has changed significantly over the years, as has the design of automobile engines that use the gasoline refined from the crude oil. This chapter tells some of the inside stories of how chemists explain chemical reactions and how chemical engineers use and control chemical reactions.

Reaction Progress

From your own experience, including the Exploration on page 523, you can see that some reactions do not proceed spontaneously at room temperature unless additional energy is added to start them off. A lit match, for example, is needed to start the combustion of candle wax in a candle, wood in a campfire, and propane in a barbeque. Consider a thought experiment for a dangerous situation in which methane gas is escaping into a closed room and is mixing with the air. Based on what you know about methane and oxygen, the predicted reaction is highly exothermic. Why is this highly exothermic reaction not spontaneous—why does an immediate reaction not occur to form the more thermally stable products carbon dioxide and water? A spark from a light switch being turned on, however, can cause an explosive reaction of the methane–air mixture. Why is this initiating energy source necessary to cause the reaction?

From your experience and from the Exploration, you may also have noticed that different reactants appear to react at different rates, even when all other variables are controlled. Why does changing one of the reactants in a chemical reaction make such a difference in the rate of the reaction? For example, different metals in contact with the same acid react at varying rates, and the same metal in contact with different acids reacts at varying rates. Consider another thought experiment where the flame of a propane torch is applied for the same period of time to different types of wood cut into identical shavings. In this case, the initiating energy is the same; however, the resulting rates of reaction are different. Some of the wood shavings burn very quickly while others burn very slowly. What is there about the different wood shavings that produces a varying rate of reaction? How can we explain this phenomenon?

Some reactants have different temperatures at which they start reacting. Also, some reactants at the same temperature react at different rates. What theoretical explanation is there for the different ignition temperatures and for the varying rates of reaction for different reactants?

Collision–Reaction Theory

Although empirical knowledge is the foundation of science, an ultimate aim of science is to understand processes by creating simple, consistent, and logical theories. Scientists develop theoretical knowledge, and communicate it by way of models and analogies. They test the resultant knowledge by judging its ability to describe, explain, and predict. Theories are often better at explaining than at predicting. The collision–reaction theory is an excellent example of this type of theory. It is easier to explain reactions using the theory than it is to make predictions of specific reactions.
Chemists created the collision–reaction theory to describe, explain, and predict characteristics of chemical reactions. Some of the main ideas of the collision–reaction theory are the following:

- A chemical sample consists of entities (atoms, ions, or molecules) that are in constant random motion at various speeds, rebounding elastically from collisions with each other. (Kinetic energy is conserved during elastic collisions.)
- A chemical reaction must involve collisions of reactant entities.
- An effective collision requires sufficient energy. Collisions with the required minimum energy have the potential to react.
- An effective collision also requires the correct orientation (positioning) of the colliding entities so that bonds can be broken and new bonds formed.
- Ineffective collisions involve entities that rebound elastically from the collision.

When looking at different reactions, chemists have noticed that some reactions appear to occur more readily than others. According to collision–reaction theory, reactions can only take place when entities collide, but not all collisions result in a reaction. If the orientation is correct and the energy is sufficient, then a reaction can occur (Figure 1). In other reactions, however, the collisions of reactant entities may involve insufficient energy or the collision may not have the correct orientation (Figure 2).

To use the collision–reaction theory more effectively, we need to consider other factors, such as the nature of the bonds present and the type of reaction occurring.

DID YOU KNOW?

**Reaction Kinetics**

In May 1884, Svante Arrhenius presented his doctoral thesis on a theory of ionic dissociation. His study jump-started branches of chemistry called physical chemistry and reaction kinetics. However, it wasn’t until the 1920s and 1930s that these topics became part of organic chemistry, until the 1940s and 1950s for inorganic chemistry, and, finally, completing the reform, into high school chemistry textbooks in the 1960s.
In summary, there are two sources of evidence that need explaining. First, why do some chemicals react faster than others, when all other variables except the type of chemical are controlled (for example, why does magnesium react faster than zinc with hydrochloric acid)? Second, why do some reactions require an initial input of external energy to react (for example, why is a match needed to start the combustion of a hydrocarbon)? Empirical chemists gather the evidence and establish empirical concepts, such as generalizations about reaction rates. Theoretical chemists create explanations for the evidence gathered by the empirical chemists. The empirical and theoretical chemists may work as a team in the same university or may be around the world from each other. Likewise, the theory might be developed ahead of the evidence. The empirical chemist may have the role of testing the theory created by the theoretician. So what concepts did the theoretical chemists come up with?

**Simulation—Collisions and Reactions**

View the animations to see models of effective and ineffective collisions. Draw models to represent the orientation of the atoms for both types of collision.

**Practice**

1. What two conditions must be met for two molecules to react?
2. Provide one scientific reason and one technological reason for understanding how chemical reactions occur.
3. Consider a thought experiment in which nitrogen and oxygen gases are mixed, as in air. No spontaneous reaction occurs under normal conditions or even by supplying high temperature and pressure. Then consider a lightning strike, which provides evidence for the production of nitrogen oxides. The evidence for this reaction is so strong that scientists list this reaction as part of the nitrogen cycle.
   (a) Write a balanced chemical equation for the reaction of nitrogen and oxygen to produce nitrogen dioxide, including the enthalpy change.
   (b) Draw and label a chemical potential energy diagram to express the enthalpy change for this reaction.
   (c) Create a hypothesis to explain why lightning is necessary to initiate this reaction.

**Activation Energy of a Reaction**

Since empirically measured reaction rates are often relatively slow, and in many cases too slow to be detectable (as in the nitrogen–oxygen reaction of air), chemists are forced to interpret the evidence as showing that normally only an extremely tiny fraction of the collisions actually produce products. The theoretical explanation for this evidence involves the concept of activation energy—an energy barrier that must be overcome for a chemical reaction to occur. Entities must reach this minimum energy before they can react. The input energy (which supplies the activation energy) may be in the form of heat, light, or electricity.

The concept of chemical activation energy, \( E_a \), can be illustrated by an analogy with gravitational potential energy. Consider the analogy of a billiard ball rolling on a smooth
track shaped as shown in Figure 3. The ball leaves point A moving to the right. As it travels on the uphill portion of the track it slows down— as kinetic energy is converted to gravitational potential energy. The ball can only successfully overcome the rise of the track to reach point B if it has a large enough initial speed (kinetic energy). We could call this situation an effective trip. The minimum kinetic energy required is analogous to the activation energy for a reaction. If the ball does not have enough kinetic energy, it will not reach the top of the track and will just roll back to point A. This is like two molecules colliding without enough energy to rearrange their bonds—they just rebound elastically.

Note that a ball that returns to point A will have the same kinetic energy it began with, but a ball that makes it to point B will have more kinetic energy (but less potential energy) because it will be moving faster. The example above is also analogous to the enthalpy change for an exothermic reaction. The enthalpy change (net chemical energy change) results in energy being immediately released to neighbouring entities. These entities then move faster, collide with more energy, and are more likely to react. For example, the energy released when the first few molecules of hydrogen and oxygen react (initiated by a spark or flame) is quickly transferred to other molecules, allowing the reaction to proceed unaided by external sources of energy (Figure 4). The reaction, once begun, is self-sustaining as long as enough reactants remain to make collisions likely. Exothermic reactions, once begun, often drive themselves.

Consider the reaction of carbon monoxide with nitrogen dioxide, plotted as potential energy of the molecules versus progress of reaction; that is, the progress over time of the molecular activity that constitutes the reaction (Figure 5, page 528).

\[
\text{CO}(g) + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \quad \Delta H^o = -224.9 \text{ kJ}
\]

In Figure 5, the molecular collision follows an energy (or reaction) pathway along the plot from left to right. The energy pathway is the relative potential energy of the chemical system as it moves from reactants through activated complex to products. The activated complex is the chemical entity containing the collided reactants. Along the flat
Figure 5
The energy pathway and the models represent a theoretical explanation of the reaction. The activation energy explains both the initiating energy required and the rate for this particular reaction.

Learning Tip
To draw these energy pathway diagrams, start with determining, if possible, the absolute or relative initial and final energy. Then add an energy pathway with an estimate of the activation energy between the initial and final values.

Figure 6
Chemical potential energy diagram for the carbon monoxide–nitrogen dioxide reaction.
Chemists infer that, if a large quantity of energy is needed to start a reaction and if the reaction progresses relatively slowly, then the activation energy is large. A spontaneous reaction at room temperature and a higher rate of reaction is interpreted as a relatively small activation energy.

Recall the chemical potential energy diagrams showing enthalpy changes in Chapter 11 and Figure 6. The new energy pathway diagrams (such as Figure 5) show the energy pathway between the initial and the final energy states. You can think of the new energy pathway diagrams as being an expanded form of chemical potential energy diagram, with the approximate energy of the activated complex also represented.

The carbon monoxide–nitrogen dioxide reaction is exothermic: the potential energy of the products is less than that of the reactants. If the reverse were true—if the potential energy of the products were greater than that of the reactants—the reaction would be endothermic. A continuous input of energy, usually heat, would be needed to keep the reaction going, and the enthalpy change would be positive (Figure 7).

**Learning Tip**

In Chapter 11 you drew mostly chemical potential energy diagrams with $E_p$ on the $y$-axis (with no values). You also saw some enthalpy change diagrams with $\Delta H$ and numerical values on the $y$-axis. For energy pathway diagrams, $E_p$ (with no values) is a more appropriate axis label because it is not possible to measure an enthalpy change, under standard conditions, for reactants to activated complex, and from activated complex to products.

**WEB Activity**

**Simulation—Collision—Reaction Theory**

View a simulation to review some key points of the collision–reaction theory including activation energy and enthalpy changes.

www.science.nelson.com
Draw energy pathway diagrams for a general endothermic and a general exothermic reaction. Label the reactants, products, enthalpy change, activation energy, and activated complex.

**Solution**

**Potential Energy Changes During an Endothermic Reaction**

<table>
<thead>
<tr>
<th>Reaction coordinate</th>
<th>$E_p$ (kJ)</th>
<th>$\Delta H$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactants</td>
<td>$E_p$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td>activated complex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>products</td>
<td>$E_p$</td>
<td></td>
</tr>
</tbody>
</table>

**Potential Energy Changes During an Exothermic Reaction**

<table>
<thead>
<tr>
<th>Reaction coordinate</th>
<th>$E_p$ (kJ)</th>
<th>$\Delta H$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactants</td>
<td>$E_p$</td>
<td>$\Delta H$</td>
</tr>
<tr>
<td>activated complex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>products</td>
<td>$E_p$</td>
<td></td>
</tr>
</tbody>
</table>

**Activation Energy and Ozone**

Research indicates that the energy of a photon of electromagnetic radiation is inversely proportional to the wavelength. The longer the wavelength, the lower the energy of the radiation. Ozone ($O_3$) is formed and destroyed naturally in the stratosphere by ultraviolet (UV) radiation from our sun providing the activation energy. Ozone is formed by converting molecular oxygen ($O_2$) into atomic oxygen ($O$). The atomic oxygen then reacts with molecular oxygen to produce ozone:

$$O_2(g) + \sim 240 \text{ nm UVC} \rightarrow O(g) + O_2(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g)$$

The ozone molecule is then split when it absorbs skin-cancer causing UVB radiation.

$$O_3(g) + 240–320 \text{ nm UVB} \rightarrow O_2(g) + O(g) \quad \text{(which then reacts to replenish the ozone)}$$

The energy supplied by the sun’s UV radiation is a measure of the activation energy for these reactions; that is, the activation energy (from UVB) for destroying ozone is lower than the activation energy (from UVC) for converting molecular oxygen to atomic oxygen. In the laboratory chemists can perform controlled experiments with electromagnetic radiation to determine the activation energy for reactions.

**WEB Activity**

**Web Quest—Neurotransmitters and Nerve Agents**

This Web Quest requires you to actively research how chemistry could be used in a dangerous and deadly way. Work as a team to develop informational posters for emergency response personnel, outlining how nerve agents work and how to treat individuals who have been exposed to nerve agents. You can explain the normal functions of nerve agents and how they react chemically to cause damage. You can also research and present the symptoms of and treatments for exposure to nerve agents.

[www.science.nelson.com](http://www.science.nelson.com)
Section 12.1 Questions

1. Describe, in your own words, what happens in a successful reaction of two molecules. Include as many key points as possible from the beginning to the end of the reaction.

2. What types of experiments led to the hypothesis that reactions have an activation energy?

3. (a) Is the reaction in Figure 8 endothermic or exothermic? 
   (b) What do (i) and (ii) represent? 
   (c) Explain the energy changes that occur at different points during the reaction progress, referring to potential and kinetic energy.

4. Enthalpy change and activation energy are two important concepts used when describing a chemical reaction. How are these two terms similar, and how are they different?

5. The combustion of hydrogen to produce water is a well-studied chemical reaction. Hydrogen may become one of the most important fuels in the future—for heat, transportation, and electricity. If possible, prepare and present your responses to the following questions electronically. 
   (a) What theoretical conditions are necessary for this reaction to occur? 
   (b) Draw an enthalpy change diagram for the combustion of hydrogen to form liquid water. Include actual enthalpy of formation values. 
   (c) Assuming a one-step reaction, draw an energy pathway diagram. 
   (d) Label the reactants, products, enthalpy change, activation energy, and activated complex.

   Use this information to answer questions 6 and 7. 

   You may have seen a video or a demonstration of the relative rates of reaction of the alkali metals—sodium, potassium, and cesium—with water (Figure 9). This evidence suggests that there is an increasing rate of reaction from sodium through cesium.

6. Complete the Purpose, Problem, Hypothesis, Prediction, Design, Materials (including cautions), and Procedure for an investigation to test the hypothesis that the activation energy decreases from sodium to cesium.

7. Draw three energy pathway diagrams with relative activation energies, for the reactions.

8. Aboriginal peoples used fire for many purposes. What technologies did they use to start a fire?

9. List the ignition temperature of a few combustible materials that interest you. Write a brief theoretical explanation for the different ignition temperatures.

10. For thousands of years, peoples living in cold climates have taken advantage of the low temperatures to help them preserve food. 
    (a) Apply the concepts learned in this section to create a hypothesis to explain why food lasts longer at low temperatures. 
    (b) Research a technology that was developed to capitalize on the benefits of cold storage. Consider the risks and benefits of this technology. 
    (c) Create an illustrated article entitled "Cold Storage: Theory and Application" suitable for publication in a popular science magazine or e-zine.
Energy transfer is an important factor in all chemical changes. Exothermic reactions, such as the combustion of gasoline in a car engine and the metabolism of fats and carbohydrates in the human body (Figure 1), release energy into the surroundings. Endothermic reactions, such as photosynthesis (Figure 2) and the decomposition of water into hydrogen and oxygen, remove energy from the surroundings. Knowledge of energy and energy changes is important to society and to industry; the study of energy changes provides chemists with important information about chemical bonds.

Just as glue holds objects together, electrical forces hold atoms together. In order to pull apart objects that are glued together, you have to supply some energy. Similarly, if atoms or ions are bonded together, energy (in the form of heat, light, or electricity) is required to separate them. In other words, bond breaking—when two entities (such as atoms or ions) move apart—requires energy.

\[
\text{bonded particles} + \text{energy} \rightarrow \text{separated particles}
\]

In contrast, bond making—when two entities move together—releases energy.

\[
\text{separated particles} \rightarrow \text{bonded particles} + \text{energy}
\]

By analogy it requires energy to lift an object away from Earth, while energy is released when an object is dropped to Earth.

The stronger the bond holding the particles together, the greater the quantity of energy required to separate them. Bond energy is the energy required to break a chemical bond. It is also the energy released when a bond is formed. Even the simplest of chemical reactions involves the breaking and forming of several individual bonds. The terms endothermic and exothermic are empirical descriptions of overall changes that scientists explain by their knowledge of bond changes.

Some reactions might involve several steps, with several unstable intermediate products along the way. For simplicity, however, we will just consider the energy changes between the initial reactants and the final products.

**Endothermic Reactions**

Consider the decomposition of water:

\[
2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \quad \Delta H^\circ = +571.6 \text{ kJ}
\]

In this reaction, hydrogen–oxygen bonds in the water molecules must be broken, and the hydrogen–hydrogen and oxygen–oxygen bonds must be formed.

Since the overall change is endothermic, the energy required to break the O—H bonds must be greater than the energy released when the H—H and O═O bonds form. In any endothermic reaction, more energy is needed to break bonds in the reactants than is released by bonds formed in the products.

**Exothermic Reactions**

For exothermic reactions, the opposite is true. More energy is released by bonds formed in the products than is needed to break bonds in the reactants. The reaction between hydrogen and chlorine (Figure 3) illustrates the energy of bond breaking and bond making. Although an activated complex may be involved in the transition from bond breaking to bond making, for simplicity, we will only look at the individual bonds that are changing. Energy is required to break the bonds in hydrogen molecules (H₂) to create hydrogen...
atoms (H). The two hydrogen atoms have higher chemical potential energy than a hydrogen molecule. Likewise, the chlorine atoms have higher potential energy than the chlorine molecules. When the hydrogen and chlorine atoms make bonds to create hydrogen chloride molecules, energy is released. Since this reaction is exothermic, the logically consistent explanation is that more energy is released by bond making than is required for bond breaking. We can communicate this explanation using a potential energy diagram.

The explanation above assumes that sufficient energy is initially added to equal or exceed the required activation energy. This energy may be provided in a variety of forms: heat, light, or electrical. In all cases, the exothermic nature of this reaction means that heat is transferred to the surrounding molecules, thus increasing their kinetic energy.

Bond energies are the fourth method that you have encountered for predicting or explaining a change in enthalpy for a chemical reaction. Although there are quantitative values for bond energies, and scientists can predict a change in enthalpy from bond energies, this is not part of our study in this course. The methods that you have studied for predicting and/or explaining a change in enthalpy are the following:
1. calorimetry: the change in enthalpy equals the change in thermal energy
2. Hess’ law: the change in enthalpy equals the sum of component enthalpy changes
3. molar enthalpies of formation: the change in enthalpy equals the enthalpies of formation of the products minus the enthalpies of formation of the reactants
4. bond energies: the change in enthalpy equals the energy released from bond making minus the energy required for bond breaking

All of these methods are logically consistent with each other: they all support each other, moving from more empirical to more theoretical. Every method also yields the same answer to the question “What is the change in enthalpy for a particular reaction?”

**SUMMARY  Bond Energy and Enthalpy Changes**

- Bond energy is the energy required to break a chemical bond; it is also the energy released when a bond is formed.
- The change in enthalpy represents the net effect from breaking and making bonds. \( \Delta_H = \text{energy released from bond making} - \text{energy required for bond breaking} \)
  - Exothermic reaction: making \( \rightarrow \) breaking (\( \Delta_H \) is negative.)
  - Endothermic reaction: breaking \( \rightarrow \) making (\( \Delta_H \) is positive.)
Section 12.2 Questions

1. Write two definitions of bond energy.

2. Explain how bond energies are related to the activation energy for a reaction.

3. Why must chemical reactions include both the breaking of bonds and the forming of bonds?

4. Draw a chemical potential energy diagram (similar to Figure 3 on page 533) for the decomposition of liquid water into hydrogen and oxygen gases. Illustrate the energy change for the breaking of water molecules into atoms and then for the subsequent formation of hydrogen and oxygen molecules.

5. (a) Explain why the decomposition of water is an endothermic process.
    (b) Explain why the burning of hydrogen is an exothermic process.

6. Predict whether the reaction of hydrogen with bromine is endothermic or exothermic. Making reference to bond energies, explain your prediction.

7. In the Exploration activity (page 523) you looked at the reactions of metals with hydrochloric acid, and in Investigation 11.3 (pages 507 and 517) you determined the enthalpy change for the reaction of magnesium with hydrochloric acid.
   (a) Draw a chemical potential energy diagram, including the enthalpy change, for the reaction of magnesium metal with hydrochloric acid.
   (b) Using the net ionic equation for this reaction, list the bonds that must be broken in the reactants and the bonds that must be formed in the products.
   (c) Suggest a possible theoretical hypothesis to explain the empirical differences in the rates of reaction of zinc, magnesium, and iron with hydrochloric acid. Identify any assumptions you are making.

8. The reaction of hydrogen with chlorine at room temperature, in the absence of light, is undetectable owing to the very slow rate of reaction. The same reaction is explosively fast, however, if exposed to sunlight. The following mechanism has been suggested for this reaction.
   \[
   \text{Cl}_2(g) + \text{H}_2(g) \rightarrow \text{Cl}_2(g) + \text{H}_2(g) \\
   \text{Cl}_2(g) + \text{H}_2(g) \rightarrow \text{HCl}(g) + \text{HCl}(g) \\
   \text{H}(g) + \text{Cl}_2(g) \rightarrow \text{HCl}(g) + \text{Cl}(g) \\
   \text{Cl}(g) + \text{Cl}(g) \rightarrow \text{Cl}_2(g)
   \]
   (a) Write the net overall reaction equation.
   (b) Identify the intermediate entities that are formed during the step-by-step reaction process.
   (c) Discuss the activation energy for the collision of molecular chlorine with molecular hydrogen, and for the collision of atomic chlorine with molecular hydrogen. Which reaction has the greater activation energy, and what evidence can you use to support your argument?

9. The reaction of hydrogen and oxygen (see Figure 4, page 527) is exothermic and self-sustaining. Write the equation for this reaction, and provide a reason why it is not likely that the reaction occurs as a single step.

Extension

10. Ozone formation and destruction are natural bond-making and bond-breaking processes in the stratosphere. (See page 530.)
   (a) What is the source of the energy for breaking bonds?
   (b) Why is shorter wavelength radiation required to break the oxygen bond(s) than to break the ozone bond(s)?
   (c) If energy is produced by making ozone from molecular and atomic oxygen, why can’t this energy be used to break more molecular oxygen into atomic oxygen in the stratosphere?
Catalysis and Reaction Rates

12.3

Empirical Effect of Catalysis

Catalysis deals with the properties and development of catalysts, and the effects of catalysts on the rates of reaction. A catalyst is a substance that increases the rate of a chemical reaction without being consumed itself in the overall process. The chemical composition and amount of a catalyst are identical at the start and at the end of a reaction. A catalyst reduces the quantity of energy required to start the reaction, and results in a catalyzed reaction producing a greater yield in the same period of time (even at a lower temperature) than an uncatalyzed reaction. Research indicates that the use of a catalyst does not alter the net enthalpy change for a chemical reaction. In green plants, for example, the process of photosynthesis can take place only in the presence of the catalyst chlorophyll (Figure 1). Most catalysts significantly accelerate reactions, even when present in very tiny amounts compared with the amount of reactants present.

The action of catalysts seriously perplexed early chemists, who had problems with the concept of something obviously being involved in a chemical reaction but not being changed by that reaction. Effective catalysts for reactions have almost all been discovered by purely empirical methods—trying everything to see what worked.

Chemists learned early that metals prepared with a large surface area (powder or shavings) catalyze many reactions, including the decomposition of hydrogen peroxide in the presence of a platinum catalyst. Many people who wear contact lenses know about this reaction. They use it daily to clean their lenses.

A common consumer example of catalysis today is the use of platinum, palladium, and rhodium in catalytic converters in car exhaust systems (Figure 2). These catalysts speed the combustion of the exhaust gases so that a higher proportion of the exhaust will be the relatively harmless, completely oxidized products. Catalysts are extremely important in chemical technology and industry because they allow the use of lower temperatures. This not only reduces energy consumption but also prevents the decomposition of reactants and products and decreases unwanted side reactions. The result is an increase in the efficiency and economic benefits of many industrial reactions. For many industrial processes the difference between success and failure depends on the use of catalysts because they make the reactions fast enough to be profitable. (For an example of this, see The Haber Process case study, in Chapter 8.)

Compounds that act as catalysts in living systems are called enzymes. Enzymes are usually extremely complex molecules (proteins). A great many physiological reactions, such as metabolism, are actually controlled by the amount of enzyme present. Enzymes are also of great importance for catalyzing reactions in the food, beverage, cleaner, and pharmaceutical industries.

Practice

1. Do technologists normally use empirical or theoretical knowledge when doing work that involves catalysts?
2. List some technological inventions that involved the use of catalysts.
3. List some natural (biological) processes that involve the use of catalysts.
4. Enzymes in your body are generally present in extremely small quantities, but any substances that affect your enzymes are almost always very toxic and dangerous. Explain why this should be so, referring to reaction rates in your explanation.
Theoretical Explanation of Catalysis

Chemists believe that catalysts accelerate a reaction by providing an alternative lower-energy pathway from reactants to products. That is, a catalyst allows the reaction to occur by a different activated complex, but resulting in the same products overall. If the new pathway has a lower activation energy, a greater fraction of molecules possess the minimum required energy and the reaction rate increases. Since the activation energy is lowered by exactly the same amount for the reverse reaction, the rate of any reverse reaction increases as well (Figure 4).

Scientists do not really understand the actual mechanism by which catalysis occurs for most reactions, and discovering effective catalysts has traditionally been an empirical process involving trial-and-error. Chemists have studied a few catalyzed reactions in detail, so they believe they understand the changes involved. Most of the catalysts (enzymes) for biological reactions work by shape and orientation. They fit substrate proteins into locations on the enzyme as a key fits into a lock, enabling only specific molecules to link or detach on the enzyme, as shown in Figure 5.
One well-understood non-biological reaction is the decomposition of methanoic (formic) acid in aqueous solution. At room temperature this reaction is very slow, with no noticeable activity (Figure 6). When strong acid is added, the solution begins to bubble. Testing indicates that carbon monoxide gas is being produced. If this reaction proceeds until all the formic acid has been consumed, the solution will still contain the same quantity of acid as was initially added. It does not seem to matter which strong acid is added, so we assume that the acting catalyst is the aqueous hydrogen ion, which is common to all aqueous acidic solutions. Figure 8 shows the energy pathway diagram of the reaction with a catalyst. Note that, like all catalysts, the H⁺ is regenerated and, therefore, is not consumed during the reaction. In a catalyzed reaction, catalysts react with one or more of the reactants, but then are regenerated by the end of the reaction.

Uncatalyzed Decomposition of Methanoic Acid

Colliding methanoic acid molecules

can change the position of a hydrogen atom on one molecule,

which breaks apart to form water and carbon monoxide.

Relative potential energy $E_p$ (kJ)

HCOOH(aq) $\rightarrow$ H⁺(aq) H₂O(l) + CO(g)

Figure 6
The uncatalyzed reaction proceeds too slowly to notice at room temperature. Note that this reaction is endothermic, requiring an overall increase in (input of) energy.

Figure 5
Note that the enzyme shape is specific for the reactant (substrate) molecules. Almost all enzymes catalyze only one specific reaction.

DID YOU KNOW?
Hot Beetle Juice
The bombardier beetle of South America has a unique way of protecting itself. When it is threatened, it pumps stored hydroquinone and hydrogen peroxide from one chamber in its body into another chamber. In the second chamber the enzymes catalase and peroxidase mix with the stored compounds. The resulting catalyzed exothermic reaction produces a hot, corrosive liquid that is sprayed at the attacker.

Figure 7
The beetle’s spray can cause a skin burn that lasts for several days.

EXTENSION
Bombardier Beetles
A British professor of thermodynamics is researching the bombardier beetle’s squirting ability, with the aim of developing a device that will relight extinguished jet engines.
Catalysts and Reaction Mechanisms

With more details on the steps during catalysis, this audio clip will enrich your understanding of how catalysts can alter a reaction mechanism and hence speed up a reaction.

www.science.nelson.com

Catalyzed Decomposition of Methanoic Acid

Formic acid, HCOOH, can also react with an aqueous H⁺ ion to form the positive intermediate ion product HCOOH₂⁺, which reacts to form water, H₂O, and the intermediate ion product HCO⁻. Finally, the HCO⁻ reacts to form CO and to regenerate the H⁺ ion.

DID YOU KNOW?

Chemical Marriage

The Chinese symbol for catalyst is the same as that used for marriage broker.

DID YOU KNOW?

Communication Through Journals

The German chemist Justus von Liebig wrote in 1834: “Chemical literature is not to be found in books, it is contained in journals.” Referenced journals are regularly published reports of research that have passed a panel of judges. (See Appendix B.4.) For example, Johann Döbereiner discovered in 1823 that platinum catalyzes the burning of hydrogen. Within three months this discovery was reported in about a dozen European science journals.

Catalysis and the Nature of Science

The practice of science uses two important kinds of reasoning—inductive and deductive. Inductive reasoning involves extending specific examples to obtain a general statement; for example, using the evidence from an experiment to form a hypothesis in the analysis section of an investigation report. Deductive reasoning involves applying a general concept such as a theory, law, or generalization to obtain (deduce) a specific instance.

Chemists use indirect and direct evidence to inductively hypothesize the reaction pathway for uncatalyzed and catalyzed reactions. They create hypotheses for the structures of the activated complexes, and hypotheses for the individual reaction steps in an overall reaction. A reaction mechanism describes the individual reaction steps and the intermediates formed during the reaction, starting with reactants and finishing with products. Intermediates are chemical entities that form with varying stability at the end of a step in a reaction mechanism. They are more stable (have lower potential energy) than the activated complexes, but less stable than the reactants and the products. The intermediate then reacts in a subsequent step and does not appear in the final reaction mixture. For example, a three-step reaction mechanism (Figure 8) can be generalized as follows:

1. Step 1: reactant(s) → activated complex 1 → intermediate 1
2. Step 2: intermediate 1 → activated complex 2 → intermediate 2
3. Step 3: intermediate 2 → activated complex 3 → product(s)

The inductive reasoning of using the evidence from an experiment to hypothesize a reaction mechanism is usually accompanied by deductive reasoning to test the logic of
the mechanism. Chemists constantly ask themselves if a hypothesis makes sense based upon all the evidence they have collected and all of their chemical experience. If the mechanism has internal consistency, all the intermediates and reaction steps seem to be correct/logical. If the mechanism has external consistency, none of the thinking behind the proposed mechanism contradicts accepted theories, laws, or generalizations.

For example, evidence from sophisticated technologies (such as spectrometers) suggests that there are two intermediates in the catalyzed decomposition of methanoic acid. The spectrophotographs indicate that the chemical formulas of the intermediates are HCOOH₂⁻(aq) and HCO⁺(aq). The same equipment provides evidence that the products are water and carbon monoxide. Other diagnostic tests on the final products provide supporting evidence.

A consistency check of the mechanism indicates that all chemical equations must be balanced and that all reactants, intermediates, and products can be accounted for by writing balanced chemical equations. Furthermore, the chemical formulas of all chemicals described are consistent with chemical formulas of known chemicals and/or with the bonding capacity of each atom in each entity. From an energy perspective, the law of conservation of energy seems to be obeyed, the chemical potential energies of the entities involved are consistent with known values, and the enthalpy change remains the same as for the uncatalyzed reaction. It all fits together in a nice logical package. There are no contradictions, no inconsistencies.

**Uses of Catalysts**

**The Oil Industry**

The oil industry uses catalysts in the cracking and reforming of crude oil and bitumen to produce more marketable fractions (such as gasoline). The science and engineering of crude oil refining has advanced tremendously, due mostly to the use of catalysts that increase the rate of the reaction while decreasing the energy (which often means decreasing the temperature) required for the chemical process. Table 1 lists the typical catalysts for cracking and reforming of crude oil.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Catalysts Used in the Oil Industry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process</strong></td>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>cracking</td>
<td>fluid catalytic cracking (high temperature)</td>
</tr>
<tr>
<td></td>
<td>hydrocracking (lower temperature, higher pressure, presence of H₂)</td>
</tr>
<tr>
<td>reforming</td>
<td>alkylation</td>
</tr>
<tr>
<td></td>
<td>catalytic reforming</td>
</tr>
</tbody>
</table>

**WEB Activity**

**Simulation—A Catalyzed Reaction**

Hydrogenation is an important industrial process. Scientific studies of hydrogenation typically start with simple reactions in order to understand the molecular process (mechanism). In this animation, you will investigate the hydrogenation of ethene using a platinum catalyst.

**DID YOU KNOW?**

**Syrup Digesters**

High-fructose corn syrup is a key ingredient in many processed foods: pop, fruit-flavoured drinks, cookies, jam, candy ... It is made by treating starch (extracted from corn) with enzymes to break it down into glucose monomers. Glucose, however, is not as sweet as the sucrose (table sugar) that has traditionally been used to sweeten foods. Fortunately, there are enzymes that convert some of the syrup’s glucose into super-sweet fructose. It is this combination of glucose and fructose that is so widely used as corn syrup. The mixture can even be tailored to the needs of the food and beverage industries. While 42% fructose syrup is perfectly satisfactory for many foods, a sweeter syrup is required by the soft drink industry: up to 55% fructose.

**Learning Tip**

You are not expected to memorize which catalyst goes with which chemical process. However, you should know that major reactions, for example, cracking, reforming, and hydrodesulfurization, use catalysts. In fact, the message is that most major chemical processes in industry involve catalysis.

**DID YOU KNOW?**

**Gasoline Production**

Gasoline is the most marketable of all products from crude oil. In the 1920s about one-quarter of a barrel of oil could be converted to gasoline. Due to the use of modern catalysts, about half of a barrel of oil can now be converted to gasoline.
Emissions control is another use of catalysts. These emissions may be nitrogen oxides (from power plants), sulfur (from gas plants), and chemicals that contribute to smog (from internal combustion engines). Table 3 shows some of the emission control reactions and their catalysts. (You do not need to memorize these reactions and catalysts.)

As you can see from the above reactions, catalysis is an extremely important branch of chemistry and chemical engineering. Catalysts play a very important role in chemical industries—for producing chemicals that we use in our work and in our homes and for controlling environmentally harmful emissions.
Enzymes
Natural product chemists have discovered many naturally occurring catalysts. Most of these catalysts are enzymes that increase the rate of specific reactions (Table 4).
Chemists are now using enzymes as catalysts for the production of chemicals not found in nature, such as pharmaceuticals and agricultural chemicals. These enzymes are designed to be highly selective in the reaction each catalyzes, effective under ambient conditions, and convenient and safe to dispose.

Table 4  Natural Enzymes as Catalysts

<table>
<thead>
<tr>
<th>Technological process</th>
<th>Description</th>
<th>Catalyst(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>detergents with enzymes (widest application of enzymes today) (Figure 9)</td>
<td>hydrolyzes (breaks down) starch</td>
<td>amylases</td>
</tr>
<tr>
<td></td>
<td>attacks cellulose fibres to remove tiny fibres and prevent pilling</td>
<td>cellulases</td>
</tr>
<tr>
<td></td>
<td>breaks down oily and fatty stains</td>
<td>lipases</td>
</tr>
<tr>
<td></td>
<td>degrades proteins</td>
<td>proteases</td>
</tr>
<tr>
<td>brewing (fermentation)</td>
<td>C₆H₁₂O₆(s) → 2 C₂H₅OH(l) + 2 CO₂(g)</td>
<td>zymase (yeast)</td>
</tr>
<tr>
<td>cleaning contact lenses</td>
<td>decomposes H₂O₂(aq) to O₂(g), to disinfect contact lenses</td>
<td>catalase</td>
</tr>
<tr>
<td>high-fructose corn syrup</td>
<td>three enzymatic steps: liquefies corn syrup, hydrolyzes sugar, isomerizes glucose</td>
<td>amylase, glucoamylase, glucose isomerase</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Natural process</th>
<th>Description</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrogen fixation</td>
<td>converts nitrogen into nitrogen compounds</td>
<td>nitrogenase</td>
</tr>
<tr>
<td>photosynthesis</td>
<td>6 CO₂(g) + 6 H₂O(l) → C₆H₁₂O₆(s) + 6 O₂(g)</td>
<td>chlorophyll</td>
</tr>
</tbody>
</table>

Evidence for an Activated Complex
Evidence for an activated complex is difficult to obtain. According to reaction theory, catalyzed and uncatalyzed reactions have different activated complexes. Most activated complexes are colourless and fairly unstable. A few, however, are coloured and exist long enough to be observed.

Purpose
The purpose of this investigation is to test the theoretical concept that a catalyzed reaction involves an activated complex different from that in an uncatalyzed reaction.

Problem
What evidence is there for the existence of a different activated complex for a catalyzed reaction?

Design
An uncatalyzed reaction is observed, and then a catalyst is added to the chemical system. Evidence for the formation of a different activated complex is sought.

To perform this investigation, turn to page 543.

SUMMARY

- A catalyst is a substance that increases the rate of a reaction without being consumed in the overall process.
- According to theory, catalysts accelerate a reaction by providing an alternative pathway with a lower activation energy.
- A catalyst does not alter the net enthalpy change of a reaction. Both catalyzed and uncatalyzed versions of the same reaction have the same ΔH.
- Catalysts are widely used in industry, consumer technologies, and biological processes.
1. Compare two reactions with the same reactants. One reaction involves a catalyst; the other does not.
   (a) What is the same for both reactions?
   (b) What is different for both reactions?

2. Consider the following reaction mechanism, in which A, B, and E may be elements or compounds, and C, D, and F are compounds:
   (1) \( 2A + B \rightarrow C \)
   (2) \( C \rightarrow D \)
   (3) \( D + E \rightarrow F \)
   (a) Which entities are intermediates?
   (b) Which entities are reactants?
   (c) Which entities are products?
   (d) What is the overall reaction equation?

3. (a) What is the activation energy for the following net forward reaction?
   \( A + B \rightarrow C + D \)
   (b) What is the activation energy for the following net reverse reaction?
   \( C + D \rightarrow A + B \)
   (c) What is the change in enthalpy (net energy change) for the net forward reaction?
   (d) What is the change in enthalpy (net energy change) for the net reverse reaction?
   (e) Which reaction (forward or reverse) is exothermic?

4. Explain what you would expect to occur if the original collision of particles in the forward reaction has a total available kinetic energy equivalent to 55 kJ.
5. Explain what you would expect to occur if the original collision of particles in the reverse reaction has a total available kinetic energy equivalent to 55 kJ.
6. How do catalysts provide solutions to technological problems? Give at least four examples.

7. Complete the Purpose, Design, Materials, Analysis, and Evaluation (part 2) sections of the following lab report.

   **Problem**
   What is the molar enthalpy of decomposition of 20 mL of 2 mol/L aqueous hydrogen peroxide without and with an iron(III) catalyst being added?

   **Hypothesis**
   The molar enthalpy of reaction does not change when a catalyst is added.

   **Evidence**
   Trial 1:
   - volume of aqueous hydrogen peroxide = 20.0 mL
   - volume of 0.1 mol/L sodium hydroxide = 5.0 mL
   - volume of aqueous iron(III) nitrate = 0 mL
   - initial temperature of hydrogen peroxide = 21.4 °C
   - final temperature of hydrogen peroxide = 23.4 °C
   - time = 10 min
   Trial 2:
   - volume of aqueous hydrogen peroxide = 20.0 mL
   - volume of 0.1 mol/L sodium hydroxide = 5.0 mL
   - volume of aqueous iron(III) nitrate = 0.3 mL
   - initial temperature of hydrogen peroxide = 21.4 °C
   - final temperature of hydrogen peroxide = 23.6 °C
   - time = 2 min

8. Find at least two examples of enzymes and industrial catalysts. Summarize your research to these questions.
   (a) For each of the enzymes or catalysts, record
      • the reaction that is catalyzed
      • how the catalyst was discovered
      • where and how the catalyst or enzyme acts
      • for an enzyme, physiological implications of its presence or deficiency, whether such a condition exists, and, if so, how it is currently treated
      • economic implications of the industrial catalysts’ use
   (b) Which of the industrial catalysts has the greatest effect on your own life? Explain.

9. Catalysts make it possible for us to modify the components of crude oil to meet our many needs and wants. Despite growing research and development into alternative sources of energy, we rely on crude oil for energy more and more each year. What are the risks and benefits of relying on fossil fuels as energy sources?

**Extension**

10. An ad claims wonderful health benefits from a new form of water created with a catalyst. What kinds of authorities would you accept for this claim?
Chapter 12 INVESTIGATIONS

INVESTIGATION 12.1

Iodine Clock Reaction

Technological problem solving often involves a systematic trial-and-error approach that is guided by knowledge and experience. Thomas Edison, the greatest inventor of all time, used this method, for example, to invent the incandescent light bulb and for inventing new batteries. Usually, one variable at a time is manipulated. In this investigation, a variety of potential catalysts are added one at a time to a reaction mixture. The rate of the reaction, as determined by the time required to get to a blue endpoint, is the responding variable. Use MSDS to find cautions. Include safety and disposal information at the end of the Materials section.

Purpose
The purpose of this investigation is to create a reaction mixture (including a catalyst) that will react as fast as possible.

Problem
What technological procedure involving a catalyst can be used to have solution A react with solution B as quickly as possible?

Evidence for an Activated Complex

Evidence for an activated complex is difficult to obtain. According to reaction theory, catalyzed and uncatalyzed reactions have different activated complexes. Most activated complexes are colourless and fairly unstable. A few, however, are coloured and exist long enough to be observed.

Purpose
The purpose of this investigation is to test the theoretical concept that a catalyzed reaction involves an activated complex that is different from that in an uncatalyzed reaction.

Problem
What evidence is there for the existence of a different activated complex for a catalyzed reaction?

Prediction
According to the theory of catalysis, a catalyst increases the rate of a reaction by creating an alternative activated complex with a lower activation energy. The evidence should show that the catalyzed reaction had a different activated complex than did the uncatalyzed reaction.

Design
An uncatalyzed reaction is observed, and then a catalyst is added to the chemical system. Evidence for the formation of a different activated complex is sought.

Materials
- 40 mL of 0.30 mol/L sodium potassium tartrate
- 40 mL of 3% H₂O₂(aq)
- 5 mL of 0.30 mol/L CoCl₂(aq)
- hot plate
- thermometers or temperature probes

Sodium potassium tartrate, hydrogen peroxide, and cobalt(II) chloride may irritate skin and eyes. Cobalt(II) chloride is also toxic by ingestion and a possible carcinogen. Handle with care.

Procedure
1. Add 40 mL of 0.30 mol/L sodium potassium tartrate solution to the beaker followed by 40 mL of hydrogen peroxide solution.
2. Heat the solution in the beaker (covered with a watch glass) to 45 °C to 50 °C. Record any evidence of a reaction and of an activated complex.
3. Remove the beaker from the hot plate and add 5 mL of 0.30 mol/L cobalt(II) chloride as a catalyst.
4. Again, cover the beaker with the watch glass and observe the reaction.
Chapter 12 SUMMARY

Outcomes

Knowledge

- analyze and label energy diagrams for a chemical reaction, including reactants, products, enthalpy change, and activation energy (all sections)
- define activation energy as the energy barrier that must be overcome for a chemical reaction to occur (12.1)
- explain the energy changes that occur during chemical reactions referring to bonds breaking and forming and changes in potential and kinetic energy (12.2)
- explain that catalysts increase reaction rates by providing alternative pathways for changes without affecting the net energy involved (12.3)

STS

- recognize the values and limitations of technological products and processes (12.1, 12.3)
- state that a goal of technology is to solve practical problems (12.2)
- evaluate technologies from a variety of perspectives (12.3)

Skills

- initiating and planning: describe procedures for safe handling, storage, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (12.3)
- performing and recording: plot chemical potential energy diagrams, enthalpy diagrams, and energy pathway diagrams indicating changes in energy for chemical reactions (all sections);
- analyzing and interpreting: interpret energy diagrams for chemical reactions (all sections)
- communication and teamwork: work collaboratively in addressing problems and apply the skills and conventions of science in communicating information and ideas and in assessing results by using appropriate SI notation, and fundamental and derived units for calculating and communicating enthalpy changes (all sections)

Key Terms

12.1 activation energy, $E_a$

12.2 bond energy

12.3 catalysis
- catalyst
- enzyme
- intermediate

MAKE a summary

1. Draw a combined potential energy diagram and energy pathway diagram to illustrate the uncatalyzed and catalyzed reaction of hydrogen and fluorine. Add labels and explanations to communicate what you have learned in this chapter, including the concept of catalysis.

2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

Go To

The following components are available on the Nelson Web site. Follow the links for Nelson Chemistry Alberta 20–30.
- an interactive Self Quiz for Chapter 12
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.
Part 1

1. Which of the following statements concerning collision–reaction theory is false?
   A. A chemical reaction must involve collisions of reactant entities.
   B. An effective collision requires sufficient energy.
   C. All collisions with the required minimum energy form new bonds.
   D. All collisions without the required minimum energy rebound elastically.

2. Catalysts speed up the rate of a chemical reaction by providing a reaction pathway that has
   A. lower activation energy
   B. higher activation energy
   C. lower net energy change
   D. higher net energy change

3. Which of the following statements regarding bond energy is false?
   A. Bond energy is the energy released when a bond is formed.
   B. Bond energy is the energy required to break a chemical bond.
   C. The change in enthalpy represents the net effect from breaking and making bonds.
   D. In an endothermic reaction the energy released from bond making is greater than the energy required for bond breaking.

4. The following statements are not all true.
   1. Catalysts are consumed in the net reaction.
   2. Catalysts are not consumed in the net reaction.
   3. Catalysts decrease the enthalpy of the products.
   4. Catalysts increase the enthalpy of the products.
   5. Catalysts decrease the overall rate of a reaction.
   6. Catalysts increase the overall rate of a reaction.
   7. Catalysts provide an alternate pathway for the reaction.
   8. Catalysts are an essential part of most industrial chemical processes.
   List, in order, the true statements about catalysts.

5. The ignition system in an automobile is designed to provide the engine with
   A. activation energy
   B. enthalpy
   C. oxygen
   D. fuel

6. The catalytic converter in an automobile is designed to
   A. provide more energy
   B. provide more oxygen
   C. improve fuel efficiency
   D. remove nitrogen oxides from the exhaust

7. Which of the following is not an example of a catalyst?
   A. enzymes in the production of sugar from starch
   B. ethene in the production of ethylene glycol
   C. V2O5(s) in the production of sulfuric acid
   D. Fe(s) in the production of ammonia

8. The structural arrangement of particles representing the highest potential energy point in a chemical reaction step is called the
   A. product
   B. catalyst
   C. reactant
   D. activated complex

9. The change in enthalpy of a chemical reaction can be predicted by all the following methods except
   A. Hess’ law
   B. stoichiometry
   C. bond energies
   D. molar enthalpies of formation

10. All the alkali metals react with water at room temperature to produce hydrogen gas and hydroxide ions. The tendency to react increases as the atomic number of the alkali metal increases. Based on this evidence, which of the alkali metals has the highest activation energy in this reaction?
    A. cesium
    B. lithium
    C. potassium
    D. sodium

Part 2

11. Carbon tetrachloride, CCl4(l), is widely used as a solvent for oils, fats, lacquers, and varnishes. Carbon tetrachloride can be produced by the reaction of methane and chlorine gas.
    \[ \text{CH}_4(g) + 4 \text{Cl}_2(g) \rightarrow \text{CCl}_4(l) + 4 \text{HCl}(g) \]
    (a) Describe the conditions required for a successful collision between methane and chlorine molecules.
    (b) How would a catalyst change the rate of the reaction?
    (c) Why does a catalyst have this effect?
    (d) Explain how bond energies affect the rate of this reaction.
    (e) Explain how bond energies affect the net energy change of this reaction.
12. Using the concept of bond energies,
   (a) explain why the oxidation of aluminium is exothermic.
   (b) explain why the decomposition of aluminium oxide is
       endothermic.

13. Draw energy pathway diagrams for the following reactions. Label
    the reactants, products, enthalpy change, activation energy,
    and activated complex.
   (a) C(s) + O_2(g) → CO_2(g) + 393.5 kJ
   (b) N_2(g) + 2 O_2(g) + 66.4 kJ → 2 NO_2(g)

14. Explain why it is important to avoid producing static
    electricity while refuelling an automobile.

15. Catalytic reforming technology is used to improve the
    quality of gasoline by converting straight-chain
    hydrocarbons to aromatic molecules, for example,
    heptane + energy → methylbenzene + hydrogen
   (Figure 1). Analyze this reaction. Your response should
   include
   • a balanced structural formula equation
   • your justification of which is greater: the energy
     released from bond making or the energy required for
     bond breaking
   • an energy pathway diagram for the reaction, with
     labels for the reactants, products, enthalpy change,
     and activation energy for the catalyzed and
     uncatalyzed reactions

Figure 1
A catalytic reforming unit

16. Use Figure 2 to answer the following questions.

   (a) What is the activation energy for the uncatalyzed
       forward reaction?
   (b) What is the activation energy for the uncatalyzed
       reverse reaction?
   (c) What is the activation energy for the catalyzed forward
       reaction?
   (d) What is the activation energy for the catalyzed reverse
       reaction?
   (e) What is the enthalpy change for the uncatalyzed
       forward reaction?
   (f) What is the enthalpy change for the uncatalyzed
       reverse reaction?
   (g) What is the enthalpy change for the catalyzed forward
       reaction?
   (h) What is the enthalpy change for the catalyzed reverse
       reaction?

Figure 2
Energy pathway diagram for the synthesis of an organic compound

(a) How is the activation energy for the uncatalyzed forward reaction?
(b) How is the activation energy for the uncatalyzed reverse reaction?
(c) How is the activation energy for the catalyzed forward reaction?
(d) How is the activation energy for the catalyzed reverse reaction?
(e) How is the enthalpy change for the uncatalyzed forward reaction?
(f) How is the enthalpy change for the uncatalyzed reverse reaction?
(g) How is the enthalpy change for the catalyzed forward reaction?
(h) How is the enthalpy change for the catalyzed reverse reaction?

17. Illustrate each of the following technological processes
    with examples. For each example, provide a word equation
    and suggest a suitable catalyst.
   (a) hydrocracking heavy oil to gasoline
   (b) pollution control in an automobile catalytic converter
   (c) production of high-fructose corn syrup
Unit 6 REVIEW

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

1. The correct units for specific heat capacity are
   A. J/(g°C)
   B. kJ/(g°C)
   C. kg/(J°C)
   D. °C/(g·J)

2. Water can be decomposed by electrical energy as shown in the following equation:
   \[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]
   \[ \Delta H = ? \]
   The value of \( \Delta H \) for the equation as written is __________ kJ (to three digits).

3. There are several electrical generating stations in Alberta that use the energy from burning coal to generate electricity. Assuming coal is pure carbon, the temperature increase in 1.00 t of water when it absorbs all the energy produced by the complete combustion of 1.00 kg of coal is calculated to be ______________ °C.

4. Which statements are true for exothermic reactions?
   ___ , ___, ___, and ___

5. Which statements are true for endothermic reactions?
   ___ , ___, ___, and ___

6. The energy barrier that must be overcome in order for a reaction to occur is referred to as the
   A. activation energy
   B. bond energy
   C. enthalpy change
   D. molar enthalpy

7. Catalysts are an essential part of most industrial chemical processes. Which of the following statements about catalysts is false?
   A. Catalysts are not consumed in the net reaction.
   B. Catalysts increase the enthalpy of the products.
   C. Catalysts increase the overall rate of a reaction.
   D. Catalysts provide an alternative pathway for the reaction.

8. Using a catalyst in a chemical reaction
   A. increases the enthalpy change of the reaction
   B. increases the activation energy of the reaction
   C. decreases the enthalpy change of the reaction
   D. decreases the activation energy of the reaction

9. A chemistry student determines in the laboratory that the molar enthalpy of combustion of methanol is –721 kJ/mol.
   \[ 2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) + \text{energy} \]
   When the energy term is written as a term in the reaction equation, for the same conditions, the value is ______________ kJ.

10. An automobile catalytic converter is a technological invention for the conversion of noxious exhaust gases. For example,
    \[ 2\text{NO}_2(g) + 2\text{CO}(g) \rightarrow \text{N}_2(g) + 2\text{CO}_2(g) \]
    \[ \Delta H^\circ = ? \]
    The standard enthalpy change for this reaction is ______________ kJ.

11. A much studied chemical reaction is communicated by the reaction equation
    \[ \text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g) \]
    \[ \Delta H = +53.0 \text{ kJ} \]
    This equation is representative of an
    A. endothermic formation reaction
    B. endothermic decomposition reaction
    C. exothermic formation reaction
    D. exothermic decomposition reaction

12. Glucose is an important natural product. Which of the following reactions involving glucose is endothermic?
    A. Formation of glucose from its elements
    B. Combustion of glucose
    C. Cellular respiration of glucose
    D. Photosynthesis involving glucose
13. Match the appropriate energy change, labelled 1 to 5 in the graph, with the following reactions. Give your answers in the same order as the energy changes listed.
- enthalpy change for the forward reaction
- enthalpy change for the reverse reaction
- activation energy for the uncatalyzed reaction
- activation energy for the catalyzed reaction
___, ___, ___, and ___

14. From the graph above, match the appropriate sections, numbered 6 to 9, with the following statements. Give your answers in the same order as the statements.
- the activated complex for the uncatalyzed reaction
- the activated complex for the catalyzed reaction
- the conversion of kinetic energy into potential energy
- the chemical potential energy of entities with varying kinetic energy
___, ___, ___, and ___

15. Combustion of a hydrocarbon, cellular respiration, and photosynthesis have much in common. Which of the following is not common to all three reactions?
A. energy
B. CO₂(g)
C. H₂O(l)
D. H₂O(g)

16. Part of the character of chemicals is their thermal stability. Using a reference, list the following organic compounds in order of increasing stability.
1. sucrose, C₁₂H₂₂O₁₁(s)
2. ethanoic acid, CH₃COOH(l)
3. ethanol, C₂H₅OH(l)
4. glucose, C₆H₁₂O₆(s)
___, ___, ___, ___

17. Enumerate four factors that influence the rate of a chemical reaction.

18. The reaction equation
A + B → C + D
represents a hypothetical reaction. Illustrate the reaction with an energy pathway diagram showing the catalyzed and uncatalyzed reactions, given that the activation energy is twice as large for the uncatalyzed reaction as for the catalyzed reaction.

19. The reaction between ammonia and hydrogen chloride gas produces a white smoke that was once widely used for "special effects" in dramatic productions.
NH₃(g) + HCl(g) → NH₄Cl(s)
ΔH° = ?
(a) Use a table of standard molar enthalpies of formation to predict the standard enthalpy change for the reaction.
(b) Predict which is greater: the energy required for breaking the bonds in the reactant molecules or the energy released by forming bonds in the product.

20. The modern method of preparing methanol combines carbon monoxide and hydrogen at high temperature and pressure, in the presence of a catalyst.
CO(g) + 2 H₂(g) → CH₃OH(l)
ΔH° = ?
(a) Explain the purpose of the catalyst.
(b) Using a reference, predict the standard enthalpy change for the reaction.
(c) Determine the quantity of energy released by the formation of 1.00 kg of methanol.

21. Some of the natural gas fields in Alberta contain hydrogen sulfide, a very poisonous gas. The sulfur is removed by burning some of the hydrogen sulfide to form sulfur dioxide, which is then reacted with the remaining hydrogen sulfide to form elemental sulfur. The overall reaction equation for the process is
16 H₂S(g) + 8 SO₂(g) → 16 H₂O(g) + 3 S₈(s)
ΔH° = ?
(a) Use a table of standard molar enthalpies of formation to predict the enthalpy change of the above reaction.
(b) Determine the standard molar enthalpy of reaction for sulfur, S₈(s).
(c) Determine the quantity of energy released by the production of 1.00 t of sulfur, S₈(s).

22. In addition to being a fuel, ethane is used to produce ethene and ethyne, the starting points for the synthesis of a host of useful compounds. Use a table of standard molar enthalpies of formation to predict the enthalpy change of the following reactions:
(a) C₂H₆(g) → C₂H₄(g) + H₂(g)
(b) C₂H₆(g) → C₂H₂(g) + 2 H₂(g)
23. Cracking (especially to produce gasoline and ethene) is the most common industrial chemical reaction in Alberta. For catalytic cracking of crude oil fractions into gasoline hydrocarbons, synthetic zeolites (aluminosilicates, Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}) are the preferred catalysts.

(a) Use the following information (only) to determine the enthalpy of cracking for the following reaction:

\[
\begin{align*}
\text{C}_{10}\text{H}_{22}(l) + \text{H}_{2}(g) & \rightarrow \text{C}_{4}\text{H}_{10}(g) + \text{C}_{6}\text{H}_{14}(l) \\
\Delta H &= \text{?} \\
2 \text{C}_{10}\text{H}_{22}(l) + 31 \text{O}_{2}(g) & \rightarrow 20 \text{CO}_{2}(g) + 22 \text{H}_{2}\text{O}(l) \\
\Delta H &= -13555.8 \text{ kJ} \\
2 \text{C}_{4}\text{H}_{10}(g) + 13 \text{O}_{2}(g) & \rightarrow 8 \text{CO}_{2}(g) + 10 \text{H}_{2}\text{O}(l) \\
\Delta H &= -5754.6 \text{ kJ} \\
2 \text{C}_{6}\text{H}_{14}(l) + 19 \text{O}_{2}(g) & \rightarrow 12 \text{CO}_{2}(g) + 14 \text{H}_{2}\text{O}(l) \\
\Delta H &= -8325.8 \text{ kJ} \\
\text{C}(s) + \frac{1}{2} \text{O}_{2}(g) & \rightarrow \text{CO}_{2}(g) \\
\Delta H &= -393.5 \text{ kJ} \\
\text{H}_{2}(g) + \frac{1}{2} \text{O}_{2}(g) & \rightarrow \text{H}_{2}\text{O}(l) \\
\Delta H &= -285.8 \text{ kJ}
\end{align*}
\]

(b) Explain how the addition of the zeolite changes the overall
(i) enthalpy of reaction
(ii) rate of reaction
(iii) activation energy

(c) View an animation of natural and synthetic zeolite.
(i) What cation is primarily used to enrich the synthetic zeolite to make an even more effective catalyst than the natural crystal?
(ii) What other cations may be present in the synthetic zeolite catalyst?

24. Catalysts are one of many technological solutions used to reduce greenhouse gas (GHG) emissions.
(a) List the four GHGs that research shows have the most effect on global warming.
(b) From research, which of carbon dioxide or methane is found to have the largest global warming potential (GWP)?
(c) The catalysts used in catalytic converters in cars are from what class of elements in the periodic table?

25. (a) Table 1 shows the increase in per capita GHG emissions since 1990. What is the percentage increase in this time?

(b) Research recent GHG emissions in Environment Canada’s Greenhouse Gas Inventory. Graph the per capita emissions over the last fifteen years or so. Comment on the trends you observe.
(c) What is the Canadian GHG emission target in tonnes per capita? If every one of us meets this target, what will be the percentage reduction in GHG emissions? Relate this to the graph you plotted in (b).

26. List five ways by which you can personally reduce GHG emissions.

27. Why do most Canadians (as indicated by polls) want to reduce the emission of GHGs?
28. At 300 K the activation energy, $E_a$, for the uncatalyzed decomposition of hydrogen peroxide into water and oxygen is measured to be 75.3 kJ/mol. For a particular concentration of the catalyst potassium iodide and again at 300 K, the activation energy is 56.5 kJ/mol.

(a) Predict the molar enthalpy of decomposition of hydrogen peroxide.

(b) Draw a potential energy diagram, including reaction pathways, to communicate all the information above.

29. Compare three different organic fuels.

Your response should include:
- A calculation of the molar enthalpy of combustion for each fuel
- A calculation of the quantities of energy released per kilogram of fuel
- A calculation of the chemical amounts of carbon dioxide released per kilogram of fuel
- An evaluation of the “environmental efficiency” in units of moles of CO$_2$ per kilogram of fuel

30. Ethanoic acid (acetic acid) is an important industrial chemical that is manufactured from the reaction of methanol and carbon monoxide using rhodium or iridium catalysts.

(a) Write the balanced chemical equation for the industrial production of ethanoic acid.

(b) Sketch a chemical potential energy diagram, and label the enthalpy change.

(c) Sketch an energy pathway diagram, and label the activation energies for the uncatalyzed and catalyzed reactions.

(d) Provide the scientific explanation and the technological purpose for using a catalyst.

31. Ethanol can be oxidized (to carbon dioxide and water) in a laboratory fume hood through a series of reactions by using a platinum or palladium wire catalyst. Use the reaction mechanism below to answer the questions.

\[
\text{CH}_3\text{CH}_2\text{OH}(l) \rightarrow \text{CH}_3\text{CHO}(l) + \text{H}_2(g)
\]

\[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)
\]

\[
\text{CH}_3\text{CHO}(l) + \frac{5}{2} \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)
\]

(a) Determine the enthalpy change for the overall reaction resulting from the above catalyzed reaction mechanism.

(b) Explain how the enthalpy change for the overall reaction is affected by catalyzing the reaction and creating an alternative pathway.

32. Statistics Canada lists the percent hydroelectric power generation by province and territory (Table 2).

<table>
<thead>
<tr>
<th>Province</th>
<th>1994</th>
<th>2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>NL</td>
<td>97.7</td>
<td>93.9</td>
</tr>
<tr>
<td>PE</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NS</td>
<td>10.4</td>
<td>8.5</td>
</tr>
<tr>
<td>NB</td>
<td>17.4</td>
<td>12.6</td>
</tr>
<tr>
<td>QC</td>
<td>96.5</td>
<td>96.3</td>
</tr>
<tr>
<td>ON</td>
<td>25.6</td>
<td>24.9</td>
</tr>
<tr>
<td>MB</td>
<td>99.0</td>
<td>97.9</td>
</tr>
<tr>
<td>SK</td>
<td>21.9</td>
<td>15.8</td>
</tr>
<tr>
<td>AB</td>
<td>3.4</td>
<td>2.8</td>
</tr>
<tr>
<td>BC</td>
<td>87.5</td>
<td>90.1</td>
</tr>
<tr>
<td>YT</td>
<td>88.9</td>
<td>87.5</td>
</tr>
<tr>
<td>NT</td>
<td>32.6</td>
<td>37.9</td>
</tr>
</tbody>
</table>

Note: NT includes NU.
Source: Table B35 on page 80 of HAatE by StatCan

(a) Analyze this data (or more recent data from the Statistics Canada Web site) to find any trends and insights concerning the percentage of hydroelectric power generation in Canada.

(b) Illustrate the percentage generation of hydroelectric power by province on a bar graph.

(c) Explain the difference between hydro use in Alberta and hydro use in one other province or territory.

(d) From an environmental perspective enumerate pros and cons for hydroelectric power stations.

(e) If a goal of technology is to provide solutions to practical problems, evaluate the solution of replacing fossil fuel power plants with hydroelectric power. Provide at least one pro and one con from at least three perspectives.

33. People living in different regions of Canada use (or in the past have used) different fuels for cooking and for heating their homes. Enumerate five different fuels used by peoples in different parts of Canada—north to south and west to east.

34. Compare methane and propane as fuels. Establish at least four criteria for evaluating these fuels. Provide quantitative and/or qualitative information for each criterion. Finally, provide a personal choice based upon the information compiled and upon your values. Share your findings as an audio-visual presentation.
35. **Table 3** lists ignition temperatures for various fuels. The piloted ignition temperature is the temperature at which the fuel will ignite when provided with a spark or flame (such as a pilot light in a furnace). The spontaneous ignition temperature is the temperature at which the fuel ignites without a spark or flame.

**Table 3** Ignition Temperatures

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Piloted ignition temperature (°C)</th>
<th>Spontaneous ignition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>204</td>
<td>651</td>
</tr>
<tr>
<td>asphalt</td>
<td>254</td>
<td>485</td>
</tr>
<tr>
<td>corn oil</td>
<td>300</td>
<td>420</td>
</tr>
<tr>
<td>ethanol</td>
<td>225</td>
<td>343</td>
</tr>
<tr>
<td>gasoline</td>
<td>199</td>
<td>245</td>
</tr>
<tr>
<td>methane</td>
<td>350</td>
<td>600</td>
</tr>
</tbody>
</table>

1 Gas that ignites with a spark or flame at any temperature. 

(a) Use concepts from Chapter 12 to _explain_ (theoretically) why gasoline ignites at or above —43 °C when a spark is provided (for example, by a spark plug).

(b) _Explain_ where the energy comes from for spontaneous ignition of propane at 450 °C.

(c) Methane ignites with a spark or flame at any temperature. Gas companies advise people to “Call before you dig.” What might produce a spark to ignite a broken natural gas line?

(d) Methane, propane, gasoline, and asphalt are hydrocarbons. Consult Table 3 to develop a hypothesis about their relative activation energies. What certainties and uncertainties do you have about the hypothesis you have written?

36. The molar enthalpy of neutralization, \( \Delta H_{\text{ne}} \), for aqueous acid–base reactions can be determined by calorimetry. If one of the reactants is in excess, then the molar enthalpy of neutralization is determined for the other reactant. Complete the Analysis portion of the lab report.

**Purpose**
The purpose of this exercise it to use calorimetry to determine the molar enthalpy of neutralization for hypoiodous acid when reacted with excess aqueous sodium hydroxide.

**Evidence**
1.00 L of 0.400 mol/L HIO(aq)
1.00 L of 0.500 mol/L NaOH(aq)
initial temperature of solutions = 21.22 °C
final temperature of mixture = 22.44 °C

37. Over the years there have been many “free energy” devices or “energy machines” advertised on the Internet. The energy output of these devices is claimed to be greater than the energy input. As a skeptic, what kind of authorities would you consult and/or what kinds of tests would you advocate to test these claims?

38. Review the focusing questions on page 474. Using the knowledge you have gained from this unit, briefly _outline_ a response to each of these questions.

**Extension**

39. When investigating reactions to produce ammonia, Haber and Bosch tested some 20 000 candidate catalysts in a trial-and-error process before discovering an iron ore from Sweden that worked well for fertilizer production. (The ore happened to contain traces of alumina and alkali metal compounds.) In the catalyzed reaction of nitrogen and hydrogen, the gases are adsorbed onto the solid iron ore catalyst.

(a) _Compare_ the activation energy for the uncatalyzed reaction (red pathway) with the largest activation energy for the catalyzed reaction (green pathway).

(b) _Explain_ why the catalyzed reaction is much faster.

(c) _Compare_ the enthalpy changes for the catalyzed and uncatalyzed reactions. Comment on the magnitude and sign.

40. Use the One-Tonne Challenge calculator to see how your energy emissions compare with the national average, and what you can do to reduce your emissions.

41. Green chemistry is a term that describes chemical industrial work involving environmental stewardship. Research two examples of green chemistry associated with energy production or use.

www.science.nelson.com