

BIG Idea Chemical reactions usually absorb or release energy.

15.1 Energy

MAIN Idea Energy can change form and flow, but it is always conserved.

15.2 Heat

MAIN Idea The enthalpy change for a reaction is the enthalpy of the products minus the enthalpy of the reactants.

15.3 Thermochemical Equations

MAIN Idea Thermochemical equations express the amount of heat released or absorbed by chemical reactions.

15.4 Calculating Enthalpy Change

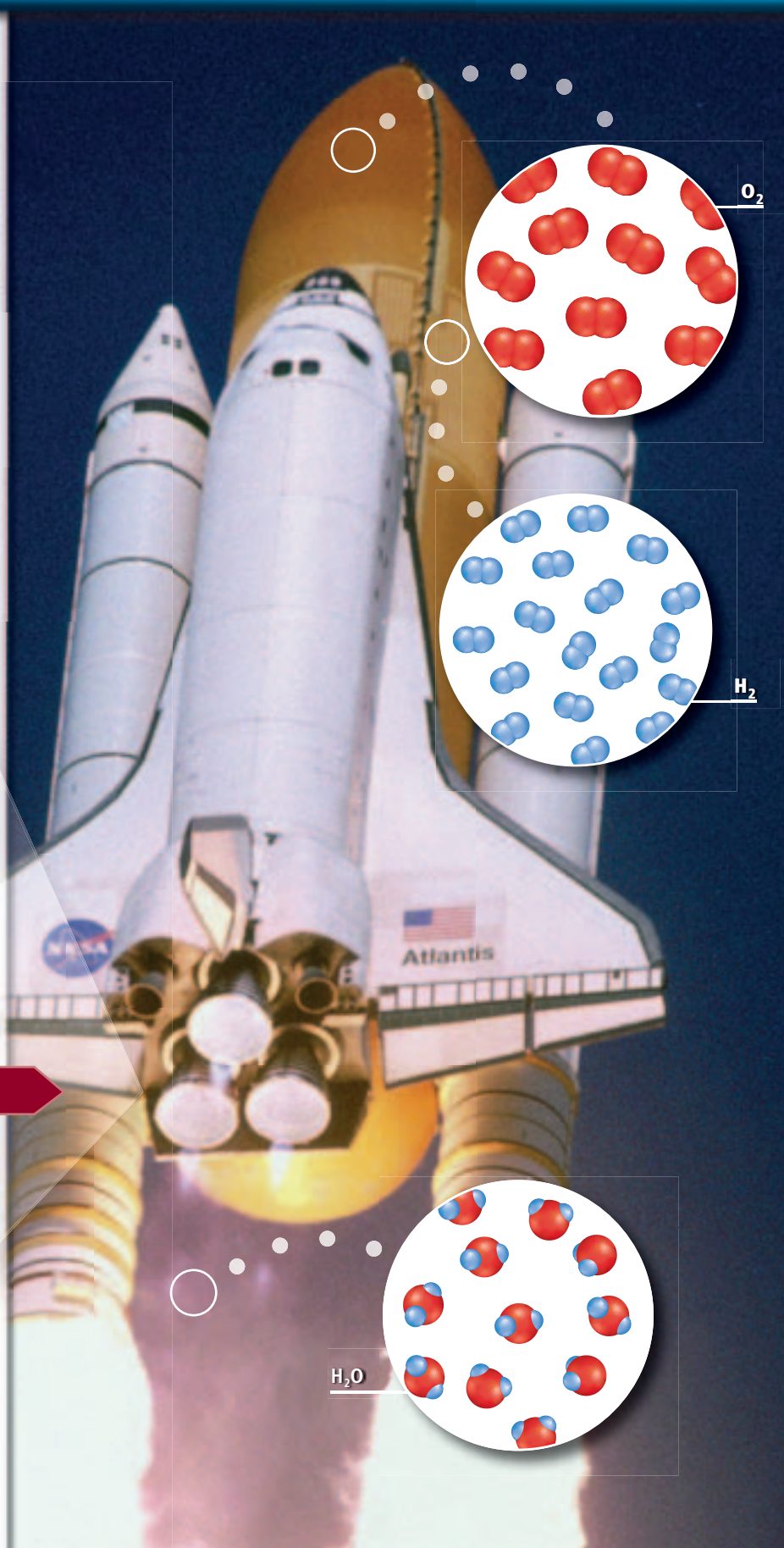
MAIN Idea The enthalpy change for a reaction can be calculated using Hess's law.

15.5 Reaction Spontaneity

MAIN Idea Changes in enthalpy and entropy determine whether a process is spontaneous.

ChemFacts

- The three main engines of the space shuttle use more than 547,000 kg of liquid oxygen and approximately 92,000 kg of liquid hydrogen.
- The engines lift a total mass of 2.04×10^6 kg.
- In about eight minutes, the space shuttle accelerates to a speed of more than 17,000 km/h.



Start-Up Activities

LAUNCH Lab

How can you make a cold pack?

Chemical cold packs are used for fast relief of pain due to injury. Some chemical cold packs contain two separate compounds that are combined in a process that absorbs heat. Which compound would make the best chemical cold pack?



Procedure

1. Read and complete the lab safety form.
2. Use a **graduated cylinder** to place 15 mL of **distilled water** into each of **three test tubes**.
3. Use a **nonmercury thermometer** to find the temperature of the distilled water. Record the initial temperature of the water in a data table.
4. Use a **balance** to measure the mass of 1.0 g of **potassium nitrate (KNO₃)**. Add the KNO₃ to Test Tube 1. **WARNING: Keep all chemicals used in this lab away from heat sources.**
5. Mix, and record the maximum or minimum temperature reached by the solution.
6. Repeat Steps 4 and 5 with samples of **calcium chloride (CaCl₂)** and **ammonium nitrate (NH₄NO₃)**.

Analysis

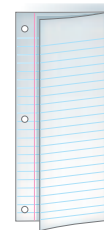
1. **Analyze and Conclude** Which is the best chemical for a chemical cold pack?
2. **Describe** an alternate use better suited for one of the other chemicals used in the lab.

Inquiry Investigate a change that you could make in the procedure that would increase the temperature change.

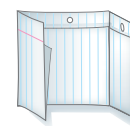
FOLDABLES™ Study Organizer

Gibbs Free Energy Equation
Make the following Foldable to organize your study of the energy equation.

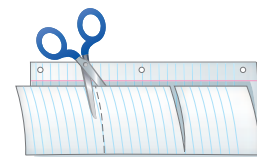
- ▶ **STEP 1** Fold a sheet of paper in half lengthwise. Make the back edge about 2 cm longer than the front edge.



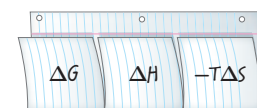
- ▶ **STEP 2** Fold into thirds.



- ▶ **STEP 3** Unfold and cut along the folds of the top flap to make three tabs.



- ▶ **STEP 4** Label the tabs as follows: ΔG , ΔH and $-T\Delta S$.



FOLDABLES Use this Foldable with Section 15.5. As you read this section, summarize what each term means and how it relates to reaction spontaneity.

Chemistry Online

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Section 15.1

Objectives

- Define energy.
- Distinguish between potential and kinetic energy.
- Relate chemical potential energy to the heat lost or gained in chemical reactions.
- Calculate the amount of heat absorbed or released by a substance as its temperature changes.

Review Vocabulary

temperature: a measure of the average kinetic energy of the particles in a sample of matter

New Vocabulary

energy
law of conservation of energy
chemical potential energy
heat
calorie
joule
specific heat

Energy

MAIN Idea Energy can change form and flow, but it is always conserved.

Real-World Reading Link Have you ever watched a roller coaster zoom up and down a track, or experienced the thrill of a coaster ride? Each time a coaster climbs a steep grade or plunges down the other side, its energy changes from one form to another.

The Nature of Energy

You are probably familiar with the term *energy*. Perhaps you have heard someone say, “I just ran out of energy,” after a strenuous game or a difficult day. Solar energy, nuclear energy, energy-efficient automobiles, and other energy-related topics are often discussed in the media.

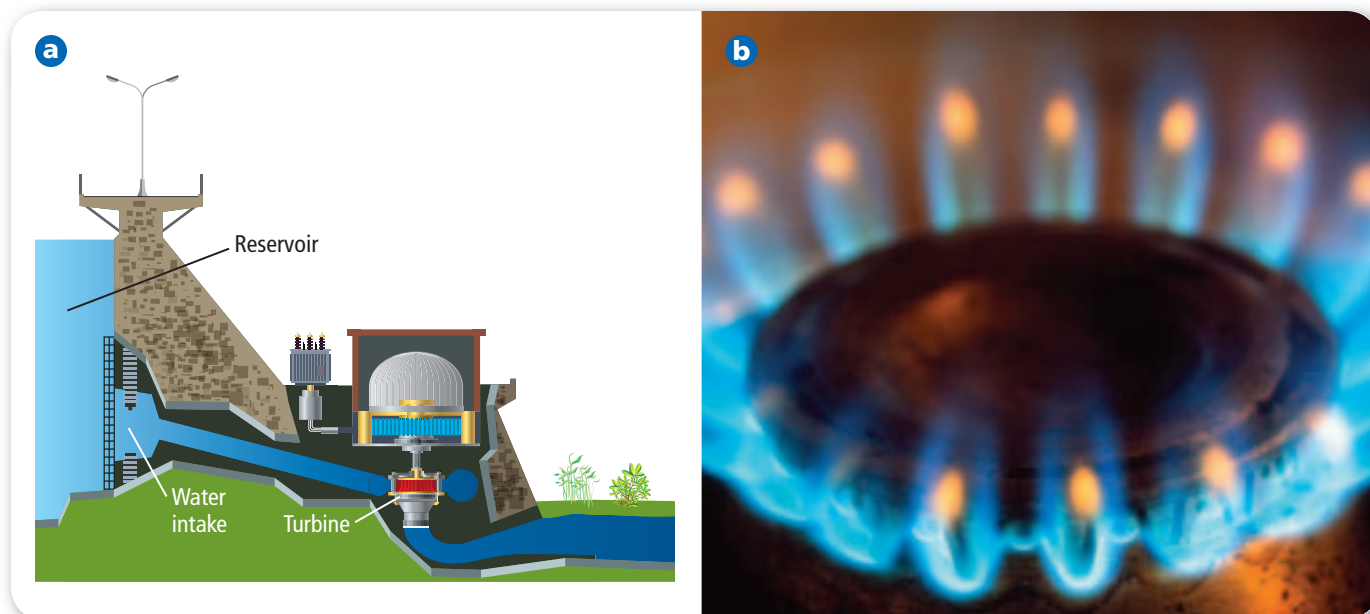
Energy cooks the food you eat and propels the vehicles that transport you. If the day is especially hot or cold, energy from burning fuels helps maintain a comfortable temperature in your home and school. Electric energy provides light and powers devices from computers and TV sets to cellular phones, MP3 players, and calculators. Energy was involved in the manufacture and delivery of every material and device in your home. Your every movement and thought requires energy. In fact, you can think of each cell in your body as a miniature factory that runs on energy derived from the food you eat.

What is energy? **Energy** is the ability to do work or produce heat. It exists in two basic forms: potential energy and kinetic energy. Potential energy is energy due to the composition or position of an object. A macroscopic example of potential energy of position is a downhill skier poised at the starting gate for a race, as shown in **Figure 15.1a**. After the starting signal is given, the skier’s potential energy changes to kinetic energy during the speedy trip to the finish line, as shown in **Figure 15.1b**. Kinetic energy is energy of motion. You can observe kinetic energy in the motion of objects and people all around you.

- Figure 15.1** At the top of the course, the skier in **a** has high potential energy because of her position. In **b**, the skier’s potential energy changes to kinetic energy.

Compare How is the potential energy of the skier different at the starting gate and at the finish line?






Chemical systems contain both kinetic energy and potential energy. Recall from Chapter 13 that the kinetic energy of a substance is directly related to the constant random motion of its representative particles and is proportional to temperature. As temperature increases, the motion of submicroscopic particles increases. The potential energy of a substance depends on its composition: the type of atoms in the substance, the number and type of chemical bonds joining the atoms, and the particular way the atoms are arranged.

Law of conservation of energy When water rushes through turbines in the hydroelectric plant shown in **Figure 15.2a**, some of the water's kinetic energy is converted to electric energy. Propane (C_3H_8) is an important fuel for cooking and heating. In **Figure 15.2b**, propane gas combines with oxygen to form carbon dioxide and water. Potential energy stored in the propane bonds is given off as heat. In both of these examples, energy changes from one form to another, but energy is conserved—the total amount of energy remains constant. To better understand the conservation of energy, suppose you have money in two accounts at a bank and you transfer funds from one account to the other. Although the amount of money in each account has changed, the total amount of your money in the bank remains the same. When applied to energy, this analogy embodies the law of conservation of energy. The **law of conservation of energy** states that in any chemical reaction or physical process, energy can be converted from one form to another, but it is neither created nor destroyed. This is also known as the first law of thermodynamics.

Chemical potential energy The energy that is stored in a substance because of its composition is called **chemical potential energy**. Chemical potential energy plays an important role in chemical reactions. For example, the chemical potential energy of propane results from the arrangement of the carbon and hydrogen atoms and the strength of the bonds that join them.

 **Reading Check** State the law of conservation of energy in your own words.

■ **Figure 15.2** Energy can change from one form to another but is always conserved. In **a**, the potential energy of water is converted to kinetic energy of motion as it falls through the intake from its high position in the reservoir. The rushing water spins the turbine to generate electric energy. In **b**, the potential energy stored in the bonds of propane molecules is converted to heat.

Table 15.1 Relationships Among Energy Units	
Relationship	Conversion Factors
1 J = 0.2390 cal	$\frac{1 \text{ J}}{0.2390 \text{ cal}}$ $\frac{0.2390 \text{ cal}}{1 \text{ J}}$
1 cal = 4.184 J	$\frac{1 \text{ cal}}{4.184 \text{ J}}$ $\frac{4.184 \text{ J}}{1 \text{ cal}}$
1 Calorie = 1 kcal	$\frac{1 \text{ Calorie}}{1000 \text{ cal}}$ $\frac{1000 \text{ cal}}{1 \text{ Calorie}}$

Heat The principle component of gasoline is octane (C_8H_{18}). When gasoline burns in an automobile's engine, some of octane's chemical potential energy is converted to the work of moving the pistons, which ultimately moves the wheels and propels the automobile. However, much of the chemical potential energy of octane is released as heat. The symbol q is used to represent **heat**, which is energy that is in the process of flowing from a warmer object to a cooler object. When the warmer object loses energy, its temperature decreases. When the cooler object absorbs energy, its temperature rises.

Measuring Heat

The flow of energy and the resulting change in temperature are clues to how heat is measured. In the metric system of units, the amount of energy required to raise the temperature of one gram of pure water by one degree Celsius (1°C) is defined as a **calorie** (cal). When your body breaks down sugars and fats to form carbon dioxide and water, these exothermic reactions generate heat that can be measured in Calories. Note that the nutritional Calorie is capitalized. That is because one nutritional Calorie equals 1000 calories, or one kilocalorie (kcal). Recall that the prefix *kilo-* means 1000. For example, one tablespoon of butter contains approximately 100 Calories. This means that if the butter was burned completely to produce carbon dioxide and water, 100 kcal (100,000 cal) of heat would be released.

The SI unit of energy and of heat is the **joule** (J). One joule is the equivalent of 0.2390 calories, and one calorie equals 4.184 joules.

Table 15.1 summarizes the relationships between calories, nutritional Calories, joules, and kilojoules (kJ) and the conversion factors you can use to convert from one unit to another.

EXAMPLE Problem 15.1

Convert Energy Units A breakfast of cereal, orange juice, and milk might contain 230 nutritional Calories. Express this energy in joules.

Math Handbook

Unit Conversion
pages 957–958

1 Analyze the Problem

You are given an amount of energy in nutritional Calories. You must convert nutritional Calories to calories and then convert calories to joules.

Known

amount of energy = 230 Calories

Unknown

amount of energy = ? J

2 Solve for the Unknown

Convert nutritional Calories to calories.

$$230 \text{ Calories} \times \frac{1000 \text{ cal}}{1 \text{ Calorie}} = 2.3 \times 10^5 \text{ cal}$$

Apply the relationship 1 Calorie = 1000 cal.

Convert calories to joules.

$$2.3 \times 10^5 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 9.6 \times 10^5 \text{ J}$$

Apply the relationship 1 cal = 4.184 J.

3 Evaluate the Answer

The minimum number of significant figures used in the conversion is two, and the answer correctly has two digits. A value of the order of 10^5 or 10^6 is expected because the given number of kilocalories is of the order of 10^2 and it must be multiplied by 10^3 to convert it to calories. Then, the calories must be multiplied by a factor of approximately 4. Therefore, the answer is reasonable.

1. A fruit-and-oatmeal bar contains 142 nutritional Calories. Convert this energy to calories.
2. An exothermic reaction releases 86.5 kJ. How many kilocalories of energy are released?
3. **Challenge** Define a new energy unit, named after yourself, with a magnitude of one-tenth of a calorie. What conversion factors relate this new unit to joules? To Calories?

Specific Heat

You have read that one calorie, or 4.184 J, is required to raise the temperature of one gram of pure water by one degree Celsius (1°C). That quantity, $4.184 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$, is defined as the specific heat (c) of water. The **specific heat** of any substance is the amount of heat required to raise the temperature of one gram of that substance by one degree Celsius. Because different substances have different compositions, each substance has its own specific heat.

To raise the temperature of water by one degree Celsius, 4.184 J must be absorbed by every gram of water. Much less energy is required to raise the temperature of an equal mass of concrete by one degree Celsius. You might have noticed that concrete sidewalks get hot during a sunny summer day. How hot depends on the specific heat of concrete, but other factors are also important. The specific heat of concrete is $0.84 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$, which means that the temperature of concrete increases roughly five times more than water's temperature when equal masses of concrete and water absorb the same amount of energy. You can see in **Figure 15.3** that people who have been walking on hot concrete surfaces might want to cool their feet in the water of a fountain.

■ **Figure 15.3** The cooler waters of the fountain are welcome after walking on the hot concrete sidewalk. The water is cooler because water must absorb five times the number of joules as concrete to reach an equivalent temperature.

Infer How would the temperature change of the concrete compare to that of the water over the course of a cool night.



Table 15.2 Specific Heats at 298 K (25°C)

Substance	Specific heat J/(g·°C)
Water(l)	4.184
Ethanol(l)	2.44
Water(s)	2.03
Water(g)	2.01
Beryllium(s)	1.825
Magnesium(s)	1.023
Aluminum(s)	0.897
Concrete(s)	0.84
Granite(s)	0.803
Calcium(s)	0.647
Iron(s)	0.449
Strontium(s)	0.301
Silver(s)	0.235
Barium(s)	0.204
Lead(s)	0.129
Gold(s)	0.129

Calculating heat absorbed Suppose that the temperature of a 5.00×10^3 -g block of concrete sidewalk increased by 6.0°C . Would it be possible to calculate the amount of heat it had absorbed? Recall that the specific heat of a substance tells you the amount of heat that must be absorbed by 1 g of a substance to raise its temperature 1°C . **Table 15.2** shows the specific heats for some common substances. The specific heat of concrete is $0.84 \text{ J}/(\text{g}\cdot^\circ\text{C})$, so 1 g of concrete absorbs 0.84 J when its temperature increases by 1°C . To determine the heat absorbed by 5.00×10^3 g of concrete you must multiply the 0.84 J by 5.00×10^3 . Then, because the concrete's temperature changed by 6.0°C , you must multiply the product of the mass and the specific heat by 6.0°C .

Equation for Calculating Heat

q represents the heat absorbed or released. c represents the specific heat of the substance. m represents the mass of the sample in grams. ΔT is the change in temperature in $^\circ\text{C}$, or $T_{\text{final}} - T_{\text{initial}}$.

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

The quantity of heat absorbed or released by a substance is equal to the product of its specific heat, the mass of the substance, and the change in its temperature.

You can use this equation to calculate the heat absorbed by the concrete block.

$$q = c \times m \times \Delta T$$
$$q_{\text{concrete}} = \frac{0.84 \text{ J}}{(\text{g}\cdot^\circ\text{C})} \times (5.00 \times 10^3 \text{ g}) \times 6.0^\circ\text{C} = 25,000 \text{ J or } 25 \text{ kJ}$$

The total amount of heat absorbed by the concrete block is 25,000 J or 25 kJ.

For comparison, how much heat would be absorbed by 5.00×10^3 g of the water in the fountain when its temperature is increased by 6.0°C ? The calculation for q_{water} is the same as it is for concrete except that you must use the specific heat of water, $4.184 \text{ J}/(\text{g}\cdot^\circ\text{C})$.

$$q_{\text{water}} = \frac{4.184 \text{ J}}{(\text{g}\cdot^\circ\text{C})} \times (5.00 \times 10^3 \text{ g}) \times 6.0^\circ\text{C} = 1.3 \times 10^5 \text{ J or } 130 \text{ kJ}$$

If you divide the heat absorbed by the water (130 kJ) by the heat absorbed by the concrete (25 J), you will find that for the same change in temperature, the water absorbed more than five times the amount of heat absorbed by the concrete block.

Calculating heat released Substances can both absorb and release heat. The same equation for q , the quantity of heat, can be used to calculate the energy released by substances when they cool off. Suppose the 5.00×10^3 -g piece of concrete reached a temperature of 74.0°C during a sunny day and cooled down to 40.0°C at night. How much heat was released? First calculate ΔT .

$$\Delta T = 74.0^\circ\text{C} - 40.0^\circ\text{C} = 34.0^\circ\text{C}$$

Then, use the equation for quantity of heat.

$$q = c \times m \times \Delta T$$
$$q_{\text{concrete}} = \frac{0.84 \text{ J}}{(\text{g}\cdot^\circ\text{C})} \times (5.00 \times 10^3 \text{ g}) \times 34.0^\circ\text{C} = 140,000 \text{ J or } 140 \text{ kJ}$$

EXAMPLE Problem 15.2

Calculate Specific Heat In the construction of bridges and skyscrapers, gaps must be left between adjoining steel beams to allow for the expansion and contraction of the metal due to heating and cooling. The temperature of a sample of iron with a mass of 10.0 g changed from 50.4°C to 25.0°C with the release of 114 J. What is the specific heat of iron?

1 Analyze the Problem

You are given the mass of the sample, the initial and final temperatures, and the quantity of heat released. You can calculate the specific heat of iron by rearranging the equation that relates these variables to solve for c .

Known

energy released = 114 J $T_i = 50.4^\circ\text{C}$
mass of iron = 10.0 g Fe $T_f = 25.0^\circ\text{C}$

Unknown

specific heat of iron, $c = ? \text{ J}/(\text{g}\cdot^\circ\text{C})$

2 Solve for the Unknown

Calculate ΔT .

$$\Delta T = 50.4^\circ\text{C} - 25.0^\circ\text{C} = 25.4^\circ\text{C}$$

Write the equation for calculating the quantity of heat.

$$q = c \times m \times \Delta T \quad \text{State the equation for calculating heat.}$$

$$\frac{c \times m \times \Delta T}{m \times \Delta T} = \frac{q}{m \times \Delta T} \quad \text{Solve for } c.$$

$$c = \frac{q}{m \times \Delta T}$$

$$c = \frac{114 \text{ J}}{(10.0 \text{ g})(25.4^\circ\text{C})} \quad \text{Substitute } q = 114 \text{ J, } m = 10.0 \text{ g, and } \Delta T = 25.4^\circ\text{C}.$$

$$c = 0.449 \text{ J}/(\text{g}\cdot^\circ\text{C}) \quad \text{Multiply and divide numbers and units.}$$

3 Evaluate the Answer

The values used in the calculation have three significant figures, so the answer is correctly stated with three digits. The value of the denominator of the equation is approximately two times the value of the numerator, so the final result, which is approximately 0.5, is reasonable. The calculated value is the same as that recorded for iron in **Table 15.2**.

Real-World Chemistry Specific Heat



Absorbing heat You might have wrapped your hands around a cup of hot chocolate to stay warm at a fall football game. In much the same way, long ago, children sometimes walked to school on wintry days carrying hot, baked potatoes in their pockets. The potatoes provided warmth for cold hands, but by the time the school bell rang, the potatoes had cooled off. At lunchtime, the cold potatoes might have been placed in or on the schoolhouse stove to warm them again for eating.

PRACTICE Problems

Extra Practice Page 986 and glencoe.com

- If the temperature of 34.4 g of ethanol increases from 25.0°C to 78.8°C, how much heat has been absorbed by the ethanol? Refer to **Table 15.2**.
- A 155-g sample of an unknown substance was heated from 25.0°C to 40.0°C. In the process, the substance absorbed 5696 J of energy. What is the specific heat of the substance? Identify the substance among those listed in **Table 15.2**.
- Challenge** A 4.50-g nugget of pure gold absorbed 276 J of heat. The initial temperature was 25.0°C. What was the final temperature?

■ **Figure 15.4** Each photoelectric cell on this panel absorbs the Sun's radiation and converts it to electricity quietly and without causing pollution.



Using the Sun's energy Because of its high specific heat, water is sometimes used to harness the energy of the Sun. After water has been heated by solar radiation, the hot water can be circulated in homes and businesses to provide heat. Radiation from the Sun could supply all the energy needs of the world and reduce or eliminate the use of carbon dioxide-producing fuels, but several factors have delayed the development of solar technologies. For example, the Sun shines for only a part of each day. In some areas, clouds often reduce the amount of available radiation. Because of this variability, effective methods for storing energy are critical.

A more promising approach to the use of solar energy is the development of photovoltaic cells, such as those shown in **Figure 15.4**. These devices convert solar radiation directly to electricity. Photovoltaic cells supply power for astronauts in space, but they are not used extensively for ordinary energy needs. That is because the cost of supplying electricity by means of photovoltaic cells is high compared to the cost of burning coal or oil.

Section 15.1 Assessment

Section Summary

- ▶ Energy is the capacity to do work or produce heat.
- ▶ Chemical potential energy is energy stored in the chemical bonds of a substance by virtue of the arrangement of the atoms and molecules.
- ▶ Chemical potential energy is released or absorbed as heat during chemical processes or reactions.

7. **MAIN Idea** Explain how energy changes from one form to another in an exothermic reaction. In an endothermic reaction.
8. **Distinguish** between kinetic and potential energy in the following examples: two separated magnets; an avalanche of snow; books on library shelves; a mountain stream; a stock-car race; separation of charge in a battery.
9. **Explain** how the light and heat of a burning candle are related to chemical potential energy.
10. **Calculate** the amount of heat absorbed when 5.50 g of aluminum is heated from 25.0°C to 95.0°C. The specific heat of aluminum is 0.897 J/(g·°C).
11. **Interpret Data** Equal masses of aluminum, gold, iron, and silver were left to sit in the Sun at the same time and for the same length of time. Use **Table 15.2** to arrange the four metals according to the increase in their temperatures from largest increase to smallest.

Section 15.2

Objectives

- Describe how a calorimeter is used to measure energy that is absorbed or released.
- Explain the meaning of enthalpy and enthalpy change in chemical reactions and processes.

Review Vocabulary

pressure: force applied per unit area

New Vocabulary

calorimeter
thermochemistry
system
surroundings
universe
enthalpy
enthalpy (heat) of reaction

Heat

MAIN Idea The enthalpy change for a reaction is the enthalpy of the products minus the enthalpy of the reactants.

Real-World Reading Link Think about standing under a hot shower, relaxing as your body absorbs heat from the water. When you jump into a cold pool, you might shiver as your body loses heat. In a similar way, some chemical reactions absorb heat whereas others release heat.

Calorimetry

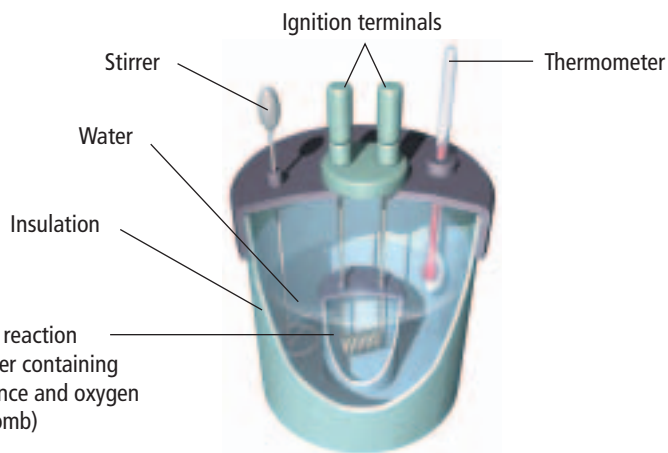
Have you ever wondered how food chemists obtain the Calorie information that appears on packaged food? The packages record the results of combustion reactions carried out in calorimeters. A **calorimeter** is an insulated device used for measuring the amount of heat absorbed or released during a chemical or physical process. A known mass of water is placed in an insulated chamber to absorb the energy released from the reacting system or to provide the energy absorbed by the system. The data to be collected is the change in temperature of this mass of water. **Figure 15.5** shows the kind of calorimeter, called a bomb calorimeter, that is used by food chemists.

Determining specific heat Satisfactory results can be obtained in your calorimetry experiments using the much simpler foam-cup calorimeter. These calorimeters are open to the atmosphere, so reactions carried out in them occur at constant pressure. You can use them to determine the specific heat of an unknown metal.

Suppose you put 125 g of water into a foam-cup calorimeter and find that its initial temperature is 25.60°C. Then you heat a 50.0-g sample of the unknown metal to 115.0°C and put the metal sample into the water. Heat flows from the hot metal to the cooler water, and the temperature of the water rises. The flow of heat stops only when the temperature of the metal and the water are equal.

■ **Figure 15.5** A sample is positioned in a steel inner chamber called the bomb, which is filled with oxygen at high pressure. Surrounding the bomb is a measured mass of water stirred by a low-friction stirrer to ensure uniform temperature. The reaction is initiated by a spark, and the temperature is recorded until it reaches its maximum.

Infer Why is it important that the stirrer does not create friction?



Bomb Calorimeter

Concepts in Motion

Interactive Figure To see an animation of calorimetry, visit glencoe.com.



■ **Figure 15.6 a.** An initial temperature of 25.60°C is recorded for the 125 g of water in the calorimeter. **b.** A 50.0-g sample of an unknown metal is heated to 115.0°C and placed in the calorimeter. **c.** The metal transfers heat to the water until metal and water are at the same temperature. The final temperature is 29.30°C.

Figure 15.6 shows the experimental procedure. Note that the temperature in the calorimeter becomes constant at 29.30°C, which is the final temperature attained by both the water and the metal. Assuming no heat is lost to the surroundings, the heat gained by the water is equal to the heat lost by the metal. This quantity of heat can be calculated using the equation you learned in Section 15.1.

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



Reading Check Define the four variables in the equation above.

First, calculate the heat gained by the water. To do this, you need the specific heat of water, 4.184 J/(g·°C).

$$q_{\text{water}} = 4.184 \text{ J}/(\text{g}\cdot^{\circ}\text{C}) \times 125 \text{ g} \times (29.30^{\circ}\text{C} - 25.60^{\circ}\text{C})$$

$$q_{\text{water}} = 4.184 \text{ J}/(\text{g}\cdot^{\circ}\text{C}) \times 125 \text{ g} \times 3.70^{\circ}\text{C}$$

$$q_{\text{water}} = 1940 \text{ J}$$

The heat gained by the water, 1940 J, equals the heat lost by the metal, q_{metal} , so you can write this equation.

$$q_{\text{metal}} = q_{\text{water}}$$

$$q_{\text{metal}} = -1940 \text{ J}$$

$$c_{\text{metal}} \times m \times \Delta T = -1940 \text{ J}$$

Now, solve the equation for the specific heat of the metal, c_{metal} , by dividing both sides of the equation by $m \times \Delta T$.

$$c_{\text{metal}} = \frac{-1940 \text{ J}}{m \times \Delta T}$$

The change in temperature for the metal, ΔT , is the difference between the final temperature of the water and the initial temperature of the metal ($29.30^{\circ}\text{C} - 115.0^{\circ}\text{C} = -85.7^{\circ}\text{C}$). Substitute the known values of m and ΔT (50.0 g and -85.7°C) into the equation and solve.

$$c_{\text{metal}} = \frac{-1940 \text{ J}}{(50.0 \text{ g})(-85.7^{\circ}\text{C})} = 0.453 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$$

The unknown metal has a specific heat of 0.453 J/(g·°C). **Table 15.2** shows that the metal could be iron.

EXAMPLE Problem 15.3

Math Handbook

Solving Algebraic
Equations
pages 954–955

Using Specific Heat A piece of metal with a mass of 4.68 g absorbs 256 J of heat when its temperature increases by 182°C. What is the specific heat of the metal? Could the metal be one of the alkaline earth metals listed in **Table 15.2**?

1 Analyze the Problem

You are given the mass of the metal, the amount of heat it absorbs, and the temperature change. You must calculate the specific heat. Use the equation for q , the quantity of heat, but solve for specific heat, c .

Known

mass of metal, $m = 4.68$ g
quantity of heat absorbed, $q = 256$ J
 $\Delta T = 182^\circ\text{C}$

Unknown

specific heat, $c = ? \text{ J}/(\text{g}\cdot^\circ\text{C})$

2 Solve for the Unknown

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

$$c = \frac{q}{m \times \Delta T}$$

$$c = \frac{256 \text{ J}}{(4.68 \text{ g})(182^\circ\text{C})} = 0.301 \text{ J}/(\text{g}\cdot^\circ\text{C})$$

State the equation for the quantity of heat, q .

Solve for c .

Substitute $q = 256$ J, $m = 4.68$ g, and $\Delta T = 182^\circ\text{C}$.

Table 15.2 indicates that the metal could be strontium.

3 Evaluate the Answer

The three quantities used in the calculation have three significant figures, and the answer is correctly stated with three digits. The calculations are correct and yield the expected unit.

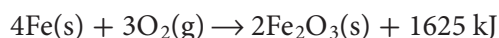
PRACTICE Problems

Extra Practice Page 986 and glencoe.com

- A 90.0-g sample of an unknown metal absorbed 25.6 J of heat as its temperature increased 1.18°C. What is the specific heat of the metal?
- The temperature of a sample of water increases from 20.0°C to 46.6°C as it absorbs 5650 J of heat. What is the mass of the sample?
- How much heat is absorbed by a 2.00×10^3 -g granite boulder ($c_{\text{granite}} = 0.803 \text{ J}/(\text{g}\cdot^\circ\text{C})$) as its temperature changes from 10.0°C to 29.0°C?
- Challenge** If 335 g of water at 65.5°C loses 9750 J of heat, what is the final temperature of the water?

Chemical Energy and the Universe

Virtually every chemical reaction and change of physical state either releases or absorbs heat. **Thermochemistry** is the study of heat changes that accompany chemical reactions and phase changes. The burning of fuels always produces heat. Some products have been engineered to produce heat on demand. For example, soldiers in the field use a highly exothermic reaction to heat their meals. You might have used a heat pack to warm your hands on a cold day. The energy released by a heat pack is produced by the following reaction and is shown in the equation as one of the products.



Determine Specific Heat

How can you determine the specific heat of a metal? You can use a coffee-cup calorimeter to determine the specific heat of a metal.

Procedure



1. Read and complete the lab safety form.
2. Make a table to record your data.
3. Pour approximately 150 mL of **distilled water** into a **250-mL beaker**. Place the beaker on a **hot plate** set on high.
4. Use a **balance** to find the mass of a **metal cylinder**.
5. Using **crucible tongs**, carefully place the metal cylinder in the beaker on the hot plate.
6. Measure 90.0 mL of distilled water using a **graduated cylinder**.
7. Pour the water into a **polystyrene coffee cup** nested in a second **250-mL beaker**.
8. Measure and record the temperature of the water using a **nonmercury thermometer**.

9. When the water on the hot plate begins to boil, measure and record the temperature as the initial temperature of the metal.
10. Carefully add the hot metal to the cool water in the coffee cup with the crucible tongs. Do not touch the hot metal with your hands.
11. Stir, and measure the maximum temperature of the water after the metal was added.

Analysis

1. **Calculate** the heat gained by the water. The specific heat of H_2O is $4.184 \text{ J/g}\cdot^\circ\text{C}$. Because the density of water is 1.0 g/mL , use the volume of water as the mass.
2. **Calculate** the specific heat of your metal. Assume that the heat absorbed by the water equals the heat lost by the metal.
3. **Compare** this experimental value to the accepted value for your metal.
4. **Describe** major sources of error in this lab. What modifications could you make in this experiment to reduce the error?

■ **Figure 15.7** In this endothermic reaction, the reacting mixture draws enough energy from the water and the board to lower the temperature of the water and the board to freezing.



Because you are interested in the heat given off by the chemical reaction going on inside the pack, it is convenient to think of the pack and its contents as the system. In thermochemistry, the **system** is the specific part of the universe that contains the reaction or process you wish to study. Everything in the universe other than the system is considered the **surroundings**. Therefore, the **universe** is defined as the system plus the surroundings.

$$\text{universe} = \text{system} + \text{surroundings}$$

What kind of energy transfer occurs during the exothermic heat-pack reaction? Heat produced by the reaction flows from the heat pack (the system) to your cold hands (part of the surroundings).

What happens in an endothermic reaction or process? The flow of heat is reversed. Heat flows from the surroundings to the system. When barium hydroxide and ammonium thiocyanate crystals, shown in **Figure 15.7**, are placed in a beaker and mixed, a highly endothermic reaction occurs. Placing the beaker on a wet board allows heat to flow from the water and board (the surroundings) into the beaker (the system). The temperature change is great enough that the beaker freezes to the board.

Enthalpy and enthalpy changes The total amount of energy a substance contains depends on many factors, some of which are still not completely understood. Therefore, it is impossible to know the total energy content of a substance. Fortunately, chemists are usually more interested in changes in energy during reactions than in the absolute amounts of energy contained in the reactants and products.

For many reactions, the amount of energy lost or gained can be measured conveniently in a calorimeter at constant pressure, as shown in the experiment in **Figure 15.6**. The foam cup is not sealed, so the pressure is constant. Many reactions take place at constant atmospheric pressure; for example, those that occur in living organisms on Earth's surface, in lakes and oceans, and those that take place in open beakers and flasks in the laboratory. The energy released or evolved from reactions carried out at constant pressure is sometimes given the symbol q_p . To more easily measure and study the energy changes that accompany such reactions, chemists have defined a property called enthalpy.

Enthalpy (H) is the heat content of a system at constant pressure.

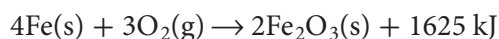
Although you cannot measure the actual energy or enthalpy of a substance, you can measure the change in enthalpy, which is the heat absorbed or released in a chemical reaction. The change in enthalpy for a reaction is called the **enthalpy (heat) of reaction** (ΔH_{rxn}). You have already learned that a symbol preceded by the Greek letter delta (Δ) means a change in the property. Thus, ΔH_{rxn} is the difference between the enthalpy of the substances that exist at the end of the reaction and the enthalpy of the substances present at the start.

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

Because the reactants are present at the beginning of the reaction and the products are present at the end, ΔH_{rxn} is defined by this equation.

$$\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$$

The sign of the enthalpy of reaction Recall the heat-pack reaction.



According to the equation, the reactants in this exothermic reaction lose heat. Therefore, $H_{\text{products}} < H_{\text{reactants}}$. When $H_{\text{reactants}}$ is subtracted from the smaller H_{products} , a negative value for ΔH_{rxn} results. Enthalpy changes for exothermic reactions are always negative. The equation for the heat-pack reaction and its enthalpy change are usually written as shown.



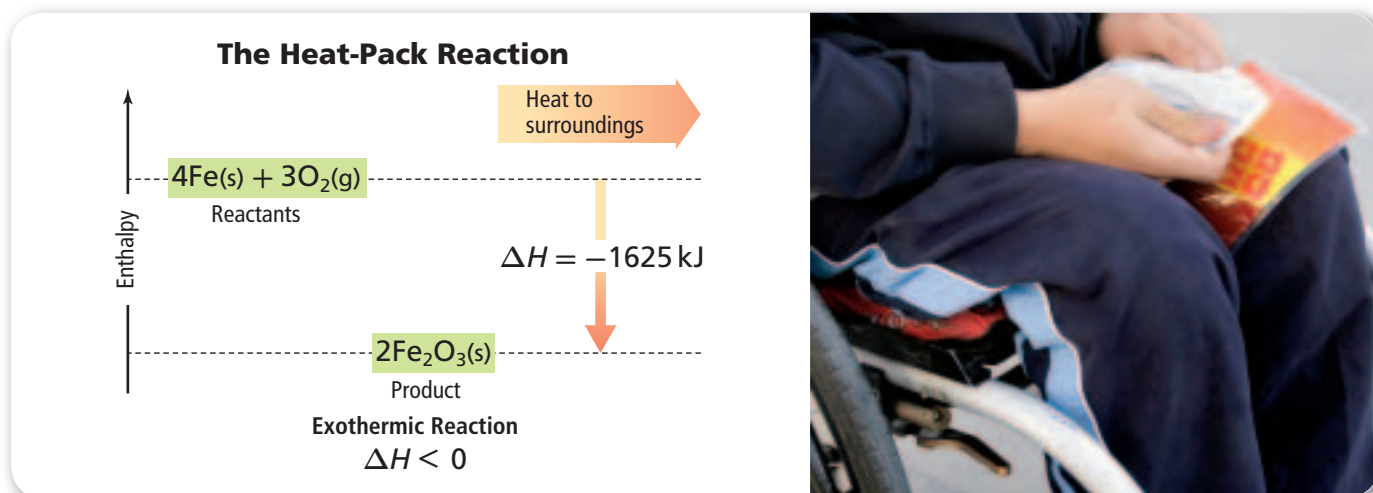
A diagram of the enthalpy change is shown in **Figure 15.8**.

Heating and Cooling Specialist

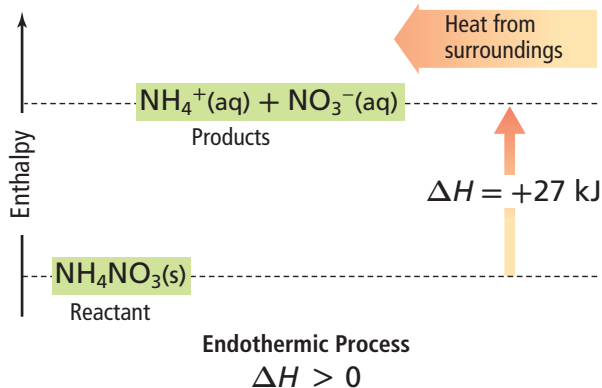
Heating and cooling system mechanics install, maintain, and repair refrigeration and heating equipment in homes and in industry. They must understand how heat is exchanged by means of exothermic and endothermic processes. They must be able to read blueprints and use a wide range of tools, from pipe cutters to computerized diagnostic devices. Such mechanics might specialize in one aspect of this field, or become proficient in all areas. For more information on chemistry careers, visit glencoe.com.

■ **Figure 15.8** The downward arrow shows that 1625 kJ of heat is released to the surroundings in the reaction between iron and oxygen to form Fe_2O_3 . A heat pack utilizing this reaction of iron and oxygen provides energy for warming cold hands.

Explain how the diagram shows that the reaction is exothermic.



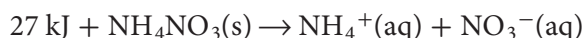
The Cold-Pack Process



■ **Figure 15.9** The upward arrow shows that 27 kJ of heat is absorbed from the surroundings in the process of dissolving NH_4NO_3 . This reaction is the basis for the cold pack. When the cold pack is placed on a person's ankle, his ankle supplies the required heat and is itself cooled.

Determine How many kilojoules per mol of ammonium nitrate are released when a cold pack is activated?

Now, recall the cold-pack process.



For this endothermic process, $H_{\text{products}} > H_{\text{reactants}}$. Therefore, when $H_{\text{reactants}}$ is subtracted from the larger H_{products} , a positive value for ΔH_{rxn} is obtained. Chemists write the equation for the cold-pack process and its enthalpy change in the following way.

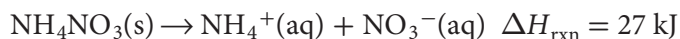


Figure 15.9 shows the energy change for the cold-pack process. In this process, the enthalpy of the products is 27 kJ greater than the enthalpy of the reactant because energy is absorbed. Thus, the sign of ΔH_{rxn} for this and all endothermic reactions and processes is positive. Recall that the sign of ΔH_{rxn} for all exothermic reactions is negative.

The enthalpy change, ΔH , is equal to q_p , the heat gained or lost in a reaction or process carried out at constant pressure. Because all reactions presented in this textbook occur at constant pressure, you might assume that $q = \Delta H_{\text{rxn}}$.

Section 15.2 Assessment

Section Summary

- ▶ In thermochemistry, the universe is defined as the system plus the surroundings.
- ▶ The heat lost or gained by a system during a reaction or process carried out at constant pressure is called the change in enthalpy (ΔH).
- ▶ When ΔH is positive, the reaction is endothermic. When ΔH is negative, the reaction is exothermic.

- ▶ **16. MAIN Idea** Describe how you would calculate the amount of heat absorbed or released by a substance when its temperature changes.
- ▶ **17. Explain** why ΔH for an exothermic reaction always has a negative value.
- ▶ **18. Explain** why a measured volume of water is an essential part of a calorimeter.
- ▶ **19. Explain** why you need to know the specific heat of a substance in order to calculate how much heat is gained or lost by the substance as a result of a temperature change.
- ▶ **20. Describe** what *the system* means in thermodynamics, and explain how the system is related to the surroundings and the universe.
- ▶ **21. Calculate** the specific heat in $\text{J}/(\text{g}\cdot^\circ\text{C})$ of an unknown substance if a 2.50-g sample releases 12.0 cal as its temperature changes from 25.0°C to 20.0°C .
- ▶ **22. Design an Experiment** Describe a procedure you could follow to determine the specific heat of a 45-g piece of metal.

Section 15.3

Objectives

- Write thermochemical equations for chemical reactions and other processes.
- Describe how energy is lost or gained during changes of state.
- Calculate the heat absorbed or released in a chemical reaction.

Review Vocabulary

combustion reaction: a chemical reaction that occurs when a substance reacts with oxygen, releasing energy in the form of heat and light

New Vocabulary

thermochemical equation
enthalpy (heat) of combustion
molar enthalpy (heat) of vaporization
molar enthalpy (heat) of fusion

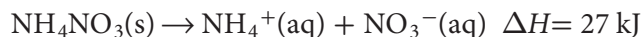
Thermochemical Equations

MAIN Idea Thermochemical equations express the amount of heat released or absorbed by chemical reactions.

Real-World Reading Link Have you ever been exhausted after a hard race or other strenuous activity? If you felt as if your body had less energy than before the event, you were right. That tired feeling relates to combustion reactions that occur in the cells of your body, the same combustion you might observe in the burning of a campfire.

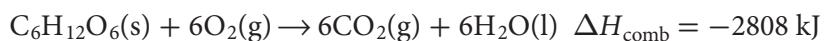
Writing Thermochemical Equations

The change in energy is an important part of chemical reactions, so chemists include ΔH as part of many chemical equations. The heat-pack and cold-pack equations are called thermochemical equations when they are written as follows.



A **thermochemical equation** is a balanced chemical equation that includes the physical states of all reactants and products and the energy change, usually expressed as the change in enthalpy, ΔH .

The highly exothermic combustion of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) occurs in the body as food is metabolized to produce energy. The thermochemical equation for the combustion of glucose is shown below.



The **enthalpy (heat) of combustion** (ΔH_{comb}) of a substance is the enthalpy change for the complete burning of one mole of the substance. Standard enthalpies of combustion for several substances are given in **Table 15.3**. Standard enthalpy changes have the symbol ΔH° . The zero superscript tells you that the enthalpy changes were determined with all reactants and products at standard conditions. Standard conditions are 1 atm pressure and 298 K (25°C) and should not be confused with standard temperature and pressure (STP).

Table 15.3

Standard Enthalpies of Combustion

Substance	Formula	$\Delta H_{\text{comb}}^\circ$ (kJ/mol)
Sucrose (table sugar)	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$	-5644
Octane (a component of gasoline)	$\text{C}_8\text{H}_{18}(l)$	-5471
Glucose (a simple sugar found in fruit)	$\text{C}_6\text{H}_{12}\text{O}_6(s)$	-2808
Propane (a gaseous fuel)	$\text{C}_3\text{H}_8(g)$	-2219
Methane (a gaseous fuel)	$\text{CH}_4(g)$	-891

Table 15.4

Standard Enthalpies of Vaporization and Fusion

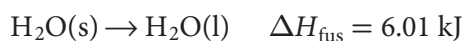
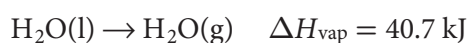
Substance	Formula	$\Delta H_{\text{vap}}^{\circ}$ (kJ/mol)	$\Delta H_{\text{fus}}^{\circ}$ (kJ/mol)
Water	H ₂ O	40.7	6.01
Ethanol	C ₂ H ₅ OH	38.6	4.94
Methanol	CH ₃ OH	35.2	3.22
Acetic acid	CH ₃ COOH	23.4	11.7
Ammonia	NH ₃	23.3	5.66

Changes of State

Many processes other than chemical reactions absorb or release heat. For example, think about what happens when you step out of a hot shower. You shiver as water evaporates from your skin. That is because your skin provides the heat needed to vaporize the water.

As heat is taken from your skin to vaporize the water, you cool down. The heat required to vaporize one mole of a liquid is called its **molar enthalpy (heat) of vaporization** (ΔH_{vap}). Similarly, if you want a glass of cold water, you might drop an ice cube into it. The water cools as it provides the heat to melt the ice. The heat required to melt one mole of a solid substance is called its **molar enthalpy (heat) of fusion** (ΔH_{fus}). Because vaporizing a liquid and melting a solid are endothermic processes, their ΔH values are positive. Standard molar enthalpies of vaporization and fusion for five common compounds are shown in **Table 15.4**.

Thermochemical equations for changes of state The vaporization of water and the melting of ice can be described by the following equations.



The first equation indicates that 40.7 kJ of energy is absorbed when one mole of water is converted to one mole of water vapor. The second equation indicates that 6.01 kJ of energy is absorbed when one mole of ice melts to form one mole of liquid water.

What happens in the reverse processes, when water vapor condenses to liquid water or liquid water freezes to ice? The same amounts of energy are released in these exothermic processes as are absorbed in the endothermic processes of vaporization and melting. Thus, the molar enthalpy (heat) of condensation (ΔH_{cond}) and the molar enthalpy of vaporization have the same numerical value but opposite signs. Similarly, the molar enthalpy (heat) of solidification (ΔH_{solid}) and the molar enthalpy of fusion have the same numerical value but opposite signs.

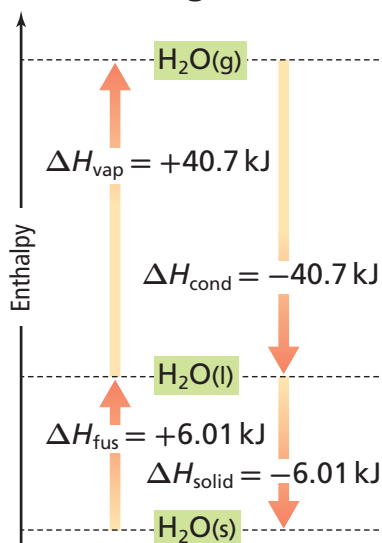
$$\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$$

$$\Delta H_{\text{fus}} = -\Delta H_{\text{solid}}$$

These relationships are illustrated in **Figure 15.10**.

■ **Figure 15.10** The upward arrows show that the energy of the system increases as water melts and then vaporizes. The downward arrows show that the energy of the system decreases as water condenses and then solidifies.

Phase Changes for Water




Concepts in Motion

Interactive Figure To see an animation of heat flow in endothermic and exothermic reactions, visit glencoe.com.

Compare the following equations for the condensation and freezing of water with the equations on the previous page for the vaporization and melting of water.



Some farmers make use of the heat of fusion of water to protect fruit and vegetables from freezing. If the temperature is predicted to drop to freezing, they flood their orchards or fields with water. When the water freezes, energy (ΔH_{fus}) is released and often warms the surrounding air enough to prevent frost damage. In the Problem-Solving Lab that follows, you will draw the heating curve of water and interpret it using the heats of fusion and vaporization.

 **Reading Check Categorize** condensation, solidification, vaporization, and fusion as exothermic or endothermic processes.

PROBLEM-SOLVING LAB

Make and Use Graphs

How can you derive the heating curve for water? Water molecules have a strong attraction to one another because they are polar. They form hydrogen bonds that affect water's properties. The polarity of water accounts for its high specific heat and relatively high enthalpies of fusion and vaporization.

Analysis

Use the data in the table to plot a heating curve of temperature versus time for a 180-g sample of water as it is heated at a constant rate from -20°C to 120°C . Draw a best-fit line through the points. Note the time required for water to pass through each segment of the graph.

Think Critically

- Analyze** each of the five regions of the graph, which are distinguished by an abrupt change in slope. Indicate how the absorption of heat changes the energy (kinetic and potential) of the water molecules.
- Calculate** the amount of heat required to pass through each region of the graph (180 g $\text{H}_2\text{O} = 10 \text{ mol H}_2\text{O}$, $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$, $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$, $c = 4.184 \text{ J/(g} \cdot ^\circ\text{C)}$). How does the length of time needed to pass through each region relate to the amount of heat absorbed?

Time and Temperature Data for Water

Time (min)	Temperature ($^\circ\text{C}$)	Time (min)	Temperature ($^\circ\text{C}$)
0.0	-20	13.0	100
1.0	0	14.0	100
2.0	0	15.0	100
3.0	9	16.0	100
4.0	26	17.0	100
5.0	42	18.0	100
6.0	58	19.0	100
7.0	71	20.0	100
8.0	83	21.0	100
9.0	92	22.0	100
10.0	98	23.0	100
11.0	100	24.0	100
12.0	100	25.0	120

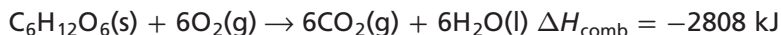
- Infer** What would the heating curve of ethanol look like? Ethanol melts at -114°C and boils at 78°C . Sketch ethanol's curve from -120°C to 90°C . What factors determine the lengths of the flat regions of the graph and the slope of the curve between the flat regions?

EXAMPLE PROBLEM 15.4

Math Handbook

Unit Conversion
pages 957–958

The Energy Released in a Reaction A bomb calorimeter is useful for measuring the energy released in combustion reactions. The reaction is carried out in a constant-volume bomb with a high pressure of oxygen. How much heat is evolved when 54.0 g glucose ($C_6H_{12}O_6$) is burned according to this equation?



1 Analyze the Problem

You are given a mass of glucose, the equation for the combustion of glucose, and ΔH_{comb} . You must convert grams of glucose to moles of glucose. Because the molar mass of glucose is more than three times the mass of glucose burned, you can predict that the energy evolved will be less than one-third ΔH_{comb} .

Known

mass of glucose = 54.0 g $C_6H_{12}O_6$
 $\Delta H_{\text{comb}} = -2808 \text{ kJ}$

Unknown

$q = ? \text{ kJ}$

2 Solve for the Unknown

Convert grams of $C_6H_{12}O_6$ to moles of $C_6H_{12}O_6$.

$$54.0 \text{ g } \cancel{C_6H_{12}O_6} \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.18 \text{ g } \cancel{C_6H_{12}O_6}} = 0.300 \text{ mol } C_6H_{12}O_6 \quad \text{Multiply by the inverse of molar mass, } \frac{1 \text{ mol}}{180.18 \text{ g}}$$

Multiply moles of $C_6H_{12}O_6$ by the enthalpy of combustion, ΔH_{comb} .

$$0.300 \text{ mol } \cancel{C_6H_{12}O_6} \times \frac{2808 \text{ kJ}}{1 \text{ mol } \cancel{C_6H_{12}O_6}} = \mathbf{842 \text{ kJ}} \quad \text{Multiply moles of glucose by } \frac{2808 \text{ kJ}}{1 \text{ mol } C_6H_{12}O_6}$$

3 Evaluate the Answer

All values in the calculation have at least three significant figures, so the answer is correctly stated with three digits. As predicted, the released energy is less than one-third ΔH_{comb} .

PRACTICE Problems

Extra Practice Page 986 and glencoe.com

- Calculate the heat required to melt 25.7 g of solid methanol at its melting point. Refer to **Table 15.4**.
- How much heat evolves when 275 g of ammonia gas condenses to a liquid at its boiling point? Use **Table 15.4** to determine ΔH_{cond} .
- Challenge** What mass of methane (CH_4) must be burned in order to liberate 12,880 kJ of heat? Refer to **Table 15.3** on page 529.

Connection to Biology When a mole of glucose is burned in a bomb calorimeter, 2808 kJ of energy is released. The same amount of energy is produced in your body when an equal mass of glucose is metabolized in the process of cellular respiration. The process takes place in every cell of your body in a series of complex steps in which glucose is broken down and carbon dioxide and water are released. These are the same products produced by the combustion of glucose in a calorimeter. The energy released is stored as chemical potential energy in the bonds of molecules of adenosine triphosphate (ATP). When energy is needed by any part of the body, molecules of ATP release their energy.

Combustion Reactions

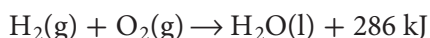
Combustion is the reaction of a fuel with oxygen. In biological systems, food is the fuel. **Figure 15.11** illustrates some of the many foods that contain glucose as well as other foods that contain carbohydrates that are readily converted to glucose in your body. You also depend on other combustion reactions to keep you warm or cool, and to transport you in vehicles. One way you might heat your home or cook your food is by burning methane gas. The combustion of one mole of methane produces 891 kJ according to this equation.



Most vehicles—cars, airplanes, boats, and trucks—run on the combustion of gasoline, which is mostly octane (C_8H_{18}). **Table 15.3** on page 529 shows that the burning of one mole of octane produces 5471 kJ. The equation for the combustion of gasoline is as follows.



Another combustion reaction is the reaction between hydrogen and oxygen.



The combustion of hydrogen provides the energy to lift the shuttle into space, as illustrated on the opening page of this chapter.

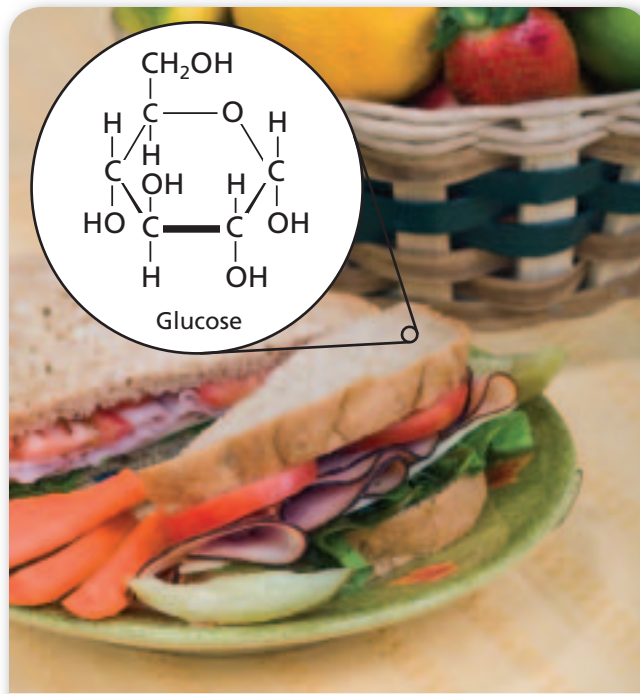


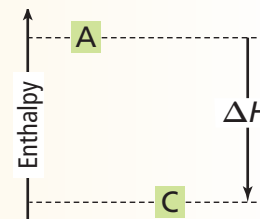
Figure 15.11 These foods are fuels for the body. They provide the glucose that is burned to produce 2808 kJ/mol to carry on the activities of life.

Section 15.3 Assessment

Section Summary

- A thermochemical equation includes the physical states of the reactants and products and specifies the change in enthalpy.
- The molar enthalpy (heat) of vaporization, ΔH_{vap} , is the amount of energy required to evaporate one mole of a liquid.
- The molar enthalpy (heat) of fusion, ΔH_{fus} , is the amount of energy needed to melt one mole of a solid.

- **26. MAIN Idea** Write a complete thermochemical equation for the combustion of ethanol ($\text{C}_2\text{H}_5\text{OH}$). $\Delta H_{\text{comb}} = -1367 \text{ kJ/mol}$
- **27. Determine** Which of the following processes are exothermic? Endothermic?
 - a. $\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$
 - b. $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{s})$
 - c. $\text{C}_5\text{H}_{12}(\text{g}) + 8\text{O}_2(\text{g}) \rightarrow 5\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
 - d. $\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{l})$
 - e. $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{l})$
- **28. Explain** how you could calculate the heat released in freezing 0.250 mol water.
- **29. Calculate** How much heat is released by the combustion of 206 g of hydrogen gas? $\Delta H_{\text{comb}} = -286 \text{ kJ/mol}$
- **30. Apply** The molar heat of vaporization of ammonia is 23.3 kJ/mol. What is the molar heat of condensation of ammonia?
- **31. Interpret Scientific Illustrations** The reaction $\text{A} \rightarrow \text{C}$ is shown in the enthalpy diagram at right. Is the reaction exothermic or endothermic? Explain your answer.



Section 15.4

Objectives

- ▶ **Apply** Hess's law to calculate the enthalpy change for a reaction.
- ▶ **Explain** the basis for the table of standard enthalpies of formation.
- ▶ **Calculate** ΔH_{rxn} using thermochemical equations.
- ▶ **Determine** the enthalpy change for a reaction using standard enthalpies of formation data.

Review Vocabulary

allotrope: one of two or more forms of an element with different structures and properties when they are in the same state

New Vocabulary

Hess's law
standard enthalpy (heat) of formation

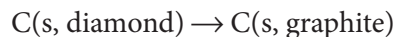
Calculating Enthalpy Change

MAIN Idea The enthalpy change for a reaction can be calculated using Hess's law.

Real-World Reading Link Maybe you have watched a two-act play or a two-part TV show. Each part tells some of the story, but you have to see both parts to understand the entire story. Like such a play or show, some reactions are best understood when you view them as the sum of two or more simpler reactions.

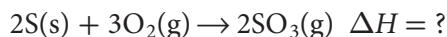
Hess's Law

Sometimes it is impossible or impractical to measure the ΔH of a reaction by using a calorimeter. Consider the reaction in **Figure 15.12**, the conversion of carbon in its allotropic form, diamond, to carbon in its allotropic form, graphite.



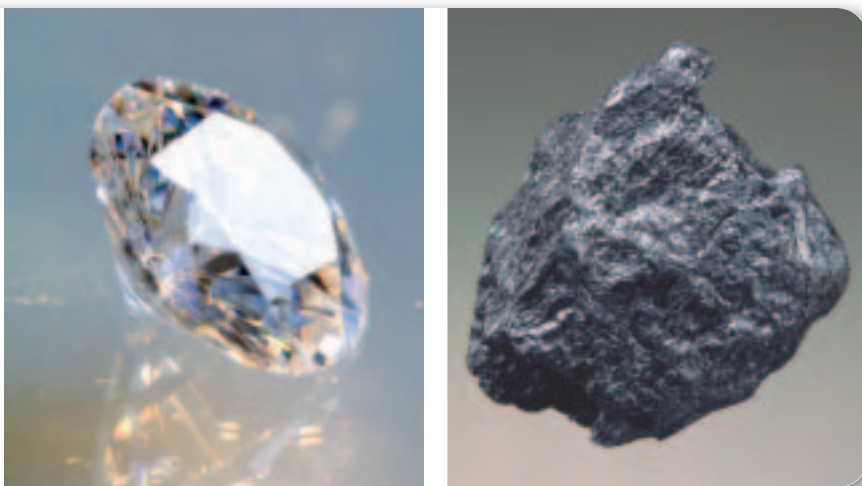
This reaction occurs so slowly that measuring the enthalpy change is impossible. Other reactions occur under conditions difficult to duplicate in a laboratory. Still others produce products other than the desired ones. For these reactions, chemists use a theoretical way to determine ΔH .

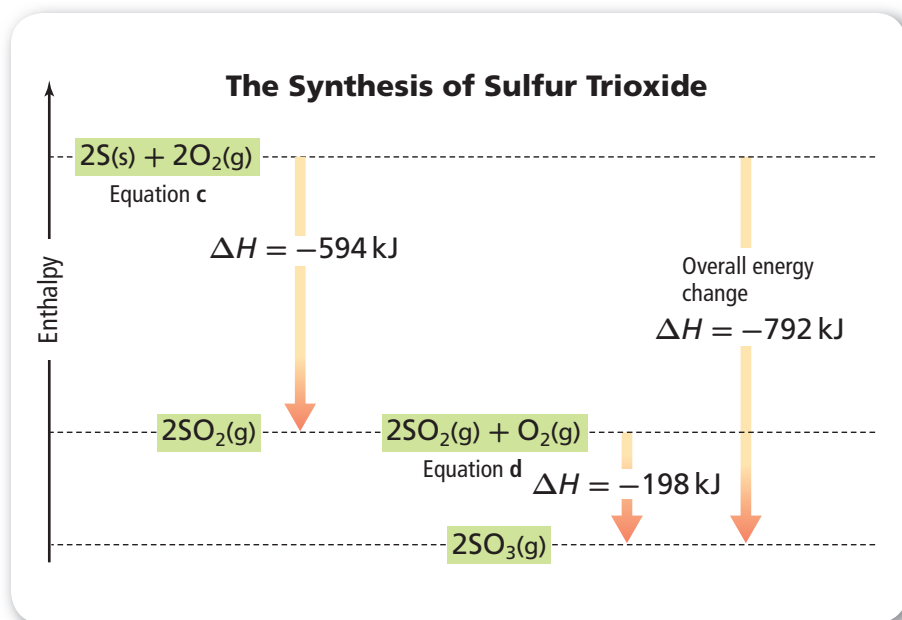
Suppose you are studying the formation of sulfur trioxide in the atmosphere. You would need to determine ΔH for this reaction.



Unfortunately, laboratory experiments to produce sulfur trioxide and determine its ΔH result in a mixture of products that is mostly sulfur dioxide (SO_2). In situations such as this, you can calculate ΔH by using Hess's law of heat summation. **Hess's law** states that if you can add two or more thermochemical equations to produce a final equation for a reaction, then the sum of the enthalpy changes for the individual reactions is the enthalpy change for the final reaction.

■ **Figure 15.12** The expression "diamonds are forever" suggests the durability of diamonds and tells you that the conversion of diamond to graphite is so slow that it would be impossible to measure its enthalpy change.

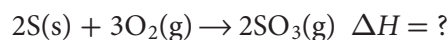




■ **Figure 15.13** The arrow on the left indicates the release of 594 kJ as S and O₂ react to form SO₂ (Equation **c**). Then, SO₂ and O₂ react to form SO₃ (Equation **d**) with the release of 198 kJ (middle arrow). The overall energy change (the sum of the two processes) is shown by the arrow on the right.

Determine the enthalpy change for the decomposition of SO₃ to S and O₂.

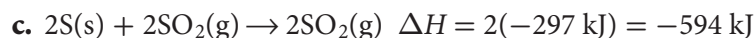
Applying Hess's law How can Hess's law be used to calculate the energy change for the reaction that produces SO₃?



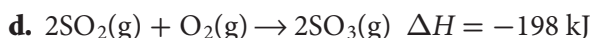
Step 1 Chemical equations are needed that contain the substances found in the desired equation and have known enthalpy changes. The following equations contain S, O₂, and SO₃.

- a. $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \quad \Delta H = -297 \text{ kJ}$
- b. $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = 198 \text{ kJ}$

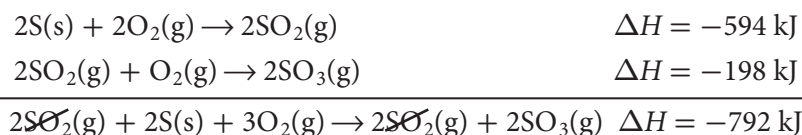
Step 2 The desired equation shows two moles of sulfur reacting, so rewrite Equation **a** for two moles of sulfur by multiplying the coefficients by two. Double the enthalpy change, ΔH because twice the energy will be released if two moles of sulfur react. With these changes, Equation **a** becomes the following (Equation **c**).



Step 3 In the desired equation, sulfur trioxide is a product rather than a reactant, so reverse Equation **b**. When you reverse an equation, you must also change the sign of its ΔH . Equation **b** then becomes Equation **d**.



Step 4 Add Equations **c** and **d** to obtain the desired reaction. Add the corresponding ΔH values. Cancel any terms that are common to both sides of the combined equation.



The thermochemical equation for the burning of sulfur to form sulfur trioxide is as follows. **Figure 15.13** diagrams the energy changes.



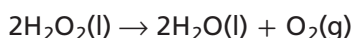
Thermochemical equations are usually written and balanced for one mole of product. Often, that means that fractional coefficients must be used. For example, the thermochemical equation for the reaction between sulfur and oxygen to form one mole of sulfur trioxide is the following.



Reading Check Compare the equation above with the thermochemical equation developed on the previous page. How are they different?

EXAMPLE PROBLEM 15.5

Hess's Law Use thermochemical Equations **a** and **b** below to determine ΔH for the decomposition of hydrogen peroxide (H_2O_2), a compound that has many uses ranging from bleaching hair to powering rocket engines.



- a.** $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)} \quad \Delta H = -572 \text{ kJ}$
b. $\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O}_2\text{(l)} \quad \Delta H = -188 \text{ kJ}$

1 Analyze the Problem

You have been given two chemical equations and their enthalpy changes. These two equations contain all the substances found in the desired equation.

Known

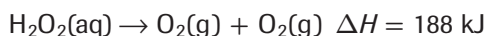
- a.** $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)} \quad \Delta H = -572 \text{ kJ}$
b. $\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O}_2\text{(l)} \quad \Delta H = -188 \text{ kJ}$

Unknown

$$\Delta H = ? \text{ kJ}$$

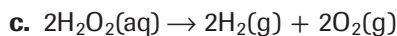
2 Solve for the Unknown

H_2O_2 is a reactant.



Reverse Equation **b** and change the sign of ΔH .

Two moles of H_2O_2 are needed.

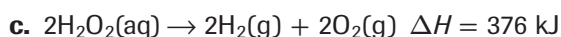


Multiply the reversed Equation **b** by two to obtain Equation **c**.

$$\Delta H \text{ for Equation c} = (188\text{kJ})(2)$$

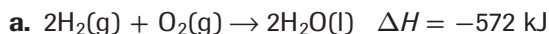
Multiply 188 kJ by two to obtain ΔH for Equation **c**.

$$= 376 \text{ kJ}$$

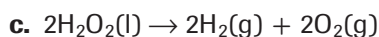


Write Equation **c** and ΔH .

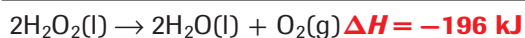
Add Equations **a** and **c**, canceling any terms common to both sides of the combined equation. Add the enthalpies of Equations **a** and **c**.



Write Equation **a**.



$$\Delta H = 376 \text{ kJ} \quad \text{Write Equation c.}$$

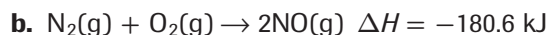
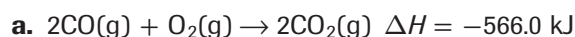


Add Equations **a** and **c**. Add the enthalpies.

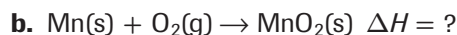
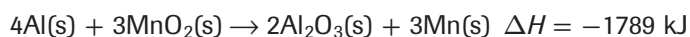
3 Evaluate the Answer

The two equations produce the desired equation. All values are accurate to the ones place, so ΔH is correctly stated.

32. Use Equations **a** and **b** to determine ΔH for the following reaction.



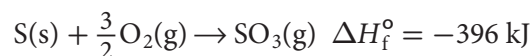
33. **Challenge** ΔH for the following reaction is -1789 kJ . Use this and Equation **a** to determine ΔH for Equation **b**.



Standard Enthalpy (Heat) of Formation

Hess's law allows you to calculate unknown ΔH values using known reactions and their experimentally determined ΔH values. However, recording ΔH values for all known chemical reactions would be a huge and unending task. Instead, scientists record and use enthalpy changes for only one type of reaction—a reaction in which a compound is formed from its elements in their standard states. The standard state of a substance means the normal physical state of the substance at 1 atm and 298 K (25°C). For example, in their standard states, iron is a solid, mercury is a liquid, and oxygen is a diatomic gas.

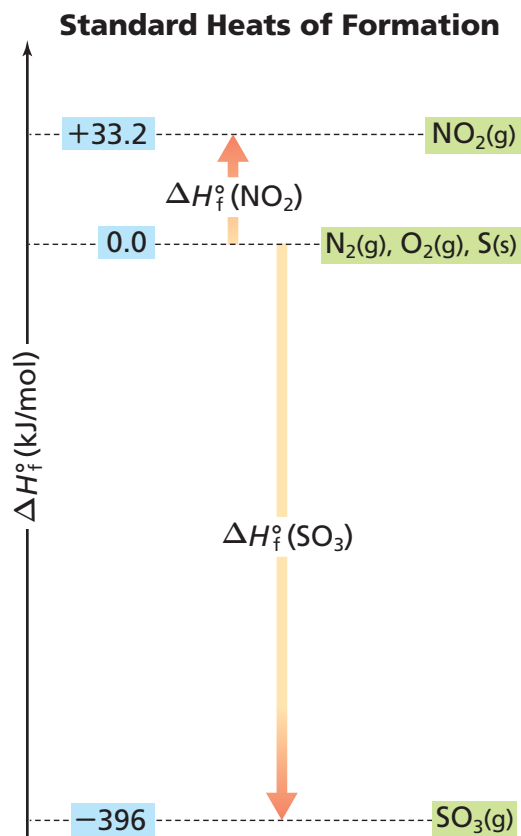
The ΔH value for such a reaction is called the standard enthalpy (heat) of formation of the compound. The **standard enthalpy (heat) of formation** (ΔH_f°) is defined as the change in enthalpy that accompanies the formation of one mole of the compound in its standard state from its elements in their standard states. A typical standard heat of formation reaction is the formation of one mole of SO_3 from its elements.



The product of this equation is SO_3 , a suffocating gas that produces acid rain when mixed with moisture in the atmosphere. The destructive results of acid precipitation are shown in **Figure 15.14**.



■ **Figure 15.14** Sulfur trioxide combines with water in the atmosphere to form sulfuric acid (H_2SO_4), a strong acid, which reaches Earth as acid precipitation. Acid precipitation slowly destroys trees and property.



■ **Figure 15.15** ΔH_f° for the elements N_2 , O_2 , and S is 0.0 kJ. When N_2 and O_2 react to form 1 mole of NO_2 , 33.2 kJ is absorbed. Thus, ΔH_f° for NO_2 is $+33.2$ kJ/mol. When S and O_2 react to form one mole of SO_3 , 396 kJ is released. Therefore, ΔH_f° for SO_3 is -396 kJ/mol.

Predict Describe the approximate location of water on the scale. The heat of formation for the reaction $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ is $\Delta H_f^\circ = -286$ kJ/mol.

Where do standard heats of formation come from?

When you state the height of a mountain, you do so relative to some point of reference—usually sea level. In a similar way, standard enthalpies of formation are stated based on the following assumption: Elements in their standard state have a ΔH_f° of 0.0 kJ. With zero as the starting point, the experimentally determined enthalpies of formation of compounds can be placed on a scale above and below the elements in their standard states. Think of the zero of the enthalpy scale as being similar to the arbitrary assignment of 0.0°C to the freezing point of water. All substances warmer than freezing water have a temperature above zero. All substances colder than freezing water have a temperature below zero.

Enthalpies of formation from experiments

Standard enthalpies of formation of many compounds have been measured experimentally. For example, consider the equation for the formation of nitrogen dioxide.



The elements nitrogen and oxygen are diatomic gases in their standard states, so their standard enthalpies of formation are zero. When nitrogen and oxygen gases react to form one mole of nitrogen dioxide, the experimentally determined ΔH for the reaction is $+33.2$ kJ. That means that 33.2 kJ of energy is absorbed in this endothermic reaction. The energy content of the product NO_2 is 33.2 kJ greater than the energy content of the reactants. On a scale on which ΔH_f° of reactants is 0.0 kJ, ΔH_f° of NO_2 is $+33.2$ kJ. **Figure 15.15** shows that on the scale of standard enthalpies of formation, NO_2 is placed 33.2 kJ above the elements from which it was formed. Sulfur trioxide (SO_3) is placed 396 kJ below zero on the scale because the formation of $\text{SO}_3(\text{g})$ is an exothermic reaction. The energy content of the sulfur trioxide, ΔH_f° , is -396 kJ. **Table 15.5** lists standard enthalpies of formation for some common compounds. A more complete list is in **Table R-11** on page 975.

Table 15.5 Standard Enthalpies of Formation

Compound	Formation Equation	$\Delta H_f^\circ(\text{kJ/mol})$
$\text{H}_2\text{S}(\text{g})$	$\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g})$	-21
$\text{HF}(\text{g})$	$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g})$	-273
$\text{SO}_3(\text{g})$	$\text{S}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$	-396
$\text{SF}_6(\text{g})$	$\text{S}(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow \text{SF}_6(\text{g})$	-1220



■ **Figure 15.16** Sulfur hexafluoride is used to etch minute and sometimes intricate patterns on silicon wafers in the production of semiconductor devices. Semiconductors are important components of modern electronic equipment, including computers, cell phones, and MP3 players.

Using standard enthalpies of formation Standard enthalpies of formation can be used to calculate the enthalpies of many reactions under standard conditions $\Delta H_{\text{rxn}}^{\circ}$ using Hess's law. Suppose you want to calculate $\Delta H_{\text{rxn}}^{\circ}$ for a reaction that produces sulfur hexafluoride. Sulfur hexafluoride is a stable, unreactive gas with some interesting applications, one of which is shown in **Figure 15.16**.

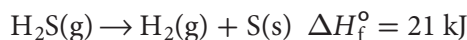


Step 1 Refer to **Table 15.5** to find an equation for the formation of each of the three compounds in the desired equation—HF, SF₆, and H₂S.

- a. $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{HF}(\text{g}) \quad \Delta H_f^{\circ} = -273 \text{ kJ}$
 b. $\text{S}(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow \text{SF}_6(\text{g}) \quad \Delta H_f^{\circ} = -1220 \text{ kJ}$
 c. $\text{H}_2(\text{g}) + \text{S}(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g}) \quad \Delta H_f^{\circ} = -21 \text{ kJ}$

Step 2 Equations **a** and **b** describe the formation of the products HF and SF₆ in the desired equation, so use Equations **a** and **b** in the direction in which they are written.

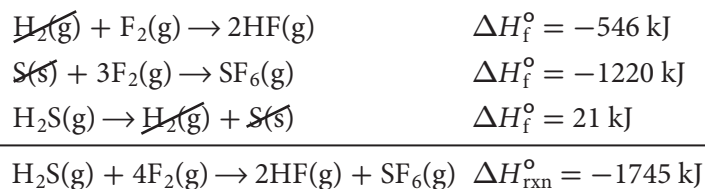
Equation **c** describes the formation of a product, H₂S, but in the desired equation, H₂S is a reactant. Reverse Equation **c** and change the sign of its ΔH_f° .



Step 3 Two moles of HF are required. Multiply Equation **a** and its enthalpy change by two.



Step 4 Add the three equations and their enthalpy changes. The elements H₂ and S cancel.



The summation equation The stepwise procedure you have just read about shows how standard heats of formation equations combine to produce the desired equation and its $\Delta H_{\text{rxn}}^{\circ}$. The procedure can be summed up in the following formula.

Summation Equation

$$\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{f}}^{\circ}(\text{products}) - \Sigma \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

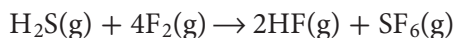
$\Delta H_{\text{rxn}}^{\circ}$ represents the standard enthalpy of the reaction.

Σ represents the sum of the terms.

$\Delta H_{\text{f}}^{\circ}(\text{products})$ and $\Delta H_{\text{f}}^{\circ}(\text{reactants})$ represent the standard enthalpies of formation of all the products and all the reactants.

$\Delta H_{\text{rxn}}^{\circ}$ is obtained by subtracting the sum of heats of formation of the reactants from the sum of the heats of formation of the products.

You can see how this formula applies to the reaction between hydrogen sulfide and fluorine.



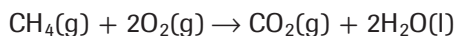
$$\Delta H_{\text{rxn}}^{\circ} = [(2)\Delta H_{\text{f}}^{\circ}(\text{HF}) + \Delta H_{\text{f}}^{\circ}(\text{SF}_6)] - [\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{S}) + (4)\Delta H_{\text{f}}^{\circ}(\text{F}_2)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(2)(-273 \text{ kJ}) + (-1220 \text{ kJ})] - [-21 \text{ kJ} + (4)(0.0 \text{ kJ})]$$

$$\Delta H_{\text{rxn}}^{\circ} = -1745 \text{ kJ}$$

EXAMPLE PROBLEM 15.6

Enthalpy Change from Standard Enthalpies of Formation Use standard enthalpies of formation to calculate $\Delta H_{\text{rxn}}^{\circ}$ for the combustion of methane.



1 Analyze the Problem

You are given an equation and asked to calculate the change in enthalpy. The formula $\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{f}}^{\circ}(\text{products}) - \Sigma \Delta H_{\text{f}}^{\circ}(\text{reactants})$ can be used with data from **Table R-11** on page 975.

Known

$$\Delta H_{\text{f}}^{\circ}(\text{CO}_2) = -394 \text{ kJ}$$

$$\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}) = -286 \text{ kJ}$$

$$\Delta H_{\text{f}}^{\circ}(\text{CH}_4) = -75 \text{ kJ}$$

$$\Delta H_{\text{f}}^{\circ}(\text{O}_2) = 0.0 \text{ kJ}$$

Unknown

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

2 Solve for the Unknown

Use the formula $\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_{\text{f}}^{\circ}(\text{products}) - \Sigma \Delta H_{\text{f}}^{\circ}(\text{reactants})$.

Expand the formula to include a term for each reactant and product. Multiply each term by the coefficient of the substance in the balanced chemical equation.

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(\text{CO}_2) + (2)\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O})] - [\Delta H_{\text{f}}^{\circ}(\text{CH}_4) + (2)\Delta H_{\text{f}}^{\circ}(\text{O}_2)]$$

Substitute CO_2 and H_2O for the products, CH_4 and O_2 for the reactants. Multiply H_2O and O_2 by two.

$$\Delta H_{\text{rxn}}^{\circ} = [(-394 \text{ kJ}) + (2)(-286 \text{ kJ})] - [(-75 \text{ kJ}) + (2)(0.0 \text{ kJ})]$$

Substitute $\Delta H_{\text{f}}^{\circ}(\text{CO}_2) = -394 \text{ kJ}$, $\Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O}) = -286 \text{ kJ}$, $\Delta H_{\text{f}}^{\circ}(\text{CH}_4) = -75 \text{ kJ}$, and $\Delta H_{\text{f}}^{\circ}(\text{O}_2) = 0.0 \text{ kJ}$ into the equation.

$$\Delta H_{\text{rxn}}^{\circ} = [-966 \text{ kJ}] - [-75 \text{ kJ}] = -966 \text{ kJ} + 75 \text{ kJ} = -891 \text{ kJ}$$

The combustion of 1 mol CH_4 releases 891 kJ.

Math Handbook

Solving Algebraic Equations
pages 954–955

E Evaluate the Answer

All values are accurate to the ones place. Therefore, the answer is correct as stated. The calculated value is the same as that given in **Table 15.3**. You can check your answer by using the stepwise procedure on page 535.

PRACTICE Problems

Extra Practice Page 986 and glencoe.com

- 34.** Show how the sum of enthalpy of formation equations produces each of the following reactions. You do not need to look up and include ΔH values.
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
 - $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$
- 35.** Use standard enthalpies of formation from **Table R-11** on page 975 to calculate $\Delta H_{\text{rxn}}^\circ$ for the following reaction.
- $$4\text{NH}_3(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$
- 36.** Determine $\Delta H_{\text{comb}}^\circ$ for butanoic acid, $\text{C}_3\text{H}_7\text{COOH}(\text{l}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$. Use data in **Table R-11** on page 975 and the following equation.
- $$4\text{C}(\text{s}) + 4\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{C}_3\text{H}_7\text{COOH}(\text{l}) \quad \Delta H = -534 \text{ kJ}$$
- 37. Challenge** Two enthalpy of formation equations, **a** and **b**, combine to form the equation for the reaction of nitrogen oxide and oxygen. The product of the reaction is nitrogen dioxide: $\text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H_{\text{rxn}}^\circ = -58.1 \text{ kJ}$
- $\frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g}) \quad \Delta H_f^\circ = 91.3 \text{ kJ}$
 - $\frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H_f^\circ = ?$
- What is ΔH_f° for Equation **b**?

Section 15.4 Assessment

Section Summary

- The enthalpy change for a reaction can be calculated by adding two or more thermochemical equations and their enthalpy changes.
- Standard enthalpies of formation of compounds are determined relative to the assigned enthalpy of formation of the elements in their standard states.

- MAIN Idea Explain** what is meant by Hess's law and how it is used to determine $\Delta H_{\text{rxn}}^\circ$.
- Explain** in words the formula that can be used to determine $\Delta H_{\text{rxn}}^\circ$ when using Hess's law.
- Describe** how the elements in their standard states are defined on the scale of standard enthalpies of formations.
- Examine** the data in **Table 15.5** on page 538. What conclusion can you draw about the stabilities of the compounds listed relative to the elements in their standard states? Recall that low energy is associated with stability.
- Calculate** Use Hess's law to determine ΔH for the reaction $\text{NO}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H = ?$ given the following reactions. Show your work.
 $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g}) \quad \Delta H = +495 \text{ kJ}$
 $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g}) \quad \Delta H = -427 \text{ kJ}$
 $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = -199 \text{ kJ}$
- Interpret Scientific Illustrations** Use the data below to draw a diagram of standard heats of formation similar to **Figure 15.15** on page 538 and use your diagram to determine the heat of vaporization of water at 298 K.
Liquid water: $\Delta H_f^\circ = -285.8 \text{ kJ/mol}$
Gaseous water: $\Delta H_f^\circ = -241.8 \text{ kJ/mol}$

Section 15.5

Objectives

- ▶ **Differentiate** between spontaneous and nonspontaneous processes.
- ▶ **Explain** how changes in entropy and free energy determine the spontaneity of chemical reactions and other processes.

Review Vocabulary

vaporization: the energy-requiring process by which a liquid changes to a gas or vapor

New Vocabulary

spontaneous process
entropy
second law of thermodynamics
free energy

Reaction Spontaneity

MAIN Idea Changes in enthalpy and entropy determine whether a process is spontaneous.

Real-World Reading Link How is it that some newer buildings appear to be falling apart when others that are much older seem to stand forever? It might be the level of maintenance and work put into them. Similarly, in chemistry, without a constant influx of energy, there is a natural tendency toward disorder.

Spontaneous Processes

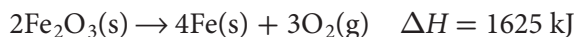
In **Figure 15.17** you can see a familiar picture of what happens to an iron object when it is left outdoors in moist air. Iron rusts slowly according to the same chemical equation that describes what happens in the heat pack you read about earlier in the chapter.



The heat pack goes into action the moment you activate it. Similarly, unprotected iron objects rust whether you want them to or not.

Rusting is spontaneous. Any physical or chemical change that once begun, occurs with no outside intervention is a **spontaneous process**. However, for many spontaneous processes, some energy from the surroundings must be supplied to get the process started. For example, you might use a match to light a Bunsen burner in your school lab.

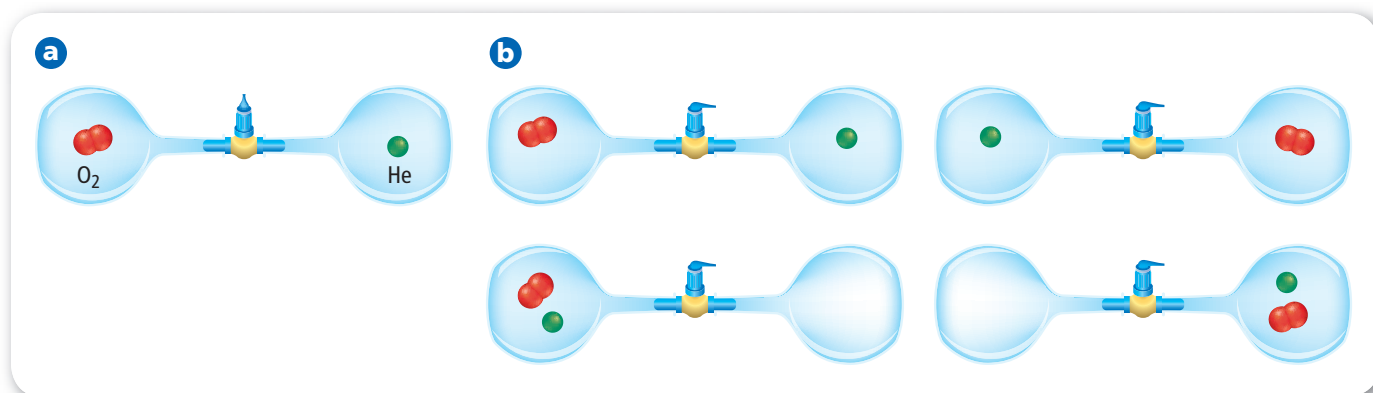
Suppose you reverse the direction of the equation for the rusting of iron. Recall that when you change the direction of a reaction, the sign of ΔH changes. The reaction becomes endothermic.



Reversing the equation will not make rust decompose spontaneously into iron and oxygen under ordinary conditions. The equation represents a reaction that is not spontaneous.

■ **Figure 15.17** Left unattended, with abundant water and oxygen in the air, the iron in this boat spontaneously converts to rust (Fe_2O_3).





The formation of rust on iron is an exothermic and spontaneous reaction. The reverse reaction is endothermic and nonspontaneous. You might conclude that all exothermic processes are spontaneous and all endothermic processes are nonspontaneous. But remember that ice melting at room temperature is a spontaneous, endothermic process. Something other than ΔH plays a role in determining whether a chemical process occurs spontaneously under a given set of conditions. That something is called entropy.

What is entropy? You're probably not surprised when the smell of brownies baking in the kitchen wafts to wherever you are in your home. And you know that gases tend to spread throughout Earth's atmosphere. Why do gases behave this way? When gases spread out, a system reaches a state of maximum entropy. **Entropy** (S) is a measure of the number of possible ways that the energy of a system can be distributed, and this is related to the freedom of the system's particles to move and number of ways they can be arranged.

Consider the two bulbs in **Figure 15.18**. When the stopcock is closed, one bulb contains a single molecule of oxygen. The other contains one atom of helium. When the stopcock is opened, the gas particles pass freely between the bulbs. Each gas particle can spread out into twice its original volume. The particles might be found in any of the four arrangements shown. The entropy of the system is greater with the stopcock open because the number of possible arrangements of the particles and the distribution of their energies is increased.

As the number of particles increases, the number of possible arrangements for a group of particles increases dramatically. If the two bulbs contained a total of ten particles, the number of possible arrangements would be 1024 times more than if the particles were confined to a single bulb. In general, the number of possible arrangements available to a system increases under the following conditions: when volume increases, when energy increases, when the number of particles increases, or when the particles' freedom of movement increases.

The second law of thermodynamics The tendency toward increased entropy is summarized in the **second law of thermodynamics**, which states that spontaneous processes always proceed in such a way that the entropy of the universe increases. Entropy is sometimes considered to be a measure of the disorder or randomness of the particles that make up a system. Particles that are more spread out are said to be more disordered, causing the system to have greater entropy than when the particles are closer together.

■ **Figure 15.18** In **a**, an oxygen molecule and a helium atom are each confined to a single bulb. When the stopcock is opened in **b**, the gas particles move freely into the double volume available. Four arrangements of the particles, which represent an increase in entropy, are possible at any given time.

VOCABULARY

SCIENCE USAGE V. COMMON USAGE

System

Science usage: the particular reaction or process being studied

The universe consists of the system and the surroundings.

Common usage: an organized or established procedure

She worked out a system in which everyone would have an equal opportunity.



Personal Tutor For an online tutorial on probability, visit glencoe.com.

Predicting changes in entropy Recall that the change in enthalpy for a reaction is equal to the enthalpy of the products minus the enthalpy of the reactants. The change in entropy (ΔS) during a reaction or process is similar.

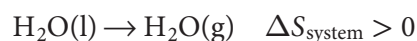
$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

If the entropy of a system increases during a reaction or process, $S_{\text{products}} > S_{\text{reactants}}$ and ΔS_{system} is positive. Conversely, if the entropy of a system decreases during a reaction or process, $S_{\text{products}} < S_{\text{reactants}}$ and ΔS_{system} is negative.

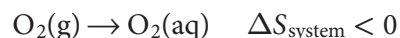
You can sometimes predict if ΔS_{system} is positive or negative by examining the equation for a reaction or process.

1. *Entropy changes associated with changes in state can be predicted.*

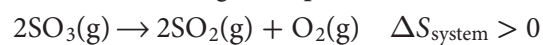
In solids, molecules have limited movement. In liquids, they have some freedom to move, and in gases, molecules can move freely within their container. Thus, entropy increases as a substance changes from a solid to a liquid and from a liquid to a gas. ΔS_{system} is positive as water vaporizes and methanol melts.



2. *The dissolving of a gas in a solvent always results in a decrease in entropy.* Gas particles have more entropy when they can move freely than when they are dissolved in a liquid or solid that limits their movements and randomness. ΔS_{system} is negative for the dissolving of oxygen in water as shown in **Figure 15.19**.



3. *Assuming no change in physical state occurs, the entropy of a system usually increases when the number of gaseous product particles is greater than the number of gaseous reactant particles.* For the following reaction, ΔS_{system} is positive because two molecules of gas react and three molecules of gas are produced.



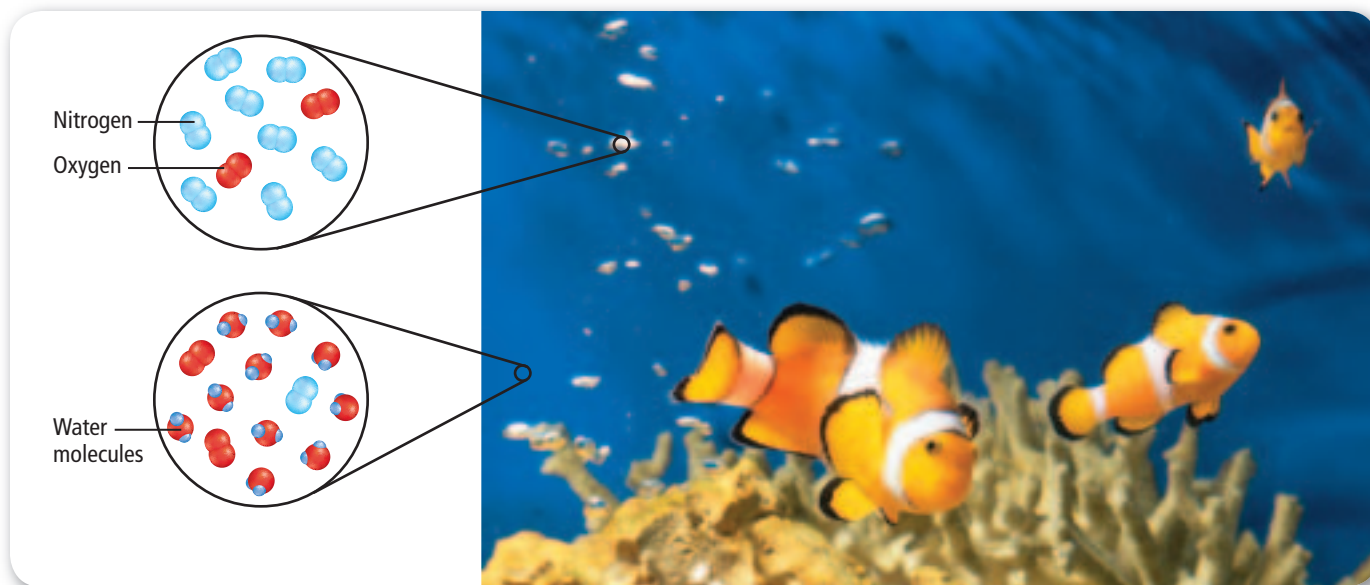
VOCABULARY

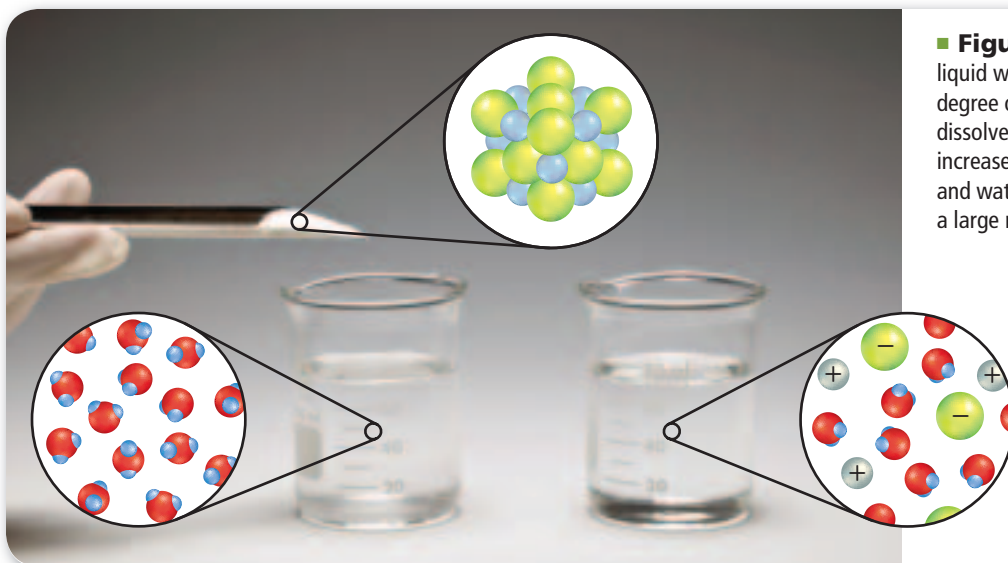
WORD ORIGIN

Random

comes from the Germanic word *rinnan*, meaning to run—a haphazard course

■ **Figure 15.19** In the bubbles, the nitrogen and oxygen gas molecules that make up most of the air can move more freely than when dissolved in the aquarium water.





■ **Figure 15.20** Sodium chloride and liquid water are pure substances, each with a degree of orderliness. When sodium chloride dissolves in water, the entropy of the system increases because sodium ions, chloride ions, and water molecules mix together to create a large number of random arrangements.

4. *With some exceptions, entropy increases when a solid or a liquid dissolves in a solvent.* The solute particles, which are together before dissolving, become dispersed throughout the solvent. The solute particles have more freedom of movement, as shown in **Figure 15.20** for the dissolving of sodium chloride in water. ΔS_{system} is positive.



5. *The random motion of the particles of a substance increases as its temperature increases.* Recall that the kinetic energy of molecules increases with temperature. Increased kinetic energy means faster movement and more possible arrangements of particles. Therefore, the entropy of any substance increases as its temperature increases. ΔS_{system} is positive.

PRACTICE Problems

Extra Practice Page 987 and glencoe.com

44. Predict the sign of ΔS_{system} for each of the following changes.
- | | |
|--|--|
| a. $\text{ClF(g)} + \text{F}_2(\text{g}) \rightarrow \text{ClF}_3(\text{g})$ | c. $\text{CH}_3\text{OH(l)} \rightarrow \text{CH}_3\text{OH(aq)}$ |
| b. $\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{aq})$ | d. $\text{C}_{10}\text{H}_8(\text{l}) \rightarrow \text{C}_{10}\text{H}_8(\text{s})$ |
45. **Challenge** Comment on the sign of ΔS_{system} for the following reaction.
 $\text{Fe(s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Zn(s)}$

Connection to Earth Science **Earth's spontaneous processes**

Volcanoes, fumaroles, hot springs, and geysers are evidence of geothermal energy in Earth's interior. Volcanoes are vents in Earth's crust from which molten rock (magma), steam, and other materials flow. When surface water moves downward through Earth's crust, it can interact with magma and/or hot rocks. Water that comes back to the surface in hot springs is heated to temperatures much higher than the surrounding air temperatures. Geysers are hot springs that spout hot water and steam into the air. Fumaroles emit steam and other gases, such as hydrogen sulfide. These geothermal processes are obviously spontaneous. Can you identify increases in entropy in these Earth processes?



■ **Figure 15.21** It is difficult to recognize this ancient Greek sculpture as the head of a lion. The particles of limestone that are loosened by wind and weather or dissolved by rain disperse randomly, destroying the precise representation of the image and increasing the entropy of the universe.

FOLDABLES

Incorporate information from this section into your Foldable.

Entropy, the Universe, and Free Energy

If you happen to break an egg, you know you cannot reverse the process and again make the egg whole. Similarly, an abandoned barn gradually disintegrates into a pile of decaying wood and a statue dissolves slowly in rainwater and disperses into the ground, as shown in **Figure 15.21**. Order turns to disorder in these processes, and the entropy of the universe increases.

What effect does entropy have on reaction spontaneity? Recall that the second law of thermodynamics states that the entropy of the universe must increase as a result of a spontaneous reaction or process. Therefore, the following is true for any spontaneous process.

$$\Delta S_{\text{universe}} > 0$$

Because the universe equals the system plus the surroundings, any change in the entropy of the universe is the sum of changes occurring in the system and surroundings.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

In nature, $\Delta S_{\text{universe}}$ tends to be positive for reactions and processes under the following conditions.

1. *The reaction or process is exothermic, which means ΔH_{system} is negative.* The heat released by an exothermic reaction raises the temperature of the surroundings and thereby increases the entropy of the surroundings. $\Delta S_{\text{surroundings}}$ is positive.
2. *The entropy of the system increases, so ΔS_{system} is positive.*

Thus, exothermic chemical reactions accompanied by an increase in entropy are all spontaneous.

Free energy Can you definitely determine if a reaction is spontaneous? In 1878, J. Willard Gibbs, a physicist at Yale University, defined a combined enthalpy-entropy function called Gibbs free energy that answers that question. For reactions or processes that take place at constant pressure and temperature, Gibbs free energy (G_{system}), commonly called **free energy**, is energy that is available to do work. Thus, free energy is useful energy. In contrast, some entropy is associated with energy that is spread out into the surroundings as, for example, random molecular motion, and cannot be recovered to do useful work. The free energy change (ΔG_{system}) is the difference between the system's change in enthalpy (ΔH_{system}) and the product of the kelvin temperature and the change in entropy ($T\Delta S_{\text{system}}$).

Gibbs Free Energy Equation

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

ΔG_{system} represents the free energy change.
 ΔH_{system} represents the change in enthalpy. T is temperature in kelvins.
 ΔS_{system} represents the change in entropy.

The free energy released or absorbed in a chemical reaction is equal to the difference between the enthalpy change and the change in entropy expressed in joules per kelvin and multiplied by the temperature in kelvins.

To calculate Gibbs free energy, it is usually necessary to convert units because ΔS is usually expressed in J/K, whereas ΔH is expressed in kJ.

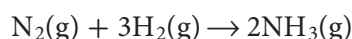
The sign of free energy When a reaction or process occurs under standard conditions (298 K and 1 atm), the standard free energy change can be expressed as follows.

$$\Delta G_{\text{system}}^{\circ} = \Delta H_{\text{system}}^{\circ} - T\Delta S_{\text{system}}^{\circ}$$

If the sign of the free energy change ($\Delta G_{\text{system}}^{\circ}$) is negative, the reaction is spontaneous. If the sign of the free energy change is positive, the reaction is nonspontaneous.

Recall that free energy is energy that is available to do work. In contrast, energy related to entropy is useless because it is dispersed and cannot be harnessed to do work.

Calculating free energy change How do changes in enthalpy and entropy affect free energy change and spontaneity for the reaction between nitrogen and hydrogen to form ammonia?



$$\Delta H_{\text{system}}^{\circ} = -91.8 \text{ kJ} \quad \Delta S_{\text{system}}^{\circ} = -197 \text{ J/K}$$

The entropy of the system decreases because 4 mol of gaseous molecules react and only 2 mol of gaseous molecules are produced. Therefore, $\Delta S_{\text{system}}^{\circ}$ is negative. A decrease in the entropy of the system tends to make the reaction nonspontaneous, but the reaction is exothermic ($\Delta H_{\text{system}}^{\circ}$ is negative), which tends to make the reaction spontaneous. To determine which of the two tendencies predominates, you must calculate $\Delta G_{\text{system}}^{\circ}$ for the reaction. First, convert $\Delta S_{\text{system}}^{\circ}$ to kilojoules.

$$\Delta S_{\text{system}}^{\circ} = -197 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -0.197 \text{ kJ/K}$$

Now, substitute $\Delta H_{\text{system}}^{\circ}$, T , and $\Delta S_{\text{system}}^{\circ}$ into the equation for $\Delta G_{\text{system}}^{\circ}$.

$$\Delta G_{\text{system}}^{\circ} = \Delta H_{\text{system}}^{\circ} - T\Delta S_{\text{system}}^{\circ}$$

$$\Delta G_{\text{system}}^{\circ} = -91.8 \text{ kJ} - (298 \text{ K})(-0.197 \text{ kJ/K})$$

$$\Delta G_{\text{system}}^{\circ} = -91.8 \text{ kJ} + 58.7 \text{ kJ} = -33.1 \text{ kJ}$$

$\Delta G_{\text{system}}^{\circ}$ for this reaction is negative, so the reaction is spontaneous.

The reaction between nitrogen and hydrogen demonstrates that the entropy of a system can decrease during a spontaneous process. However, it can do so only if the entropy of the surroundings increases more than the entropy of the system decreases. Thus, the entropy of the universe (system + surroundings) always increases in any spontaneous process. **Table 15.6** shows how reaction spontaneity depends on the signs of ΔH_{system} and ΔS_{system} .

VOCABULARY

ACADEMIC VOCABULARY

Demonstrate

to show clearly

People are standing by to demonstrate how the device works.

Table 15.6

Reaction Spontaneity

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

Concepts in Motion

Interactive Table Explore reaction spontaneity, at glencoe.com.

ΔH_{system}	ΔS_{system}	ΔG_{system}	Reaction Spontaneity
negative	positive	always negative	always spontaneous
negative	negative	negative or positive	spontaneous at lower temperatures
positive	positive	negative or positive	spontaneous at higher temperatures
positive	negative	always positive	never spontaneous

EXAMPLE Problem 15.7

Determine Reaction Spontaneity For a process, $\Delta H_{\text{system}} = 145 \text{ kJ}$ and $\Delta S_{\text{system}} = 322 \text{ J/K}$. Is the process spontaneous at 382 K?

Math Handbook

Solving Algebraic Equations
pages 954–955

1 Analyze the Problem

You must calculate ΔG_{system} to determine spontaneity.

Known

$$T = 382 \text{ K}$$

$$\Delta H_{\text{system}} = 145 \text{ kJ}$$

$$\Delta S_{\text{system}} = 322 \text{ J/K}$$

Unknown

$$\text{sign of } \Delta G_{\text{system}} = ?$$

2 Solve for the Unknown

Convert ΔS_{system} to kJ/K

$$322 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 0.322 \text{ kJ/K}$$

Convert ΔS_{system} to kJ/K.

Solve the free energy equation.

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

State the Gibbs free energy equation.

$$\Delta G_{\text{system}} = 145 \text{ kJ} - (382 \text{ K})(0.322 \text{ kJ/K})$$

Substitute $T = 382 \text{ K}$, $\Delta H_{\text{system}} = 145 \text{ kJ}$,
and $\Delta S_{\text{system}} = 0.322 \text{ kJ/K}$

$$\Delta G_{\text{system}} = 145 \text{ kJ} - 123 \text{ kJ} = \mathbf{22 \text{ kJ}}$$

Multiply and subtract numbers.

Because ΔG_{system} is positive, the reaction is nonspontaneous.

3 Evaluate the Answer

Because ΔH is positive and the temperature is not high enough to make the second term of the equation greater than the first, ΔG_{system} is positive. The significant figures are correct.

PRACTICE Problems

Extra Practice Page 987 and glencoe.com

46. Determine whether each of the following reactions is spontaneous.

a. $\Delta H_{\text{system}} = -75.9 \text{ kJ}$, $T = 273 \text{ K}$, $\Delta S_{\text{system}} = 138 \text{ J/K}$

c. $\Delta H_{\text{system}} = 365 \text{ kJ}$, $T = 388 \text{ K}$, $\Delta S_{\text{system}} = -55.2 \text{ J/K}$

b. $\Delta H_{\text{system}} = -27.6 \text{ kJ}$, $T = 535 \text{ K}$, $\Delta S_{\text{system}} = -55.2 \text{ J/K}$

d. $\Delta H_{\text{system}} = 452 \text{ kJ}$, $T = 165 \text{ K}$, $\Delta S_{\text{system}} = 55.7 \text{ J/K}$

47. **Challenge** Given $\Delta H_{\text{system}} = -144 \text{ kJ}$ and $\Delta S_{\text{system}} = -36.8 \text{ J/K}$ for a reaction, determine the lowest temperature in kelvins at which the reaction would be spontaneous.

Section 15.5 Assessment

Section Summary

- Entropy is a measure of the disorder or randomness of a system.
- Spontaneous processes always result in an increase in the entropy of the universe.
- Free energy is the energy available to do work. The sign of the free energy change indicates whether the reaction is spontaneous.

48. **MAIN Idea** Compare and contrast spontaneous and nonspontaneous reactions.

49. **Describe** how a system's entropy changes if the system becomes more disordered during a process.

50. **Decide** Does the entropy of a system increase or decrease when you dissolve a cube of sugar in a cup of tea? Define the system, and explain your answer.

51. **Determine** whether the system $\Delta H_{\text{system}} = -20.5 \text{ kJ}$, $T = 298 \text{ K}$, and $\Delta S_{\text{system}} = -35.0 \text{ J/K}$ is spontaneous or nonspontaneous.

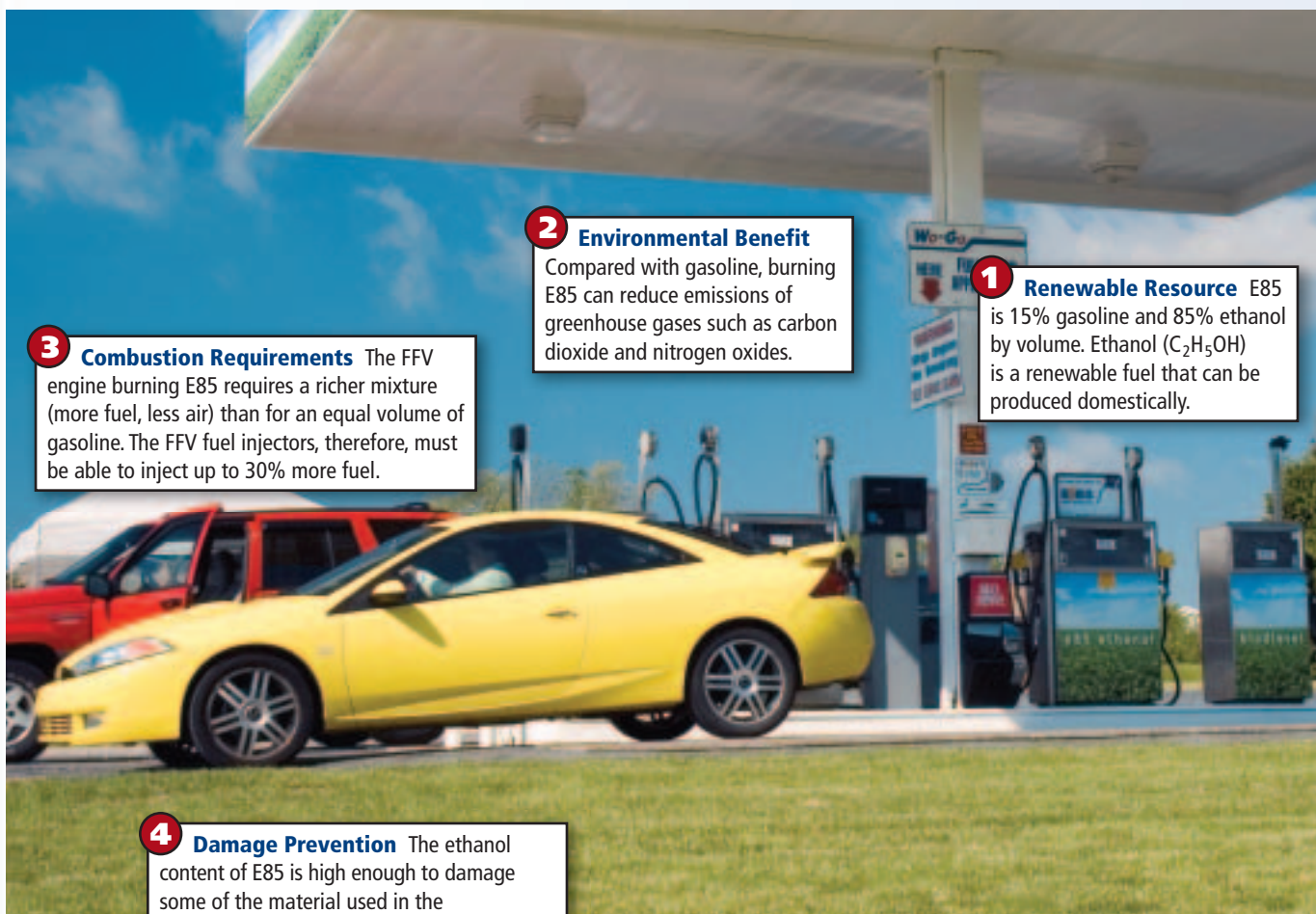
52. **Outline** Use the blue and red headings to outline the section. Under each heading, summarize the important ideas discussed.

HOW IT WORKS



Driving the Future: Flexible Fuel Vehicles

The service stations of the not-too-distant future will not only deliver various grades of gasoline, but they will also pump a fuel called E85. This fuel can be used in a flexible-fuel vehicle, or FFV. Conventional vehicles operate on 100% gasoline or on a blend of 10% ethanol and 90% gasoline. FFVs, however, operate on all these blends and E85, which is 85% ethanol. E85 has the advantage of not being highly dependent on fossil fuels.



3 Combustion Requirements The FFV engine burning E85 requires a richer mixture (more fuel, less air) than for an equal volume of gasoline. The FFV fuel injectors, therefore, must be able to inject up to 30% more fuel.

2 Environmental Benefit Compared with gasoline, burning E85 can reduce emissions of greenhouse gases such as carbon dioxide and nitrogen oxides.

1 Renewable Resource E85 is 15% gasoline and 85% ethanol by volume. Ethanol (C_2H_5OH) is a renewable fuel that can be produced domestically.

4 Damage Prevention The ethanol content of E85 is high enough to damage some of the material used in the construction of conventional vehicles. Therefore, the FFV fuel tank is made of stainless steel. The fuel lines are also made of stainless steel or lined with nonreactive materials.

WRITING in Chemistry

Write thermochemical equations for the complete combustion of 1 mol octane (C_8H_{18}), a component of gasoline, and 1 mol ethanol (ΔH_{comb} of $C_8H_{18} = -5471$ kJ/mol; ΔH_{comb} of $C_2H_5OH = -1367$ kJ/mol). Which releases the greater amount of energy per mole of fuel? Which releases more energy per kilogram of fuel? Discuss the significance of your findings. Visit glencoe.com to learn more about the use of E85 in flexible-fuel vehicles.

INTERNET: MEASURE CALORIES

Background: The burning of a potato chip releases heat stored in the substances contained in the chip. Using calorimetry, you will approximate the amount of energy contained in a potato chip.

Question: *How many Calories are in a potato chip?*

Materials

large potato chip or other snack food
250-mL beaker
100-mL graduated cylinder
evaporating dish
nonmercury thermometer
ring stand with ring
wire gauze
matches
stirring rod
balance

Safety Precautions

WARNING: *Hot objects might not appear to be hot. Do not heat broken, chipped, or cracked glassware. Tie back long hair. Do not eat any items used in the lab.*

Procedure

1. Read and complete the lab safety form.
2. Measure the mass of a potato chip and record it in a data table.
3. Place the potato chip in an evaporating dish on the metal base of the ring stand. Position the ring and wire gauze so that they will be 10 cm above the top of the potato chip.
4. Measure the mass of an empty 250-mL beaker and record it in your data table.
5. Using a graduated cylinder, measure 50 mL of water and pour it into the beaker. Measure the mass of the beaker and water and record it in your data table.
6. Measure and record the initial temperature of the water.
7. Place the beaker on the wire gauze on the ring stand. Use a match to ignite the bottom of the potato chip.
8. Gently stir the water in the beaker while the chip burns. Measure and record the highest temperature attained by the water.
9. **Cleanup and Disposal** Wash all lab equipment and return it to its designated place.



Analyze and Conclude

1. **Classify** Is the reaction exothermic or endothermic? Explain how you know.
2. **Observe and Infer** Describe the reactant and products of the chemical reaction. Was the reactant (potato chip) completely consumed? What evidence supports your answer?
3. **Calculate** Determine the mass of the water and its temperature change. Use the equation $q = c \times m \times \Delta T$ to calculate how much heat, in joules, was transferred to the water by the burning of the chip.
4. **Calculate** Convert the quantity of heat from joules/chip to Calories/chip.
5. **Calculate** From the information on the chip container, determine the mass in grams of one serving. Determine how many Calories are contained in one serving. Use your data to calculate the number of Calories released by the combustion of one serving.
6. **Error Analysis** Compare your calculated Calories per serving with the value on the chip's container. Calculate the percent error.
7. **Compare** your class results with other students by posting your data at glencoe.com.

INQUIRY EXTENSION

Predict Do all potato chips have the same number of calories? Make a plan to test several different brands of chips.

**BIG Idea** Chemical reactions usually absorb or release energy.**Section 15.1 Energy****MAIN Idea** Energy can change form and flow, but it is always conserved.**Vocabulary**

- calorie (p. 518)
- chemical potential energy (p. 517)
- energy (p. 516)
- heat (p. 518)
- joule (p. 518)
- law of conservation of energy (p. 517)
- specific heat (p. 519)

Key Concepts

- Energy is the capacity to do work or produce heat.
- Chemical potential energy is energy stored in the chemical bonds of a substance by virtue of the arrangement of the atoms and molecules.
- Chemical potential energy is released or absorbed as heat during chemical processes or reactions.

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

Section 15.2 Heat**MAIN Idea** The enthalpy change for a reaction is the enthalpy of the products minus the enthalpy of the reactants.**Vocabulary**

- calorimeter (p. 523)
- enthalpy (p. 527)
- enthalpy (heat) of reaction (p. 527)
- surroundings (p. 526)
- system (p. 526)
- thermochemistry (p. 525)
- universe (p. 526)

Key Concepts

- In thermochemistry, the universe is defined as the system plus the surroundings.
- The heat lost or gained by a system during a reaction or process carried out at constant pressure is called the change in enthalpy (ΔH).
- When ΔH is positive, the reaction is endothermic. When ΔH is negative, the reaction is exothermic.

Section 15.3 Thermochemical Equations**MAIN Idea** Thermochemical equations express the amount of heat released or absorbed by chemical reactions.**Vocabulary**

- enthalpy (heat) of combustion (p. 529)
- molar enthalpy (heat) of fusion (p. 530)
- molar enthalpy (heat) of vaporization (p. 530)
- thermochemical equation (p. 529)

Key Concepts

- A thermochemical equation includes the physical states of the reactants and products and specifies the change in enthalpy.
- The molar enthalpy (heat) of vaporization, ΔH_{vap} , is the amount of energy required to evaporate one mole of a liquid.
- The molar enthalpy (heat) of fusion, ΔH_{fus} , is the amount of energy needed to melt one mole of a solid.

Section 15.4 Calculating Enthalpy Change**MAIN Idea** The enthalpy change for a reaction can be calculated using Hess's law.**Vocabulary**

- Hess's law (p. 534)
- standard enthalpy (heat) of formation (p. 537)

Key Concepts

- The enthalpy change for a reaction can be calculated by adding two or more thermochemical equations and their enthalpy changes.
- Standard enthalpies of formation of compounds are determined relative to the assigned enthalpy of formation of the elements in their standard states.

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

Section 15.5 Reaction Spontaneity**MAIN Idea** Changes in enthalpy and entropy determine whether a process is spontaneous.**Vocabulary**

- entropy (p. 543)
- free energy (p. 546)
- second law of thermodynamics (p. 543)
- spontaneous process (p. 542)

Key Concepts

- Entropy is a measure of the disorder or randomness of a system.
- Spontaneous processes always result in an increase in the entropy of the universe.
- Free energy is the energy available to do work. The sign of the free energy change indicates whether the reaction is spontaneous.

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

Section 15.1

Mastering Concepts

- Compare and contrast temperature and heat.
- How does the chemical potential energy of a system change during an endothermic reaction?
- Describe a situation that illustrates potential energy changing to kinetic energy.
- Cars** How is the energy in gasoline converted and released when it burns in an automobile engine?
- Nutrition** How does the nutritional Calorie compare with the calorie? What is the relationship between the Calorie and a kilocalorie?
- What quantity has the units $\text{J}/(\text{g}\cdot^{\circ}\text{C})$?



■ Figure 15.22

- Describe what might happen in **Figure 15.22** when the air above the surface of the lake is colder than the water.
- Ethanol has a specific heat of $2.44 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$. What does this mean?
- Explain how the amount of energy required to raise the temperature of an object is determined.

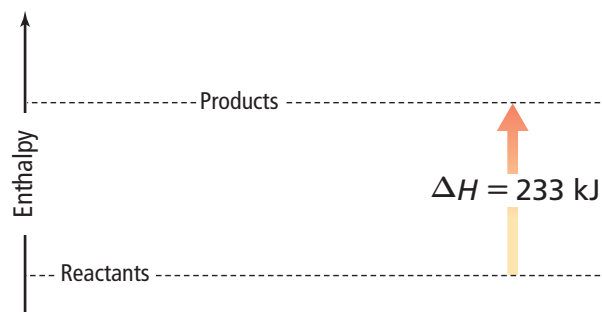
Mastering Problems

- Nutrition** A food item contains 124 nutritional Calories. How many calories does the food item contain?
- How many joules are absorbed in a process that absorbs 0.5720 kcal?
- Transportation** Ethanol is being used as an additive to gasoline. The combustion of 1 mol of ethanol releases 1367 kJ of energy. How many Calories are released?
- To vaporize 2.00 g of ammonia, 656 calories are required. How many kilojoules are required to vaporize the same mass of ammonia?
- The combustion of one mole of ethanol releases 326.7 Calories of energy. How many kilojoules are released?
- Metallurgy** A 25.0-g bolt made of an alloy absorbed 250 J of heat as its temperature changed from 25.0°C to 78.0°C . What is the specific heat of the alloy?

Section 15.2

Mastering Concepts

- Why is a foam cup used in a student calorimeter rather than a typical glass beaker?



■ Figure 15.23

- Is the reaction shown in **Figure 15.23** endothermic or exothermic? How do you know?
- Give two examples of chemical systems and define the universe in terms of those examples.
- Under what condition is the heat (q) evolved or absorbed in a chemical reaction equal to a change in enthalpy (ΔH)?
- The enthalpy change for a reaction, ΔH , is negative. What does this indicate about the chemical potential energy of the system before and after the reaction?
- What is the sign of ΔH for an exothermic reaction? An endothermic reaction?

Mastering Problems

- How many joules of heat are lost by 3580 kg of granite as it cools from 41.2°C to -12.9°C ? The specific heat of granite is $0.803 \text{ J}/(\text{g}\cdot^{\circ}\text{C})$.
- Swimming Pool** A swimming pool measuring $20.0 \text{ m} \times 12.5 \text{ m}$ is filled with water to a depth of 3.75 m. If the initial temperature is 18.4°C , how much heat must be added to the water to raise its temperature to 29.0°C ? Assume that the density of water is 1.000 g/mL .
- How much heat is absorbed by a 44.7-g piece of lead when its temperature increases by 65.4°C ?
- Food Preparation** When 10.2 g of canola oil at 25.0°C is placed in a wok, 3.34 kJ of heat is required to heat it to a temperature of 196.4°C . What is the specific heat of the canola oil?
- Alloys** When a 58.8-g piece of hot alloy is placed in 125 g of cold water in a calorimeter, the temperature of the alloy decreases by 106.1°C , while the temperature of the water increases by 10.5°C . What is the specific heat of the alloy?

Section 15.3

Mastering Concepts

79. Write the sign of ΔH_{system} for each of the following changes in physical state.
- $\text{C}_2\text{H}_5\text{OH}(\text{s}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
 - $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
 - $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{g})$
 - $\text{NH}_3(\text{l}) \rightarrow \text{NH}_3(\text{s})$
80. The molar enthalpy of fusion of methanol is 3.22 kJ/mol. What does this mean?
81. Explain how perspiration can help cool your body.
82. Write the thermochemical equation for the combustion of methane. Refer to Table 15.3.

Mastering Problems

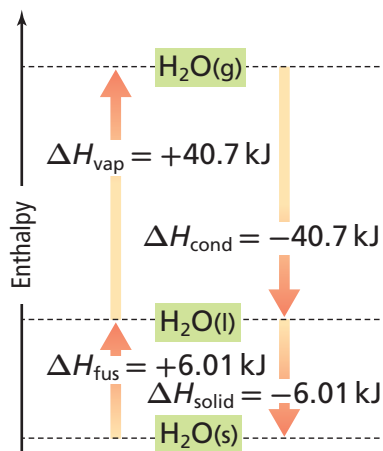


Figure 15.24

83. Use information from Figure 15.24 to calculate how much heat is required to vaporize 4.33 mol of water at 100°C.
84. **Agriculture** Water is sprayed on oranges during a frosty night. If an average of 11.8 g of water freezes on each orange, how much heat is released?
85. **Grilling** What mass of propane (C_3H_8) must be burned in a barbecue grill to release 4560 kJ of heat? The ΔH_{comb} of propane is -2219 kJ/mol .
86. **Heating with Coal** How much heat is liberated when 5.00 kg of coal is burned if the coal is 96.2% carbon by mass and the other materials in the coal do not react? ΔH_{comb} of carbon is -394 kJ/mol .
87. How much heat is evolved when 1255 g of water condenses to a liquid at 100°C?
88. A sample of ammonia ($\Delta H_{\text{solid}} = -5.66 \text{ kJ/mol}$) liberates 5.66 kJ of heat as it solidifies at its melting point. What is the mass of the sample?

Section 15.4

Mastering Concepts

89. For a given compound, what does the standard enthalpy of formation describe?
90. How does ΔH for a thermochemical equation change when the amounts of all substances are tripled and the equation is reversed?

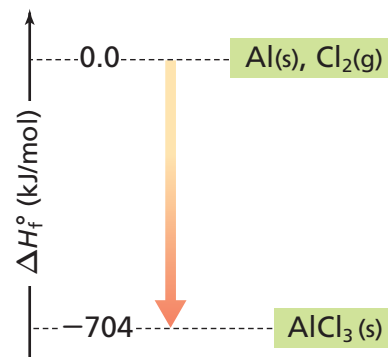
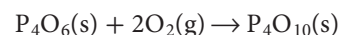


Figure 15.25

91. Use Figure 15.25 to write the thermochemical equation for the formation of 1 mol of aluminum chloride (a solid in its standard state) from its constituent elements in their standard states.

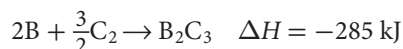
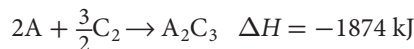
Mastering Problems

92. Use standard enthalpies of formation from Table R-11 on page 975 to calculate $\Delta H_{\text{rxn}}^\circ$ for the following reaction.



93. Use Hess's law and the following thermochemical equations to produce the thermochemical equation for the reaction $\text{C}(\text{s, diamond}) \rightarrow \text{C}(\text{s, graphite})$. What is ΔH for the reaction?
- $\text{C}(\text{s, graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = -394 \text{ kJ}$
 - $\text{C}(\text{s, diamond}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = -396 \text{ kJ}$

94. Use Hess's law and the changes in enthalpy for the following two generic reactions to calculate ΔH for the reaction $2\text{A} + \text{B}_2\text{C}_3 \rightarrow 2\text{B} + \text{A}_2\text{C}_3$.



Section 15.5

Mastering Concepts

95. Under what conditions is an endothermic chemical reaction in which the entropy of the system increases likely to be spontaneous?

96. Predict how the entropy of the system changes for the reaction $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. Explain.
97. Which of these reactions would you expect to be spontaneous at relatively high temperatures? At relatively low temperatures? Explain.
- $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{g})$
 - $\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$
 - $\text{CH}_3\text{OH}(\text{s}) \rightarrow \text{CH}_3\text{OH}(\text{l})$
98. Explain how an exothermic reaction changes the entropy of the surroundings. Does the enthalpy change for such a reaction increase or decrease ΔG_{system} ? Explain.

Mastering Problems

99. Calculate ΔG_{system} for each process, and state whether the process is spontaneous or nonspontaneous.
- $\Delta H_{\text{system}} = 145 \text{ kJ}$, $T = 293 \text{ K}$, $\Delta S_{\text{system}} = 195 \text{ J/K}$
 - $\Delta H_{\text{system}} = -232 \text{ kJ}$, $T = 273 \text{ K}$, $\Delta S_{\text{system}} = 138 \text{ J/K}$
 - $\Delta H_{\text{system}} = -15.9 \text{ kJ}$, $T = 373 \text{ K}$, $\Delta S_{\text{system}} = -268 \text{ J/K}$
100. Calculate the temperature at which $\Delta G_{\text{system}} = 0$ if $\Delta H_{\text{system}} = 4.88 \text{ kJ}$ and $\Delta S_{\text{system}} = 55.2 \text{ J/K}$.
101. For the change $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$, $\Delta G_{\text{system}}^\circ$ is 8.557 kJ and $\Delta H_{\text{system}}^\circ$ is 44.01 kJ . What is $\Delta S_{\text{system}}^\circ$ for the change?
102. Is the following reaction to convert copper(II) sulfide to copper(II) sulfate spontaneous under standard conditions? $\text{CuS}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{CuSO}_4(\text{s})$. $\Delta H_{\text{rxn}}^\circ = -718.3 \text{ kJ}$, and $\Delta S_{\text{rxn}}^\circ = -368 \text{ J/K}$. Explain.
103. Calculate the temperature at which $\Delta G_{\text{system}} = -34.7 \text{ kJ}$ if $\Delta H_{\text{system}} = -28.8 \text{ kJ}$ and $\Delta S_{\text{system}} = 22.2 \text{ J/K}$.

Mixed Review

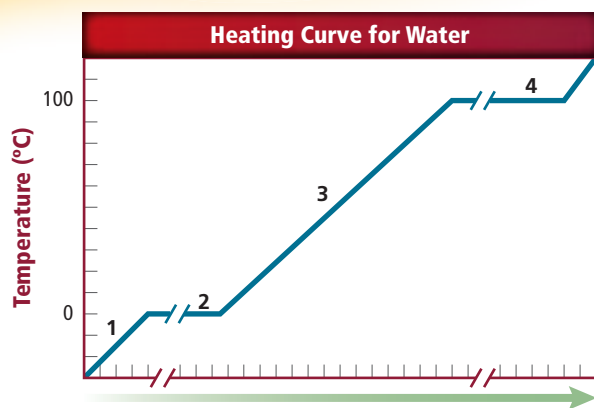


Figure 15.26

104. Heat was added consistently to a sample of water to produce the heating curve in Figure 15.26. Identify what is happening in Sections 1, 2, 3, and 4 on the curve.

105. **Bicycling** Describe the energy conversions that occur when a bicyclist coasts down a long grade, then struggles to ascend a steep grade.
106. **Hiking** Imagine that on a cold day you are planning to take a thermos of hot soup with you on a hike. Explain why you might fill the thermos with hot water first before filling it with the hot soup.
107. Differentiate between the enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{H}_2\text{O}(\text{g})$. Why is it necessary to specify the physical state of water in the following thermochemical equation $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l or g})$ $\Delta H = ?$

Think Critically



Figure 15.27

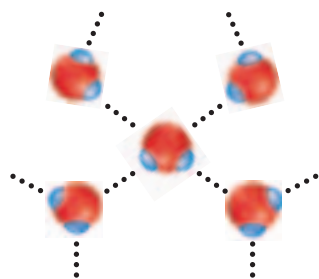
108. **Analyze** both of the images in Figure 15.27 in terms of potential energy of position, chemical potential energy, kinetic energy, and heat.
109. **Apply** Phosphorus trichloride is a starting material for the preparation of organic phosphorous compounds. Demonstrate how thermochemical equations **a** and **b** can be used to determine the enthalpy change for the reaction $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{s})$.
- $\text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightarrow 4\text{PCl}_3(\text{l}) \quad \Delta H = -1280 \text{ kJ}$
 - $\text{P}_4(\text{s}) + 10\text{Cl}_2(\text{g}) \rightarrow 4\text{PCl}_5(\text{s}) \quad \Delta H = -1774 \text{ kJ}$
110. **Calculate** Suppose that two pieces of iron, one with a mass exactly twice the mass of the other, are placed in an insulated calorimeter. If the original temperatures of the larger piece and the smaller piece are 90.0°C and 50.0°C , respectively, what is the temperature of the two pieces when thermal equilibrium has been established? Refer to Table R-9 on page 975 for the specific heat of iron.
111. **Predict** which of the two compounds, methane gas (CH_4) or methanal vapor (CH_2O), has the greater molar enthalpy of combustion. Explain your answer. (*Hint: Write and compare the balanced chemical equations for the two combustion reactions.*)

Challenge Problem

- 112.** A sample of natural gas is analyzed and found to be 88.4% methane (CH_4) and 11.6% ethane (C_2H_6) by mass. The standard enthalpy of combustion of methane to gaseous carbon dioxide (CO_2) and liquid water (H_2O) is -891 kJ/mol . Write the equation for the combustion of gaseous ethane to carbon dioxide and water. Calculate the standard enthalpy of combustion of ethane using standard enthalpies of formation from **Table R-11** on page 975. Using that result and the standard enthalpy of combustion of methane in **Table 15.3**, calculate the energy released by the combustion of 1 kg of natural gas.

Cumulative Review

- 113.** Why is it necessary to perform repeated experiments in order to support a hypothesis? (*Chapter 1*)
- 114.** Phosphorus has the atomic number 15 and an atomic mass of 31 amu. How many protons, neutrons, and electrons are in a neutral phosphorus atom? (*Chapter 4*)
- 115.** What element has the electron configuration $[\text{Ar}]4s^13d^5$? (*Chapter 5*)
- 116.** Name the following molecular compounds. (*Chapter 8*)
- S_2Cl_2
 - CS_2
 - SO_3
 - P_4O_{10}
- 117.** Determine the molar mass for the following compounds. (*Chapter 10*)
- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
 - $\text{Fe}(\text{OH})_3$



■ **Figure 15.28**

- 118.** What kind of chemical bond is represented by the dotted lines in **Figure 15.28**? (*Chapter 12*)
- 119.** A sample of oxygen gas has a volume of 20.0 cm^3 at -10.0°C . What volume will this sample occupy if the temperature rises to 110°C ? (*Chapter 13*)
- 120.** What is the molarity of a solution made by dissolving 25.0 g of sodium thiocyanate (NaSCN) in enough water to make 500 mL of solution? (*Chapter 14*)
- 121.** List three colligative properties of solutions. (*Chapter 14*)

Additional Assessment**WRITING in Chemistry**

- 122. Alternate Fuels** Use library and Internet sources to explain how hydrogen might be produced, transported, and used as a fuel for automobiles. Summarize the benefits and drawbacks of using hydrogen as an alternative fuel for internal combustion engines.
- 123. Wind Power** Research the use of wind as a source of electrical power. Explain the possible benefits, disadvantages, and limitations of its use.

DBQ Document-Based Questions

Cooking Oil A university research group burned four cooking oils in a bomb calorimeter to determine if a relationship exists between the enthalpy of combustion and the number of double bonds in an oil molecule. Cooking oils typically contain long chains of carbon atoms linked by either single or double bonds. A chain with no double bonds is said to be saturated. Oils with one or more double bonds are unsaturated. The enthalpies of combustion of the four oils are shown in **Table 15.7**. The researchers calculated that the results deviated by only 0.6% and concluded that a link between saturation and enthalpy of combustion could not be detected by the experimental procedure used.

Data obtained from: <http://Heat of Combustion Oils>, April 1998. University of Pennsylvania.

Table 15.7 Combustion Results for Oils

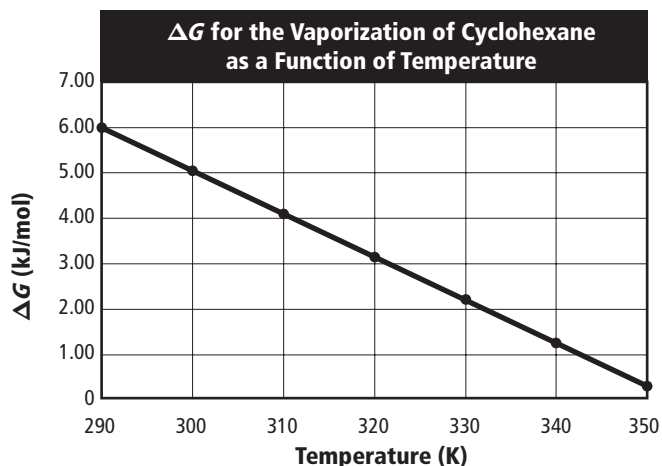
Type of Oil	ΔH_{comb} (kJ/g)
Soy oil	40.81
Canola oil	41.45
Olive oil	39.31
Extra-virgin olive oil	40.98

- 124.** Which of the oils tested provided the greatest amount of energy per unit mass when burned?
- 125.** According to the data, how much energy would be liberated by burning 0.554 kg of olive oil?
- 126.** Assume that 12.2 g of soy oil is burned and that all the energy released is used to heat 1.600 kg of water, initially at 20.0°C . What is the final temperature of the water?
- 127.** Oils can be used as fuels. How many grams of canola oil would have to be burned to provide the energy to vaporize 25.0 g of water. ($\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$).

Cumulative Standardized Test Practice

Multiple Choice

Use the graph below to answer Questions 1 to 3.



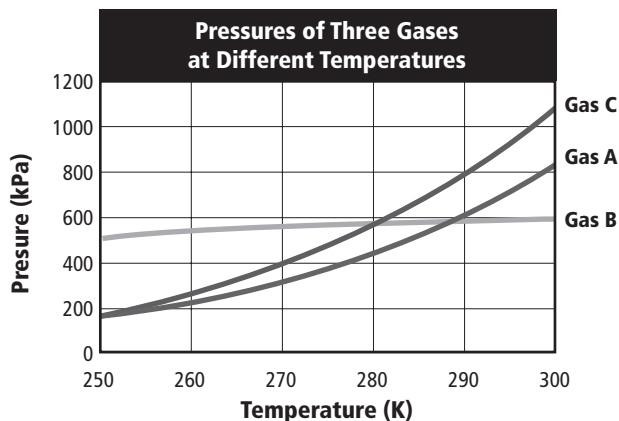
- In the range of temperatures shown, the vaporization of cyclohexane
 - does not occur at all.
 - will occur spontaneously.
 - is not spontaneous.
 - occurs only at high temperatures.
- What is the standard free energy of vaporization, $\Delta G_{\text{vap}}^{\circ}$, of cyclohexane at 300 K?
 - 5.00 kJ/mol
 - 3.00 kJ/mol
 - 3.00 kJ/mol
 - 2.00 kJ/mol
- When $\Delta G_{\text{vap}}^{\circ}$ is plotted as a function of temperature, the slope of the line equals $\Delta S_{\text{vap}}^{\circ}$ and the y -intercept of the line equals $\Delta H_{\text{vap}}^{\circ}$. What is the approximate standard entropy of the vaporization of cyclohexane?
 - 50.0 J/mol·K
 - 10.0 J/mol·K
 - 5.0 J/mol·K
 - 100 J/mol·K
- The metal yttrium, atomic number 39, forms
 - positive ions.
 - negative ions.
 - both positive and negative ions.
 - no ions at all.
- Given the reaction $2\text{Al} + 3\text{FeO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Fe}$, what is the mole-to-mole ratio between iron(II) oxide and aluminum oxide?
 - 2:3
 - 1:1
 - 3:2
 - 3:1

Use the table below to answer Question 6.

Electronegativity of Selected Elements						
H						
2.20						
Li	Be	B	C	N	O	F
0.98	1.57	2.04	2.55	3.04	3.44	3.98
Na	Mg	Al	Si	P	S	Cl
0.93	1.31	1.61	1.90	2.19	2.58	3.16

- Which bond is the most electronegative?
 - H-H
 - H-C
 - H-N
 - H-O
- Element Q has an oxidation number of +2, while Element M has an oxidation number of -3. Which is the correct formula for a compound made of elements Q and M?
 - Q_2M_3
 - M_2Q_3
 - Q_3M_2
 - M_3Q_2
- Wavelengths of light shorter than about 4.00×10^{-7} m are not visible to the human eye. What is the energy of a photon of ultraviolet light having a frequency of $5.45 \times 10^{16} \text{ s}^{-1}$? (Planck's constant is $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$.)
 - $3.61 \times 10^{-17} \text{ J}$
 - $1.22 \times 10^{-50} \text{ J}$
 - $8.23 \times 10^{49} \text{ J}$
 - $3.81 \times 10^{-24} \text{ J}$

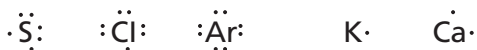
Use the graph below to answer Question 9.



- What is the predicted pressure of Gas B at 310 K?
 - 500 kPa
 - 600 kPa
 - 700 kPa
 - 900 kPa

Short Answer

Use the figure below to answer Questions 11 to 13.

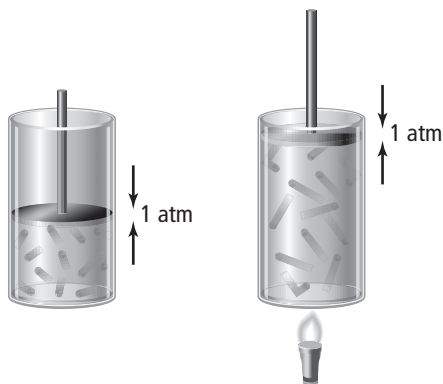


- Explain why argon is not likely to form a compound.
- Draw the structure of calcium chloride using electron-dot models. What is the chemical formula for calcium chloride?
- Use electron-dot models to explain what charge sulfur will most likely have when it forms an ion.

Extended Response

Use the information below to answer Questions 13 and 14.

A sample of gas occupies a certain volume at a pressure of 1 atm. If the pressure remains constant, heating causes the gas to expand, as shown below.



- State the gas law that describes why the gas in the second canister occupies a greater volume than the gas in the first canister.
- If the volume in the first container is 2.1 L at a temperature of 300 K, to what temperature must the second canister be heated to reach a volume of 5.4 L? Show your setup and the final answer.

SAT Subject Test: Chemistry

- The specific heat of ethanol is $2.44 \text{ J/g}\cdot^\circ\text{C}$. How many kilojoules of energy are required to heat 50.0 g of ethanol from -20.0°C to 68.0°C ?
 A. 10.7 kJ D. 1.22 kJ
 B. 8.30 kJ E. 5.86 kJ
 C. 2.44 kJ
- If 3.00 g of aluminum foil, placed in an oven and heated from 20.0°C to 662.0°C , absorbs 1728 J of heat, what is the specific heat of aluminum?
 A. $0.131 \text{ J/g}\cdot^\circ\text{C}$ D. $2.61 \text{ J/g}\cdot^\circ\text{C}$
 B. $0.870 \text{ J/g}\cdot^\circ\text{C}$ E. $0.261 \text{ J/g}\cdot^\circ\text{C}$
 C. $0.897 \text{ J/g}\cdot^\circ\text{C}$

Use the table below to answer Questions 17 and 18.

Density and Electronegativity Data for Elements

Element	Density (g/ml)	Electronegativity
Aluminum	2.698	1.6
Fluorine	1.696×10^{-3}	4.0
Sulfur	2.070	2.6
Copper	8.960	1.9
Magnesium	1.738	1.3
Carbon	3.513	2.6

- A sample of metal has a mass of 9.250 g and occupies a volume of 5.250 mL. Which metal is it?
 A. aluminum D. copper
 B. magnesium E. sulfur
 C. carbon
- Which pair is most likely to form an ionic bond?
 A. carbon and sulfur
 B. aluminum and magnesium
 C. copper and sulfur
 D. magnesium and fluorine
 E. aluminum and carbon

NEED EXTRA HELP?

If You Missed Question . . .	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Review Section . . .	15.5	15.5	15.5	8.5	11.1	8.5	7.3	5.1	13.1	5.3	5.3	5.3	13.1	13.1	15.2	15.2	2.1	8.5