

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)

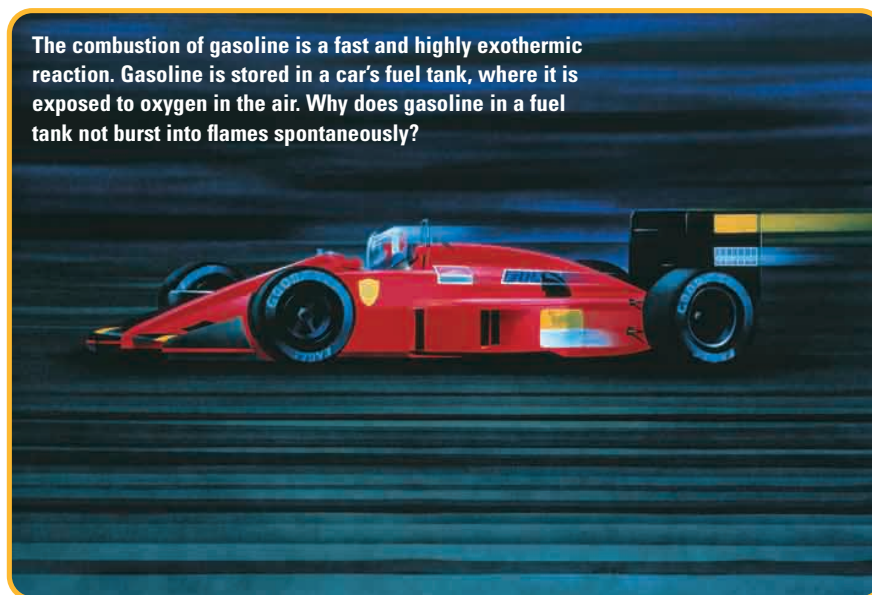
Racing cars, such as the one shown below, can reach speeds that are well above 200 km/h. In contrast, the maximum speed of many farm tractors is only about 25 km/h. Just as some vehicles travel more quickly than others, some chemical reactions occur more quickly than others. For example, compare the 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

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.

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

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*



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	3.12×10^{-3}
10.0	4.41×10^{-3}
15.0	5.40×10^{-3}
20.0	6.24×10^{-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.

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

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 3.12×10^{-3} mol/(L · 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 2.3×10^{-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.

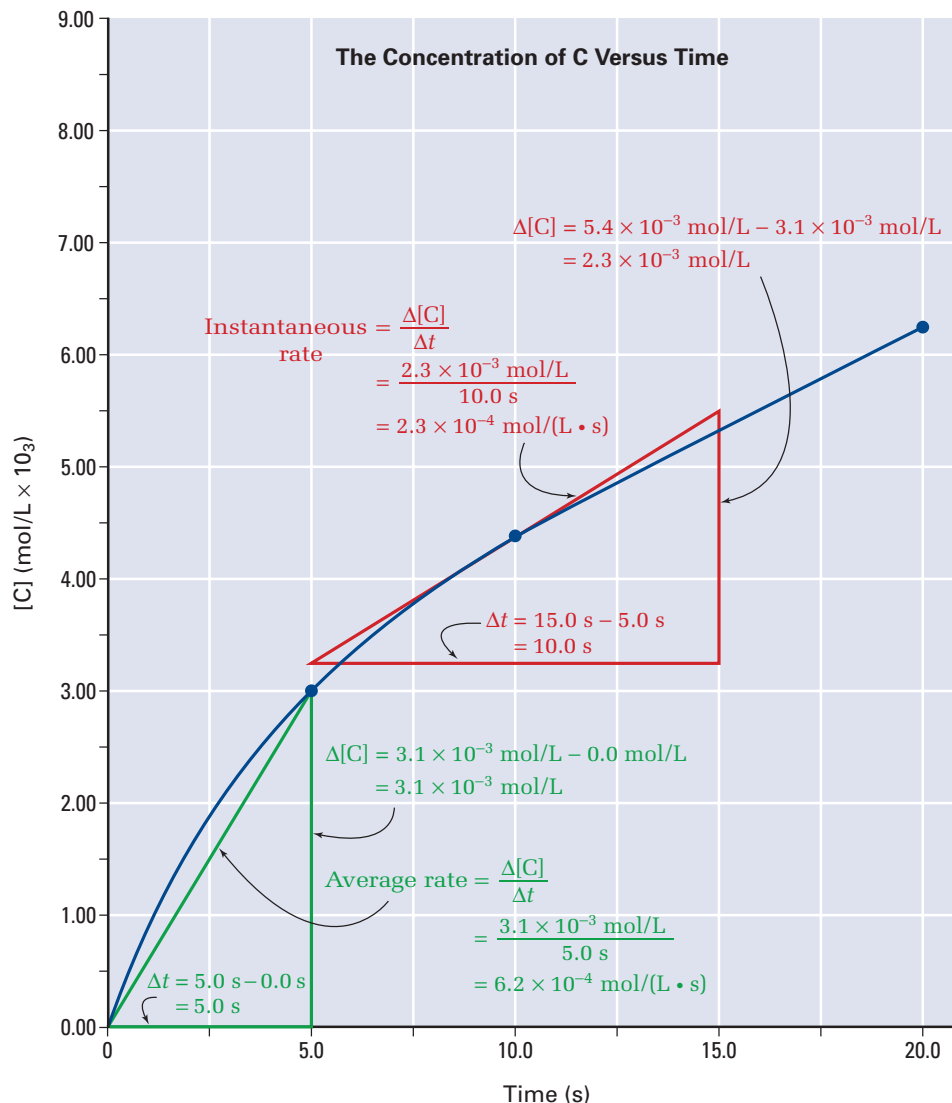


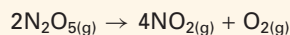
Figure 6.2 The slope of a tangent drawn to a concentration-time curve represents the instantaneous rate of the reaction. The slope of a secant is used to determine the average rate of a reaction.

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.

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.



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 ₂] (mol/L)
0.00	0.0
6.00 × 10 ²	2.1 × 10 ⁻³
1.20 × 10 ³	3.6 × 10 ⁻³
1.80 × 10 ³	4.8 × 10 ⁻³
2.40 × 10 ³	5.6 × 10 ⁻³
3.00 × 10 ³	6.4 × 10 ⁻³
3.60 × 10 ³	6.7 × 10 ⁻³
4.20 × 10 ³	7.1 × 10 ⁻³
4.80 × 10 ³	7.5 × 10 ⁻³
5.40 × 10 ³	7.7 × 10 ⁻³
6.00 × 10 ³	7.8 × 10 ⁻³

Procedure

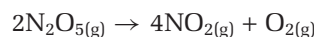
- Using graph paper or spreadsheet software, plot and label a graph that shows the rate of formation of oxygen gas. The concentration of O₂ (in mol/L) is the dependent variable and time (in s) is the independent variable.
- Draw a secant to the curve in the interval from $t = 0$ s to $t = 4800$ s.
- Draw a tangent to the curve at $t = 1200$ s and at $t = 4800$ 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 $t = 1200$ s and at $t = 4800$ 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 O₂ that is produced, 4 mol of NO₂ are also produced. This means that the rate of production of NO₂ is four times greater than the rate of production of O₂. Therefore, the rate of production of O₂ is one quarter the rate of production of NO₂. You can express the relationship between O₂ production and NO₂ production as follows.

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

When 1 mol of O₂ is produced, 2 mol of N₂O₅ are consumed. Therefore, the rate of production of O₂ is half the rate of disappearance of N₂O₅. 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 N_2O_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, N_2O_5 , decomposes to form nitrogen dioxide and oxygen.



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 N_2O_5 and rate of formation of O_2 ?

What Is Required?

Since N_2O_5 is a reactant, you need to calculate its rate of disappearance. O_2 is a product, so you need to find its rate of formation.

What Is Given?

You know the rate of formation of 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 NO_2 are produced for every 2 mol of N_2O_5 that decompose, the rate of disappearance of N_2O_5 is $\frac{2}{4}$, or $\frac{1}{2}$, the rate of formation of NO_2 . Similarly, 1 mol of O_2 is formed for every 4 mol of NO_2 . Therefore, the rate of production of O_2 is $\frac{1}{4}$ the rate of NO_2 production.

Act on Your Strategy

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

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

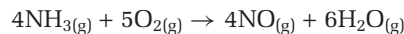
Check Your Solution

From the coefficients in the balanced chemical equation, you can see that the rate of decomposition of N_2O_5 is $\frac{2}{4}$, or $\frac{1}{2}$, the rate of formation of NO_2 . The rate of production of O_2 is $\frac{1}{4}$ the rate of decomposition of N_2O_5 .

Practice Problems

1. Cyclopropane, C_3H_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 mol/s , at what rate is propene being produced?

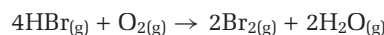
2. Ammonia, NH_3 , reacts with oxygen to produce nitric oxide, NO , and water vapour.



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

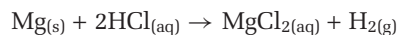
What is the corresponding rate of production of water?

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



How does the rate of decomposition of HBr (in $\text{mol/(L} \cdot \text{s)}$) compare with the rate of formation of Br_2 (also in $\text{mol/(L} \cdot \text{s)}$)? 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 s , the mass of $Mg_{(s)}$ changes by -0.011 g .

(a) What is the corresponding rate of consumption of $HCl_{(aq)}$ (in mol/s)?

(b) Calculate the corresponding rate of production of $H_{2(g)}$ (in L/s) at 20°C and 101 kPa .

PROBLEM TIP

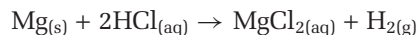
Recall, from your previous chemistry course, that 1.00 mol of any gas occupies a volume of 24.0 L at 20°C and 101 kPa .

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 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 H_3O^+ or 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, H_3O^+ , and chloride, Cl^- . The MgCl_2 that is produced exists as three separate ions in solution: one Mg^{2+} ion and two 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 N_2O_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.)



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

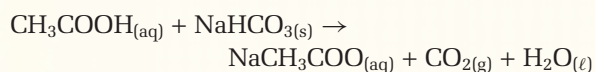
When a reaction generates gas, chemists can monitor the volume of gas produced. In Investigation 6-A, you will determine average reaction rates by recording the time taken to produce a fixed volume of gas. You will perform several trials of the same reaction to investigate the effects that temperature,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

PROBEWARE

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

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 CO_2 .

In this investigation, you will determine reaction rates by recording the time taken to produce a fixed volume of CO_2 . You will collect the 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, NaHCO_3

2.0 g powdered CaCO_3
 2.0 g solid 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

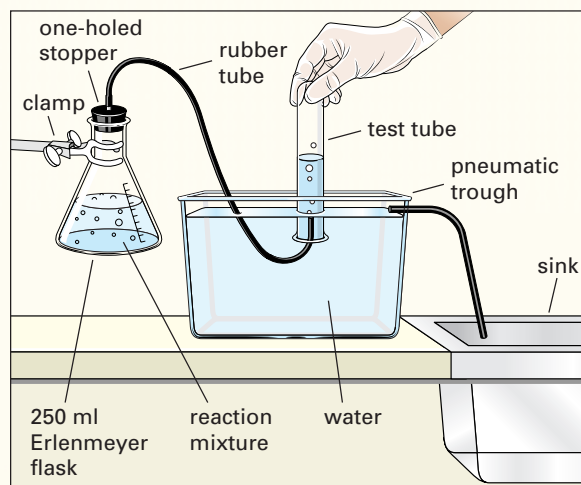


- Beware of shock hazard if an electric kettle or hot plate is used.
- Wear safety glasses at all times.

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 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.

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

Trial	Mass of NaHCO ₃ (g)	Volume of vinegar (mL)	Volume of distilled water (mL)	Time to fill test tube with CO ₂ (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		

- 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 NaHCO₃ to the flask, and put in the stopper. Record the time taken to fill the tube completely with CO₂.
- Complete trials 2 to 4 with the indicated quantities.
- Determine the volume of CO₂ 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

- 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 CO₂. Determine the average rate of production of CO₂ (in mL/s).
- 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 CO₂. Determine the average rate of production of CO₂ (in mL/s).

Part 3 The Effect of Reactants and Surface Area

- Repeat trial 3 in Part 1, using 1.00 g of powdered calcium carbonate, CaCO₃, instead of NaHCO₃. All the reactants should be at room temperature. Record the time taken to fill the tube with CO₂. Determine the average rate of production of CO₂ (in mL/s).
- Repeat step 1, using 1.00 g of solid CaCO₃ (marble chips) instead of powdered CaCO₃.

Analysis

- Draw a graph to show your results for Part 1. Plot average reaction rate (in mL CO₂/s) on the y-axis. Plot [CH₃COOH] (in mol/L) on the x-axis. Vinegar is 5.0% (m/v) CH₃COOH.
- As quantitatively as possible, state a relationship between [CH₃COOH] and the average rate of the reaction.
- Compare the average reaction rate for corresponding concentrations of vinegar at the three different temperatures tested.
- What effect did a 10°C temperature change have on the reaction rate? Be as quantitative as possible.
- What effect did using CaCO₃ instead of NaHCO₃ have on the reaction rate?
- What effect did the surface area of the CaCO₃ have on the reaction rate?

Conclusion

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

Application

- 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?

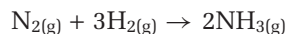
Factors That Affect Reaction Rate

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, NH_3 , from nitrogen and hydrogen.



This reaction must be carried out with high concentrations of reactants, at a temperature of 400°C to 500°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 $[\text{NO}_2] = 0.0 \text{ mol}/\text{L}$.
- (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: 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, MnO_4^- , is purple. All the other species in the reaction are colourless.
- (e) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$