

# Rates of Chemical Reactions

## Chapter Preview

- 6.1** Expressing and Measuring Reaction Rates
- 6.2** The Rate Law: Reactant Concentration and Rate
- 6.3** Theories of Reaction Rates
- 6.4** Reaction Mechanisms and Catalysts

## Prerequisite Concepts and Skills

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

- balancing chemical equations (Concepts and Skills Review)
- expressing concentration in units of mol/L (Concepts and Skills Review)

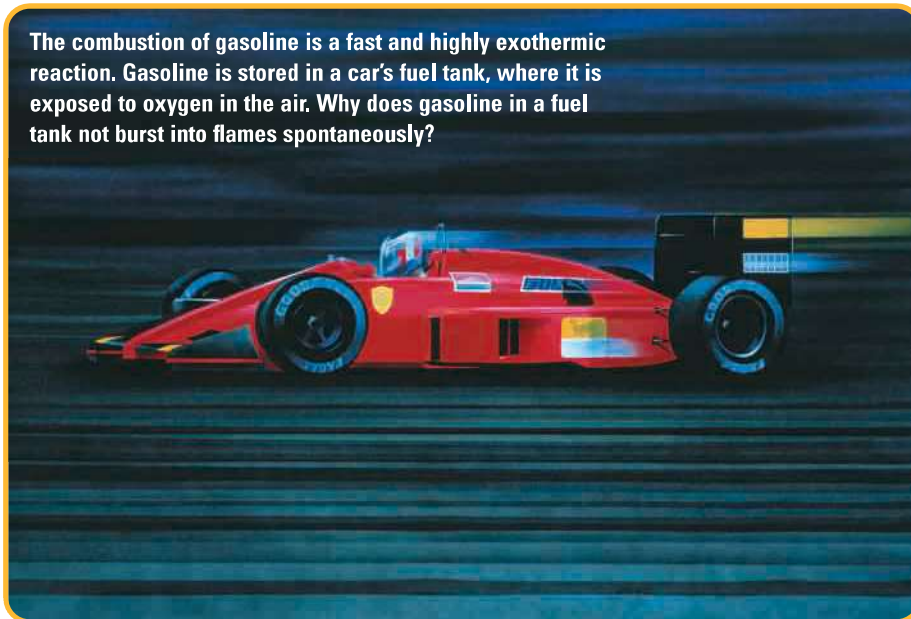
**R**acing cars, such as the one shown below, can reach speeds that are well above 200 km/h. In contrast, the maximum speed of many farm tractors is only about 25 km/h. Just as some vehicles travel more quickly than others, some chemical reactions occur more quickly than others. For example, compare the two reactions that occur in vehicles: the decomposition of sodium azide in an air bag and the rusting of iron in steel.

When an automobile collision activates an air bag, sodium azide,  $\text{NaN}_{3(\text{g})}$ , decomposes to form sodium,  $\text{Na}_{(\text{s})}$ , and nitrogen gas,  $\text{N}_{2(\text{g})}$ . (The gas inflates the bag.) This chemical reaction occurs almost instantaneously. It inflates the air bag quickly enough to cushion a driver's impact in a collision.

On the other hand, the reaction of iron with oxygen to form rust proceeds quite slowly. Most Canadians know that the combination of road salt and wet snow somewhat increases the rate of the reaction. Even so, it takes several years for a significant amount of rust to form on the body of a car. This is a good thing for car owners—if rusting occurred as fast as the reaction in an inflating air bag, cars would flake to pieces in seconds.

Why do some reactions occur slowly while others seem to take place instantaneously? How do chemists measure, compare, and express the rates at which chemical reactions occur? Can chemists predict and control the rate of a chemical reaction? These questions will be answered in Chapter 6.

**The combustion of gasoline is a fast and highly exothermic reaction. Gasoline is stored in a car's fuel tank, where it is exposed to oxygen in the air. Why does gasoline in a fuel tank not burst into flames spontaneously?**



# Expressing and Measuring Reaction Rates

## 6.1

### Section Preview/ Specific Expectations

In this section, you will

- **describe**, with the help of a graph, reaction rate as a function of the change of concentration of a reactant or product with respect to time
- **examine** various methods that are used to monitor the rate of a chemical reaction
- **determine** and **distinguish** between the average rate and the instantaneous rate of a chemical reaction
- **review** the factors that affect reaction rate
- **communicate** your understanding of the following terms: *reaction rate, average rate, instantaneous rate, catalyst*

As you learned in the Unit 3 opener, nitroglycerin is an explosive that was used to clear the way for railroads across North America. It decomposes instantly. The reactions that cause fruit to ripen, then rot, take place over a period of days. The reactions that lead to human ageing take place over a lifetime.

How quickly a chemical reaction occurs is a crucial factor in how the reaction affects its surroundings. Therefore, knowing the rate of a chemical reaction is integral to understanding the reaction.

### Expressing Reaction Rates

The change in the amount of reactants or products over time is called the **reaction rate**. How do chemists express reaction rates? Consider how the rates of other processes are expressed. For example, the Olympic sprinter in Figure 6.1 can run 100 m in about 10 s, resulting in an average running rate of 100 m/10 s or about 10 m/s.

The running rate of a sprinter is calculated by dividing the distance travelled by the interval of time the sprinter takes to travel this distance. In other words, running rate (speed) is expressed as a change in distance divided by a change in time. In general, a change in a quantity with respect to time can be expressed as follows.

$$\begin{aligned}\text{Rate} &= \frac{\text{Change in quantity}}{\text{Change in time}} \\ &= \frac{\text{Quantity}_{\text{final}} - \text{Quantity}_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \\ &= \frac{\Delta \text{Quantity}}{\Delta t}\end{aligned}$$

Chemists express reaction rates in several ways. For example, a reaction rate can be expressed as a change in the amount of reactant consumed or product made per unit of time, as shown below. (The letter A represents a compound.)

$$\begin{aligned}\text{Rate of reaction} &= \frac{\text{Amount of } A_{\text{final}} - \text{Amount of } A_{\text{initial}} \text{ (in mol)}}{t_{\text{final}} - t_{\text{initial}} \text{ (in s)}} \\ &= \frac{\Delta \text{Amount of } A}{\Delta t} \text{ (in mol/s)}\end{aligned}$$

When a reaction occurs between gaseous species or in solution, chemists usually express the reaction rate as a change in the concentration of the reactant or product per unit time. Recall, from your previous chemistry course, that the concentration of a compound (in mol/L) is symbolized by placing square brackets, [ ], around the chemical formula. The equation below is the equation you will work with most often in this section.

$$\begin{aligned}\text{Rate of reaction} &= \frac{\text{Concentration of } A_{\text{final}} - \text{Concentration of } A_{\text{initial}} \text{ (in mol/L)}}{t_{\text{final}} - t_{\text{initial}} \text{ (in s)}} \\ &= \frac{\Delta[A]}{\Delta t} \text{ (in mol/(L} \cdot \text{s))}\end{aligned}$$



**Figure 6.1** The running rate (speed) of a sprinter is expressed as a change in distance over time.

Reaction rates are always positive, by convention. A rate that is expressed as the change in concentration of a product is the rate at which the concentration of the product is increasing. The rate that is expressed in terms of the change in concentration of a reactant is the rate at which the concentration of the reactant is decreasing.

## Average and Instantaneous Rates of Reactions

If reactions always proceeded at a constant rate, it would be straightforward to find reaction rates. You would just need the initial and final concentrations and the time interval. Reaction rates, however, are not usually constant. They change with time. How does this affect the way that chemists determine reaction rates?

Consider the following reaction.



Now examine the graph in Figure 6.2. The blue line on the graph shows the concentration of product C as the reaction progresses, based on the data in Table 6.1.

**Table 6.1** Concentration of C During a Reaction at Constant Temperature

Time (s)	[C] (mol/L)
0.0	0.00
5.0	$3.12 \times 10^{-3}$
10.0	$4.41 \times 10^{-3}$
15.0	$5.40 \times 10^{-3}$
20.0	$6.24 \times 10^{-3}$

The **average rate** of a reaction is the average change in the concentration of a reactant or product per unit time over a given time interval. For example, using the data in Table 6.1, you can determine the average rate of the reaction from  $t = 0.0$  s to  $t = 5.0$  s.

$$\begin{aligned}\text{Average rate} &= \frac{\Delta[\text{C}]}{\Delta t} \\ &= \frac{(3.12 \times 10^{-3} \text{ mol/L}) - 0.00 \text{ mol/L}}{5.0 \text{ s} - 0.0 \text{ s}} \\ &= 6.2 \times 10^{-4} \text{ mol/(L} \cdot \text{s)}\end{aligned}$$

You can see this calculation in Figure 6.2. On a concentration-time graph, the average rate of a reaction is represented by the slope of a line that is drawn between two points on the curve. This line is called a *secant*.

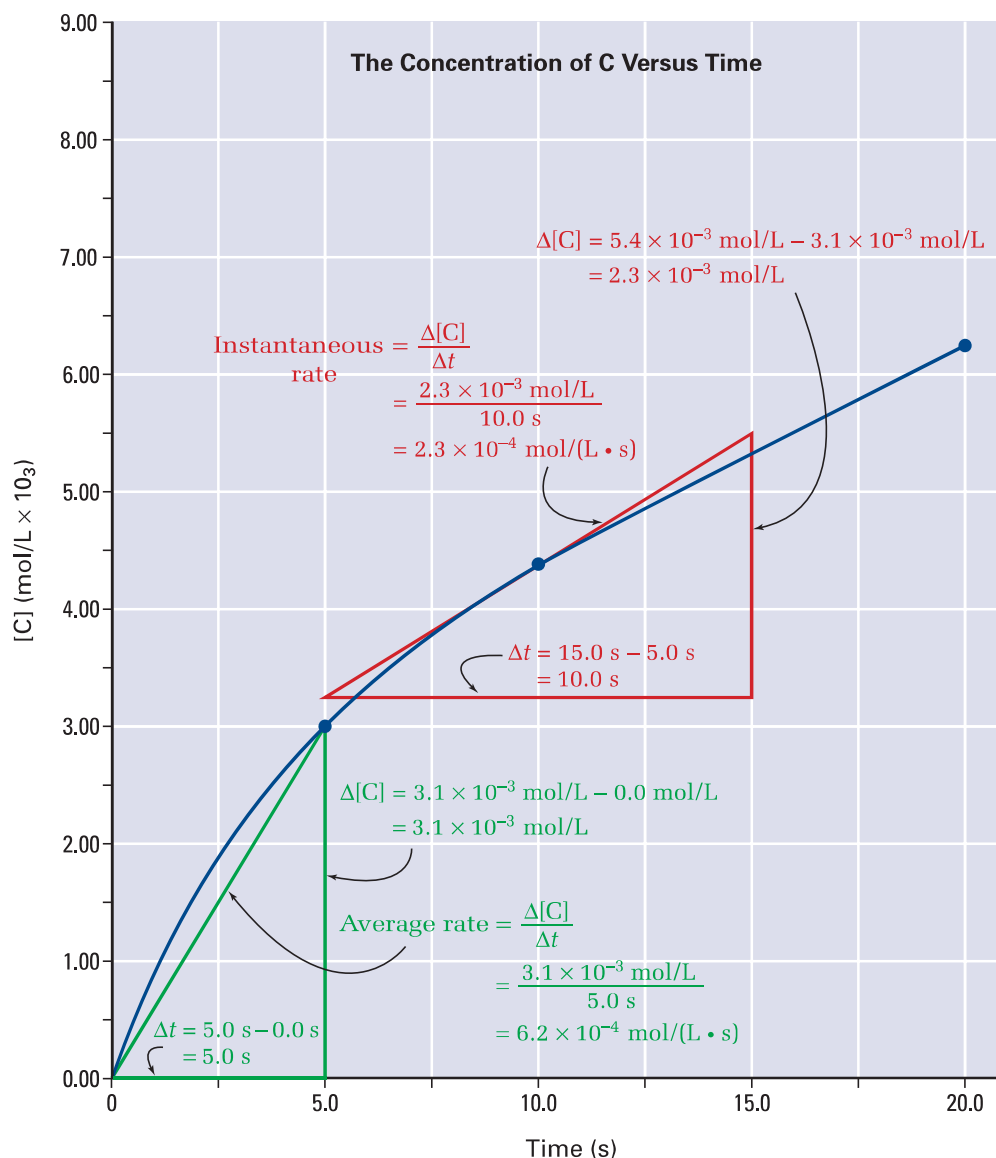
The average rate of a reaction gives an overall idea of how quickly the reaction is progressing. It does not, however, tell you how fast the reaction is progressing at a specific time. For example, suppose that someone asked you how fast the reaction in Figure 6.2 was progressing over 20.0 s. You would probably calculate the average rate from  $t = 0.0$  s to  $t = 20.0$  s. You would come up with the answer  $3.12 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}$ . (Try this calculation yourself.) What would you do, however, if you were asked how fast the reaction was progressing at exactly  $t = 10.0$  s?

The **instantaneous rate** of a reaction is the rate of the reaction at a particular time. To find the instantaneous rate of a reaction using a concentration-time graph, draw a tangent line to the curve and find the slope of the tangent. A *tangent* line is like a secant line, but it touches the curve at only one point. It does not intersect the curve.

The slope of the tangent is the instantaneous rate of the reaction. Figure 6.2 shows the tangent line at  $t = 10.0$  s. As shown on the graph, the slope of the tangent (therefore the instantaneous rate) at  $t = 10.0$  s is  $2.3 \times 10^{-4}$  mol/(L · s).

Notice that near the beginning of the reaction, when the concentration of the reactants is relatively high, the slope of the tangent is greater (steeper). This indicates a faster reaction rate. As the reaction proceeds, the reactants are used up and the slope of the tangent decreases.

In your previous courses in science or physics, you probably learned the difference between *instantaneous* velocity and *average* velocity. How did you use a displacement-time graph to determine instantaneous velocity and average velocity? Write a memo that explains instantaneous rate and average rate to a physicist, by comparing reaction rate with velocity.



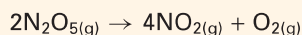
**Figure 6.2** The slope of a tangent drawn to a concentration-time curve represents the instantaneous rate of the reaction. The slope of a secant is used to determine the average rate of a reaction.

In the following ThoughtLab, you will use experimental data to draw a graph that shows the change in concentration of the product of a reaction. Then you will use the graph to help you determine the instantaneous rate and average rate of the reaction.





A chemist carried out a reaction to trace the rate of decomposition of dinitrogen pentoxide.



The chemist collected the following data at a constant temperature.

Time (s)	[O <sub>2</sub> ] (mol/L)
0.00	0.0
$6.00 \times 10^2$	$2.1 \times 10^{-3}$
$1.20 \times 10^3$	$3.6 \times 10^{-3}$
$1.80 \times 10^3$	$4.8 \times 10^{-3}$
$2.40 \times 10^3$	$5.6 \times 10^{-3}$
$3.00 \times 10^3$	$6.4 \times 10^{-3}$
$3.60 \times 10^3$	$6.7 \times 10^{-3}$
$4.20 \times 10^3$	$7.1 \times 10^{-3}$
$4.80 \times 10^3$	$7.5 \times 10^{-3}$
$5.40 \times 10^3$	$7.7 \times 10^{-3}$
$6.00 \times 10^3$	$7.8 \times 10^{-3}$

### Procedure

- Using graph paper or spreadsheet software, plot and label a graph that shows the rate of formation of oxygen gas. The concentration of O<sub>2</sub> (in mol/L) is the dependent variable and time (in s) is the independent variable.

- Draw a secant to the curve in the interval from  $t = 0 \text{ s}$  to  $t = 4800 \text{ s}$ .
- Draw a tangent to the curve at  $t = 1200 \text{ s}$  and at  $t = 4800 \text{ s}$ .
- Determine the slope of the secant. What is the average rate of the reaction over the given time interval? Include proper units, and pay attention to significant digits.
- Determine the slope of each tangent. What is the instantaneous reaction rate at  $t = 1200 \text{ s}$  and at  $t = 4800 \text{ s}$ ? Include proper units, and pay attention to significant digits.

### Analysis

- Why are the units for the average rate and the instantaneous rate the same?
- For a given set of data, two students determined different average reaction rates. If neither student made an error in the calculations, account for the difference in their reaction rates.
- Propose a reason for the difference in the instantaneous rates at 1200 s and 4800 s.
- When chemists compare the rates of reactions carried out under different conditions, they often compare the rates near the beginning of the reactions. What advantage(s) do you see in this practice? **Hint:** Think of slow reactions.

## Reaction Rates in Terms of Products and Reactants

In the ThoughtLab, you analyzed the rate of the following reaction in terms of the production of oxygen.



There are two other ways to represent the rate of this reaction:

- in terms of the rate of the disappearance of dinitrogen pentoxide
- in terms of the production of nitrogen dioxide

For every 1 mol of O<sub>2</sub> that is produced, 4 mol of NO<sub>2</sub> are also produced. This means that the rate of production of NO<sub>2</sub> is four times greater than the rate of production of O<sub>2</sub>. Therefore, the rate of production of O<sub>2</sub> is one quarter the rate of production of NO<sub>2</sub>. You can express the relationship between O<sub>2</sub> production and NO<sub>2</sub> production as follows.

$$\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

When 1 mol of O<sub>2</sub> is produced, 2 mol of N<sub>2</sub>O<sub>5</sub> are consumed. Therefore, the rate of production of O<sub>2</sub> is half the rate of disappearance of N<sub>2</sub>O<sub>5</sub>. You can represent this relationship as follows:

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Notice that the expression involving  $\text{N}_2\text{O}_5$  (the reactant) has a negative sign. A change in concentration is calculated using the expression below.

$$\text{Change in concentration} = \text{Concentration}_{\text{final}} - \text{Concentration}_{\text{initial}}$$

Since the concentration of a reactant always decreases as a reaction progresses, the change in concentration is always negative. By convention, however, *a rate is always expressed as a positive number*. Therefore, expressions that involve reactants must be multiplied by  $-1$  to become positive.

Examine the Sample Problem below to see how to express reaction rates in terms of products and reactants. Then try the Practice Problems that follow.



#### Electronic Learning Partner

To learn more about reaction rates expressed as changes in concentration over time, go to the Chemistry 12 Electronic Learning Partner.

### Sample Problem

#### Expressing Reaction Rates

##### Problem

Dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , decomposes to form nitrogen dioxide and oxygen.



$\text{NO}_2$  is produced at a rate of  $5.0 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})$ . What is the corresponding rate of disappearance of  $\text{N}_2\text{O}_5$  and rate of formation of  $\text{O}_2$ ?

##### What Is Required?

Since  $\text{N}_2\text{O}_5$  is a reactant, you need to calculate its rate of disappearance.  $\text{O}_2$  is a product, so you need to find its rate of formation.

##### What Is Given?

You know the rate of formation of  $\text{NO}_2$  and the balanced chemical equation.

##### Plan Your Strategy

First check that the chemical equation is balanced. Then use the molar coefficients in the balanced equation to determine the relative rates of disappearance and formation.

Since 4 mol of  $\text{NO}_2$  are produced for every 2 mol of  $\text{N}_2\text{O}_5$  that decompose, the rate of disappearance of  $\text{N}_2\text{O}_5$  is  $\frac{2}{4}$ , or  $\frac{1}{2}$ , the rate of formation of  $\text{NO}_2$ . Similarly, 1 mol of  $\text{O}_2$  is formed for every 4 mol of  $\text{NO}_2$ . Therefore, the rate of production of  $\text{O}_2$  is  $\frac{1}{4}$  the rate of  $\text{NO}_2$  production.

##### Act on Your Strategy

$$\begin{aligned}\text{Rate of disappearance of } \text{N}_2\text{O}_5 &= \frac{1}{2} \times 5.0 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s}) \\ &= 2.5 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})\end{aligned}$$

$$\begin{aligned}\text{Rate of production of } \text{O}_2 &= \frac{1}{4} \times 5.0 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s}) \\ &= 1.2 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})\end{aligned}$$

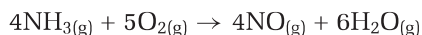
##### Check Your Solution

From the coefficients in the balanced chemical equation, you can see that the rate of decomposition of  $\text{N}_2\text{O}_5$  is  $\frac{2}{4}$ , or  $\frac{1}{2}$ , the rate of formation of  $\text{NO}_2$ . The rate of production of  $\text{O}_2$  is  $\frac{1}{4}$  the rate of decomposition of  $\text{N}_2\text{O}_5$ .

## Practice Problems

1. Cyclopropane,  $\text{C}_3\text{H}_6$ , is used in the synthesis of organic compounds and as a fast-acting anesthetic. It undergoes rearrangement to form propene. If cyclopropane disappears at a rate of  $0.25 \text{ mol/s}$ , at what rate is propene being produced?

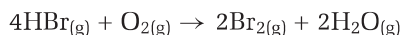
2. Ammonia,  $\text{NH}_3$ , reacts with oxygen to produce nitric oxide,  $\text{NO}$ , and water vapour.



At a specific time in the reaction, ammonia is disappearing at rate of  $0.068 \text{ mol}/(\text{L} \cdot \text{s})$ .

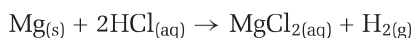
What is the corresponding rate of production of water?

3. Hydrogen bromide reacts with oxygen to produce bromine and water vapour.



How does the rate of decomposition of  $\text{HBr}$  (in  $\text{mol}/(\text{L} \cdot \text{s})$ ) compare with the rate of formation of  $\text{Br}_2$  (also in  $\text{mol}/(\text{L} \cdot \text{s})$ )? Express your answer as an equation.

4. Magnesium metal reacts with hydrochloric acid to produce magnesium chloride and hydrogen gas.



Over an interval of  $1.00 \text{ s}$ , the mass of  $\text{Mg}_{(s)}$  changes by  $-0.011 \text{ g}$ .

(a) What is the corresponding rate of consumption of  $\text{HCl}_{(aq)}$  (in  $\text{mol/s}$ )?

(b) Calculate the corresponding rate of production of  $\text{H}_{2(g)}$  (in  $\text{L/s}$ ) at  $20^\circ\text{C}$  and  $101 \text{ kPa}$ .

### PROBLEM TIP

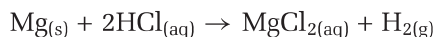
Recall, from your previous chemistry course, that  $1.00 \text{ mol}$  of any gas occupies a volume of  $24.0 \text{ L}$  at  $20^\circ\text{C}$  and  $101 \text{ kPa}$ .

## Methods for Measuring Reaction Rates

How do chemists collect the data they need to determine a reaction rate? To determine empirically the rate of a chemical reaction, chemists must monitor the concentration or amount of at least one reactant or product. There are a variety of techniques available. The choice of technique depends on the reaction under study and the equipment available.

### Monitoring Mass, pH, and Conductivity

Consider the reaction of magnesium with hydrochloric acid.



Hydrogen gas is released in the reaction. You can track the decrease in mass, due to the escaping hydrogen, by carrying out the reaction in an open vessel on an electric balance. The decrease in mass can be plotted against time. Some electronic balances can be connected to a computer, with the appropriate software, to record mass and time data automatically as the reaction proceeds.

Another technique for monitoring the reaction above involves pH. Since  $\text{HCl}$  is consumed in the reaction, you can record changes in pH with respect to time. Figure 6.3 shows a probe being used to monitor the changing pH of a solution.



**Figure 6.3** If the concentration of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions changes over the course of a reaction, a chemist can use a pH meter to monitor the reaction.

A third technique involves electrical conductivity. Dissolved ions in aqueous solution conduct electricity. The electrical conductivity of the solution is proportional to the concentration of ions. Therefore, reactions that occur in aqueous solution, and involve a change in the quantity of dissolved ions, undergo a change in electrical conductivity. In the reaction above, hydrochloric acid is a mix of equal molar amounts of two ions: hydronium,  $\text{H}_3\text{O}^+$ , and chloride,  $\text{Cl}^-$ . The  $\text{MgCl}_2$  that is produced exists as three separate ions in solution: one  $\text{Mg}^{2+}$  ion and two  $\text{Cl}^-$  ions. Since there is an increase in the concentration of ions as the reaction proceeds, the conductivity of the solution also increases with time.

### Monitoring Pressure

When a reaction involves gases, the pressure of the system often changes as the reaction progresses. Chemists can monitor this pressure change. For example, consider the decomposition of dinitrogen pentoxide, shown in the following chemical reaction.



When 2 mol of  $\text{N}_2\text{O}_5$  gas decompose, they form 5 mol of gaseous products. Therefore, the pressure of the system increases as the reaction proceeds, provided that the reaction is carried out in a closed container. Chemists use a pressure sensor to monitor pressure changes.

### Monitoring Colour

Colour change can also be used to monitor the progress of a reaction. The absorption of light by a chemical compound is directly related to the concentration of the compound. For example, suppose you add several drops of blue food colouring to a litre of water. If you add a few millilitres of bleach to the solution, the intensity of the colour of the food dye diminishes as it reacts. You can then monitor the colour change. (Do not try this experiment without your teacher's supervision.)

For accurate measurements of the colour intensity of a solution, chemists use a device called a *spectrophotometer*. (See Figure 6.4.)



**PROBEWARE**

If you have access to probeware, do Probeware Investigation 6-A, or a similar investigation from a probeware company.

**Figure 6.4** This photograph shows a simple spectrophotometer, which measures the amount of visible light that is absorbed by a coloured solution. More sophisticated devices can measure the absorption of ultraviolet and infrared radiation.

### Monitoring Volume

When a reaction generates gas, chemists can monitor the volume of gas produced. In Investigation 6-A, you will determine average reaction rates by recording the time taken to produce a fixed volume of gas. You will perform several trials of the same reaction to investigate the effects that temperature, concentration of reactants, and surface area of reactants have on the reaction rate. You will also perform one trial using a different reactant.

## Investigation 6-A

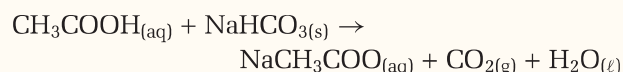
Predicting

Performing and recording

Analyzing and interpreting

## Studying Reaction Rates

You have probably already encountered the reaction of vinegar with baking soda. The carbon dioxide that is produced can be used to simulate a volcano, for example, or to propel a toy car or rocket.



Other carbonate-containing compounds, such as calcium carbonate, can also react with vinegar to produce  $\text{CO}_2$ .

In this investigation, you will determine reaction rates by recording the time taken to produce a fixed volume of  $\text{CO}_2$ . You will collect the  $\text{CO}_2$  by downward displacement of water.

## Question

How do factors such as concentration, temperature, a different reactant, and surface area affect the rate of this reaction?

## Prediction

Read the Procedure. *Quantitatively* predict the effects of changes to the concentration and temperature. *Qualitatively* predict the effects of changes to the reactant and surface area.

## Materials

electronic balance  
pneumatic trough  
stopwatch  
250 mL Erlenmeyer flask  
retort stand and clamp  
one-holed rubber stopper, fitted with a piece of glass tubing (must be airtight)  
1 m rubber hose to fit glass tubing (must be airtight)  
25 or 100 mL graduated cylinder  
large test tube  
weighing paper, weighing boat, or small beaker  
100 mL vinegar (at room temperature)  
10 g baking soda,  $\text{NaHCO}_3$

2.0 g powdered  $\text{CaCO}_3$   
2.0 g solid  $\text{CaCO}_3$  (marble chips)  
scoopula  
thermometer  
wash bottle with distilled water (at room temperature)  
warm-water bath (prepared using a large beaker and a hot plate or electric kettle)  
ice bath (ice cubes and water)  
paper towel

## Safety Precautions

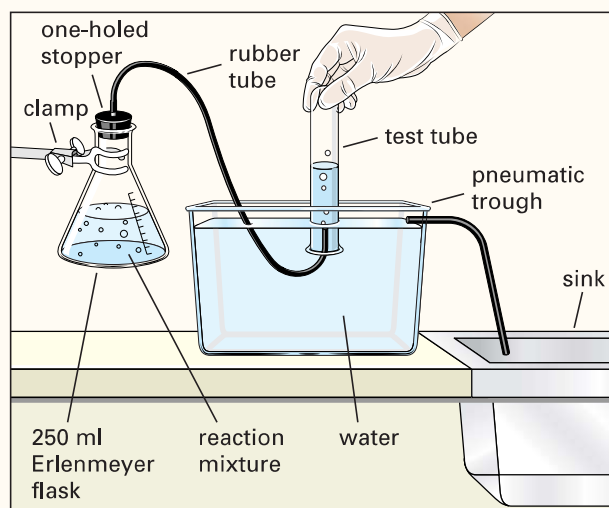


- Beware of shock hazard if an electric kettle or hot plate is used.
- Wear safety glasses at all times.

## Procedure

## Part 1 The Effect of Concentration

1. The distilled water and vinegar that you are going to use should be at room temperature. Measure and record the temperature of either the vinegar or the distilled water.
2. Assemble the apparatus for the collection of  $\text{CO}_2$ , by downward displacement of water, as shown below.





**Note:** To invert a test tube filled with water, place a piece of paper over the mouth of the filled test tube before inverting it.

3. Copy the table below into your notebook, to record your data.

Trial	Mass of NaHCO <sub>3</sub> (g)	Volume of vinegar (mL)	Volume of distilled water (mL)	Time to fill test tube with CO <sub>2</sub> (s)	Average reaction rate (mL/s)
1	1.00	20.0	0.0		
2	1.00	15.0	5.0		
3	1.00	10.0	10.0		
4	1.00	5.0	15.0		

4. For trial 1, add 20.0 mL of vinegar to the flask. Have the stopwatch ready. The end of the rubber tubing should be in place under the water-filled test tube in the pneumatic trough. Quickly add 1.00 g of NaHCO<sub>3</sub> to the flask, and put in the stopper. Record the time taken to fill the tube completely with CO<sub>2</sub>.
5. Complete trials 2 to 4 with the indicated quantities.
6. Determine the volume of CO<sub>2</sub> you collected by filling the gas collection test tube to the top with water and then pouring the water into a graduated cylinder.

### Part 2 The Effect of Temperature

1. Repeat trial 3 in Part 1 using a mixture of 10 mL of water and 10 mL of vinegar that has been cooled to about 10°C below room temperature in an ice bath. Measure and record the temperature of the mixture immediately before the reaction. Record the time taken to fill the test tube with CO<sub>2</sub>. Determine the average rate of production of CO<sub>2</sub> (in mL/s).
2. Use a hot-water bath to warm a mixture of 10 mL of distilled water and 10 mL of vinegar to about 10°C above room temperature. Repeat trial 3 in Part 1 using this heated mixture. Measure and record the temperature of the vinegar-water mixture immediately before the reaction. Record the time taken to fill the test tube with CO<sub>2</sub>. Determine the average rate of production of CO<sub>2</sub> (in mL/s).

### Part 3 The Effect of Reactants and Surface Area

1. Repeat trial 3 in Part 1, using 1.00 g of powdered calcium carbonate, CaCO<sub>3</sub>, instead of NaHCO<sub>3</sub>. All the reactants should be at room temperature. Record the time taken to fill the tube with CO<sub>2</sub>. Determine the average rate of production of CO<sub>2</sub> (in mL/s).
2. Repeat step 1, using 1.00 g of solid CaCO<sub>3</sub> (marble chips) instead of powdered CaCO<sub>3</sub>.

### Analysis

1. Draw a graph to show your results for Part 1. Plot average reaction rate (in mL CO<sub>2</sub>/s) on the y-axis. Plot [CH<sub>3</sub>COOH] (in mol/L) on the x-axis. Vinegar is 5.0% (m/v) CH<sub>3</sub>COOH.
2. As quantitatively as possible, state a relationship between [CH<sub>3</sub>COOH] and the average rate of the reaction.
3. Compare the average reaction rate for corresponding concentrations of vinegar at the three different temperatures tested.
4. What effect did a 10°C temperature change have on the reaction rate? Be as quantitative as possible.
5. What effect did using CaCO<sub>3</sub> instead of NaHCO<sub>3</sub> have on the reaction rate?
6. What effect did the surface area of the CaCO<sub>3</sub> have on the reaction rate?

### Conclusion

7. State the effect of each factor on the reaction rate. Compare your results with your prediction.

### Application

8. The rate of this reaction can be expressed by the following equation:  
Rate =  $k[\text{CH}_3\text{COOH}]^m$ , where  $k$  is a constant and  $m$  is usually equal to 0, 1, or 2.  
What value of  $m$  do your results suggest?

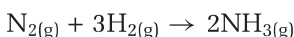
## Factors That Affect Reaction Rate

Chemists have made the following observations about factors that affect reaction rate. You may already be familiar with some of these observations, from your previous studies of chemical reactions and from Investigation 6-A.

### Summary of Some Factors That Affect Reaction Rate

1. The rate of a reaction can be increased by increasing the temperature.
2. Increasing the concentrations of the reactants usually increases the rate of the reaction.
3. A **catalyst** is a substance that increases the rate of a reaction. The catalyst is regenerated at the end of the reaction and can be re-used. You will learn more about catalysts in section 6.4.
4. Increasing the available surface area of a reactant increases the rate of a reaction.
5. The rate of a chemical reaction depends on what the reactants are.

Chemists and engineers use these and other factors to manipulate the rate of a particular reaction to suit their needs. For example, consider the synthesis of ammonia,  $\text{NH}_3$ , from nitrogen and hydrogen.



This reaction must be carried out with high concentrations of reactants, at a temperature of  $400^\circ\text{C}$  to  $500^\circ\text{C}$ , in the presence of a catalyst. Otherwise, the rate of production of ammonia is too slow to be economically feasible.

## Section Summary

In this section, you learned how to express reaction rates and how to analyze reaction rate graphs. You also learned how to determine the average rate and instantaneous rate of a reaction, given appropriate data. Then you examined different techniques for monitoring the rate of a reaction. Finally, you carried out an investigation to review some of the factors that affect reaction rate. In the next section, you will learn how to use a rate law equation to show the quantitative relationships between reaction rate and concentration.

## Section Review

- 1 **C** In your own words, explain why the rate of a chemical reaction is fastest at the beginning of the reaction.
- 2 **K/U** Show why the expression for the rate of disappearance of a reactant is always negative, even though rates are always positive, by convention.
- 3 **K/U** Under what circumstances is the rate at which the concentration of a reactant decreases numerically equal to the rate at which the concentration of a product increases?

- 4 **I** In the following reaction, the rate of production of sulfate ions is  $1.25 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{s})$ .
- $$2\text{HCrO}_4^- + 3\text{HSO}_3^- + 5\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 5\text{H}_2\text{O}$$
- (a) What is the corresponding rate at which  $[\text{HSO}_3^-]$  decreases over the same time interval?
- (b) What is the corresponding rate at which  $[\text{HCrO}_4^-]$  decreases over the same time interval?
- 5 **K/U** In this section, you examined the following techniques for monitoring the progress of a reaction. State the conditions that must change as a reaction proceeds, to allow each technique to be used.
- (a) using a pH meter
- (b) using a spectrophotometer
- (c) using a conductivity meter
- (d) monitoring pressure
- 6 **I** Refer to the table in the ThoughtLab on page 270. Redraw the table, adding one column for  $[\text{N}_2\text{O}_5]$  and one column for  $[\text{NO}_2]$ .
- (a) Calculate  $[\text{NO}_2]$  at each time interval, based on  $[\text{O}_2]$ . Assume initial  $[\text{NO}_2] = 0.0 \text{ mol/L}$ .
- (b) On the same set of axes, draw and label a concentration-time graph with two curves: one for  $[\text{NO}_2]$  and one for  $[\text{O}_2]$ .
- (c) What do you notice about the shapes of the two curves?
- (d) Determine the instantaneous rate at  $t = 1200$  and  $t = 4800$  for each compound. How do the instantaneous rates compare?
- (e) Is it possible to use the information in the table to calculate  $[\text{N}_2\text{O}_5]$  at each time interval? Explain your answer.
- (f) On a concentration-time graph, sketch the shape of a curve that represents  $[\text{N}_2\text{O}_5]$  versus time.
- 7 **C** For each reaction, suggest one or more techniques for monitoring the progress of the reaction. Explain your answers.
- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_{2(\ell)} + \text{Br}_{2(\text{aq})} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHBrCH}_2\text{Br}_{(\ell)}$   
**Hint:**  $\text{Br}_2$  is brownish-orange. The other compounds are colourless.
- (b)  $\text{H}_2\text{O}_{2(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\ell)} + \frac{1}{2}\text{O}_{2(\text{g})}$
- (c)  $\text{CaCO}_{3(\text{s})} + \text{H}_2\text{SO}_{4(\text{aq})} \rightarrow \text{CaSO}_{4(\text{aq})} + \text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\ell)}$
- (d)  $5\text{Fe}^{2+}_{(\text{aq})} + \text{MnO}_4^{-}_{(\text{aq})} + 8\text{H}^{+}_{(\text{aq})} \rightarrow \text{Mn}^{2+}_{(\text{aq})} + 5\text{Fe}^{3+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\ell)}$   
**Hint:** The permanganate ion,  $\text{MnO}_4^-$ , is purple. All the other species in the reaction are colourless.
- (e)  $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})}$

## 6.2

# The Rate Law: Reactant Concentration and Rate

### Section Preview/ Specific Expectations

In this section, you will

- **express** the rate of a reaction as a rate law equation
- **explain** the concept of half-life for a reaction
- **determine** the rate law equation and rate constant for a reaction from experimental data
- **communicate** your understanding of the following terms: *rate law equation, rate constant, overall reaction order, first-order reaction, second-order reaction, initial rates method, half-life ( $t_{1/2}$ )*

The rate of a chemical reaction depends on several factors, as you learned in section 6.1. One of the factors that affect reaction rate is the concentrations of the reactants. You know that the rates of most chemical reactions increase when the concentrations of the reactants increase. Is there a more specific relationship? In this section, you will explore the quantitative relationships between the rate of a reaction and the concentrations of the reactants.

### Relating Reactant Concentrations and Rate

Consider the general reaction below.



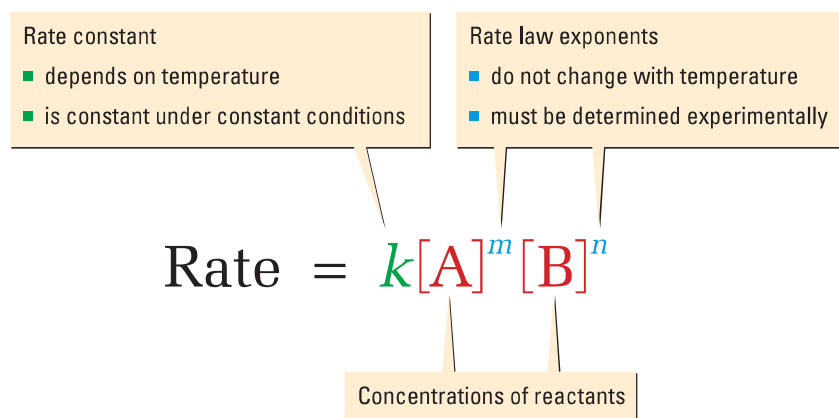
This reaction occurs at a constant temperature. The reactant formulas are represented by A and B. The stoichiometric coefficients are represented by  $a$  and  $b$ . In this section, you will study reaction rates that are not affected by the concentrations of the products. Therefore, you do not need to use symbols for the products.

In general, the rate of a reaction increases when the concentrations of the reactants increase. The dependence of the rate of a reaction on the concentrations of the reactants is given by the following relationship.

$$\text{Rate} \propto [A]^m[B]^n$$

This relationship can be expressed in a general equation called the **rate law equation**. The rate law equation is shown in Figure 6.5. For any reaction, the rate law equation expresses the relationship between the concentrations of the reactants and the rate of the reaction. The letter  $k$  represents a proportionality constant called the **rate constant**. There is a different rate constant for each reaction at any given temperature.

The exponents  $m$  and  $n$  must be determined by experiment. They do not necessarily correspond to the stoichiometric coefficients of their reactants. They are usually 1 or 2, but values of 0, 3, and even fractions can occur.



**Figure 6.5** This diagram explains the components of the rate law.

The values of the exponents in the rate law equation establish the order of the reaction. If a given reactant is found to have an exponent of 1, the reaction is said to be *first order* in this reactant. Similarly, if the exponent of a reactant is 2, the reaction is *second order* in this reactant. The sum of the exponents ( $m + n$ ) is known as the **overall reaction order**. For example, the rate law equation below represents a reaction that is first order in A, second order in B, and third order ( $1 + 2$ ) overall.

$$\text{Rate} = k[\text{A}]^1[\text{B}]^2$$

Chemists carry out experiments to determine the rate law equation for a given reaction at a given temperature. Later in the section, you will work with data and do this yourself. First, however, it is necessary to examine further the rate constant and reaction order.

## The Rate Constant

The magnitude of the rate constant,  $k$ , indicates the speed of a reaction. A small rate constant indicates a slow reaction. A large rate constant indicates a fast reaction. For example, a first-order reaction with a rate constant of  $10^2 \text{ s}^{-1}$  will be essentially complete in less than 0.10 s. By contrast, a first-order reaction with a rate constant of  $10^{-3} \text{ s}^{-1}$  will take about 2 h.

As a reaction proceeds, the reaction rate decreases because the concentrations of the reactants decrease. The value of the rate constant, however, remains the same throughout the reaction. In other words, for a given reaction under constant conditions, the value of  $k$  remains constant.

What happens if the temperature changes? Since the rate of a chemical reaction depends on temperature, so does  $k$ . Because a chemical reaction depends on temperature, chemists who study reaction rates must work at constant temperature. Furthermore, the value of  $k$  must be accompanied by the temperature at which the reaction occurred. For example, for the second order decomposition of hydrogen iodide,  $k = 2.7 \times 10^{-3} \text{ L}/(\text{mol} \cdot \text{s})$  at  $440^\circ\text{C}$ . When the temperature is increased to  $500^\circ\text{C}$ ,  $k = 3.9 \times 10^{-3} \text{ L}/(\text{mol} \cdot \text{s})$ .

## Defining First-Order Reactions

A **first-order reaction** has an overall order of 1. The decomposition of dinitrogen pentoxide,  $\text{N}_2\text{O}_5$ , is an example of a first-order reaction.



Experiments have shown that this reaction is first order in  $\text{N}_2\text{O}_5$ . In other words, the rate law equation is written as follows:

$$\text{Rate} = k[\text{N}_2\text{O}_5]^1$$

Because the overall order of the reaction is one, it is a first-order reaction.

Reactions with more than one reactant can also be first-order reactions. For example, consider the following reaction.



Experiments have shown that the reaction is first order in  $(\text{CH}_3)_3\text{CBr}$ , and zero order in water. In other words, the rate of the reaction does not depend, at all, on the concentration of water. The rate law equation is written as follows:

$$\text{Rate} = k[(\text{CH}_3)_3\text{CBr}_{(\text{l})}]^1[\text{H}_2\text{O}_{(\text{l})}]^0$$

The overall reaction order is 1 ( $1 + 0$ ). The reaction is first order.

### CONCEPT CHECK

Chemists can trace the progress of the chemical reaction shown on the left by monitoring its conductivity. Explain why.



You frequently encounter first-order relationships in everyday life. For example, if one soft drink costs \$1.50, two soft drinks cost \$3.00, three cost \$4.50, and so on. This first-order relationship can be represented by the following equation.

$$\text{Cost} = \$1.50 (\text{Number of soft drinks})^1$$

## Defining Second-Order Reactions

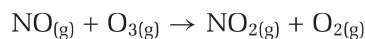
A **second-order reaction** has an overall reaction order of 2. An example of a second-order reaction is the decomposition of hydrogen iodide.



Chemists have determined, by experiment, that this reaction is second order in hydrogen iodide. Therefore, the rate law equation is written as follows:

$$\text{Rate} = k[\text{HI}]^2$$

Another example of a second-order reaction is the reaction between nitric oxide and ozone.



By experiment, chemists have determined that the reaction is first order in nitric oxide and first order in ozone, as shown below:

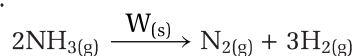
$$\text{Rate} = k[\text{NO}]^1[\text{O}_3]^1$$

The overall order of the reaction is 2 (1 + 1). Therefore, the reaction is a second order reaction.

For a non-chemistry example of a second-order relationship, consider the equation for the simple parabola,  $y = x^2$ . When  $x = 3$ ,  $y = 9$ . When  $x = 12$ , the value of  $y$  increases to  $12^2 = 144$ . In other words, when the value of  $x$  increases by 4, the value of  $y$  increases by a factor of  $4^2$  ( $16 \times 9 = 144$ ).

## Other Reactions

There are also other types of reactions, besides first-order and second-order reactions. For example, consider the decomposition of ammonia on a tungsten, W, catalyst.



The rate law equation for this reaction has been found experimentally.

$$\text{Rate} = k[\text{NH}_3]^0 = k$$

The rate of decomposition of ammonia on a tungsten catalyst is *independent* of the concentration of ammonia, since  $[\text{NH}_3]^0 = 1$ . In other words, the rate of the reaction is a constant.

Many reactions have overall orders that are higher than 2. Some reactions have overall orders that are fractions. In this text, however, you will concentrate on first-order and second-order reactions.

## The Initial Rates Method

As you have learned, the values of the exponents in a rate law equation must be determined experimentally. Chemists determine the values of  $m$  and  $n$  by carrying out a series of experiments. Each experiment has a different, known set of initial concentrations. All other factors, such as temperature, remain constant. Chemists measure and compare the initial rate of each reaction. Thus, this method is called the **initial rates method**.



### CHEM

#### FACT

For the decomposition reaction of hydrogen iodide, the value of the exponent of  $[\text{HI}]$  in the rate law equation is the same as its molar coefficient in the balanced chemical equation. This is not always the case. The values of the exponents in a rate law equation *must* be determined *by experiment*.



### Electronic Learning Partner

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

There are several reasons for using initial rates. One reason is that chemists do not need to follow each reaction to its end. This saves time, especially when studying slow reactions.

### Rate Experiments

To see how the initial rates method works, consider the following reaction:



The general rate law equation for this reaction is given below.

$$\text{Rate} = k[\text{N}_2\text{O}_5]^m$$

To determine the value of  $m$ , a chemist performs three experiments. A different initial concentration of dinitrogen pentoxide,  $[\text{N}_2\text{O}_5]_0$ , is used for each experiment. The subscript 0 represents  $t = 0$ . Table 6.2 shows the results of these experiments.

**Table 6.2** Data for Rate Experiments

Experiment	Initial $[\text{N}_2\text{O}_5]_0$ (mol/L)	Initial rate (mol/(L · s))
1	0.010	$4.8 \times 10^{-6}$
2	0.020	$9.6 \times 10^{-6}$
3	0.030	$1.5 \times 10^{-5}$

The value of  $m$  can be determined using at least two different methods. By inspection, you can see that when the concentration of  $\text{N}_2\text{O}_5$  is doubled (experiments 1 and 2), the rate also doubles. When the concentration of  $\text{N}_2\text{O}_5$  is tripled (experiments 1 and 3), the rate also triples. This indicates a first-order relationship, as follows:

$$\text{Rate} = k[\text{N}_2\text{O}_5]^1$$

Alternatively, you can compare the rate law equation for each experiment using ratios. This method is useful when the relationship between concentration and rate is not immediately obvious from the data.

Write the rate expressions for experiments 1 and 2 as follows:

$$\begin{aligned}\text{Rate}_1 &= k(0.010)^m \\ &= 4.8 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}\end{aligned}$$

$$\begin{aligned}\text{Rate}_2 &= k(0.020)^m \\ &= 9.6 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}\end{aligned}$$

Create a ratio to compare the two rates.

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k(0.010 \text{ mol/L})^m}{k(0.020 \text{ mol/L})^m} = \frac{4.8 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}}{9.6 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}}$$

Since  $k$  is a constant for reactions that occur at a constant temperature, you can cancel out  $k$ .

$$\begin{aligned}\frac{\cancel{k}(0.010 \text{ mol/L})^m}{\cancel{k}(0.020 \text{ mol/L})^m} &= \frac{4.8 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}}{9.6 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}} \\ (0.5)^m &= 0.5 \\ m &= 1 \text{ (by inspection)}\end{aligned}$$

### CONCEPT CHECK

Check your value of  $m$  by setting up a ratio for experiments 1 and 3 (or experiments 2 and 3). Solve for  $m$ , and compare.

## CONCEPT CHECK

Notice that the units of the rate constant are determined by your calculation. For a first-order reaction, the units are always  $\text{s}^{-1}$ . Show why this is the case. What are the units for a second-order reaction?

## Determining the Rate Constant

Once you know the rate law equation for a reaction, you can calculate the rate constant using the results from any of the experiments. The rate law equation for the previous rate experiments is written as follows:

$$\text{Rate} = k[\text{N}_2\text{O}_5]^1$$

You can use data from any of the three experiments to calculate  $k$ . Substituting data from experiment 1, you can solve for  $k$ .

$$4.8 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s}) = k(0.010 \text{ mol}/\text{L})$$

$$\begin{aligned} k &= \frac{4.8 \times 10^{-6} \text{ mol}/(\text{L} \cdot \text{s})}{0.010 \text{ mol}/\text{L}} \\ &= 4.8 \times 10^{-6} \text{ s}^{-1} \end{aligned}$$

Therefore, for the temperature at which the experiments were carried out,  $4.8 \times 10^{-6} \text{ s}^{-1}$  is the rate constant. Using data from experiment 2 would give the same value of  $k$ .

## Sample Problem

### Finding a Rate Law Equation

#### Problem

Chlorine dioxide,  $\text{ClO}_2$ , reacts with hydroxide ions to produce a mixture of chlorate and chlorite ions.



The rate data in the table below were determined at a constant temperature. Find the rate law equation and the value of  $k$ .

Experiment	Initial $[\text{ClO}_2]$ (mol/L)	Initial $[\text{OH}^-]$ (mol/L)	Initial rate of formation of products (mol/(L · s))
1	0.0150	0.0250	$1.30 \times 10^{-3}$
2	0.0150	0.0500	$2.60 \times 10^{-3}$
3	0.0450	0.0250	$1.16 \times 10^{-2}$

#### What Is Required?

You need to find the value of  $m$ ,  $n$ , and  $k$  in the general rate law equation for the reaction.

$$\text{Rate} = k[\text{ClO}_2]^m[\text{OH}^-]^n$$

#### What Is Given?

You know the initial concentrations of the reactants and the initial rates for three experiments.

#### Plan Your Strategy

**Step 1** Find two experiments in which  $[\text{ClO}_2]$  remains constant and  $[\text{OH}^-]$  changes. Compare the rates and concentrations to solve for  $n$ . Then find two experiments in which  $[\text{OH}^-]$  remains constant and  $[\text{ClO}_2]$  changes. Compare rates and concentrations to find  $m$ .

**Step 2** Use the data and your calculated values for  $m$  and  $n$  to solve for  $k$ , using the following equation.

$$\text{Rate} = k[\text{ClO}_2]^m[\text{OH}^-]^n$$

**PROBLEM TIP**

When you set up your ratio to compare rates, it does not matter which rate is the numerator, and which is the denominator. It is often easier to see the solution, however, if the larger rate is the numerator.

**Act on Your Strategy**

**Step 1** Begin with experiments 1 and 2, where  $[\text{ClO}_2]$  is constant, to determine the order of the reaction with respect to  $\text{OH}^-$ .

Set up a ratio for the two rates as shown. Notice that you can cancel out  $[\text{ClO}_2]$  because you chose experiments in which  $[\text{ClO}_2]$  did not change.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k(0.0150 \text{ mol/L})^m(0.0150 \text{ mol/L})^n}{k(0.0500 \text{ mol/L})^m(0.0250 \text{ mol/L})^n} = \frac{2.60 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}{1.30 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}$$

Because  $k$  is a constant, you can cancel it out.

$$\frac{\cancel{k}(0.0500 \text{ mol/L})^m}{\cancel{k}(0.0250 \text{ mol/L})^m} = \frac{2.60 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}{1.30 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}$$

$$(2)^n = 2$$

$$n = 1 \text{ (by inspection)}$$

Therefore, the reaction is first order with respect to  $\text{OH}^-$ .

Set up a ratio for experiments 1 and 3, in which  $[\text{OH}^-]$  is constant and  $[\text{ClO}_2]$  changes. You can cancel out the  $[\text{OH}^-]$  terms right away.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k(0.0450 \text{ mol/L})^m(0.0250 \text{ mol/L})^n}{k(0.0150 \text{ mol/L})^m(0.0250 \text{ mol/L})^n} = \frac{1.16 \times 10^{-2} \text{ mol/(L} \cdot \text{s)}}{1.30 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}$$

Since  $k$  is a constant, you can cancel it out.

$$\frac{\cancel{k}[0.0450 \text{ mol/L}]^m}{\cancel{k}[0.0150 \text{ mol/L}]^m} = \frac{1.16 \times 10^{-2} \text{ mol/(L} \cdot \text{s)}}{1.30 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}$$

$$(3)^m = 8.92 \approx 9$$

$$m = 2 \text{ (by inspection)}$$

The reaction is second order with respect to  $\text{ClO}_2$ .

Therefore, the rate law equation is written as follows:

$$\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$$

The reaction is second order in  $\text{ClO}_2$ , first order in  $\text{OH}^-$ , and third order overall.

**Step 2** To find the value of the rate constant, substitute data from any of the three experiments into the rate law equation. Using the data from experiment 1 gives the following equation.

$$1.30 \times 10^{-3} \text{ mol/(L} \cdot \text{s)} = k(0.0150 \text{ mol/L})^2(0.0250 \text{ mol/L})$$

Solve for  $k$ .

$$k = \frac{1.30 \times 10^{-3} \text{ mol/(L} \cdot \text{s)}}{(0.0150 \text{ mol/L})^2(0.0250 \text{ mol/L)}}$$

$$= 231 \text{ L}^2/(\text{mol}^2 \cdot \text{s)}$$

Therefore, the rate constant at the temperature of the experiment is  $231 \text{ L}^2/(\text{mol}^2 \cdot \text{s})$ . The rate law equation is

$$\text{Rate} = 231 \text{ L}^2/(\text{mol}^2 \cdot \text{s})[\text{ClO}_2]^2[\text{OH}^-].$$

**Check Your Solution**

To check your values of  $m$  and  $n$ , solve by inspection. When  $[\text{ClO}_2]$  is constant and  $[\text{OH}^-]$  doubles, the rate also doubles and the reaction is first order in  $\text{OH}^-$ . When  $[\text{OH}^-]$  is constant and  $[\text{ClO}_2]$  triples, the rate increases by a factor of 9. Recall that  $3^2 = 9$ , indicating a second-order relationship. To check your value of  $k$ , substitute data from experiment 2 or 3. You should get the same answer. Also check the units and the number of significant digits for  $k$ .

## Practice Problems

5. When heated, ethylene oxide decomposes to produce methane and carbon monoxide.

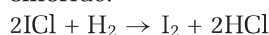


At 415°C, the following initial rate data were recorded.

Experiment	$[\text{C}_2\text{H}_4\text{O}]_0$ (mol/L)	Initial rate (mol/(L · s))
1	0.002 85	$5.84 \times 10^{-7}$
2	0.004 28	$8.76 \times 10^{-7}$
3	0.005 70	$1.17 \times 10^{-6}$

Determine the rate law equation and the rate constant at 415°C.

6. Iodine chloride reacts with hydrogen to produce iodine and hydrogen chloride.

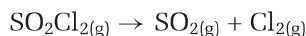


At temperature  $T$ , the following initial rate data were recorded.

Experiment	$[\text{ICl}]_0$ (mol/L)	$[\text{H}_2]_0$ (mol/L)	Initial rate (mol/(L · s))
1	0.20	0.050	0.0015
2	0.40	0.050	0.0030
3	0.20	0.200	0.0060

Determine the rate law equation and the rate constant at temperature  $T$ .

7. Sulfuryl chloride (also known as chlorosulfuric acid and thionyl chloride),  $\text{SO}_2\text{Cl}_2$ , is used in a variety of applications, including the synthesis of pharmaceuticals, rubber-based plastics, dyestuff, and rayon. At a certain temperature, the rate of decomposition of sulfuryl chloride was studied.



$[\text{SO}_2\text{Cl}_2]$ (mol/L)	Initial rate (mol/(L · s))
0.150	$3.3 \times 10^{-6}$
0.300	$6.6 \times 10^{-6}$
0.450	$9.9 \times 10^{-6}$

- (a) Write the rate law equation for the decomposition of sulfuryl chloride.
- (b) Determine the rate constant,  $k$ , for the reaction, with the appropriate units.
8. Consider the following reaction.
- $$2\text{A} + 3\text{B} + \text{C} \rightarrow \text{products}$$
- This reaction was found to obey the following rate law equation.
- $$\text{Rate} = k[\text{A}]^2[\text{B}][\text{C}]$$
- Copy the following table into your notebook. Then use the given information to predict the blank values. Do not write in this textbook.

Experiment	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial [C] (mol/L)	Initial rate (mol/(L · s))
1	0.10	0.20	0.050	0.40
2	0.10	(a)	0.10	0.40
3	0.20	0.050	(b)	0.20
4	(c)	0.025	0.040	0.45
5	0.10	0.010	0.15	(d)

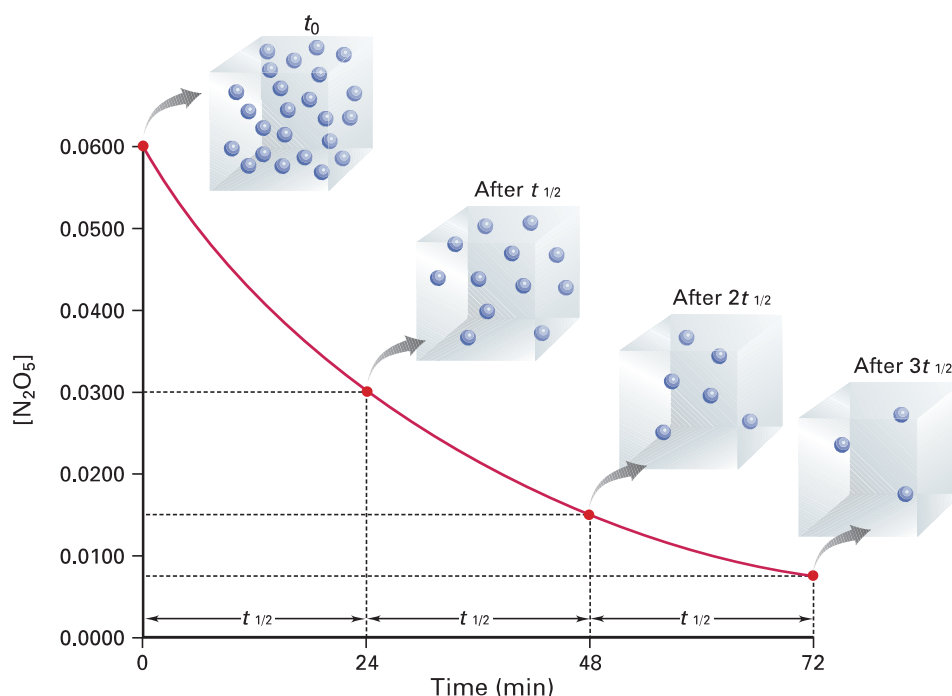


## The Half-Life of a Reaction

You have seen that a large rate constant indicates a fast reaction, while a small rate constant indicates a slow reaction. It is not always easy, however, to determine how long a reaction will take to be completed just by looking at the value of  $k$ . How can you relate the speed of a reaction to the units of  $s^{-1}$  for a first-order reaction?

The **half-life**,  $t_{1/2}$ , of a reaction is the time that is needed for the reactant mass or concentration to decrease by one half of its initial value. The SI units for half-life are seconds. Usually, however, half-life is expressed in whatever units of time are appropriate to the reaction. For example, the half-life of a very fast reaction may be measured in microseconds. The half-life of a slow reaction may be measured in days. Knowing the half-life of a reaction is an easy way to tell how fast or how slow a reaction is.

Examine Figure 6.6 to see how half-life and reactant concentration are related for the first-order decomposition of dinitrogen pentoxide.



**Figure 6.6** This graph shows  $[N_2O_5]$  versus time for the first three half-lives of the decomposition reaction of  $N_2O_5$  at  $44^\circ C$ . The spheres in the cubes represent  $[N_2O_5]$ .

The half-life of any first-order reaction is always a constant, and it depends on  $k$ . In other words, any first-order reaction (that is, any reaction with a rate law equation in the form  $\text{Rate} = k[A]$ ) has a half-life that is independent of the initial concentration of the reactant, A. The half-life of *any first-order reaction* can be calculated using the following equation.

$$t_{1/2} = \frac{0.693}{k}$$

In this equation,  $k$  is the first-order rate constant. It has units of  $s^{-1}$ .

Examine the Sample Problem on the next page to learn how to calculate the half-life of a first-order reaction. Then try the Practice Problems that follow.

### Math LINK

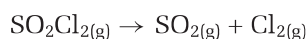
Where does the equation for half-life come from? Each rate law has an associated *integrated rate law*. (A calculus teacher may be able to show you how to arrive at the integrated rate law.) For first-order reactions, the integrated rate law is  $\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$ , where A is a reactant. Show that  $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$  for all first-order reactions. Then use the integrated rate law to arrive at the equation for half-life.

## Sample Problem

### Calculating the Half-Life of a First-Order Reaction

#### Problem

The decomposition of sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , is a first-order reaction.



$$\text{Rate} = k[\text{SO}_2\text{Cl}_2]$$

At  $320^\circ\text{C}$ , the rate constant is  $2.2 \times 10^{-5} \text{ s}^{-1}$ .

- (a) Calculate the half-life of the reaction, in hours.
- (b) How long does the sulfuryl chloride take to decrease to  $\frac{1}{8}$  of its original concentration?

#### What Is Required?

- (a) You need to find the half-life,  $t_{1/2}$ , of the reaction.
- (b) You need to find the time required for  $[\text{SO}_2\text{Cl}_2]$  to decrease to  $\frac{1}{8}$  of its initial value,  $[\text{SO}_2\text{Cl}_2]_0$ .

#### What Is Given?

You know the rate equation and the rate constant.

$$\text{Rate} = k[\text{SO}_2\text{Cl}_2]$$

$$k = 2.2 \times 10^{-5} \text{ s}^{-1}$$

#### Plan Your Strategy

- (a) To find  $t_{1/2}$ , use the following equation.

$$t_{1/2} = \frac{0.693}{k}$$

- (b) Each half-life reduces the initial concentration of the reactant,  $[\text{A}]_0$ , by one half.

$$\text{After } 1 \ t_{1/2}, [\text{A}] = \frac{1}{2} [\text{A}]_0$$

$$\begin{aligned} \text{After } 2 \ t_{1/2}, [\text{A}] &= \frac{1}{2} \times \left(\frac{1}{2} [\text{A}]_0\right) \\ &= \frac{1}{4} [\text{A}]_0 \end{aligned}$$

$$\begin{aligned} \text{After } 3 \ t_{1/2}, [\text{A}] &= \frac{1}{2} \times \left(\frac{1}{4} [\text{A}]_0\right) \\ &= \frac{1}{8} [\text{A}]_0 \end{aligned}$$

The concentration of reactant remaining after 3 half-lives is  $\frac{1}{8}$ , or  $(\frac{1}{2})^3$ , of the original amount.

#### Act on Your Strategy

- (a) Solve for  $t_{1/2}$ .

$$\begin{aligned} t_{1/2} &= \frac{0.693}{2.2 \times 10^{-5} \text{ s}^{-1}} \\ &= 3.2 \times 10^4 \text{ s} \end{aligned}$$

Convert the units of your answer to hours.

$$\begin{aligned} t_{1/2} &= \frac{3.2 \times 10^4 \text{ s}}{(60 \text{ s/min})(60 \text{ min/h})} \\ &= 8.8 \text{ h} \end{aligned}$$

The half-life of the reaction, in hours, is 8.8 h.

#### PROBLEM TIP

In general, the concentration of reactant that is left after  $n$  half-lives have passed,  $[\text{A}]_t$ , can be expressed as follows.

$$[\text{A}]_t = x[\text{A}]_0 = \left(\frac{1}{2}\right)^n \times [\text{A}]_0$$

(b) Determine how many half-lives correspond to  $\frac{1}{8} \times [\text{SO}_2\text{Cl}_2]_0$ .

$$\frac{1}{8} \times [\text{SO}_2\text{Cl}_2]_0 = \left(\frac{1}{2}\right)^n \times [\text{SO}_2\text{Cl}_2]_0$$

$$\frac{1}{8} = \left(\frac{1}{2}\right)^n$$

$$n = 3 \text{ (by inspection)}$$

Determine the time span that corresponds to 3 half-lives.

$$3 \times 8.8 \text{ h} = 26 \text{ h}$$

It would take 26 h for the concentration of  $\text{SO}_2\text{Cl}_2$  to decrease to  $\frac{1}{8}[\text{SO}_2\text{Cl}_2]_0$ .

### Check Your Solution

The units and significant digits for half-life are correct. The small rate constant of  $2.2 \times 10^{-5}$  corresponds to a slow reaction with a long half-life. Three half-lives corresponds to  $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{8}$  of the initial concentration.

## Practice Problems

9. Cyclopropane,  $\text{C}_3\text{H}_6$ , has a three-membered hydrocarbon ring structure. It undergoes rearrangement to propene. At  $1000^\circ\text{C}$ , the first-order rate constant for the decomposition of cyclopropane is  $9.2 \text{ s}^{-1}$ .

(a) Determine the half-life of the reaction.

(b) What percent of the original concentration of cyclopropane will remain after 4 half-lives?

10. Peroxyacetyl nitrate (PAN),  $\text{H}_3\text{CCO}_2\text{ONO}_2$ , is a constituent of photochemical smog. It undergoes a first-order decomposition reaction with  $t_{1/2} = 32 \text{ min}$ .

(a) Calculate the rate constant in  $\text{s}^{-1}$  for the first-order decomposition of PAN.

(b) 128 min after a sample of PAN began to decompose, the concentration of PAN in the air is  $3.1 \times 10^{13}$  molecules/L. What was the concentration of PAN when the decomposition began?

11. In general, a reaction is essentially over after 10 half-lives. Prove that this generalization is reasonable.

12. The half-life of a certain first-order reaction is 120 s. How long do you estimate that it will take for 90% of the original sample to react?

## Section Summary

In this section, you learned how to relate the rate of a chemical reaction to the concentrations of the reactants using the rate law. You classified reactions based on their reaction order. You determined the rate law equation from empirical data. Then you learned about the half-life of a first-order reaction. As you worked through sections 6.1 and 6.2, you may have wondered *why* factors such as concentration and temperature affect the rates of chemical reactions. In the following section, you will learn about some theories that have been developed to explain the effects of these factors.

## Section Review

- 1 **K/U** The following reaction is second order in A and first order in B.

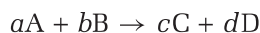


What is the rate law equation for the reaction below?

(Assume that A, B, and C are the same compounds for each reaction.)



- 2 **K/U** Consider the general reaction below.



Based on this equation, is it correct to write the following rate law equation by inspection? Explain your answer.

$$\text{Rate} = k[A]^a[B]^b$$

- 3 **K/U** Consider the following rate law equation.

$$\text{Rate} = k[A]^2[B]$$

(a) How does the reaction rate change if [A] decreases by a factor of 2 and [B] increases by a factor of 4?

(b) How does the reaction rate change if [A] and [B] are doubled?

- 4 **K/U** Consider the following rate law equation.

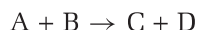
$$\text{Rate} = k[\text{HCrO}_4^-][\text{HSO}_3^-]^2[\text{H}^+]$$

(a) What is the order with respect to each reactant?

(b) What is the overall reaction order?

(c) What are the units for the rate constant?

- 5 **I** The data in the table below were collected for the following reaction.

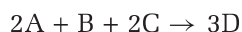


Experiment	[A] <sub>0</sub> (mol/L)	[B] <sub>0</sub> (mol/L)	Initial rate (mol/(L · s))
1	0.020	0.020	$5.0 \times 10^{-3}$
2	0.040	0.020	$1.0 \times 10^{-2}$
3	0.040	0.060	$9.0 \times 10^{-2}$

(a) What is the rate law equation for the reaction?

(b) Calculate the value of the rate constant, with proper units.

- 6 **I** The data in the table below were collected, at 25°C, for the following reaction.



Determine the rate law equation and the value of  $k$  at 25°C, with proper units.

Experiment	[A] <sub>0</sub> (mol/L)	[B] <sub>0</sub> (mol/L)	[C] <sub>0</sub> (mol/L)	Initial rate (mol/(L · s))
1	0.20	0.10	0.10	$4.0 \times 10^{-4}$
2	0.20	0.30	0.20	$1.2 \times 10^{-3}$
3	0.20	0.10	0.30	$4.0 \times 10^{-4}$
4	0.60	0.30	0.40	$3.6 \times 10^{-3}$

- 7 **I** A first-order decomposition reaction has a rate constant of  $2.34 \times 10^{-2} \text{ year}^{-1}$ . What is the half-life of the reaction? Express your answer in years and in seconds.

# Theories of Reaction Rates

## 6.3

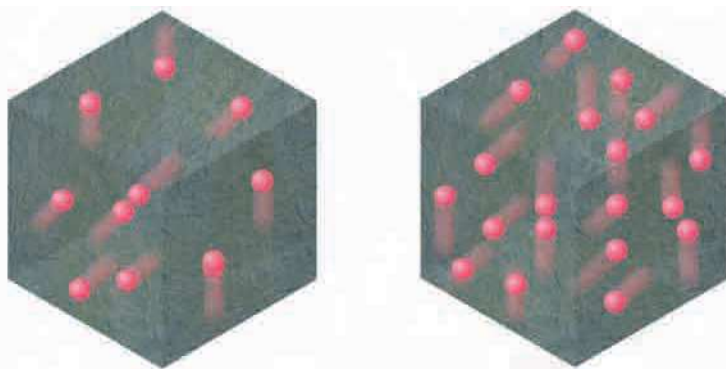
In section 6.2, you explored the rate law, which defines the relationship between the concentrations of reactants and reaction rate. Why, however, does the rate of a reaction increase with increased concentrations of reactants? Why do increased temperature and surface area increase reaction rates? To try to explain these and other macroscopic observations, chemists develop theories that describe what happens as reactions proceed on the molecular scale. In this section, you will explore these theories.

### Collision Theory

Why do factors such as temperature and concentration increase or decrease the rate of a reaction? To answer this question, chemists must first answer another question: What causes a reaction to occur? One obvious answer is that a reaction occurs when two reactant particles collide with one another. This answer is the basis for **collision theory**: In order for a reaction to occur, reacting particles (atoms, molecules, or ions) must collide with one another.

### The Effect of Concentration on Reactant Rates

You can use simple collision theory to begin to understand why factors such as concentration affect reaction rate. If a collision is necessary for a reaction to occur, then it makes sense that the rate of the reaction will increase if there are more collisions per unit time. More reactant particles in a given volume (that is, greater concentration) will increase the number of collisions between the particles per second. Figure 6.7 illustrates this idea.



**Figure 6.7** At increased reactant concentrations, there is an increased number of collisions per second.

### Collision Theory and Surface Area

You can also use simple collision theory to explain why increasing the surface area of a solid-phase reactant speeds up a reaction. With greater surface area, more collisions can occur. This explains why campfires are started with paper and small twigs, rather than logs. Figure 6.8 shows an example of the effect of surface area on collision rate.

#### Section Preview/ Specific Expectations

In this section, you will

- **explain**, using the collision theory and potential energy diagrams, how different factors, such as temperature and concentration, control the rate of a chemical reaction
- **analyze** simple potential energy diagrams of chemical reactions
- **communicate** your understanding of the following terms: *collision theory*, *activation energy ( $E_a$ )*, *transition state theory*, *potential energy diagram*, *transition state*, *activated complex*



#### Electronic Learning Partner

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



**Figure 6.8** Mixtures of grain or coal dust and air are potentially explosive, as shown in this grain elevator explosion.



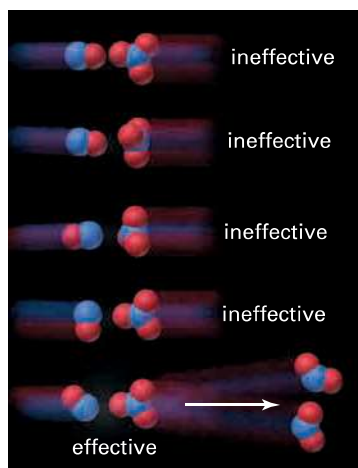
## Beyond Collision Theory

Simple collision theory recognizes that a collision between reactants is necessary for a reaction to proceed. Does every collision result in a reaction? Consider a 1 mL sample of gas at room temperature and atmospheric pressure. In the sample, about  $10^{28}$  collisions per second take place between gas molecules. If each collision resulted in a reaction, *all* gas phase reactions would be complete in about a nanosecond ( $10^{-9}$  s)—a truly explosive rate! As you know from section 6.2, however, gas phase reactions can occur quite slowly. This suggests that *not every collision between reactants results in a reaction*.

In order for a collision between reactants to result in a reaction, the collision must be *effective*. An effective collision—one that results in the formation of products—must satisfy the following two criteria. You will investigate these criteria over the next few pages.

For a collision to be effective, it must satisfy both of these criteria:

1. correct orientation of reactants
2. sufficient collision energy



**Figure 6.9** Only one of these five possible orientations of NO and NO<sub>3</sub> will lead to the formation of a product.

### Orientation of Reactants

Reacting particles must collide with the proper orientation relative to one another. This is also known as having the correct *collision geometry*. The importance of proper collision geometry can be illustrated by the following reaction.

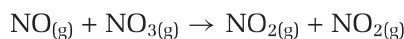


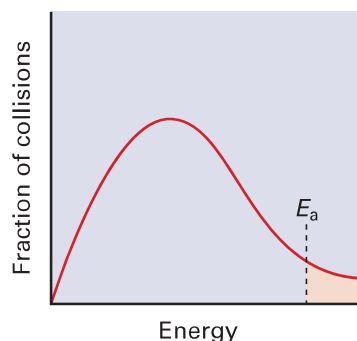
Figure 6.9 shows five of the many possible ways in which NO and NO<sub>3</sub> can collide. Only one of these five possibilities has the correct collision geometry for a reaction to occur. As shown in the figure, only a certain orientation of reactants prior to collision leads to the formation of two molecules of nitrogen dioxide.

### Activation Energy

In addition to collision geometry, there is a second factor that determines whether a collision will result in a reaction: the energy of the collision. The reactants must collide with energy that is sufficient to begin to break the bonds in the reactants and to begin to form the bonds in the products. In most reactions, only a small fraction of collisions have sufficient energy for a reaction to occur. The **activation energy**,  $E_a$ , of a reaction is the minimum collision energy that is required for a successful reaction.

The collision energy depends on the kinetic energy of the colliding particles. As you know, temperature is a measure of the average kinetic energy of the particles in a substance. If you plot the number of collisions in a substance at a given temperature against the kinetic energy of each collision, you get a curve like the one in Figure 6.10. The type of distribution that is shown by this curve is known as a *Maxwell-Boltzmann distribution*. The dotted line indicates the activation energy. The shaded part of the graph indicates the collisions with energy that is equal to or greater than the activation energy.

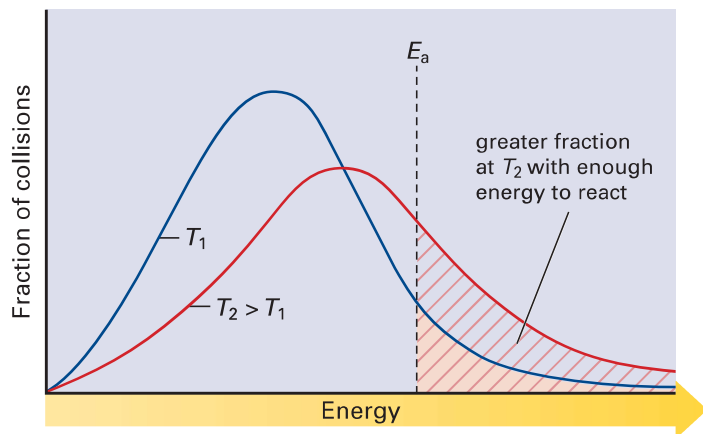
How does the distribution of kinetic energy change as the temperature of a substance increases? Figure 6.11 shows the distribution of kinetic



**Figure 6.10** The area under a Maxwell-Boltzmann distribution graph represents the distribution of the kinetic energy of collisions at a constant temperature. At a given temperature, only a certain fraction of the molecules in a sample have enough kinetic energy to react.

energy in a sample of reacting gases at two different temperatures,  $T_1$  and  $T_2$ , where  $T_2 > T_1$ . The activation energy is indicated by the dashed vertical line. Two observations are apparent from the graph:

1. At both temperatures, a relatively small fraction of collisions have sufficient kinetic energy—the activation energy—to result in a reaction.
2. As the temperature of a sample increases, the fraction of collisions with sufficient energy to cause a reaction increases significantly.



For many reactions, the rate roughly doubles for every  $10^\circ\text{C}$  rise in temperature.

## Transition State Theory

**Transition state theory** is used to explain what happens when molecules collide in a reaction. It examines the transition, or change, from reactants to products. The kinetic energy of the reactants is transferred to potential energy as the reactants collide, due to the law of conservation of energy. This is analogous to a bouncing basketball. The kinetic energy of the ball is converted to potential energy, which is stored in the deformed ball as it hits the floor. The potential energy is converted to kinetic energy as the ball bounces away.

You can represent the increase in potential energy during a chemical reaction using a **potential energy diagram**: a diagram that charts the potential energy of a reaction against the progress of the reaction. Examples of potential energy diagrams are shown in Figures 6.12 and 6.13 on the next page. The y-axis represents potential energy. The x-axis, labelled “Reaction progress,” represents the progress of the reaction through time.

The “hill” in each diagram illustrates the activation energy barrier of the reaction. A slow reaction has a high activation energy barrier. This indicates that relatively few reactants have sufficient kinetic energy for a successful reaction. A fast reaction, by contrast, has a low activation energy barrier.

A potential energy diagram for an exothermic reaction is shown in Figure 6.12. The reactants at the beginning of the reaction are at a higher energy level than the products. The overall difference in potential energy is the enthalpy change,  $\Delta H$ . *There is no way to predict the activation energy of a reaction from its enthalpy change.* A highly exothermic reaction may be very slow because it has a high activation energy. Conversely, a reaction that is very fast may release very little heat. The enthalpy change of a reaction is determined by finding the overall energy that is

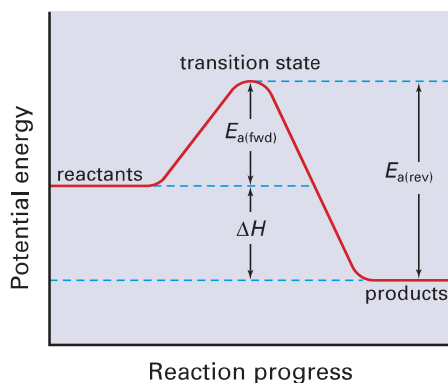


Go to the Chemistry 12 Electronic Learning Partner to learn more about collision geometry.

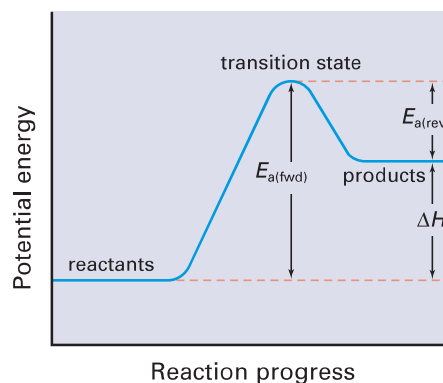
**Figure 6.11** At increased temperatures, more particles collide with enough energy to react.

transferred. The activation energy of a reaction is determined by analyzing the reaction rate.

A potential energy diagram for an endothermic reaction is shown in Figure 6.13. The reactants at the beginning of the reaction are at a lower energy level than the products. The overall difference in potential energy between reactants and products is the enthalpy change.

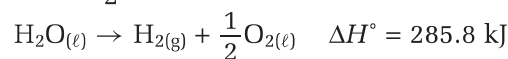
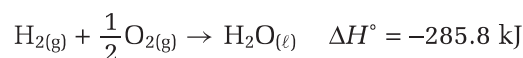


**Figure 6.12** A potential energy diagram for an exothermic reaction



**Figure 6.13** A potential energy diagram for an endothermic reaction

You may already know that many reactions can proceed in two directions. For example, hydrogen and oxygen react to form water. Water, however, can also undergo electrolysis, forming hydrogen and oxygen. This is the reverse of the first reaction.



The enthalpy change of the first reaction is the same as the enthalpy change of the second reaction, with the opposite sign. (You can show this using Hess's law.) How are the activation energies of forward and reverse reactions related? For an exothermic reaction, the activation energy of the reverse reaction,  $E_{\text{a}(\text{rev})}$  equals  $E_{\text{a}(\text{fwd})} + \Delta H$ . For an endothermic reaction,  $E_{\text{a}(\text{rev})}$  equals  $E_{\text{a}(\text{fwd})} - \Delta H$ . Figures 6.12 and 6.13 show the activation energies of forward and reverse reactions.

The top of the activation energy barrier on a potential energy diagram represents the **transition state**, or change-over point, of the reaction. The chemical species that exists at the transition state is referred to as the **activated complex**. The activated complex is a transitional species that is neither product nor reactant. It has partial bonds and is highly unstable. There is a subtle difference between the transition state and the activated complex. The transition state refers to the top of the “hill” on a potential energy diagram. The *chemical species* that exists at this transition point is called the activated complex.

### Tracing a Reaction With a Potential Energy Diagram

Consider the substitution reaction between a hydroxide,  $\text{OH}^-$ , ion and methyl bromide,  $\text{BrCH}_3$ . Methanol,  $\text{CH}_3\text{OH}$ , and a bromide,  $\text{Br}^-$ , ion are formed.

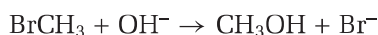
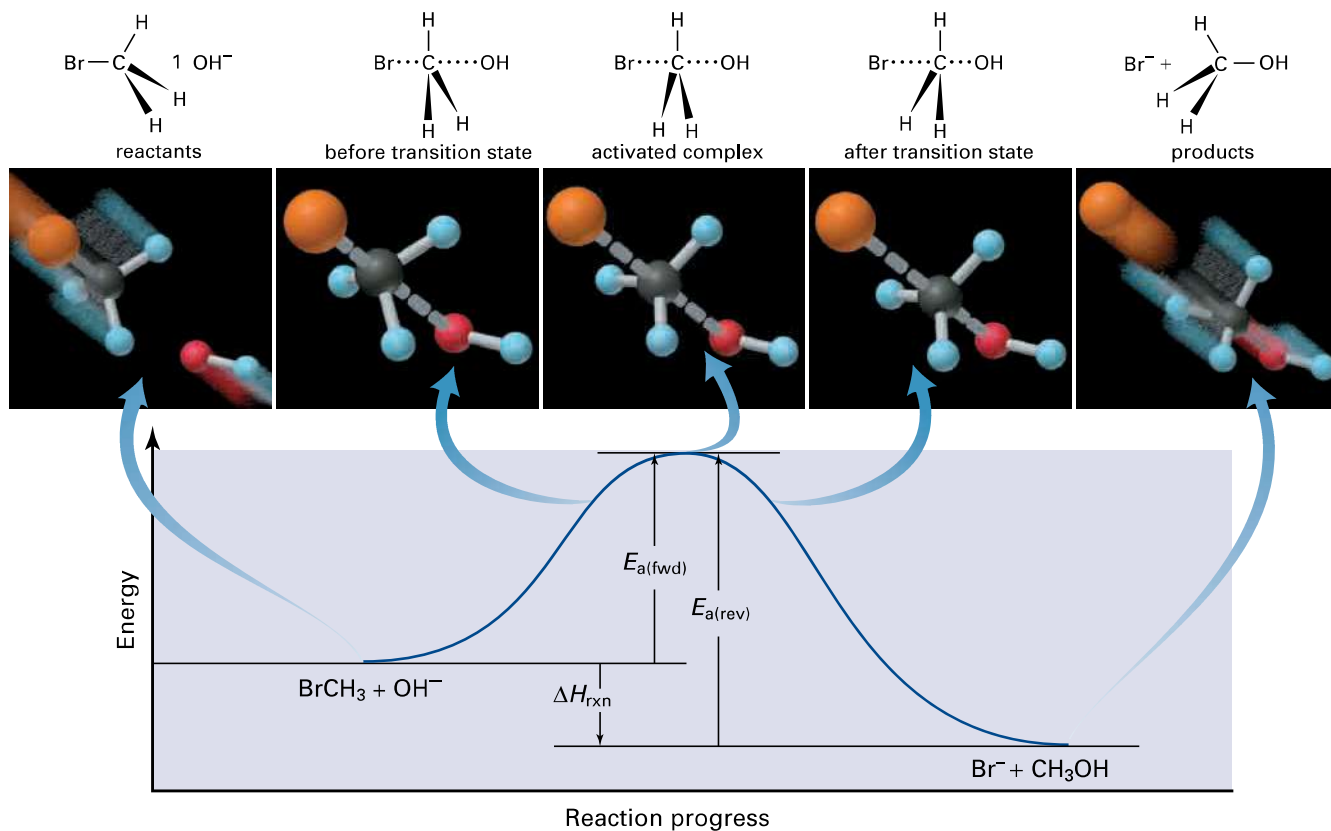


Figure 6.14 is a potential energy diagram for this reaction. It includes several “snapshots” as the reaction proceeds.



**Figure 6.14** As the reactants collide, chemical bonds break and form.

For a successful reaction to take place,  $\text{BrCH}_3$  and  $\text{OH}^-$  must collide in a favourable orientation. The  $\text{OH}^-$  ion must approach  $\text{BrCH}_3$  from the side that is *opposite* to the Br atom. When this occurs, a partial bond is formed between the O of the  $\text{OH}^-$  ion and the C atom. Simultaneously, the  $\text{C}-\text{Br}$  bond is weakened.

Because the activated complex contains partial bonds, it is highly unstable. It can either break down to form products or it can decompose to re-form the reactants. The activated complex is like a rock teetering on top of a mountain. It could fall either way.

## Sample Problem

### Drawing a Potential Energy Diagram

#### Problem

Carbon monoxide,  $\text{CO}$ , reacts with nitrogen dioxide,  $\text{NO}_2$ . Carbon dioxide,  $\text{CO}_2$ , and nitric oxide,  $\text{NO}$ , are formed. Draw a potential energy diagram to illustrate the progress of the reaction. (You do not need to draw your diagram to scale). Label the axes, the transition state, and the activated complex. Indicate the activation energy of the forward reaction,  $E_{\text{a(fwd)}} = 134 \text{ kJ}$ , as well as  $\Delta H = -226 \text{ kJ}$ . Calculate the activation energy of the reverse reaction,  $E_{\text{a(rev)}}$ , and show it on the graph.

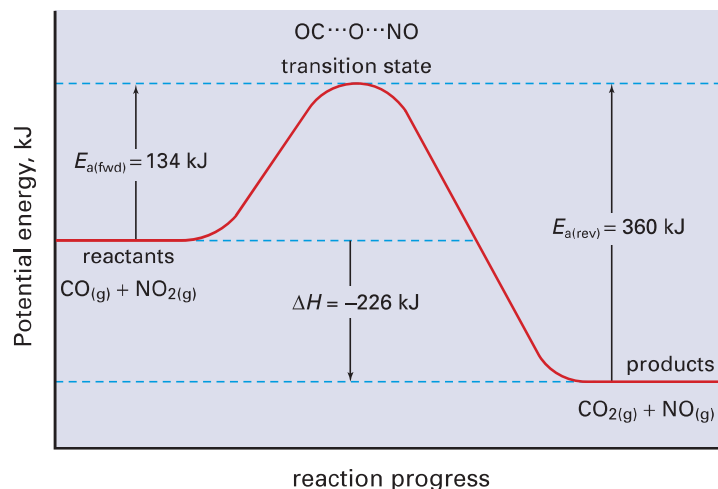
Continued ...

**Solution**

Since  $E_{a(\text{rev})} = \Delta H + E_{a(\text{fwd})}$

$$\begin{aligned} E_{a(\text{rev})} &= 226 \text{ kJ} + 134 \text{ kJ} \\ &= 360 \text{ kJ} \end{aligned}$$

The activation energy of the reverse reaction is 360 kJ.

**Check Your Solution**

Look carefully at the potential energy diagram. Check that you have labelled it completely. Since the forward reaction is exothermic, the reactants should be at a higher energy level than the products, and they are. The value of  $E_{a(\text{rev})}$  is reasonable.

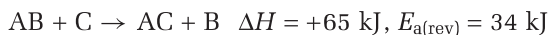
**Practice Problems**

13. The following reaction is exothermic.



Draw and label a potential energy diagram for the reaction. Propose a reasonable activated complex.

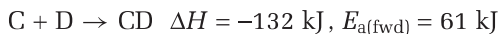
14. Consider the following reaction.



Draw and label a potential energy diagram for this reaction.

Calculate and label  $E_{a(\text{fwd})}$ . Include a possible structure for the activated complex.

15. Consider the reaction below.



Draw and label a potential energy diagram for this reaction. Calculate and label  $E_{a(\text{rev})}$ . Include a possible structure for the activated complex.

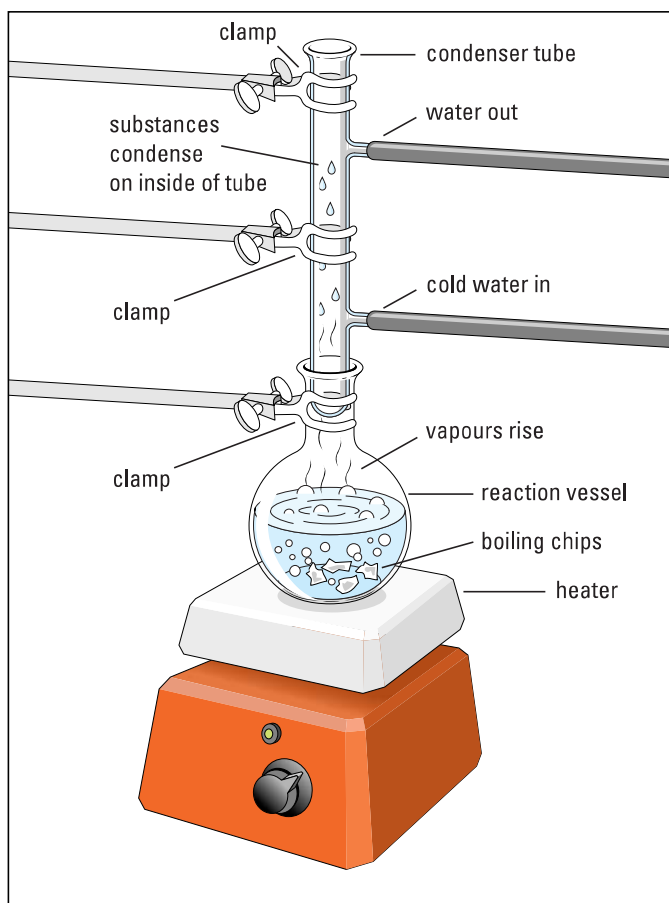
16. In the upper atmosphere, oxygen exists in forms other than  $\text{O}_{2(\text{g})}$ . For example, it exists as ozone,  $\text{O}_{3(\text{g})}$ , and as single oxygen atoms,  $\text{O}_{(\text{g})}$ . Ozone and atomic oxygen react to form two molecules of oxygen. For this reaction, the enthalpy change is  $-392 \text{ kJ}$  and the activation energy is  $19 \text{ kJ}$ . Draw and label a potential energy diagram. Include a value for  $E_{a(\text{rev})}$ . Propose a structure for the activated complex.

## Temperature Dependence of Reaction Rates: Applications

As you saw in Figure 6.11, when reactions occur at higher temperatures, the percent of particles that have sufficient kinetic energy to react ( $E_a$ ) increases. Since a greater percent of reactant particles have enough energy to react, the rate of the reaction increases.

Chemists exploit the temperature dependence of reaction rates by carrying out chemical reactions at elevated temperatures to speed them up. In organic chemistry, especially, reactions are commonly performed under *reflux*: that is, while boiling the reactants. To prevent reactants and products from escaping as gases, a water-cooled condenser tube is fitted to the reaction vessel. The tube condenses the vapours to liquids and returns them to the reaction vessel. Figure 6.15 shows an experiment performed under reflux.

At home, you take advantage of the temperature dependence of chemical reactions all the time. For example, to keep your food fresh, you store it in a refrigerator. If you have ever left milk or vegetables in the refrigerator for several weeks, however, you have probably observed that refrigeration does not *stop* food from spoiling. Instead, it decreases the *rate* of the reactions that cause spoilage. When you want to cook your food quickly, you increase the temperature of the stove. This increases the rate of the reactions that take place as the food cooks.



**Figure 6.15** As the reactants are boiled under reflux, the vapours condense and are returned to the reaction vessel. In this way, a chemical reaction can be carried out at the boiling point of the reactants at atmospheric pressure, with no loss of reactants, products, or solvent.

Web  LINK

[www.mcgrawhill.ca/links/chemistry12](http://www.mcgrawhill.ca/links/chemistry12)

The chirping rate of a cricket is dependent on temperature, much like chemical reaction rates are. Why does this suggest that a cricket is a cold-blooded creature? Search the Internet to determine the mathematical relationship between ambient temperature and the chirping rate of a cricket. Start your search by going to the web site above and clicking on **Web Links**.



## Section Summary

In this section, you used collision theory and transition state theory to explain how reaction rates are affected by various factors. You considered simple reactions, consisting of a single-step collision between reactants. Not all reactions are simple, however. In fact, most chemical reactions take place via several steps, occurring in sequence. In the next section, you will learn about the steps that make up reactions and discover how these steps relate to reaction rates.

## Section Review

- 1 K/U** In your own words, describe how collision theory explains that increased concentrations result in increased reaction rates.
- 2 I** Suppose that you have a solid sample of an organic substance. You are going to burn the substance in an analytical furnace and determine whether or not any unburned matter remains. The substance is somewhat hard, and you receive it in a solid chunk.
  - (a)** Suggest two ways to increase the rate of burning so that your analysis will take less time.
  - (b)** Explain why your suggestions would work, using the theories you learned in this section.
- 3 K/U** Consider the following reaction.
$$\text{A}_2 + \text{B}_2 \rightarrow 2\text{AB} \quad E_{\text{a(fwd)}} = 143 \text{ kJ}, E_{\text{a(rev)}} = 75 \text{ kJ}$$
  - (a)** Is the reaction endothermic or exothermic in the forward direction?
  - (b)** Draw and label a potential energy diagram. Include a value for  $\Delta H$ .
  - (c)** Suggest a possible activated complex.
- 4 C** Consider two exothermic reactions. Reaction (1) has a much smaller activation energy than reaction (2).
  - (a)** Sketch a potential energy diagram for each reaction, showing how the difference in activation energy affects the shape of the graph.
  - (b)** How do you think the rates of reactions (1) and (2) compare? Explain your answer.
- 5 C** Your friend is confused about the difference between the enthalpy change and the activation energy of a chemical reaction. Write a few paragraphs, in which you define each term and distinguish between them. Use potential energy diagrams to illustrate your answer.
- 6 MC** In a coal-fired electric generating plant, the coal is pulverized before being mixed with air in the incinerator. Use collision theory to explain why the coal is pulverized.
- 7 C** People who have been submerged in very cold water, and presumed drowned, have sometimes been revived. By contrast, people who have been submerged for a similar period of time in warmer water have not survived. Suggest reasons for this difference.
- 8 C** Create a graphic organizer to summarize how the theories you have studied in section 6.3 explain the effects of concentration, temperature, and surface area on reaction rates.

# Reaction Mechanisms and Catalysts

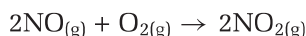
## 6.4

Chemical reactions are like factories, where goods (products) are created from raw materials (reactants). An assembly line, like the one shown in Figure 6.16, involves many steps. An automobile is not formed from its components in just one step. Similarly, most chemical reactions do not proceed immediately from products to reactants. They take place via a number of steps. While you can go inside a factory to see all the steps that are involved in making an automobile or a piece of clothing, you cannot observe a chemical equation on a molecular scale as it proceeds. Chemists can experimentally determine the reactants and products of a reaction, but they must use indirect evidence to suggest the steps in-between.

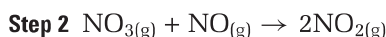
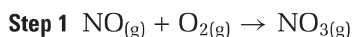
### Elementary Reactions

A **reaction mechanism** is a series of steps that make up an overall reaction. Each step, called an **elementary reaction**, involves a single molecular event, such as a simple collision between atoms, molecules, or ions. An elementary step can involve the formation of different molecules or ions, or it may involve a change in the energy or geometry of the starting molecules. It cannot be broken down into further, simpler steps.

For example, consider the following reaction.



Chemists have proposed the following two-step mechanism for this reaction. Each step is an elementary reaction.



When you add the two elementary reactions, you get the overall reaction. Notice that  $\text{NO}_3$  is present in both elementary reactions, but it is not present in the overall reaction. It is produced in the first step and consumed in the second step.

Molecules (or atoms or ions) that are formed in an elementary reaction and consumed in a subsequent elementary reaction are called **reaction intermediates**. Even though they are not products or reactants in the overall reaction, reaction intermediates are essential for the reaction to take place. They are also useful for chemists who are trying to find evidence to support a proposed reaction mechanism. You will explore this idea in Investigation 6-B.

### The Molecularity of Elementary Reactions

The term **molecularity** refers to the number of reactant particles (molecules, atoms, or ions) that are involved in an elementary reaction.

In the reaction mechanism you just saw, each elementary reaction consisted of two molecules colliding and reacting. When two particles collide and react, the elementary reaction is said to be **bimolecular**.

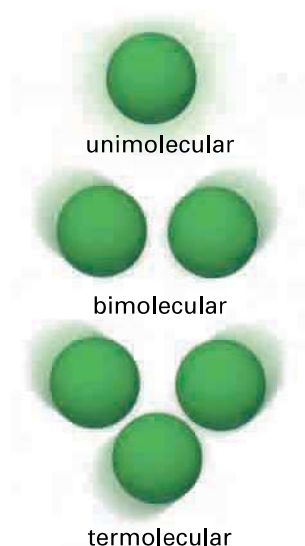
#### Section Preview/ Specific Expectations

In this section, you will

- **demonstrate** an understanding that most reactions occur as a series of elementary reactions in a reaction mechanism
- **evaluate** a proposed mechanism for a chemical reaction
- **determine**, through experiment, the reaction rate and rate law equation for a chemical reaction
- **communicate** your understanding of the following terms: *reaction mechanism, elementary reaction, reaction intermediates, molecularity, bimolecular, unimolecular, termolecular, rate-determining step, homogeneous catalyst, heterogeneous catalyst, enzymes, active site, substrate*

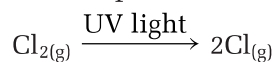


**Figure 6.16** Like most chemical reactions, building a car on an assembly line takes more than one step.



**Figure 6.17** This figure shows the molecularity of elementary reactions. Termolecular reactions are rare.

A **unimolecular** elementary reaction occurs when one molecule or ion reacts. For example, when one molecule of chlorine absorbs ultraviolet light, the Cl—Cl bond breaks. The product is two chlorine atoms.



An elementary reaction may also involve three particles colliding in a **termolecular** reaction. Termolecular elementary steps are rare, because it is unlikely that three particles will collide all at once. Think of it this way. You have probably bumped into someone accidentally, many times, on the street or in a crowded hallway. How many times, however, have you and two other people collided at exactly the same time? Figure 6.17 models unimolecular, bimolecular, and termolecular reactions.

### Rate Law Equations for Elementary Reactions

In section 6.2, you learned that the rate law equation for a chemical reaction cannot be determined just by looking at the chemical equation. It must be found by experiment. Elementary reactions are the exception to this rule. *For an elementary reaction, the exponents in the rate law equation are the same as the stoichiometric coefficients for each reactant in the chemical equation.* Table 6.3 shows how rate laws correspond to elementary reactions.

**Table 6.3** Elementary Reactions and Their Rate Laws

Elementary reaction	Rate law
$A \rightarrow \text{products}$	$\text{Rate} = k[A]$
$A + B \rightarrow \text{products}$	$\text{Rate} = k[A][B]$
$2A \rightarrow \text{products}$	$\text{Rate} = k[A]^2$
$2A + B \rightarrow \text{products}$	$\text{Rate} = k[A]^2[B]$

### Proposing and Evaluating Mechanisms

You can take apart a grandfather clock to take a look at its mechanism. You can physically examine and take apart its gears and springs to determine how it works.

When chemists investigate the mechanism of a reaction, they are not so lucky. Determining the mechanism of a chemical reaction is a bit like figuring out how a clock works just by looking at its face and hands. For this reason, reaction mechanisms are *proposed* rather than definitively stated. Much of the experimental evidence that is obtained to support a mechanism is indirect. Researchers need a lot of creativity as they propose and test mechanisms.

One of the ways that researchers provide evidence for proposed mechanisms is by proving the existence of a reaction intermediate. Although a reaction intermediate usually appears for a very short time and cannot be isolated, there are other ways to show its presence. For example, if a reaction intermediate is coloured while other reactants are colourless, a spectrophotometer will show when the reaction intermediate is formed. You may even be able to see a fleeting colour change without a spectrophotometer.

When chemists propose a mechanism, they must satisfy the following criteria:

- The equations for the elementary steps must combine to give the equation for the overall reaction.
- The proposed elementary steps must be reasonable.
- The mechanism must support the experimentally determined rate law.

### The Rate-Determining Step

How do chemists determine whether a proposed mechanism supports the experimentally determined rate law? They must consider how the rates of the elementary reactions relate to the rate of the overall reaction.

Elementary reactions in mechanisms all have different rates. Usually one elementary reaction, called the **rate-determining step**, is much slower. Hence, it determines the overall rate.

To understand the rate-determining step, consider a two-step process. Suppose that you and a friend are making buttered toast for a large group of people. The first step is toasting the bread. The second step is buttering the toast. Suppose that toasting two slices of bread takes about two minutes, but buttering the toast takes only a few seconds.

The rate at which the toast is buttered does not have any effect on the overall rate of making buttered toast, because it is much faster than the rate at which the bread is toasted. The overall rate of making buttered toast, therefore, depends only on the rate of toasting the bread. In other words, two pieces of buttered toast will be ready every two minutes. This is the same as the rate for the first step in the “buttered toast mechanism.” Thus, toasting the bread is the rate-determining step in the mechanism.

**Step 1** Bread → Toast (slow, rate-determining)

**Step 2** Toast + Butter → Buttered toast (fast)

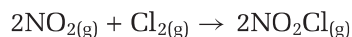
Now suppose that the butter is frozen nearly solid. It takes you about five minutes to scrape off enough butter for one piece of toast. Pieces of toast pile up, waiting to be buttered. In this case, the rate of making buttered toast depends on the rate of spreading the butter. The rate of toasting is fast relative to the rate of buttering.

**Step 1** Bread → Toast (fast)

**Step 2** Toast + Frozen butter → Buttered toast (slow, rate-determining)

### The Rate-Determining Step and the Rate Law

How does the rate-determining step relate to the rate law for the overall equation? Consider the reaction of nitrogen dioxide with chlorine.



Experiments show that this reaction has the following rate equation.

$$\text{Rate} = k[\text{NO}_2][\text{Cl}_2]$$

The proposed mechanism for the reaction is shown below.

**Step 1**  $\text{NO}_{2(g)} + \text{Cl}_{2(g)} \rightarrow \text{NO}_2\text{Cl}_{(g)} + \text{Cl}_{(g)}$  (slow)

**Step 2**  $\text{NO}_{2(g)} + \text{Cl}_{(g)} \rightarrow \text{NO}_2\text{Cl}_{(g)}$  (fast)

The mechanism seems reasonable, because the steps add up to give the overall reaction. Both steps are plausible, because they are bimolecular elementary reactions. Does the reaction mechanism support, however, the experimentally determined rate law?



## CHEM

### FACT

Rate-determining steps can occur anywhere in a reaction mechanism. If a slow step is not the first step of the mechanism, however, the overall rate law is more complicated to determine. One reason is that fast reactions occurring early in a mechanism are often reversible—both the forward and reverse reactions take place. (You will learn more about these reactions in Unit 4.)

The first step in the mechanism is slow when compared with the second step. Therefore, the rate-determining step is step 1. Since the rate of the overall reaction depends on the rate of the slow step, the rate law equation for the rate-determining step should match the rate law for the overall reaction.

By definition, the rate law equation for step 1 is written as follows:

$$\text{Rate}_1 = k_1[\text{NO}_2][\text{Cl}_2]$$

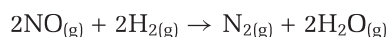
The rate law of the rate-determining step in the proposed mechanism matches the experimentally determined rate law. Since the proposed mechanism is consistent with the overall rate law equation, it is a reasonable mechanism.

## Sample Problem

### Evaluating a Proposed Mechanism

#### Problem

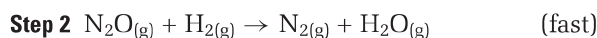
Consider the reaction below.



The experimentally determined rate law is written as follows:

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

A chemist proposes the mechanism below for the reaction.



Determine whether the proposed mechanism is reasonable.

#### What Is Required?

You need to determine whether the proposed mechanism is reasonable. To do this, you need to answer the following questions:

- Do the steps add up to the overall reaction?
- Are the steps reasonable in terms of their molecularity?
- Is the proposed mechanism consistent with the experimentally determined rate law?

#### What Is Given?

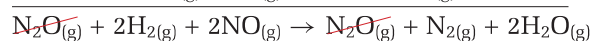
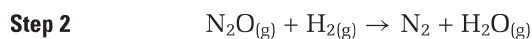
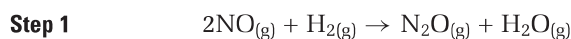
You know the proposed mechanism, the overall reaction, and the rate law for the overall reaction.

#### Plan Your Strategy

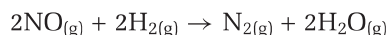
Add the two reactions, and cancel out reaction intermediates. Check the molecularity of the steps. Determine the rate law equation for the rate-determining step, and compare it to the overall rate law equation.

#### Act on Your Strategy

Add the two steps.



or





The two steps add up to give the overall reaction. The second step is bimolecular, so it is chemically reasonable. The first step is termolecular, which is possible but rare. In the proposed mechanism, step 1 is the rate-determining reaction. The rate law equation for the first step is written as follows:

$$\text{Rate}_1 = k_1[\text{NO}_2]^2[\text{H}_2]$$

The rate law equation for the slow step matches the rate law equation for the overall reaction.

Based on the equations for the elementary reactions, the molecularity of these reactions, and the rate law for the rate-determining step, the reaction mechanism seems reasonable.

### Check Your Solution

The reaction intermediate in the proposed mechanism is  $\text{N}_2\text{O}$ . When adding the two steps, you were able to cancel out  $\text{N}_2\text{O}$ .

## Practice Problems

17.  $\text{NO}_{2(g)}$  and  $\text{F}_{2(g)}$  react to form  $\text{NO}_2\text{F}_{(g)}$ . The experimentally determined rate law for the reaction is written as follows:

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

A chemist proposes the following mechanism. Determine whether the mechanism is reasonable.



18. A researcher is investigating the following overall reaction.  
 $2\text{C} + \text{D} \rightarrow \text{E}$

The researcher claims that the rate law equation for the reaction is written as follows:

$$\text{Rate} = k[\text{C}][\text{D}]$$

- (a) Is the rate law equation possible for the given reaction?  
 (b) If so, suggest a mechanism that would match the rate law. If not, explain why not.
19. A chemist proposes the following reaction mechanism for a certain reaction.
- Step 1**  $\text{A} + \text{B} \rightarrow \text{C}$  (slow)  
**Step 2**  $\text{C} + \text{A} \rightarrow \text{E} + \text{F}$  (fast)
- (a) Write the equation for the chemical reaction that is described by this mechanism.  
 (b) Write a rate law equation that is consistent with the proposed mechanism.
20. Consider the reaction between 2-bromo-2-methylpropane and water.  
 $(\text{CH}_3)_3\text{CBr}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow (\text{CH}_3)_3\text{COH}_{(aq)} + \text{H}^+_{(aq)} + \text{Br}^-_{(aq)}$   
 Rate experiments show that the reaction is first order in  $(\text{CH}_3)_3\text{CBr}$ , but zero order in water. Demonstrate that the accepted mechanism, shown below, is reasonable.
- Step 1**  $(\text{CH}_3)_3\text{CBr}_{(aq)} \rightarrow (\text{CH}_3)_3\text{C}^+_{(aq)} + \text{Br}^-_{(aq)}$  (slow)  
**Step 2**  $(\text{CH}_3)_3\text{C}^+_{(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow (\text{CH}_3)_3\text{COH}_2^+_{(aq)}$  (fast)  
**Step 3**  $(\text{CH}_3)_3\text{COH}_2^+_{(aq)} \rightarrow \text{H}^+_{(aq)} + (\text{CH}_3)_3\text{COH}_{(aq)}$  (fast)

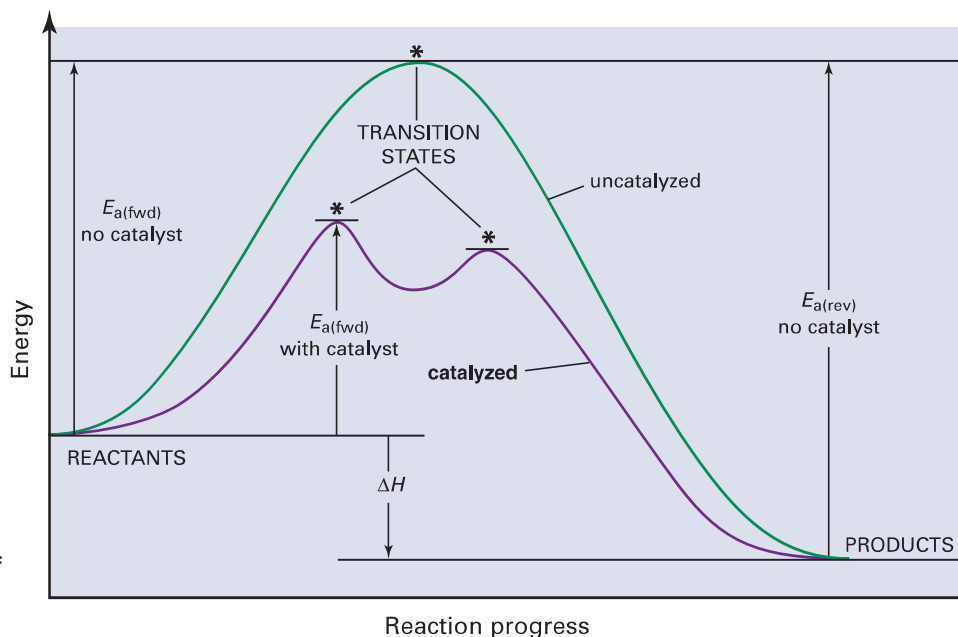


## Catalysts

A catalyst is a substance that increases the rate of a chemical reaction without being consumed by the reaction. Catalysts are of tremendous importance in all facets of chemistry, from the laboratory to industry. Many industrial reactions, for example, would not be economically viable without catalysts. Well over three million tonnes of catalysts are produced annually in North America.

### How a Catalyst Works

A catalyst works by lowering the activation energy of a reaction so that a larger fraction of the reactants have sufficient energy to react. It lowers the activation energy by providing an alternative mechanism for the reaction. The potential energy diagram in Figure 6.18 shows the activation energy for an uncatalyzed reaction and the activation energy for the same reaction with the addition of a catalyst.

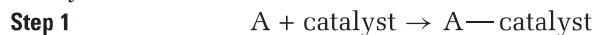


**Figure 6.18** A catalyst lowers the activation energy of a reaction by providing an alternative mechanism. A catalyst also increases the rate of the reverse reaction. What effect does a catalyst have on  $\Delta H$  of a reaction?

In Figure 6.18, the catalyzed reaction consists of a two-step mechanism. The uncatalyzed reaction consists of a one-step mechanism. To see how a catalyst works, in general, consider a simple, one-step, bimolecular reaction:



A catalyst can increase the rate of this reaction by providing an alternative mechanism with lower activation energy. A possible mechanism for the catalyzed reaction is shown below.



Both steps are faster than the original, uncatalyzed reaction. Therefore, although the overall reaction of the catalyzed mechanism has the same reactants and products as the uncatalyzed reaction, the catalyzed mechanism is faster. The chemical species  $A - \text{catalyst}$  is a reaction intermediate. It is produced in step 1 but consumed in step 2. By contrast, the catalyst is *regenerated* in the reaction. It appears as a reactant in step 1 and as

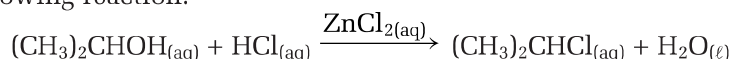
a product in step 2. Although the catalyst changes *during* the overall reaction, it is regenerated unchanged at the *end* of the overall reaction.

Figure 6.19 shows the reaction of sodium potassium tartrate with  $\text{H}_2\text{O}_2$ , catalyzed by cobaltous chloride,  $\text{CoCl}_2$ . The  $\text{CoCl}_2$  is pink in solution. Notice that the contents of the beaker briefly change colour to dark green, suggesting the formation of a reaction intermediate. Also notice that you can see the regeneration of the catalyst when the reaction is over.

Catalysts are divided into two categories, depending on whether or not they are in the same phase as the reactants.

### Homogeneous Catalysts

A **homogeneous catalyst** exists in the same phase as the reactants. Homogeneous catalysts most often catalyze gaseous and aqueous reactions. For example, aqueous zinc chloride,  $\text{ZnCl}_2$ , is used to catalyze the following reaction.

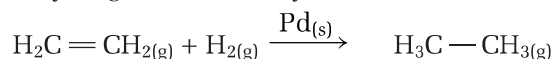


The reaction takes place in aqueous solution, and the catalyst is soluble in water. Therefore,  $\text{ZnCl}_2$  is a homogeneous catalyst when it is used with this reaction.

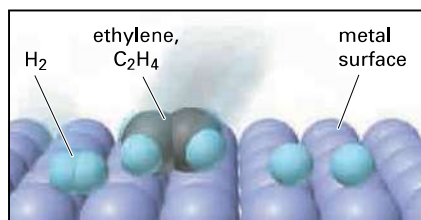
### Heterogeneous Catalysts

A **heterogeneous catalyst** exists in a phase that is different from the phase of the reaction it catalyzes. An important industrial use of heterogeneous catalysts is the addition of hydrogen to an organic compound that contains  $\text{C}=\text{C}$  double bonds. This process is called *hydrogenation*.

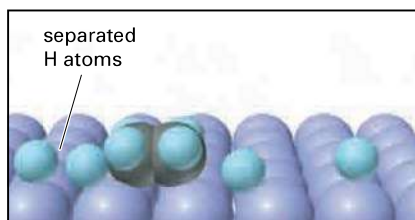
Consider the hydrogenation of ethylene, shown below.



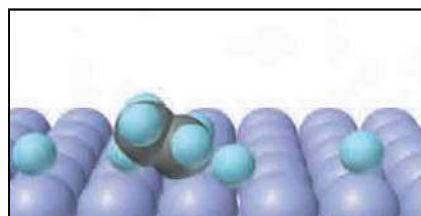
Without a catalyst, the reaction is very slow. When the reaction is catalyzed by a metal such as palladium or platinum, however, the rate increases dramatically. The ethylene and hydrogen molecules form bonds with the metal surface. This weakens the bonds of the hydrogen and ethylene. The  $\text{H}-\text{H}$  bonds of the hydrogen molecules break, and the hydrogen atoms are somewhat stabilized because of their attraction to the metal. The hydrogen atoms react with the ethylene, forming ethane. Figure 6.20 shows the hydrogenation of ethylene to ethane.



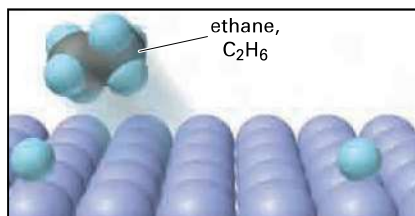
1  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  approach and bond to metal surface.



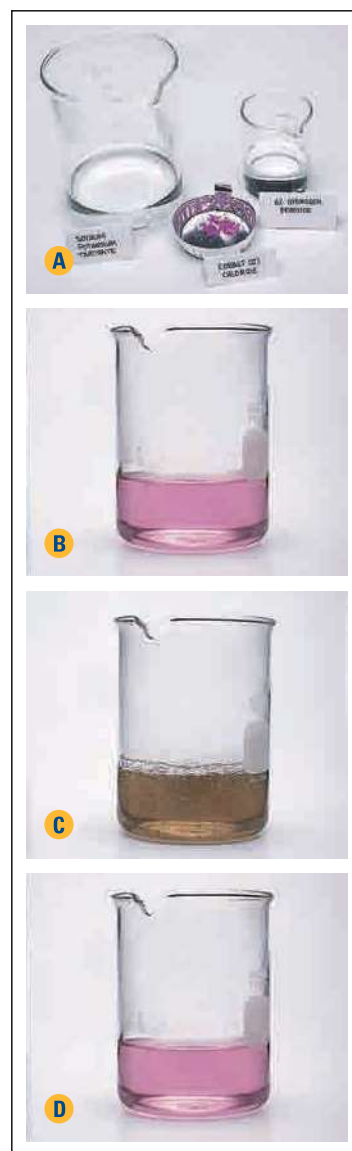
2 Rate-limiting step is  $\text{H}-\text{H}$  bond breakage.



3 One H atom bonds to  $\text{C}_2\text{H}_4$ .



4 Another  $\text{C}-\text{H}$  bond forms, and  $\text{C}_2\text{H}_6$  leaves the surface.



**Figure 6.19** The reaction of Rochelle's salt, sodium potassium tartrate, with hydrogen peroxide is catalyzed with  $\text{CoCl}_2$  at  $70^\circ\text{C}$ .

Photograph A shows the reactants before mixing.

Photograph B was taken immediately after  $\text{CoCl}_2$  was added. Notice the pink colour. Photograph C was taken after about 20 s.

Photograph D was taken after about 2 min.

**Figure 6.20** Platinum metal is used as a heterogeneous catalyst for the hydrogenation of gaseous ethylene to ethane.

[www.mcgrawhill.ca/links/chemistry12](http://www.mcgrawhill.ca/links/chemistry12)

You probably know that compounds called chlorofluorocarbons (CFCs) are responsible for depleting the ozone layer in Earth's stratosphere. Did you know, however, that CFCs do their destructive work by acting as homogeneous catalysts? Use the Internet to find out how CFCs catalyze the decomposition of ozone in the stratosphere. To start your research, go to the web site above and click on **Web Links**. Communicate your findings as a two-page press release.

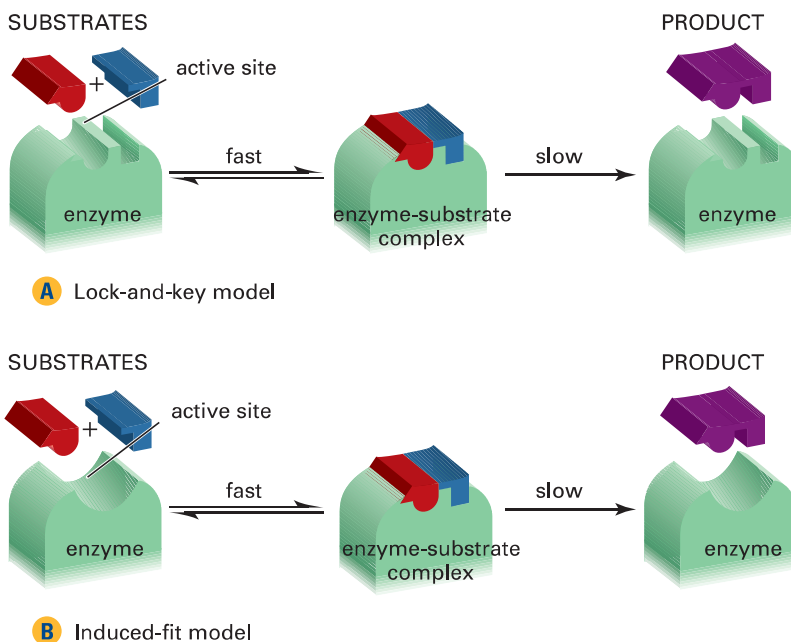
You may find the term “hydrogenation” familiar. Some food products, such as margarine and peanut butter, contain hydrogenated vegetable oils. Hydrogenation is used in the food industry to convert liquid vegetable oils, which contain carbon-carbon double bonds, to solid fats, such as shortening, which are fully saturated.

## Biological Catalysts

Your body depends on reactions that are catalyzed by amazingly efficient and specific biological catalysts. Biological catalysts are enormous protein molecules called **enzymes**. Their molecular masses range from 15 000 to 1 000 000 g/mol.

Only a small portion of the enzyme, called the **active site**, is actually involved in the catalysis reaction. In terms of the enzyme's overall shape, the active site is like a nook or a fold in its surface. The reactant molecule, called the **substrate** in an enzyme reaction, binds to the active site. The enzyme works by stabilizing the reaction's transition state.

Two models currently exist to explain how an enzyme and its substrate interact. One model, called the *lock and key model*, suggests that an enzyme is like a lock, and its substrate is like a key. The shape of the active site on the enzyme exactly fits the shape of the substrate. A second model, called the *induced fit model*, suggests that the active site of an enzyme changes its shape to fit its substrate. Figure 6.21 shows both models.



**Figure 6.21** Diagram A shows the lock and key model of enzyme function. Diagram B shows the induced-fit model of enzyme function.

Enzymes are involved in many functions of the human body, including digestion and metabolism. For example, the enzyme lactase is responsible for catalyzing the breakdown of lactose, a sugar found in milk. People who are lactose-intolerant are usually missing lactase, or they have insufficient amounts. If you are lactose-intolerant, you can take commercially produced supplements that contain lactase.

In the following ThoughtLab, you will investigate other ways in which industries use and produce catalysts.



Many reactions that produce useful compounds proceed too slowly to be used in industries. Some reactions need to be carried out at high temperatures or pressures to proceed quickly. These conditions, however, are often expensive to maintain. Therefore, chemists and engineers use catalysts to speed up the reactions in order to obtain products at a reasonable rate and under reasonable conditions. Similarly, many necessary biological reactions would proceed too slowly to sustain life without the presence of enzymes.

### Procedure

1. As a class, hold a brainstorming session to create a list of catalysts that are used in industries and a list of enzymes. Come to class prepared with several suggestions. (You may need to do some initial research.) Two examples in each category are given below.
  - *industrial catalysts*: catalytic converter,  $V_2O_5$  catalyst in synthesis of  $H_2SO_{4(aq)}$  (contact process)
  - *enzymes*: pepsin, pepsin
2. Choose one catalyst and one enzyme from each brainstormed list.
3. Using electronic and print resources, research your substances.
4. Prepare a brief report about each substance. Your report should include answers to the Analysis questions below. If you prefer, present your research as a web page.
5. Include a list of the sources you used. You should include at least three electronic sources and one print source for each substance.

### Analysis

1. Your report about industrial catalysts should answer the following questions.
  - (a) What is the chemical formula of the catalyst? Is the catalyst heterogeneous or homogeneous?
  - (b) What process does the catalyst speed up? Include products, reactants, the reaction mechanism (if possible), and information about the uncatalyzed reaction.
  - (c) What technology is required to support the catalyzed reaction (for example, the design of a catalytic converter)?
  - (d) What is the importance and relevance, to Canadians, of the industry associated with the catalyst?
2. Your report about enzymes should answer the questions below.
  - (a) What chemical process is the enzyme involved in?
  - (b) How does the enzyme fit into an overall biological process?
  - (c) Are there any ways in which the enzyme can be prevented from doing its job? Explain.
  - (d) Is the enzyme mass-produced by industry? If so, how? For what purpose is it mass-produced?

In the Thought Lab above, you may have included the enzyme catalase in your brainstormed list. Catalase in your blood is responsible for the “fizzing” you see when you use a dilute hydrogen peroxide solution to disinfect a cut. When dilute hydrogen peroxide is poured on a cut, it decomposes to oxygen gas and water. The decomposition reaction is catalyzed by catalase.

Have you ever opened an old bottle of hydrogen peroxide and noticed that it has lost its potency? The hydrogen peroxide has decomposed, leaving you with a bottle of water. At room temperature, in the absence of a catalyst, the decomposition of  $H_2O_2$  occurs very slowly, over a period of months or years. With the help of a catalyst, however, the rate of the reaction can be increased to the point where it can be easily studied in a high school laboratory.

In Investigation 6-B, you will write a detailed procedure to determine the rate law for the catalyzed decomposition of hydrogen peroxide. Instead of using catalase to catalyze the reaction, you will use an inorganic catalyst.



## Investigation 6-B

Predicting

Performing and recording

Analyzing and interpreting

# Determining the Rate Law for a Catalyzed Reaction

Hydrogen peroxide,  $\text{H}_2\text{O}_2$ , can be purchased as a dilute solution in a pharmacy or supermarket. It is used, among other things, as a topical antiseptic for minor cuts. In this investigation, you will use the  $\text{I}^-$  ion, in the form of aqueous  $\text{NaI}$ , to catalyze the decomposition of  $\text{H}_2\text{O}_2$ .

## Questions

What are the exponents  $m$  and  $n$ , and the rate constant, in the following general rate law equation?

$$\text{Rate} = k[\text{H}_2\text{O}_2]^m[\text{I}^-]^n$$

## Prediction

Will the catalyzed decomposition be first order or second order with respect to  $\text{H}_2\text{O}_2$  and with respect to  $\text{I}^-$ ?

## Materials

100 mL beaker  
250 mL Erlenmeyer flask  
60 mL 6% (m/v)  $\text{H}_2\text{O}_2(\text{aq})$   
60 mL 1.0 mol/L  $\text{NaI}(\text{aq})$   
3 graduated cylinders (10 mL)  
2 medicine droppers or plastic pipettes  
masking tape or grease pencil  
electronic top-loading balance,  
accurate to two decimal places

### Option 1

pneumatic trough  
one-holed rubber stopper, fitted with a piece  
of glass tubing (must be airtight)  
1 m rubber hose to fit glass tubing  
(must be airtight)  
graduated cylinder to collect gas

### Option 2

balance, preferably accurate to three decimal places

## Safety Precautions



- The reaction mixture will get hot. Handle the Erlenmeyer flask near the top.
- 6% hydrogen peroxide solution is an irritant. Wear safety glasses, latex gloves, and a laboratory apron.

## Procedure

- Copy the following table into your notebook, to record your observations. Give your table a title.

Experiment	$\text{H}_2\text{O}_2$		$\text{NaI}$		$\text{O}_2$ produced in 60 s (mL or g)
	Volume of 6% $\text{H}_2\text{O}_2$ (mL)	Volume of distilled water (mL)	Volume of 1.0 mol/L $\text{NaI}$ (mL)	Volume of distilled water (mL)	
1	10.0	0	10.0	0	
2	8.0	2.0	10.0	0	
3	6.0	4.0	10.0	0	
4	4.0	6.0	10.0	0	
5	10.0	0	8.0	2.0	
6	10.0	0	6.0	4.0	
7	10.0	0	4.0	6.0	

- The rate of production of oxygen gas can be monitored in different ways. Depending on the equipment you have available, choose option 1 or option 2.
  - Option 1:** You can collect the oxygen gas by downward displacement of water. Collect the oxygen produced in the first 60 s of the reaction in an upside-down graduated cylinder. Refer to Investigation 6-A to see how to set up an apparatus for collecting the gas.
  - Option 2:** If you have an electronic balance that is accurate to 0.001 g, you can monitor the change in mass as oxygen is released in the first 60 s of the reaction.

**Note:** Gently swirl the reaction mixture for the first 5 s. To help the bubbles of oxygen leave the solution, gently swirl the reaction flask every 15 s. Stop swirling at 45 s.

3. For your chosen option, write out a complete procedure based on the table on the previous page. Include a diagram showing the experimental set-up, and detailed safety precautions. Have your teacher approve your procedure, and then carry it out.

### Analysis

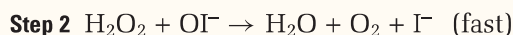
1. For each experiment, determine the initial rate of reaction. That is, convert the volume or mass of  $O_2$  within the time interval to get an initial rate of  $\text{mol } O_2/(\text{L} \cdot \text{s})$ . Using the stoichiometry of the reaction, convert this initial rate to a rate of decomposition of  $H_2O_2$  in  $\text{mol}/(\text{L} \cdot \text{s})$ .
2. (a) For the experiments in which  $[H_2O_2]$  was kept constant, plot a graph of reaction rate (y-axis) versus  $[NaI]$ . From the shape of the graph, determine if the reaction is first order or second order with respect to  $NaI$ .  
(b) For the experiments in which  $[NaI]$  was kept constant, plot a graph of reaction rate (y-axis) versus  $[H_2O_2]$ . From the shape of the graph, determine if the reaction is first order or second order with respect to  $H_2O_2$ .
3. Determine the value of  $k$  for the reaction, with proper units. Pay close attention to significant digits.

### Conclusion

4. Write the rate law equation for the reaction.

### Applications

5. The iodide ion-catalyzed decomposition of hydrogen peroxide to oxygen gas and water is believed to occur via the following mechanism.



- (a) Show that these two steps are consistent with the overall stoichiometry of the reaction.
  - (b) Is this mechanism consistent with your experimentally obtained rate law? Explain.
  - (c) How does this mechanism account for the fact that the  $I^-$  ion is a catalyst?
  - (d) What is the role of the hypoiodite,  $IO^-$ , ion in the mechanism? How do you know?
  - (e) Draw and label a potential energy-reaction coordinate diagram that is consistent with this mechanism. Be sure to illustrate any reaction intermediates.
  - (f) Postulate a possible activated complex for step 1 of the proposed mechanism.
6. The rate of decomposition of  $H_2O_2$  can be increased using other catalysts, such as  $Mn^{2+}$  and  $Fe^{2+}$ .
    - (a) How do you expect  $\Delta H$  for the decomposition reaction to change if different catalysts are used?
    - (b) Do you expect the rate law to change? Explain.





**Dr. Maud L. Menten**

Dr. Maud L. Menten, a leading researcher in the field of biochemistry, was born in Port Lambton, Ontario, in 1879. She grew up in rural British Columbia, where she had to take a canoe across the Fraser River every day to get to school. Later, Menten returned to Ontario to attend the University of Toronto. Upon receiving her medical degree in 1911, she became one of the first female doctors in Canada.

Menten soon received international recognition for her study of enzymes. From 1912 to 1913, she worked at Leonor Michaelis' lab at the University of Berlin. While conducting experiments on the breakdown of sucrose by the enzyme called invertase, Menten and Michaelis were able to refine the work of Victor Henri to explain how enzymes function. A few years earlier, Henri had proposed that enzymes bind directly to their substrates. Michaelis and Menten obtained the precise measurements that were needed to support Henri's hypothesis. Using the recently developed concept of pH, they were able to buffer their chemical reactions and thereby control the conditions of their experiments more

successfully than Henri. Their findings, published in 1913, provided the first useful model of enzyme function.

In the ground-breaking scientific paper that presented their work, Menten and Michaelis also derived an important mathematical formula. This formula describes the rate at which enzymes break down their substrates. It correlates the speed of the enzyme reaction with the concentrations of the enzyme and the substrate. Called the Michaelis-Menten equation, it remains fundamental to our understanding of how enzymes catalyze reactions.

Menten remained an avid researcher all her life. She worked long days, dividing her time between teaching at the University of Pittsburgh's School of Medicine and working as a pathologist at the Children's Hospital of Pittsburgh. She also worked with her peers and students on more than 70 papers that dealt with a wide range of medical topics. In addition to her work with Michaelis, Menten's contributions to science include pioneering techniques for studying the chemical composition of tissues and for investigating the nature of hemoglobin in human red blood cells.

It was not until 1949, only a year before retiring from the University of Pittsburgh, that Menten obtained a full professorship. Shortly after retiring, Menten joined the Medical Research Institute of British Columbia to do cancer research. Sadly, ill health forced her to cease her scientific work only a few years later. She spent her remaining days in Leamington, Ontario.

Although she was a brilliant medical researcher, Menten's enthusiasm overflowed beyond the boundaries of science. She was a world traveller, a mountain climber, a musician, and a student of languages. She was even a painter, whose work made its way into art exhibitions.

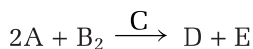
In honour of her lifetime of achievements, Maud L. Menten was inducted into the Canadian Medical Hall of Fame in 1998.

## Section Summary

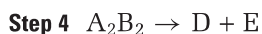
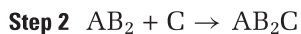
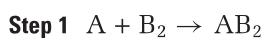
In this section, you learned that chemical reactions usually proceed as a series of steps called elementary reactions. You related the equations for elementary reactions to rate laws. You learned how the relative speed of the steps in a reaction mechanism help to predict the rate law of an overall reaction. Finally, you learned how a catalyst controls the rate of a chemical reaction by providing a lower-energy reaction mechanism. In this chapter, you compared activation energies of forward and reverse reactions. In the next unit, you will study, in detail, reactions that proceed in both directions.

## Section Review

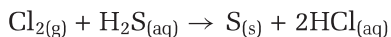
- 1 **K/U** In your own words, describe an elementary reaction.
- 2 **K/U** Distinguish between an overall reaction and an elementary reaction. Include a discussion of rate law.
- 3 **K/U** Why do chemists say that a reaction mechanism is *proposed*?
- 4 **K/U** What three criteria must a proposed reaction mechanism satisfy, for it to be accepted?
- 5 **C** Explain the difference between a reaction intermediate and an activated complex in a reaction mechanism.
- 6 **K/U** Consider the reaction below.



A chemist proposes the following reaction mechanism.



- (a) Show that the proposed mechanism can account for the overall reaction.
  - (b) What is the role of  $AB_2C$  and  $AB_2$ ?
  - (c) What is the role of  $C$ ?
  - (d) Given a proposed reaction mechanism, how can you differentiate, in general, between a reaction intermediate and a catalyst?
- 7 **I** Chlorine gas reacts with aqueous hydrogen sulfide (also known as hydrosulfuric acid) to form elemental sulfur and hydrochloric acid.

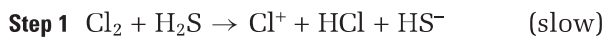


The experimentally obtained rate law equation is written as follows:

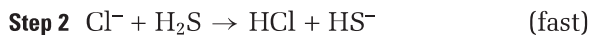
$$\text{Rate} = k[Cl_2][H_2S]$$

Which of the following mechanisms is consistent with this information? Explain your answer.

*Mechanism A*



*Mechanism B*

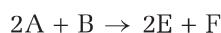


- 8 **C** Consider the following general endothermic reaction.



- (a) Explain why a catalyst has no effect on the enthalpy change. Illustrate your answer with a potential energy diagram.
- (b) Explain the effect of a catalyst on a reaction that has similar products and reactants, but is an exothermic reaction. Illustrate your answer with a potential energy diagram.

- 9 **K/U** Consider the general reaction shown below.



The experimentally determined rate law equation is written as follows:

$$\text{Rate} = k[A][B]$$

A proposed mechanism for the reaction has the first step below.

**Step 1**  $A + B \rightarrow C + F$  (rate-determining step)

Assuming a two-step mechanism, write a possible second elementary reaction for this mechanism.

- 10 **MC** Historians suspect that many ancient Romans suffered from lead poisoning. The ancient Romans used lead for their plumbing system (hence, the Latin name for the element). Lead is a poison because it can form strong bonds with proteins, including enzymes. Lead and other heavy metals react with enzymes by binding to functional groups on their active sites. When lead binds to a protein, such as an enzyme, the protein often precipitates out of solution.
- (a) Based on your understanding of enzymes and the information above, explain why lead's ability to form strong bonds with the active sites of enzymes makes lead toxic to humans.
- (b) Egg whites and milk are used as antidotes for heavy metal poisoning. The victim must ingest the egg white or milk soon after the lead has been ingested. Then the victim's stomach must be pumped. Explain why this antidote works. Why must the stomach be pumped?
- (c) Would the antidote described in part (b) work for someone who suffers from long-term exposure to lead by ingestion? Explain why or why not.

# CHAPTER 6 Review

## Reflecting on Chapter 6

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

- Use a graph to describe the rate of reaction as a function of the change of concentration of a reactant or product with respect to time.
- Distinguish between an average rate and an instantaneous rate of a reaction.
- Express the rate of a reaction as a rate law equation.
- Explain what the term “half-life” means. Calculate the half-life of a first-order reaction.
- Use collision theory and transition state theory to explain how concentration, temperature, surface area, and the nature of reactants control the rate of a chemical reaction.
- Use a potential energy diagram to demonstrate your understanding of the relationships between activation energy, reactants, products, enthalpy change, and the activated complex.
- Explain why most reactions occur as a series of elementary reactions. Show how the rate law for a rate-determining step relates to the rate law for an overall reaction.
- Explain how a catalyst increases the rate of a chemical reaction.

## Reviewing Key Terms

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

reaction rate	average rate
instantaneous rate	catalyst
rate law equation	rate constant
overall reaction order	first-order reaction
second-order reaction	initial rates method
half-life ( $t_{1/2}$ )	collision theory
activation energy ( $E_a$ )	transition state theory
potential energy diagram	transition state
activated complex	reaction mechanism
elementary reaction	reaction intermediates
molecularity	bimolecular
unimolecular	termolecular
rate-determining step	homogeneous catalyst
heterogeneous catalyst	enzymes
active site	substrate

## Knowledge/Understanding

- The way that chemists monitor the rate of a chemical reaction depends on the reaction. What conditions of a reacting system must change for the each instrument or method below to be useful?
  - balance
  - downward displacement of water
  - spectrophotometer
- In your own words, describe how collision theory explains why increased surface area increases the rate of a reaction.
- Agitation (stirring) often increases the rate of a reaction. Use collision theory to explain why.
- At elevated temperatures, ammonia reacts with oxygen as follows:
 
$$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$$
  - Write an equation that shows the relationship between the rate of reaction expressed in terms of each reactant and product.
  - The average rate of production of nitrogen monoxide is  $6.2 \times 10^{-2} \text{ mol}/(\text{L} \cdot \text{s})$ . What is the average rate of change in the concentration of ammonia?
- State two requirements for an effective collision between reactants.
- State the difference between a homogeneous catalyst and a heterogeneous catalyst.

## Inquiry

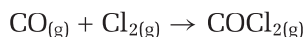
- The rate of decomposition of hydrogen peroxide was studied at a particular temperature.
 
$$\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$$
  - The initial concentration of hydrogen peroxide was  $0.200 \text{ mol/L}$ .  $10.0 \text{ s}$  later, it was measured to be  $0.196 \text{ mol/L}$ . What was the initial rate of the reaction, expressed in  $\text{mol}/(\text{L} \cdot \text{s})$ ?
  - $0.500 \text{ L}$  of hydrogen peroxide solution was used for the experiment. What mass was lost as  $\text{O}_2$  bubbled out of solution in this initial  $10.0 \text{ s}$  interval?
- The following first-order reaction has a rate of  $3.8 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{s})$  when  $[\text{A}] = 0.38 \text{ mol/L}$ .  $\text{A} \rightarrow \text{products}$ 
  - Calculate the value of  $k$  and the half-life of the reaction.

(b) What did you assume when answering part (a)?

9. The units of  $k$ , the rate constant, depend on the overall order of a reaction. For what overall reaction order does the rate constant have the same units as the reaction rate?

10. The rate constant of a first-order reaction is  $4.87 \times 10^{-2} \text{ s}^{-1}$  at a particular temperature. Calculate the half-life of this reaction.

11. Phosgene,  $\text{COCl}_2$ , is a highly toxic gas that is heavier than air. It can be produced by reacting carbon monoxide with chlorine in a very slow reaction.



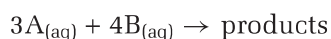
The following initial rate data were collected at a particular temperature.

Experiment	Initial $[\text{CO}]$ (mol/L)	Initial $[\text{Cl}_2]$ (mol/L)	Initial rate (mol/(L · s))
1	0.500	0.0500	$6.45 \times 10^{-30}$
2	0.0500	0.0500	$6.65 \times 10^{-31}$
3	0.0500	0.500	$6.50 \times 10^{-30}$
4	0.0500	0.00500	$6.60 \times 10^{-32}$

- (a) Write the rate law equation for this reaction.  
(b) Calculate the value of the rate constant.

Make sure that you use the proper units.

12. The following reaction was studied using the method of initial rates.

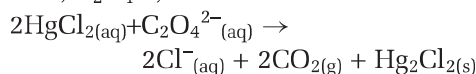


The following data were collected.

Experiment	Initial $[\text{A}]$ (mol/L)	Initial $[\text{B}]$ (mol/L)	Initial rate (mol/(L · s))
1	0.200	0.200	5.00
2	0.600	0.200	45.0
3	0.200	0.400	10.0
4	0.600	0.400	90.0

- (a) Write the rate law equation.  
(b) What is the overall reaction order?  
(c) Calculate the value of the rate constant, with the proper units.

13. Mercury(II) chloride,  $\text{HgCl}_2$ , reacts with oxalate ions,  $\text{C}_2\text{O}_4^{2-}$ , as follows:



The reaction rate was monitored by measuring the mass of  $\text{Hg}_2\text{Cl}_2$  formed as a function of time.

Experiment	Initial $[\text{Hg}_2\text{Cl}_2]$ (mol/L)	Initial $[\text{C}_2\text{O}_4^{2-}]$ (mol/L)	Initial rate (mol/(L · s))
1	0.0788	0.113	$1.35 \times 10^{-6}$
2	0.0788	0.225	$5.33 \times 10^{-6}$
3	0.039	0.225	$2.63 \times 10^{-6}$

- (a) Write the rate law equation for the reaction.  
(b) Calculate the value of the rate constant, with the appropriate units.  
(c) Calculate the initial rate of the reaction when  $[\text{HgCl}_2] = 0.0400 \text{ mol/L}$  and  $[\text{C}_2\text{O}_4^{2-}] = 0.150 \text{ mol/L}$ .

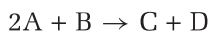
14. A chemical reaction between compounds A and B is first order in A and first order in B. Find the unknown information in the table below.

Experiment	Rate (mol/(L · s))	$[\text{A}]$ (mol/L)	$[\text{B}]$ (mol/L)
1	0.10	0.20	0.050
2	0.40	(a)	0.050
3	0.80	0.40	(b)

15. A chemical reaction between compounds C and D is first order in C and second order in D. Find the unknown information in the table below.

Experiment	Rate (mol/(L · s))	$[\text{A}]$ (mol/L)	$[\text{B}]$ (mol/L)
1	0.10	1.0	0.20
2	(a)	2.0	0.20
3	(b)	2.0	0.40

16. Consider the reaction below.

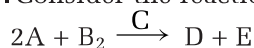


At  $20^\circ\text{C}$ , the activation energy of the forward reaction is  $59.9 \text{ kJ/mol}$  and the activation energy of the reverse reaction is  $72.0 \text{ kJ/mol}$ .

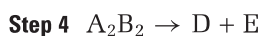
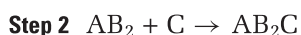
- (a) What is the enthalpy change for the reaction?  
(b) Sketch a potential energy diagram for the reaction.



17. Consider the reaction below.



A chemist proposes the following reaction mechanism.



Suggest a rate law equation corresponding to each of the following situations. Remember that a rate law equation may include only the concentration of reactants and catalyst, if any. If you think that it is impossible to predict a rate law for any of the situations, explain why. State any assumptions you make for each situation.

- (a) Step 1 is the rate determining step.  
(b) Step 2 is the rate determining step.  
(c) Step 3 is the rate determining step.

## Communication

18. Explain why chemical reactions are fastest at the beginning.
19. Explain why a rate constant must always be accompanied by the temperature at which it was determined.
20. Your friend is having trouble understanding how a rate-determining step in a reaction mechanism determines the rate of the overall reaction. Invent a new analogy to explain the idea to your friend, using a process from everyday life that involves slow and fast steps.
21. Write a few paragraphs to distinguish between an activated complex and a reaction intermediate. Include equations and diagrams in your explanation.
22. "For an endothermic reaction, the activation energy will always be greater than the enthalpy change for the reaction."  
(a) Do you agree or disagree with this statement? Explain your answer.  
(b) Replace the word "endothermic" with "exothermic." Do you agree or disagree with this statement now? Explain your answer.
23. (a) Explain, in your own words, what is meant by the term "activation energy."  
(b) How can the idea of activation energy be used to explain the temperature dependence of rate?  
(c) How can activation energy be used to explain why a catalyst increases the rate of a chemical reaction?

## Making Connections

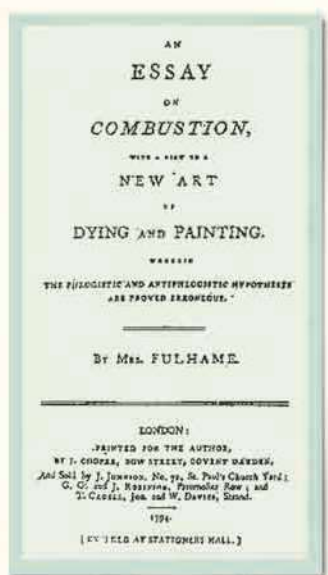
24. Suppose that you are using a Polaroid™ camera outdoors during the winter. You want your photographs to develop faster. Suggest a way to accomplish this.
25. Why are catalytic converters not very effective immediately after starting a vehicle in the winter? Suggest a way to correct this problem.

### Answers to Practice Problems and Short Answers to Section Review Questions

**Practice Problems:** 1. 0.25 mol/s 2. 0.10 mol/(L · s)  
3.  $\Delta[\text{Br}_2]/\Delta t = -0.5\Delta[\text{HBr}]/\Delta t$  4.(a)  $9.0 \times 10^{-4}$  mol/s  
(b) 0.011 L/s 5. Rate =  $(2.05 \times 10^{-4} \text{ s}^{-1})[\text{C}_2\text{H}_4\text{O}]$   
6. Rate =  $(0.15 \text{ L}/(\text{mol} \cdot \text{s}))[\text{ICl}][\text{H}_2]$  7.(a) Rate =  $k[\text{SO}_2\text{Cl}_2]$   
(b)  $k = 2.2 \times 10^{-5} \text{ s}^{-1}$  8.(a) 0.10 (b) 0.025 (c) 0.34 (d) 0.060  
9.(a) 0.075 s (b) 6.2% 10.(a)  $3.6 \times 10^{-4} \text{ s}^{-1}$   
(b)  $5.0 \times 10^{14}$  molecules/L 11. Only 0.1% of the reactants are left. 12. about 400 s 13. Products are at lower energy than reactants. 14.  $E_{a(\text{fwd})} = 99 \text{ kJ}$  15.  $E_{a(\text{rev})} = 193 \text{ kJ}$   
16.  $E_{a(\text{rev})} = 411 \text{ kJ}$  17. Yes: Steps add to give overall reaction. Both steps are bimolecular. Rate law for slow step matches experimental rate law. 18.(a) yes (b)  $C + D \rightarrow B$  (slow);  $B + C \rightarrow E$  (fast) 19.(a)  $A + 2B \rightarrow E + F$  (b) Rate =  $k[A][B]$   
20. Steps add to give overall reaction. Steps are bimolecular or unimolecular. Rate law for slow step matches experimental rate law.  
**Section Review:** 6.1: 4.(a)  $1.25 \times 10^{-3} \text{ mol}/(\text{L} \cdot \text{s})$   
(b)  $8.33 \times 10^{-4} \text{ mol}/(\text{L} \cdot \text{s})$  6.2 1. Rate =  $k[A]^2[B]$  2. no 3.(a) no change (b) increase by a factor of 8 4.(a) 1, 2, 1 (b) 4  
(c)  $\text{L}^3/(\text{mol}^3 \cdot \text{s})$  5.(a) Rate =  $k[A][B]^2$   
(b)  $6.2 \times 10^2 \text{ L}^2/(\text{mol}^2 \cdot \text{s})$  6. Rate =  $(0.020 \text{ L}^2/(\text{mol}^2 \cdot \text{s}))[\text{A}][\text{B}]$   
7. 29.6 years;  $9.33 \times 10^8 \text{ s}$  6.3: 3.(a) endothermic  
(b)  $\Delta H = 68 \text{ kJ}$  6.4: 6.(b) reaction intermediates (c) catalyst  
7. mechanism A 9.  $A + C \rightarrow 2E$  (fast)



## Developing a Bulletin About Catalysts and Enzymes



### Background

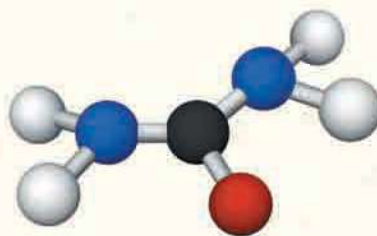
Scientists have studied the amazing properties of enzymes and catalysts for more than 200 years. In 1794, the English chemist Elizabeth Fulhame published a book called *An Essay on Combustion*. Her book included many of the first recorded ideas about the role of catalysis in chemical processes. In particular, Fulhame was interested in the catalytic properties of the hydrogen and oxygen atoms in water.

Fulhame's ideas about inorganic catalysts were swept under by the fast and furious debate of her scientific era. Many of the most prominent scientists of her day were arguing over whether organic reactions needed living organisms to occur. Many scientists believed that a *vital force* was present in living organisms and was essential for the formation of all organic compounds. For example, the fermentation of sugar into alcohol takes place through the action of yeast, a living organism.

Scientists argued that it was impossible to produce alcohol, an organic compound, without the action of yeast, or some other living organism.

Although no one realized it at the time, Fulhame's ideas on catalysts were directly relevant to the debate on vital force. There is no mysterious vital force in living organisms. Instead, organic reactions in living organisms depend on organic catalysts called enzymes.

In 1828, the German chemist Friedrich Wohler discovered that urea, an organic compound, could be produced in a laboratory without any help from a living organism. Wohler's discovery inspired other scientists to hypothesize that the fermentation of sugar into alcohol could also occur without the presence of living organisms, such as yeast. Some scientists went further, and insisted that yeast was not even a living organism.



Urea

Eventually, scientists proved that fermentation did not require whole cells of yeast. Fermentation could still occur if non-living extracts of yeast were present. Through further study and experimentation, the important component in the yeast extract was identified as an enzyme. If earlier scientists had considered Fulhame's ideas on catalysts, they might have arrived at the truth about enzymes sooner!

Over time, scientists have built up a large body of knowledge about many different catalysts and enzymes. This knowledge has been put to good use in industry. Difficult and expensive industrial processes have been made faster, cheaper, and easier through the use of catalysts and enzymes. For example, enzymes are used in the pharmaceutical industry, in paper-making and recycling processes, and in the petroleum industry. Many more industrial uses of catalysts and enzymes are possible, and research into catalysts continues.

In this project, you will research some of the many catalysts and enzymes that are used in Canadian industries. Then you will create an information bulletin to present your findings.

## Challenge

Design, produce, and distribute an information bulletin to inform your community about the use of catalysts or enzymes in Canadian industries. Choose one or more of the following options:

- If there is a local industry you can study, focus on different aspects of this industry's use of catalysts.
- Study a catalyst that is used by several different industries.
- Compile a variety of uses of catalysts and enzymes across Canada.
- Analyze a cutting-edge technology that involves catalysts or enzymes.
- Analyze the historical development and use of a particular enzyme or catalyst.

## Materials

Set up your information bulletin in the format of a brochure or leaflet, suitable to be distributed to classmates and other students in your school. Alternatively, present your information bulletin as a web page, so that you can share your research with a wider audience.

## Design Criteria

- A** As a class, develop a product rubric to assess the bulletins. For example, you may wish to evaluate how interesting the bulletins are, or whether they are easy for non-chemistry students to understand.
- B** Your bulletin should be interesting, visually attractive, factual, and aimed at a wide audience.

## Action Plan

- 1 Decide whether you will work on your own, with a partner, or as part of a small group.
- 2 Decide what you want your bulletin to look like. The following questions will help you decide on a format.
  - How many topics will you cover in your bulletin?
  - How long will each article in your bulletin be?

After you complete this project, answer the following questions to assess your work.

- Assess the interest level of the information you gathered. Did you obtain information of interest to Grade 12 chemistry students? Did you obtain information of interest to non-science students?
- Assess the scientific accuracy and complexity of the information you gathered. Did you use at least three major sources? If you used web sites, were they run by reputable organizations? Did you include information above and beyond the content of this course?
- Assess your communication skills. Did you explain detailed chemical information in a clear and understandable way?

- Will you study a local industry, or cover a variety of Canadian industries?
- Will you examine one enzyme or catalyst in detail, or will you give an overview of many different catalysts and/or enzymes?
- How can you ensure that your bulletin is visually attractive and interesting?
- How can you motivate readers? For example, you may want to include activities (such as puzzles and quizzes) or a brief list of interesting facts.

- 3 If you are working as part of a group, assign a task to each member of the group.

## Evaluate

Print out your bulletin. Display it on a poster board in a hallway of your school, or in a local public building. If your bulletin is in the form of a web page, present it to the class and then post it on the Internet or on your school's Intranet.

Web

LINK

[www.mcgrawhill.ca/links/chemistry12](http://www.mcgrawhill.ca/links/chemistry12)

Go to the web site above, and click on **Web Links** to find appropriate sites to start your research.

## Knowledge/Understanding

### Multiple Choice

In your notebook, write the letter for the best answer to each question.

- The  $\Delta H^\circ_f$  of an element in its standard state is defined to be
    - 0 kJ/mol
    - 10 kJ/mol
    - 10 kJ/mol
    - greater than 0 kJ/mol
    - a unique value for each element
  - 10.9 kJ of energy is needed to vaporize 60.0 g of liquid  $\text{Br}_2$  vapour at  $60^\circ\text{C}$ . What is the molar heat of vaporization of  $\text{Br}_2$  at  $60^\circ\text{C}$ ?
    - 3.64 kJ/mol
    - 7.27 kJ/mol
    - 14.6 kJ/mol
    - 29.1 kJ/mol
    - 10.9 kJ/mol
  - What is the molar heat of vaporization of water, given the following thermochemical equations?
 
$$\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(g)} + 241.8 \text{ kJ}$$

$$\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)} + 285.8 \text{ kJ}$$
    - 44.0 kJ/mol
    - 527.6 kJ/mol
    - 44.0 kJ/mol
    - 527.6 kJ/mol
    - 241.8 kJ/mol
  - Which substance has a standard enthalpy of formation,  $\Delta H^\circ_f$ , equal to zero?
    - gold,  $\text{Au}_{(s)}$
    - water,  $\text{H}_2\text{O}_{(l)}$
    - carbon monoxide,  $\text{CO}_{(s)}$
    - zinc,  $\text{Zn}_{(g)}$
    - water,  $\text{H}_2\text{O}_{(g)}$
  - Which of the following statements are true?
    - The reaction vessel cools when an endothermic reaction occurs.
    - An endothermic reaction has a negative value of  $\Delta H$ .
    - Heat is liberated when an exothermic reaction occurs.
    - I and II
    - I, II, and III
    - I and III only
    - II and III only
    - none of them
  - Which of the following processes are exothermic?
    - boiling water
    - freezing water
    - condensing steam
    - melting ice
  - I and II only
  - II and III only
  - I and IV only
  - II, III, and IV only
  - II and IV only
- Which factor does not affect the rate of a chemical reaction in aqueous solution?
    - the enthalpy change of the reaction
    - the activation energy of the reaction
    - the collision frequency of the reacting particles
    - the relative orientation of the colliding particles
    - the temperature of the solution
  - Which statement about an activated complex is true?
    - It is a stable substance.
    - It has lower chemical potential energy, or enthalpy, than reactants or products.
    - It occurs only in endothermic reactions.
    - It occurs at the transition state of the reaction.
    - It always breaks down to form product molecules.
  - A catalyst changes the
    - mechanism of a reaction
    - enthalpy change of a reaction
    - activation energy of a reaction
    - I only
    - III only
    - I and III only
    - II and III only
    - I, II, and III
  - The overall rate of any chemical reaction is most closely related to
    - the number of steps in the reaction mechanism
    - the overall reaction
    - the fastest step in the reaction mechanism
    - the slowest step in the reaction mechanism
    - the average rate of all the steps in the reaction mechanism

### Short Answer

In your notebook, write a sentence or a short paragraph to answer each question.

- Distinguish between an open system and an insulated system.
- In your own words, define the terms "system" and "surroundings." Use an example.

13. In a chemical reaction, bonds are formed and broken.
  - (a) How would you characterize the enthalpy change of bond breaking?
  - (b) How would you characterize the enthalpy change of bond formation?
  - (c) State the relationship between the enthalpy change of the overall reaction (exothermic or endothermic) and bond breakage and formation.
14. “The reactants have more potential energy than the products.” What kind of reaction does this statement describe? Justify your answer.
15. What is the relationship between the initial quantity of reactants for a reaction and the enthalpy change for a reaction? Use a thermochemical equation in your answer.
16. Compare and contrast enthalpy of vaporization and enthalpy of condensation.
17. What are the characteristics of a good constant-pressure calorimeter?
18. A wooden or plastic spoon, rather than a metal spoon, should be used to stir hot soup. Explain why, in terms of specific heat capacity.
19. Butane,  $\text{C}_4\text{H}_{10}$ , is the fuel that is used in disposable lighters. Consider the following equation for the complete combustion of butane.
$$\text{C}_4\text{H}_{10(g)} + 6.5\text{O}_{2(g)} \rightarrow 4\text{CO}_{2(g)} + 5\text{H}_2\text{O}_{(l)}$$
  - (a) Write a separate balanced chemical equation for the formation of  $\text{C}_4\text{H}_{10}$ , the formation of  $\text{CO}_2$ , and the formation of  $\text{H}_2\text{O}$ , directly from the elements in their standard states.
  - (b) Algebraically combine these equations to get the balanced chemical equation for the complete combustion of  $\text{C}_4\text{H}_{10}$ .
20. The enthalpy of formation of an element in its standard state is zero. Explain why the enthalpy of formation of  $\text{I}_{2(g)}$  is 21 kJ/mol, not 0 kJ/mol.
21. Briefly state why it is useful to know the half-life of a reaction.
22. The rate of a chemical reaction is dependent on its  $\Delta H$ . Do you agree or disagree with this statement? Briefly justify your answer.
23. What is the relationship between the units of the rate constant,  $k$ , and the overall reaction order?
24. List the factors that affect the rate of a chemical reaction.
25. Draw and label a potential energy diagram for the following exothermic reaction. Include  $E_a$ , the activated complex, and  $\Delta H$ .
$$\text{A} + \text{B} \rightarrow \text{AB}$$
26. Distinguish between the instantaneous rate and the initial rate of a chemical reaction. Under what circumstances would these two rates be the same?

## Inquiry

27. A student wants to determine the enthalpy change associated with dissolving solid sodium hydroxide,  $\text{NaOH}$ , in water. The student dissolves 1.96 g of  $\text{NaOH}$  in 100.0 mL of water in a coffee-cup calorimeter. The initial temperature of the water is  $23.4^\circ\text{C}$ . After the  $\text{NaOH}$  dissolves, the temperature of the water rises to  $28.7^\circ\text{C}$ .
  - (a) Use these data to determine the enthalpy of dissolution of sodium hydroxide, in kJ/mol  $\text{NaOH}$ . Assume that the heat capacity of the calorimeter is negligible.
  - (b) Suppose that the heat capacity of the calorimeter was not negligible. Explain how the value of  $\Delta H$  that you calculated in part (a) would compare with the *actual*  $\Delta H$ .
  - (c) Draw and label an enthalpy diagram for this reaction.
28. Some solid ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , is added to a coffee-cup calorimeter that contains water at room temperature. After the  $\text{NH}_4\text{NO}_3$  has dissolved, the temperature of the solution drops to near  $0^\circ\text{C}$ . Explain this observation.
29. Consider the following chemical equations and their enthalpy changes.
$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow$$
$$\text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(g)} \quad \Delta H = -8.0 \times 10^2 \text{ kJ}$$
$$\text{CaO}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Ca(OH)}_{2(aq)} \quad \Delta H = -65 \text{ kJ}$$
What volume of methane, at  $20^\circ\text{C}$  and 100 kPa, would have to be combusted in order to release the same amount of energy as the reaction of  $1.0 \times 10^2 \text{ g}$  of  $\text{CaO}$  with sufficient water? (The volume of 1.00 mol of any gas at  $20^\circ\text{C}$  and 100 kPa is 24 L.)

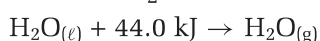
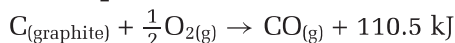
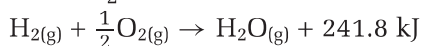
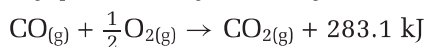
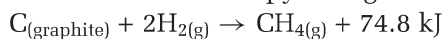


30. The complete combustion of 1.00 mol of sucrose (table sugar),  $C_{12}H_{22}O_{11}$ , yields  $5.65 \times 10^3$  kJ.
- (a) Write a balanced thermochemical equation for the combustion of sucrose.
- (b) Calculate the amount of energy that is released when 5.00 g of sucrose (about one teaspoon) is combusted.

31. Carbon monoxide reacts with hydrogen gas to produce a mixture of methane, carbon dioxide, and water. (This mixture is known as substitute natural gas.)



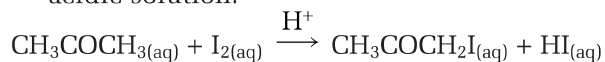
Use the following thermochemical equations to determine the enthalpy change of the reaction.



32. The decomposition of aqueous hydrogen peroxide,  $H_2O_2$ , can be catalyzed by different catalysts, such as aqueous sodium iodide,  $NaI$ , or aqueous iron(II) nitrate,  $Fe(NO_3)_2$ .

- (a) The enthalpy change, in kJ/mol of  $H_2O_2$ , would be the same for this reaction, regardless of the catalyst. Explain why, with the help of a potential energy diagram.
- (b) Design an investigation to verify your explanation in part (a). Do not attempt to carry out the investigation without the supervision of your teacher.

33. Acetone,  $CH_3COCH_3$ , reacts with iodine in acidic solution.



The experimentally observed rate law equation is written as follows:

$$\text{Rate} = k[CH_3COCH_3][H^+]$$

- (a) What is the effect on the reaction rate if the concentration of  $CH_3COCH_3$  is doubled?
- (b) What is the effect on the reaction rate if the concentration of  $I_2$  is doubled?
34. Consider the heterogeneous reaction of solid magnesium with hydrochloric acid.
- $$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

The general rate law of this reaction is given below.

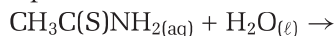
$$\text{Rate} = k[Mg]^m[HCl]^n$$

Several trials of the reaction are carried out, each using a piece of magnesium ribbon of a fixed length. This is analogous to constant concentration. The general rate law equation can now be written as follows:

$$\text{Rate} = k'[HCl]^n, \text{ where } k' = k[Mg]^m$$

Design an investigation to determine the value of  $n$  in the rate law equation. Assume that you have a stock solution of 6.0 mol/L  $HCl$ , magnesium ribbon, a stopwatch, and any standard laboratory glassware available. If you want to carry out your investigation, have your teacher approve the procedure first.

35. Thioacetamide,  $CH_3CSNH_2$ , reacts with water as shown in the balanced chemical equation below.



The experimentally observed rate law equation is written as follows:

$$\text{Rate} = k[H_3O^+][CH_3C(S)NH_2]$$

- (a) Do you expect the reaction rate to change if some solid  $NaOH$  is added to the reaction vessel? Explain.
- (b) Do you expect the reaction rate to change if 250 mL of water is added to 250 mL of the reacting solution? Explain.
- (c) How will the reaction rate change if the reaction is carried out at  $40^\circ C$  instead of at  $20^\circ C$ ?

## Communication

36. If a solution of acid accidentally comes in contact with your skin, you are told to run the affected area under cold water for several minutes. Explain why it is not advisable to simply neutralize the acid with a basic solution.
37. A classmate is having difficulty understanding how the concepts of system, insulated system, and surroundings are related to exothermic and endothermic reactions. Write a note to explain to your classmate how the concepts are related. Use diagrams to help clarify your explanation.
38. Consider the following data for the complete combustion of the  $C_1$  to  $C_8$  alkanes.

Name	Formula	$\Delta H_{\text{comb}}$ (kJ/mol of alkane)
methane	CH <sub>4</sub>	$-8.90 \times 10^2$
ethane	C <sub>2</sub> H <sub>6</sub>	$-1.56 \times 10^3$
propane	C <sub>3</sub> H <sub>8</sub>	$-2.22 \times 10^3$
butane	C <sub>4</sub> H <sub>10</sub>	$-2.88 \times 10^3$
pentane	C <sub>5</sub> H <sub>12</sub>	$-3.54 \times 10^3$
hexane	C <sub>6</sub> H <sub>14</sub>	$-4.16 \times 10^3$
heptane	C <sub>7</sub> H <sub>16</sub>	$-4.81 \times 10^3$
octane	C <sub>8</sub> H <sub>18</sub>	$-5.45 \times 10^3$

- (a) Using either graph paper or spreadsheet software, plot a graph of  $\Delta H_{\text{comb}}$  (y-axis) versus the number of C atoms in the fuel (x-axis).
- (b) Extrapolate your graph to predict  $\Delta H_{\text{comb}}$  of decane, C<sub>10</sub>H<sub>22</sub>.
- (c) From your graph, develop an equation to determine  $\Delta H_{\text{comb}}$  of a straight-chain alkane, given the number of carbons. Your equation should be of the form  $\Delta H = \dots$
- (d) Use the equation you developed in part (c) to determine  $\Delta H_{\text{comb}}$  of C<sub>10</sub>H<sub>22</sub>. How does this value compare with the value of  $\Delta H$  you determined by extrapolation from the graph? Explain why.
- (e) Methane, ethane, propane, and butane are all gases at room temperature. You know that equal volumes of different gases contain the same number of moles under identical conditions of temperature and pressure. Which of these gases do you think would make the best fuel? Explain your answer.
39. A chemistry student wrote the following sentences to remind herself of important concepts. Write a paragraph to expand on each concept. Use examples and diagrams where appropriate.
- (a) Hess's law can be used to determine the enthalpy change of a reaction, instead of measuring the enthalpy change in a laboratory.
- (b) A pH meter can be used to monitor the progress of a reaction.
- (c) The rate law equation for a reaction is dictated by the rate-determining step in the reaction's mechanism.
- (d) A catalyst speeds up a reaction, but it does not affect the enthalpy change of the reaction.
40. Suppose that you are having a new home built in a rural area, where natural gas is not available. You have two choices for fuelling your furnace:
- propane, C<sub>3</sub>H<sub>8</sub>, delivered as a liquid under pressure and stored in a tank
  - home heating oil, delivered as a liquid (not under pressure) and stored in a tank
- What factors do you need to consider in order to decide on the best fuel? What assumptions do you need to make?
41. Suppose that you read the following statement in a magazine: 0.95 thousand cubic feet of natural gas is equal to a gigajoule, GJ, of energy. Being a media-literate student, you are sceptical of this claim and wish to verify it. The following assumptions/information may be useful.
- Natural gas is pure methane.
  - Methane undergoes complete combustion.
  - H<sub>2</sub>O<sub>(l)</sub> is formed, rather than H<sub>2</sub>O<sub>(g)</sub>.
  - 1.00 mol of any gas occupies 24 L at 20°C and 100 kPa.
  - 1 foot = 12 inches; 1 inch = 2.54 cm; 1 L = 1 dm<sup>3</sup>
42. Many taxis and delivery vehicles, especially in large cities, have been converted to burn propane, C<sub>3</sub>H<sub>8</sub>, rather than gasoline. This is done to save money. For most vehicles, the conversion to propane must be done at the owner's expense. Suppose that a taxi owner wants to calculate how far a taxi needs to be driven in order to recoup the conversion cost. List the information that the owner needs in order to do the calculation. Also list any simplifying assumptions.

## Making Connections

40. Suppose that you are having a new home built in a rural area, where natural gas is not available. You have two choices for fuelling your furnace:
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### COURSE CHALLENGE



#### The Chemistry of Human Health

Consider the following points as you plan your Chemistry Course Challenge:

- How can you determine and compare rates of chemical reactions?
- What are some key differences between inorganic catalysts and enzymes?
- How are enzymes important for maintaining human health?