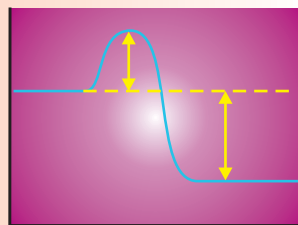


# UNIT 4



## Chemical Kinetics

### Unit Outcomes

*At the end of this unit, you should be able to:*

- *explain what is meant by reaction rate and perform activities that determine it;*
- *demonstrate an understanding of the dependence of reaction rate on the nature of reactants, the surface area of solid reactants, the concentration of the reactants, temperature of a system and the presence and nature of catalysts;*
- *determine reaction rates, using experimental data and calculations;*
- *describe how reaction rate theories (collision theory and transition-state theory) explain changes in reaction rates;*
- *determine the rate laws and order of reactions from data on initial concentrations and reaction rates;*
- *understand that most reactions occur as a series of elementary steps in reaction mechanisms;*
- *appreciate the importance of chemical kinetics in industry and in living organisms; and*
- *demonstrate scientific enquiry skills, including observing, predicting, comparing and contrasting, communicating, asking questions, drawing conclusions, applying concepts, relating cause and effect, making generalizations and problem solving.*

**MAIN CONTENTS**

- 4.1 Rate of Reaction
  - Determination of rate of reaction
  - Factors that influence reaction rates
- 4.2 Theories of Reaction Rates
  - Collision theory
  - Transition state theory
- 4.3 Rate Equation or Rate law
  - Order of reaction and rate constant
  - Concentration– Time equation (Integrated Rate law)
  - The Half–life of a reaction
- 4.4 Reaction Mechanism
  - Molecularity of an Elementary Reaction
  - Rate determining step

**Start-up Activity**

Form a group and determine the approximate time taken for completion of following chemical changes:

- a Burning of a piece of paper.
- b Conversion of milk to curd.
- c Ripening of grapes.
- d Charring of sugar.
- e Formation of fossil fuels.

Discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

1. Why do some chemical reactions proceed quickly, whereas others require days, months or even years to give products?
2. Is the rate of reaction (speed) fixed for a particular type of reaction?
3. How will the rate of reaction get altered when subjected to small changes in temperature, concentration etc.?
4. How can we measure the rate of reaction?

5. Is the rate of reaction defined for both:
  - i) reversible and irreversible reactions, and
  - ii) slow and fast reactions.
6. How does a study of the rate of a chemical reaction inform us about the way in which reactants combine to form products?

## INTRODUCTION

In Grade 9 chemistry, you learned that not all chemical reactions proceed at equal speed. For example, rusting of iron could start while ripening of fruits may be completed in a few days. On the other hand, weathering of stone may take more than a decade and the breakdown of plastics in the environment takes more than hundred years. However, other reactions, like the combustion of gasoline or the explosion of gunpowder occur in a few seconds. Can you add more examples from your daily life?

Now, let us define Chemical kinetics. Chemical kinetics is the area of chemistry concerned with the speeds, or rates, at which reactions occur. The word “**kinetic**” suggests movement or change. Chemical kinetics refers to the **rate of reaction**, which is the change over times in the concentration of a reactant or a product.

In this unit, you will study the fundamental concepts of chemical kinetics. You will explore rate of reaction, factors affecting rate of reaction, theories of rate of reaction, rate equations or rate laws, and reaction mechanisms.

### Historical Note



**Peter Waage (right) and  
Cato Guldberg (left)**

**Peter Waage** (1833–1900) and **Cato Guldberg** (1836–1902) were Norwegian chemists. They pioneered the development of chemical kinetics in 1864 by formulating the law of mass action.

## 4.1 RATE OF REACTION

*At the end of this section, you should be able to:*

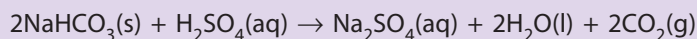
- define chemical kinetics;
- define reaction rate;
- express reaction rate in terms of the disappearance of the reactants and the appearance of the products;
- perform an activity to measure rate of reaction;
- calculate a reaction rate from given data;
- list the factors that affect reaction rate;
- explain how the nature of reactants, the surface area of solid reactants, temperature and concentration or pressure affect rate of reaction, by giving examples;
- explain activation energy;
- define catalyst, positive catalyst and negative catalyst;
- distinguish between homogeneous and heterogeneous catalysis;
- distinguish between biological and non-biological catalysts;
- draw an energy diagram that represents activation energy and shows the effect of catalysts;
- distinguish between homogeneous and heterogeneous reactions; and
- perform an activity to show the effect of the nature of reactants, surface area, concentration, temperature and catalyst on reaction rate.

### Activity 4.1



Form a group and discuss the following:

For the given reaction,



1. What happens to the concentration of a reactant as the time of reaction increases?
2. What about the concentration of a product over the time?
3. In your notebook, sketch a graph of changes in reactant and product concentration over time. In order to do this write time as the x-axis and concentration as the y-axis?
4. What do you learn from the graph?

Share your ideas with the rest of the class.

From your background knowledge of chemistry, do you remember the definition of a chemical reaction? What is the difference between reversible and irreversible chemical reactions? Consider a flask containing hydrogen, iodine, and hydrogen iodide. The hydrogen iodide, **HI** is decomposing more rapidly than the  $\text{H}_2$  and  $\text{I}_2$  can combine to produce it. The chemical equation representing the formation of HI from this reaction of hydrogen and iodine is represented as:



The rate of appearance of HI in the above reaction is defined as the rate of reaction from left to right.

For the disappearance of HI,



the rate of disappearance of **HI** is then defined as the rate of reaction from right to left.

### *How do you think that the rate of reaction is measured?*

Rate of reaction is the change in concentration of a reactant or a product over a given period of time. During the course of a reaction, the concentrations of the reactants decrease while those of the products increase. Thus, the rate of a reaction is calculated by dividing the change in the concentrations of reactants or products by the time taken for the change to occur.

For a simple reaction,



the rate of reaction is expressed in terms of a reactant concentration as

$$r = - \frac{\Delta[\text{A}]}{\Delta t} = - \frac{[\text{A}]_f - [\text{A}]_i}{\Delta t} \quad \dots(4.1)$$

where  $r$  is rate of reaction, **A** is a reactant, **B** is a product,  $[\text{A}]_i$  and  $[\text{A}]_f$  are initial and final concentration of **A** respectively,  $\Delta[\text{A}]$  is change in concentration of **A** and  $\Delta t$  is the change in time. Note that concentration is usually expressed in mole per litre.

From [equation 4.1](#), can you determine the unit for expressing rate of reaction?

The rate of a reaction can be expressed in units of  $\text{mol L}^{-1} \text{s}^{-1}$ . The final concentration of the reactant,  $[\text{A}]_f$ , is smaller than the initial concentration of the reactant,  $[\text{A}]_i$ . Thus, the difference,  $\Delta[\text{A}] = [\text{A}]_f - [\text{A}]_i$ , is negative. This indicates that the reactant is being consumed. However, the rate of a reaction is a positive quantity. Thus, a negative sign

is introduced in the rate expression to make the rate positive.

*Can you write a rate of reaction in terms of concentration of a product?*

In terms of product concentration, the rate of a reaction is given by:

$$r = \frac{\Delta[B]}{\Delta t} = \frac{[B]_f - [B]_i}{\Delta t} \quad \dots(4.2)$$

where  $[B]$  is the molar concentration of a product in moles per litre,  $\text{mol L}^{-1}$ . For a given product, the final concentration of  $B$ ,  $[B]_f$ , is greater than the initial concentration of  $B$ ,  $[B]_i$ . Thus, the difference,  $\Delta B = [B]_f - [B]_i$  is positive, and the rate of a reaction is also positive. Therefore, there is no need to introduce a negative sign to the rate expression when rate of a reaction is calculated by using product concentration. This change can be shown using a graph.

### *Reaction Rate and Stoichiometry*

You have seen that, for stoichiometrically simple reactions of the type  $A \longrightarrow B$ , the rate of reaction can be expressed either in terms of the decrease in reactant concentration over time,  $-[A] / \Delta t$ , or in terms of the increase in product concentration with time,  $\Delta[B] / \Delta t$ . For more complex reactions, you must be careful in writing the rate expressions. Consider, for example, the reaction



For two moles of  $A$  that disappear one mole of  $B$  is formed. That is, the rate of disappearance of  $A$  is twice as the rate of appearance of  $B$ . The reaction rate may be written as:

$$r = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{or} \quad r = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction



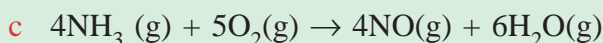
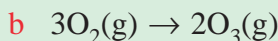
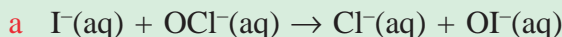
The rate of reaction is given by:

$$r = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} \quad \dots(4.3)$$

where  $r$  is the rate of reaction, **A** and **B** are reactants, **C** and **D** are products, and **a**, **b**, **c**, **d** are stoichiometric coefficients.

### Example 4.1

1. Write the rate expressions for the following reactions, in terms of the disappearance of the reactants and the appearance of the products:



**Solution:**

- a Since all of the stoichiometric coefficients are equal,

$$r = -\frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{OCl}^-]}{\Delta t} = \frac{\Delta[\text{Cl}^-]}{\Delta t} = \frac{\Delta[\text{OI}^-]}{\Delta t}$$

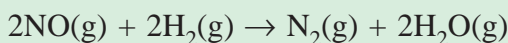
- b Here, the coefficients are 3 and 2, so,

$$r = -\frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t}$$

- c In this reaction

$$r = -\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

2. In the reaction of nitric oxide with hydrogen,



If the rate of disappearance of NO is  $5.0 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$ ,

What is the rate of reaction for the formation of  $\text{N}_2$ ?

**Solution:**

The rate of reaction for the formation of  $\text{N}_2$

$$r = \frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{2} (5.0 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1})$$

$$r = 2.5 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

## Exercise 4.1

1. Define the rate of reaction.
2. For the reaction:



express rate of reaction in terms of the concentration of:

- a)  $\text{H}_2$
  - b)  $\text{HI}$
3. For the reaction:



- a) express the rate of reaction in terms of the concentration of  $\text{NOCl}$ .
  - b) relate the rate of reaction of  $\text{NOCl}$  with the rate of reaction of  $\text{NO}$  and  $\text{Cl}_2$ .
4. The reaction for the formation of ammonia is given as:



Write the rate reaction for:

- a) the formation of  $\text{NH}_3$ .
- b) the disappearance of  $\text{N}_2$  and  $\text{H}_2$ .

### 4.1.1 Determination of Rate of Reaction

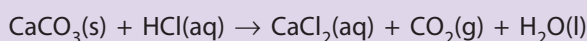
You studied in the previous grade that there are different ways in which reactions are monitored. These include change of colour, volume of gas evolved, amount of precipitate formed and loss or gain of mass. In addition, you learned how to draw a graph showing how the rate of a chemical reaction changes over time and how the rate relates to the slope.

#### Activity 4.2



Form a group and discuss the following:

The results obtained during the reaction between excess of powdered calcium carbonate and hydrochloric acid, are given in the following table:





<b>Volume of CO<sub>2</sub>/cm<sup>3</sup></b>	0	20	35	47	56	64	69	73	77	80
<b>Time/s</b>	0	10	20	30	40	50	60	70	80	100

a Plot these data on graph paper.

b At what time is the reaction most rapid?

c What is the rate of reaction after 50 seconds?

d What volume of gas has formed after 15 seconds?

e How long did it take for 40 cm<sup>3</sup> of carbon dioxide to form?

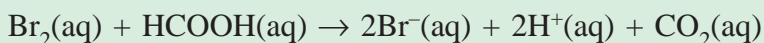
f Why does the rate of reaction gradually slow down?

Share your ideas with the rest of the class.

The rate of reaction can be determined both quantitatively and qualitatively. Qualitatively, an idea about the rate of reaction can be obtained by observing either the speed of disappearance of the reactants or the speed of appearance (formation) of the products.

### Example 4.2

In aqueous solutions, molecular bromine reacts with formic acid (HCOOH) as follows:



Molecular bromine is reddish-brown in colour. All the other species in the reaction are colourless. As the reaction progresses, the concentration of Br<sub>2</sub> steadily decreases and the colour fades. Measuring the change (decrease) in bromine concentration over time (measuring at some initial time and then again at some final time) allows us to determine the average rate of the reaction during that interval.

$$r = -\frac{\Delta[\text{Br}_2]}{\Delta t} = -\frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

where  $r$  is the average rate. Use the data provided in Table 4.1.

**Table 4.1 Rates of reaction between molecular bromine and formic acid at 25 °C**

Time (s)	[Br <sub>2</sub> ] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s)}$
0.0	0.0120	$4.20 \times 10^{-5}$	$3.50 \times 10^{-3}$
50.0	0.0101	$3.52 \times 10^{-5}$	$3.49 \times 10^{-3}$
100.0	0.00846	$2.96 \times 10^{-5}$	$3.50 \times 10^{-3}$
150.0	0.00710	$2.49 \times 10^{-5}$	$3.51 \times 10^{-3}$
200.0	0.0596	$2.09 \times 10^{-5}$	$3.51 \times 10^{-3}$
250.0	0.0500	$1.75 \times 10^{-5}$	$3.50 \times 10^{-3}$
300.0	0.0420	$1.48 \times 10^{-5}$	$3.52 \times 10^{-3}$
350.0	0.0353	$1.23 \times 10^{-5}$	$3.48 \times 10^{-3}$
400.0	0.0296	$1.04 \times 10^{-5}$	$3.51 \times 10^{-3}$

Now, you can calculate the average rate at the end of the first 50-second (s) time interval, as follows:

$$r = - \frac{(0.0101 - 0.0120)\text{M}}{50.0 \text{ s}} = 3.80 \times 10^{-5} \text{ M/s}$$

If the first 100 s is chosen as the time interval, the average rate will be given by:

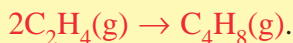
$$r = - \frac{(0.00846 - 0.0120)\text{M}}{100.0\text{s}} = 3.54 \times 10^{-5} \text{ M/s}$$

The above calculations demonstrate that the average rate of reaction depends on the time interval we choose. Thus, in general, the rate of reaction at the beginning is fast and it decreases as the reaction proceeds.

*What could be the possible reason for this decrease in the rate of reaction?*

### Exercise 4.2

Consider the reaction:



From the experimental data given in table, plot a graph for the consumption of ethylene, C<sub>2</sub>H<sub>4</sub>, versus time.

- Calculate the rate of reaction between the time interval 10 s to 30 s.
- Calculate the rate of reaction at 45 s.

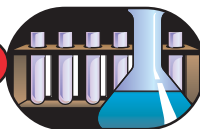
time s	0	10	20	40	60	100
$[\text{C}_2\text{H}_4]$ mol L <sup>-1</sup>	0.884	0.621	0.479	0.328	0.250	0.169

Instantaneous rate of reaction is defined as the rate of a reaction for a given instant of time and it is calculated by drawing a tangent to the graph at that instant of time.

Earlier, we measured the rates of reaction that occurred in a few seconds. We can also measure the rates of very fast reactions occurring in micro ( $10^{-6}$ ) or nano ( $10^{-9}$ ) seconds. For example, the rate of electron transfer in photosynthesis can be measured.

The following experiment demonstrates the rate of reaction between marble chips ( $\text{CaCO}_3$ ) and dilute hydrochloric acid,  $\text{HCl}$ .

## Experiment 4.1



### *Measuring Rate of Reaction*

**Objective:** To measure the rate of reaction between marble chips ( $\text{CaCO}_3$ ) and dilute  $\text{HCl}$ .

**Apparatus:** Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

**Chemicals:** 2 M dilute  $\text{HCl}$  solution, and marble chips/ $\text{CaCO}_3$ .

#### *Procedure:*

1. Set up the apparatus as shown in **Figure 4.1**, but without the marble chips at first.
2. Add 20 g of pure marble chips, in a clean 100 mL conical flask.
3. Add 40 mL of 2 M dilute hydrochloric acid to the conical flask.
4. Plug the cotton wool in position immediately.
5. Read the mass of the flask and its contents and start the stopwatch.
6. Record the mass at one minute intervals for 10 minutes.



**Figure 4.1** Laboratory set up for the measurement of rate of reaction.

**Observations and analysis:**

1. Use the following table to record your observations.

<b>Time (minutes)</b>	0	1	2	3	4	5	6	7	8	9	10
<b>Mass (g)</b>											
<b>Decrease in mass (g)</b>											

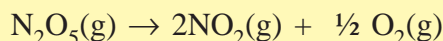
Plot a graph with time (minutes) on the horizontal axis and rate on the vertical axis. Draw a smooth curve through as many points as possible. Note that in this experiment change in mass is proportional to change in concentration.

2. What happens to the mass during the reaction? Explain this with the help of balanced equation.
3. What information can be obtained from the slope of this graph at any point?
4. Why is the graph:

- a steep at the start of the reaction?
- b less steep in the middle of the reaction?
- c horizontal at the end of the reaction?
5. Calculate:
- a The average rate of the reaction.
- b The rate of reaction at 2 minutes.
6. Describe how the rate of reaction changes with time.
7. Can we measure the rate of this reaction by measuring the amount /volume of  $\text{CO}_2$  evolved?
8. Draw a graph of the expected result by plotting volume of  $\text{CO}_2$  evolved vs time.

### Exercise 4.3

For the reaction,



The rates of reaction of  $\text{N}_2\text{O}_5(\text{g})$ , and  $\text{NO}_2(\text{g})$  as a function of time at  $45^\circ\text{C}$  is given in the table below

Time (min)	$\text{N}_2\text{O}_5$ (M)	$\text{NO}_2$ (M)
0	$1.24 \times 10^{-2}$	0
10	$0.92 \times 10^{-2}$	$0.64 \times 10^{-2}$
20	$0.68 \times 10^{-2}$	$1.12 \times 10^{-2}$
30	$0.50 \times 10^{-2}$	$1.48 \times 10^{-2}$
40	$0.37 \times 10^{-2}$	$1.74 \times 10^{-2}$
50	$0.28 \times 10^{-2}$	$1.92 \times 10^{-2}$

Use the data given in the table and calculate the rate of:

- a formation of  $\text{NO}_2$  over the first 10 minutes.
- b decomposition of  $\text{N}_2\text{O}_5$  during the time interval  $t = 30$  min to  $t = 50$  minutes.

## 4.1.2 Factors Influencing the Reaction Rates

### Activity 4.3



Form a group and try to dissolve 2 teaspoons of sugar crystals in cold water, in warm water and in hot water simultaneously. Repeat the same steps using sugar powder. You may also try the same activity with oil, instead of water. Now, discuss each of the following questions and share your findings with the rest of the class.

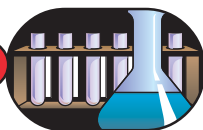
1. Why do you think sugar crystals dissolve more easily in hot water than in cold water?
2. Explain why powdered sugar dissolved easily as compared to equivalent amounts of sugar crystals?

In general, different chemical reactions have different rates. Even a chemical reaction involving the same reactants may have different rates under different conditions. Change in temperature, concentration, nature of reactant, surface area and availability of a catalyst, result in changes in rate of reaction.

Consider the **Experiment 4.2** to study the effect of the nature of reactants on rate of reaction.

### i) Nature of Reactants

### Experiment 4.2



#### *Effect of Nature of Reactants on Rate of Reaction*

**Objective:** To study the effect of nature of reactant for the reaction of copper and magnesium metals with hydrochloric acid.

**Apparatus:** Balance, test tubes, test tube stand.

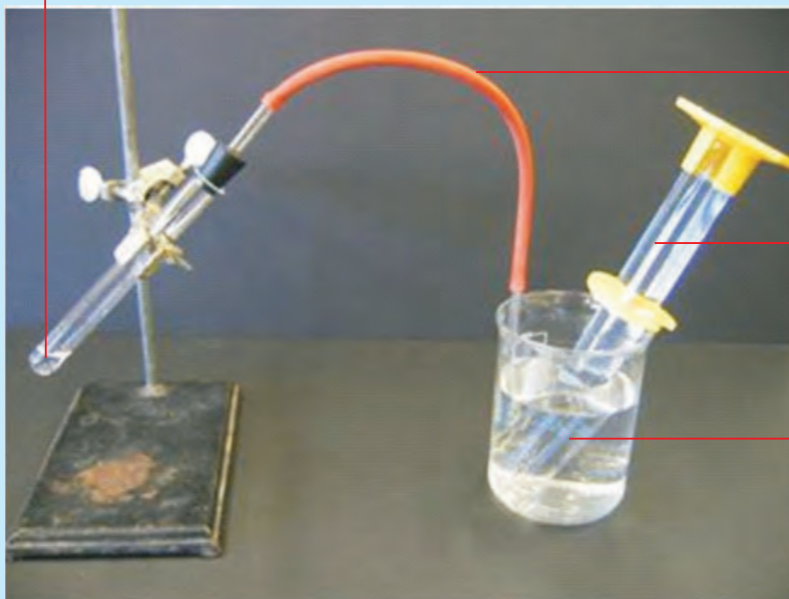
**Chemicals:** Copper (Cu), magnesium (Mg), 2 M hydrochloric acid (HCl).

**Procedure:**

1. Measure equal masses of copper and magnesium metals using a balance.
2. Record the weighed mass of these metals and add each to separate test tubes.
3. Assemble the test tubes as shown in **Figure 4.2**.
4. Add equal volume of 5 mL of 1 M HCl to both the test tubes. Be sure to wear your safety goggles and gloves.

5. Observe relative rates of reaction in both test tubes and record your observations.

Test tube  
containing  
Mg and HCl



Gas  
delivery  
tube

Graduated  
cylinder  
filled with tap  
water and  
turned upside  
down

Beaker  
containing  
water

**Figure 4.2 Reaction of magnesium with HCl.**

**Observations and analysis:**

1. Which of these two metals, copper or magnesium, reacts faster? Why?
2. Write the balanced chemical equation for the reaction of copper and magnesium with HCl.
3. What do you learn from this experiment?
4. Perform a similar activity using different metals such as aluminium, and zinc. In which case do you expect the reaction to be faster and why?

The rate of a reaction depends on the chemical nature of the substances participating in the reaction. The combination of two oppositely charged ions usually occurs very rapidly. For example, the reaction of an acid with a base is,



The acid-base reaction of **HCl** and **NaOH** is much faster than the decomposition of hydrogen peroxide, which involves the reorganization of molecules.



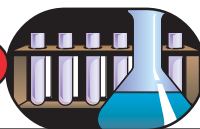
Even similar reactions may have different rates under the same conditions. For example, consider the reaction of **calcium** with water compared with the reaction of **iron** with water. The reaction of **calcium** with cold water is moderate, while that of iron is very slow in fact iron reacts with steam to form iron oxide.



Consider the **Experiment 4.3** to study the effect of surface area on rate of reaction.

## ii) Surface Area of Reactants

### Experiment 4.3



#### *Effect of surface Area on Reaction Rate*

**Objective:** To study the effect of surface area of reactants on the rate of reaction using cube chalk and powdered chalk with dilute hydrochloric acid.

**Apparatus:** Direct reading balance, 100 mL conical flask, stopwatch, cotton wool.

**Chemicals:** Cube chalk, powdered chalk and 2M dilute HCl solution

**Procedure:** Repeat **Experiment 4.1** but use 20 g of small cubical chalk and then powdered chalk in place of marble chips.

**Observations:** In which case is the evolution of gas is faster?

#### *Observations and analysis:*

1. Compare the rate curve, average rate and reaction rate at 2 minutes with that of **Experiment 4.1**. Explain your observations.
2. Sketch a graph for the consumption of each size of chalk (cube chalk and powdered chalk) against time on the same graph sheet.
3. State the conclusion of the experiment.

Which form of Zinc metal is easier to dissolve in dilute **HCl**, large pieces of **Zn** or powdered **Zn**? Why?



A reaction between substances that are in different physical phases (solid, liquid, gas) is called a *heterogeneous reaction*. In this case, bringing the reacting molecules or ions together may be difficult. For example, the reaction between steam and red hot iron, proceeds very slowly if the iron is in one large block, but it goes rapidly if the metal is powdered and spread out so as to expose a large surface to the steam.



In general, the area of contact between the phases determines the rate of reaction in heterogeneous reaction. When the size of particles is minimized, contact between the atoms, ions, or molecules in the solid state maximizes with those in a different phase.

A reaction of substances when both are in the gaseous or liquid phase, is referred to as a **homogeneous reaction**. The question of contact between the reactive molecules in a **homogeneous reaction** is not an important one, for the molecules and ions are free to move and collisions are frequent.

Consider **Experiment 4.4** to study the effect of concentration of acid on the rate of reaction between  $\text{CaCO}_3$  and hydrochloric acid.

### Exercise 4.4

1. Write the factors affecting the rate of chemical reaction.
2. Describe the differences between homogeneous reaction and heterogeneous reaction.

### iii) Concentration of Reactants

#### Experiment 4.4



#### *Effect of Concentration on Reaction Rate*

**Objective:** To study the effect of concentrations of hydrochloric acid on rate of reaction with marble chips.

**Apparatus:** Direct reading balance, 100 mL conical flask, stopwatch, cotton wool

**Chemicals:** 1 M HCl, 2 M HCl dilute solutions and marble chips ( $\text{CaCO}_3$ ).

**Procedure:**

Repeat experiment 4.1 but use 1 M dilute HCl in place of 2 M dilute HCl.

**Observations and analysis:**

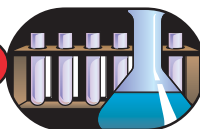
1. Compare the rate of reaction with that in **Experiment 4.1**. Which reaction is more vigorous? Explain.
2. Which of the two reactions will produce more carbon dioxide? Explain your answer.
3. What would happen to the rate curve and average rate if:
  - a 1M HCl is replaced with 4 M dilute HCl? Explain.
  - b 1M HCl is replaced with 0.5 M dilute HCl? Explain.
- 4 Sketch a graph for each of 0.5 M, 1 M, 2 M and 4 M dilute HCl against time on the same graph sheet.

***Why does wood burn more rapidly in pure oxygen than in air?***

When the concentration of one or more reactants increases, rate of reaction increases. This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction. In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction. However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

The examples of rate of reaction being affected by different factors can be seen in both biotic and abiotic components. For example, growth of cancer cells depends on the nutrient levels, temperature, pH, etc. The rate of growth of cancer cells has been measured as a function of glucose (nutrient) concentration. The cells grow as the glucose concentration decreases.

In **Experiment 4.5**, you will study the effect of temperature on the rate of reaction of  $\text{Na}_2\text{S}_2\text{O}_3$  with HCl.

iv) *Temperature of Reactants***Experiment 4.5***Effect of Temperature on Reaction Rate*

**Objective:** To study the effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid.

**Apparatus:** 100 mL beakers, test tubes, thermometers, white paper, pencil.

**Chemicals:** 0.5 M dilute HCl solution, 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution, pieces of ice.

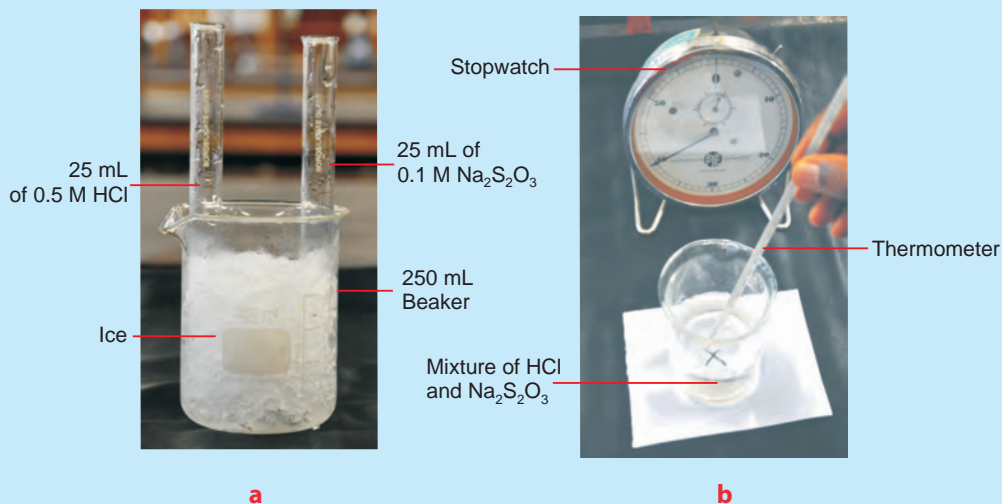
**Procedure:**

1. Take 25 mL of 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution in a test tube and 25 mL of 0.5 M HCl solution in another test tube.
2. Prepare 3 such sets and maintain them at different temperatures.  
Set (i) at  $0^\circ\text{C}$  [by keeping them in a ice bath as shown in **Figure 4.3 (a)**].  
Set (ii) at room temperature.  
Set (iii) at  $40^\circ\text{C}$  (by heating the two solutions in a water bath).
3. Put a cross sign on a white cardboard and place a clean dry 100 mL beaker above it.
4. Now, pour the contents of set (i) in the beaker and start a stopwatch immediately.
5. Carefully stir the mixture with thermometer and record the time taken for the cross to disappear [**Figure 4.3 (b)**].
6. Repeat steps 3, 4, and 5 with set 2 and set 3 respectively.
7. Tabulate your results as temperature in  $^\circ\text{C}$  versus time in minutes.

**Observations and analysis:**

1. What was the appearance of the mixture at the start of the reaction, and at the end of the reaction? Explain the changes using the equation for the reaction.
2. Plot the graph of time (minutes) on the horizontal axis against rate on the vertical axis.

3. Under which condition of temperature does the cross take:
  - a the shortest time to disappear, and
  - b the longest time to disappear.
4. Draw a conclusion about the relationship between the average reaction rate and temperature.



**Figure 4.3 Laboratory Setup for the study of the effect of temperature on reaction of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and HCl.**

Temperature usually has a major effect on the rate of reaction. Molecules at higher temperatures have more thermal energy. Generally, an increase in the temperature of a reaction mixture increases the rate of reaction of chemical reactions. This is because as the temperature of the reaction mixture raises, the average kinetic energy of the reacting particles increases. So, they collide more frequently and with greater energy.

The effect of temperature on rate of reaction can be experienced in our daily life. For example,

- a the food is kept in refrigerator to slow down the rate of decomposition of food; and
- b during heart surgery, the body of patient is cooled to slowdown the rates of biological reactions.

Temperature not only affects the rate of reaction but can even change the course of a reaction. For example,

At 200°C,



At even higher temperature,

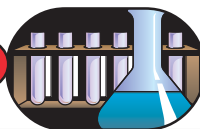


Now, you will perform Experiment 4.6 to study the effect of a catalyst on the rate of decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2$ .

### v) Presence of a Catalyst

#### Effect of Catalyst on Rate of Reaction

### Experiment 4.6



**Objective:** To investigate the effect of a catalyst on rate of reaction of decomposition reaction of hydrogen peroxide.

**Apparatus:** Conical flask, gas syringe, delivery tube.

**Chemicals:** 0.5% by volume  $\text{H}_2\text{O}_2$  solution,  $\text{MnO}_2$ .

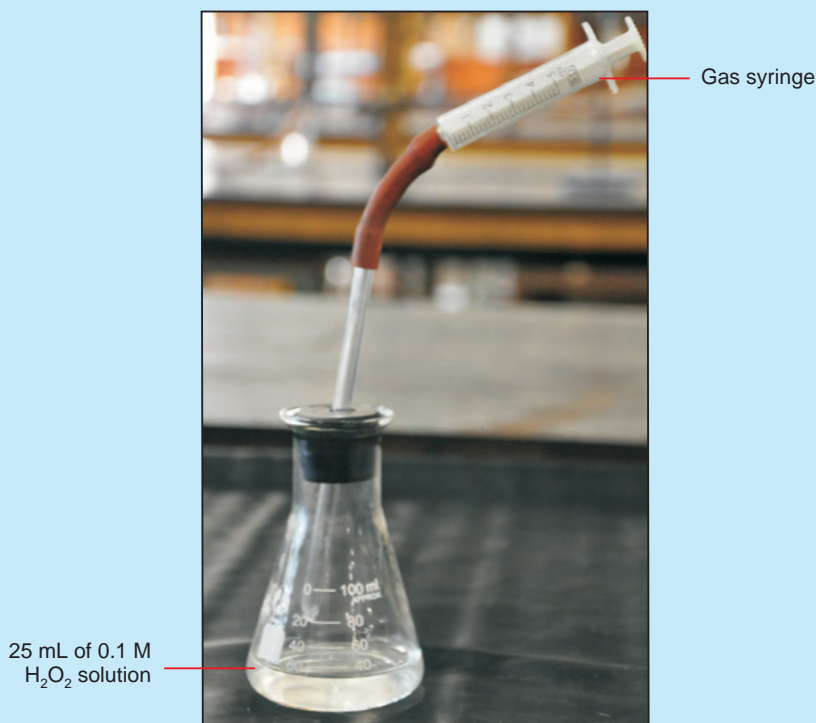
#### Procedure:

1. Set-up the apparatus as shown in **Figure 4.4**. Set the volume of the gas syringe at 0 mL. Add 25.0 mL of 0.1 M  $\text{H}_2\text{O}_2$  solution, but without manganese (IV) oxide,  $\text{MnO}_2$ , and start stopwatch immediately.
2. Record the volume of gas collected in gas syringe at minute intervals until each reaction is almost complete.
3. Repeat steps 1 and 2 with 1 g of  $\text{MnO}_2$ .

#### Observations and analysis:

1. Identify the gas and write a balanced chemical equation for the reaction.
2. Under which condition does gas syringe contains more of the gas at any one time? Give an explanation for this observation.
3. Describe the appearance of  $\text{MnO}_2$  before and after the reaction.
4. Plot graphs of rate on the vertical axis and time (minutes) on the horizontal axis for two different sets of readings. Which set of reading were used? Why?
5. Draw conclusion about the reaction rate:
  - a in the presence of a catalyst;

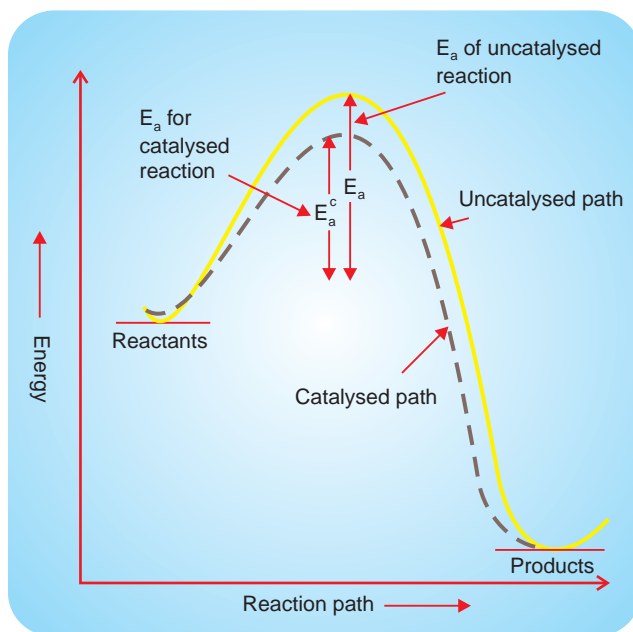
b in the absence of a catalyst.



**Fig 4.4 Investigating the effect of manganese (IV) oxide on hydrogen peroxide.**

### *How do inhibitors extend the shelf-life of a package of food?*

A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy,  $E_a$ , which is the minimum energy needed to start a chemical reaction. A catalyst may undergo physical changes and it may even form temporary chemical bonds with the reactants but it is recovered unchanged in original form at the end of the reaction. Although a catalyst speeds up the reaction, it does not alter the position of equilibrium. The effect of catalysts on the rate of chemical reaction is illustrated in **Figure 4.5**.



**Figure 4.5 Comparison of activation energies of a catalysed and an uncatalysed reaction.**

Chemical catalysts can be either positive or negative. Positive Catalyst increases the rate of reaction by lowering the Activation Energy,  $E_a$ .

**Example (1) :**  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$  ;  $\text{V}_2\text{O}_5(\text{s})$  as catalyst.

Negative Catalyst or Inhibitors decreases the rate of reaction by increasing the value of  $E_a$ .

**Example (2) :**  $\text{OCl}^-(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{OI}^-(\text{aq}) + \text{Cl}^-(\text{aq})$  ;  $\text{OH}^-(\text{aq})$  as inhibitor.

Example(1) represents **heterogeneous catalysts** as state of reactants and catalyst is different while example (2) represents **homogeneous catalyst** as both reactants and catalyst are in same state.

The role of a catalyst is highly specific to a particular reaction.

**Example :**  $\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$  ; **Ni(s)** is used as catalyst.

$\text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{HCHO}(\text{g})$ ; **Cu (s)** is used as catalyst.

A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar. Many of the most highly specific catalysts are those designed by nature. The chemical reactions in living things are controlled by biochemical catalysts called **enzymes**.

### Exercise 4.5

1. Explain what happens to the rate of reaction when temperature increases.
2. Define the term catalyst.
3. Explain the effect of surface area on the rate of reaction.
4. You are provided with a piece of zinc metal, dilute HCl (2M), zinc dust, ice-bath, test tube stand, water bath and Bunsen burner. Using the material provided, devise an activity to study the factors affecting reaction rate.

## 4.2. THEORIES OF REACTION RATES

*At the end of this section, you should be able to:*

- state collision theory;
- define activation energy;
- describe how collision theory can be used to explain changes in reaction rate;
- state the transition-state theory;
- define activated complex (transition state);
- describe how transition-state theory explains changes in reaction rate; and
- sketch and label the energy profiles of reactions that are exothermic and endothermic.

Two important theories help us to explain why different reactions occur at different rates. These are the collision theory and the transition-state theory. These two theories are distinct but in complete agreement, each emphasizing different aspects of reaction processes.

### 4.2.1. Collision Theory

Have you ever played billiards? Certain collisions result in scoring points while others are not fruitful enough as they lack in either power of impact or lack in angle placement.



## Activity 4.4



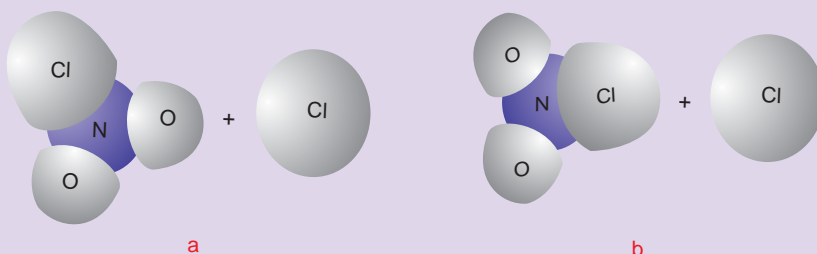
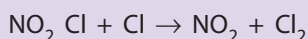
Form a group and discuss each of the following questions;

- Ethanol can easily burn in air due to the following reaction.



In actual practice, you are required to use a lighter (igniter) to start the reaction. Why?

- Consider the following reaction



Which of the above collisions might be successful to form the product?

Share your ideas with the rest of the class.

## Concentration and Collision Theory

The fundamental concept of the collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact). The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate} \propto \frac{\text{number of collisions}}{\text{second}}$$

According to collision theory, the more collisions there are, the faster the rate of reaction would be. However, not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective. Effective collisions are collisions that result in a reaction to form the desired products. Ineffective collisions are collisions that do not result in a reaction to form the desired products.

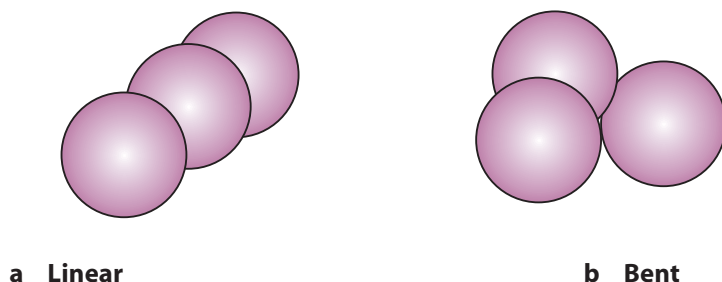
In order for a collision between reactants to be effective, the reacting species must be in proper orientation to each other at the time of collision, they must collide with sufficient energy to break or rearrange bonds. The minimum energy required for a reaction to occur during a collision of reacting species is called the activation energy,  $E_a$ .

Postulates of collision theory are summarized below.

For a reaction to occur between reactants:

1. The particles of the reacting substances must collide.
2. The particles of the reacting species must have proper orientation.
3. The particles of the reactants must collide with energy greater than or equal to the energy of activation.

According to **collision theory**, only collisions with proper orientation of reacting species possessing sufficient energy result in a reaction. The collision can either be linear or non-linear (bent).



**Figure 4.6 Orientation of molecules.**

Generally,  $E_a$  for activated complex formed in linear orientation is less than that is formed in bent orientation. Hence, orientation (a) is favoured over orientation (b).

**Concentration** is one of the factors that influence the rate of reaction of a chemical reaction. **Collision theory** accounts for the observed increase in the rate of any reaction when the **concentrations** of reactants are increased. Increasing the concentrations of the reacting species results in higher number of collisions per unit time, and the reaction rate is correspondingly higher.

### **Temperature and Collision Theory**

According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature. As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably. This causes the particles of the reactants to collide more frequently and with greater energy. This results in an increase in reaction rate.

## 4.2.2. Transition State Theory

### Activity 4.5



Form a group and try to explore which among the following reactions absorb energy (endothermic) or release energy (exothermic):

- a Burning of candle.
- b Dissolution of ammonium chloride in water.
- c Photosynthesis.
- d Respiration.

Now discuss each of the following questions and, share your ideas with the rest of the class.

1. Prepare a table of two columns and two rows. In the first column, write exothermic reaction and in the second column, write endothermic reaction. In the second row, write one important way in which the two types of reactions differ.
2. Draw a potential energy diagram for each, (use the x-axis for the progress of the reaction (time), and the y-axis for potential energy).
3. Write two examples of endothermic and exothermic reactions.

Share your ideas with the rest of the class.

Transition-state theory was developed in 1935 simultaneously by Henry Eyring, Meredith Gwynne Evans and Michael Polanyi. It is also referred to as “**activated-complex theory**”. According to transition-state theory, the collision between two reacting species results in the formation of an activated complex or transition state. An activated complex or transition state is a short-lived, high energy state species that is temporarily formed by the collision of reactant molecules before they form products.

These species can either form products or fall apart to give the original reactants. In the activated complex, the original bonds are lengthened and weakened, and the new bonds are only partially formed. Remember that chemical reactions involve the formation and breaking of chemical bonds and are accompanied by changes in potential energy, which is related to bond energy. Let us consider the reaction:

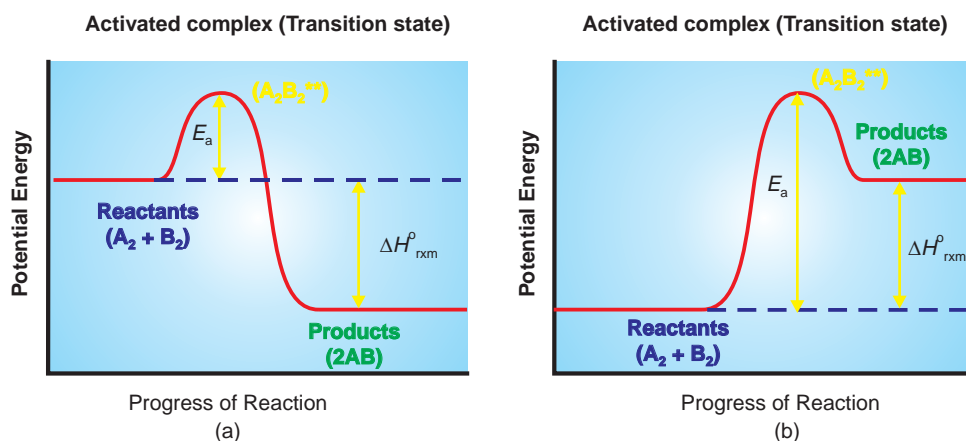


where  $A_2$  and  $B_2$  are the reactants, and  $AB$  is a the product. Refer to Figure 4.7. As the reactants,  $A_2$  and  $B_2$ , approach each other and collide, they begin climbing up the left side of the potential-energy hill, or barrier. If they have less energy than the energy of activation,  $E_a$ , they fail to climb the barrier and, instead, roll back down its left side. In this case, no reaction occurs.

If, however, they have energy that is at least equal to the energy of activation, they climb the barrier, roll down the other side, and convert to product.

In this concept, the level of activation energy required for a reaction is seen as the height of a barrier between the reactants and products. To convert from the reactant condition to the product condition, particles must climb the barrier.

The potential-energy curves in Figure 4.7 include representations of the barrier.



**Figure 4.7** Reaction energy diagrams for a) exothermic and b) endothermic reactions.

The formation of an activated complex in the form of an equation can be shown as,



where  $A_2B_2^\ddagger$  is the activated complex or transition state.

As shown in Figure 4.7, the activated complex corresponds to the peak of the energy barrier. According to transition-state theory, the rate of reaction depends on the rate at

which reactants can climb to the top of the barrier and form an activated complex. On the other hand, the activation energy,  $E_a$ , is the energy that must be absorbed by the reactants to allow them to reach the transition state or the activated complex and cross the energy barrier.

For the exothermic reaction illustrated in **Figure 4.7(a)**, the products have lower energy than the reactants and the standard reaction enthalpy is less than zero  $\Delta H_r^\circ < 0$ .

In **Figure 4.7(b)**, the thus energy of the products is higher than that of the reactants, thus for an endothermic reaction,  $\Delta H_r^\circ > 0$ .

### Exercise 4.6

1. Define activation energy?
2. Describe transition-state theory.
3. How does a catalyst affect the rate of a reaction?
4. During a course of reaction, can only one activated complex be formed for a particular type of reaction?
5. Discuss the relationship between collision and rate of chemical reaction.

## 4.3 RATE EQUATION OR RATE LAW

*At the end of this section, you should be able to:*

- define rate law, order of reaction and rate constant;
- determine reaction order;
- calculate rate constants from given experimental data;
- describe the role of the rate constant in the theoretical determination of a reaction rate;
- explain the zero order, first order and second-order reactions, using concentration-versus- time curves;
- calculate that concentration and time the reaction mixture for different order reactions and plot their graphs; define half life;
- define half-life; and
- calculate the half lives of zero-order, first-order and second-order reactions from experimental data.

### 4.3.1 Order of Reaction and Rate Constant

#### Activity 4.6



You have studied that rate of a reaction increases with increase in concentration of reactants. Form a group and discuss each of the following questions and share your ideas with the rest of the class.

1. How many folds does the rate of reaction increases if concentration of a reactant is doubled?
2. Do all the reactants affect reaction rate in equivalent amount?
3. Does the reaction rate changes in the same ratio every time?
4. Why do you think chemists want to know the order of a reaction and the rate constant for a reaction?

The rate law or rate equation for a chemical reaction is an equation which links the reaction rate with the concentrations or pressures of reactants and certain constant parameters (*normally rate coefficients and partial reaction order*). To determine the rate equation for a particular system, one combines the reaction rate with a mass balance for the system.

For a simple reaction,



Where **A** is reactant and **B** is the product. The rate law or rate equation for this reaction is written as:

$$\text{Rate} \propto [A]^x \quad \text{or} \quad \text{Rate} = k[A]^x \quad \dots(4.4)$$

where  $[A]$  expresses the concentration of A (usually in moles per liter) and  $k$  is the rate constant of the reaction, and “ $x$ ” is the order of the reaction. Note that “ $x$ ” is not stoichiometric coefficient in the balanced equation and it is determined experimentally. The order of reaction is the power to which the reactant's concentration is raised in the rate law expression.

For reactions involving more than one reactant, the order of a reaction is the sum of the powers to which all concentrations are raised in the rate law expression. For the general reaction.



we can write the rate law expression as:

$$r = k[A]^x [B]^y \quad \dots(4.5)$$

The reaction is  $x^{\text{th}}$  order in A,  $y^{\text{th}}$  order in B, and  $(x + y)^{\text{th}}$  order overall. Note that the order of a reaction is not necessarily the same as the stoichiometric coefficients in the balanced equation for the reaction. The value of the rate constant,  $k$ , depends on conditions such as temperature, concentration and surface area of the adsorbent or light irradiation.

Consider a reaction with the rate equation,

$$r = k[A]^2 [B]$$

The reaction with the rate equation given above is described as “**second-order in A**” and “**first-order in B.**” The overall reaction order is described as a third-order reaction overall, because the sum of the exponents on  $[A]$  and  $[B]$  is 3.

Some examples of the order of generalized rate equations for simple reactions are given in **Table 4.2**.

**Table 4.2 Rate equation and reaction order for simple reaction rate**

Rate equation	Overall reaction order
$k[A]^0$	zero
$k[A]$	first
$k[A]^2$	second
$k[A][B]$	second
$k[A]^3$	third
$k[A]^2[B]$	third
$k[A][B][C]$	third
$k[A]^{3/2}[B]$	5/2

### Example 4.3

The rate equation for the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in excess  $\text{O}_2$  is:



$$\text{Rate} = k[\text{SO}_2] [\text{SO}_3]^{-1/2}$$

- a What is the order of the reaction with respect to each substance in the rate equation?
- b What happens to the rate of reaction as  $[\text{SO}_3]$  increases?

**Solution:**

- a The reaction is first-order with respect to  $\text{SO}_2$ , and is negative one-half order with respect to  $\text{SO}_3$ .
- b As the concentration of  $\text{SO}_3$  increases, the rate of reaction decreases.

To find the experimental rate equation by the method of initial rates, it is necessary to gather concentration-time data in a series of separate experiments. Each experiment must have a different initial concentration of one or more reactants. The experiments must be performed at the same temperature. The initial rate for each experiment can be found from the concentration-versus-time curve.

Suppose a reaction of the type,



is under study. The data are inspected to find how the initial rate varies with the initial concentration of A,  $[\text{A}]_0$ . The objective is to find the value of the exponent in the rate equation,  $\text{rate} = k[\text{A}]^m$ , where  $m$  is the order of the reaction. For a first-order reaction,  $m = 1$ , and the rate varies directly with  $[\text{A}]_0$ . If  $[\text{A}]_0$  is doubled, the rate is doubled; if  $[\text{A}]_0$  is tripled, the rate is tripled; and so on (see Table 4.3). For a second-order reaction,  $m = 2$  and the rate is increased by a factor of  $2^2$ , or 4, if  $[\text{A}]_0$  is doubled, and so on. If the reaction is zero-order in A, changes in the concentration of A has no effect on the reaction rate. The order for each of several reactants can be found by varying one initial concentration at a time, while keeping the others constant.

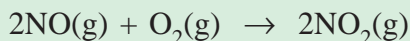
**Table 4.3 Change in initial rate with change in  $[\text{A}]_0$  for rate =  $k[\text{A}]^m$**

For a reaction of	If $[\text{A}]_0$ is doubled	If $[\text{A}]_0$ is tripled
Zero-order ( $m = 0$ )	rate is unchanged	rate is unchanged
First-order ( $m = 1$ )	rate is doubled	rate is tripled
Second-order ( $m = 2$ )	rate is quadrupled ( $\times 2^2$ )	rate is 9 times greater ( $\times 3^2$ )



### Example 4.4

The kinetics of the reaction,



was studied at 80 K by varying the initial pressures of the reactants individually and finding the initial reaction rates. The following data are typical of such a study.

Experiment	$p_{\text{init}}(\text{NO})$ (Torr)	$p_{\text{init}}(\text{O}_2)$ (Torr)	Rate of $\text{NO}_2$ formation (Torr/s)
a	1630	1630	$6.13 \times 10^{-8}$
b	3260	1630	$24.5 \times 10^{-8}$
c	1630	3260	$12.2 \times 10^{-8}$

- a What is the order of reaction with respect to each reactant?  
 b What is the value of the rate constant?

#### Solution:

- a Order of reaction with respect to each reactant can be determined as follows. Holding the  $\text{O}_2$  pressure constant, while doubling the NO pressure, quadrupled the rate, indicating that the reaction is second order in NO. With constant NO pressure, doubling the  $\text{O}_2$  pressure caused the rate to double, showing that the reaction is first-order in  $\text{O}_2$ . The rate equation for the formation of  $\text{NO}_2$  becomes

$$\text{Rate of NO}_2 \text{ formation} = k p_{\text{NO}}^2 p_{\text{O}_2}$$

- b The value of the rate constant. The experimental data can be used in the rate equation to find the value of  $k$ . For the data from experiment a, for example:

$$k = \frac{\text{Rate of NO}_2 \text{ formation}}{p_{\text{NO}}^2 p_{\text{O}_2}}$$

$$\Rightarrow k = \frac{6.13 \times 10^{-8} \text{ Torr/s}}{(1630 \text{ Torr})^2 \times 1630 \text{ Torr}} = 1.42 \times 10^{-17} \text{ Torr}^{-2} \text{ s}^{-1}$$

The best value for  $k$  is taken as an average of the  $k$  values calculated for each run: in this case, it is  $1.41 \times 10^{-17} \text{ Torr}^{-2} \text{ s}^{-1}$ .

From experimental observations, in 1889, Svante Arrhenius, observed that a mathematical relationship connects activation energy, temperature, and the rate constant. This relationship is known as the Arrhenius equation and is written as:

$$k = Ae^{-E_a/RT} \quad \dots(4.6)$$

where,  $k$  is a rate constant at temperature  $T$ ,  $A$  is a constant,  $R$  is an ideal-gas constant, and  $E_a$  = activation energy.

Equation (4.6) shows the fraction of collisions in an elementary reaction in which the particles have enough energy to react. The constant  $A$  corrects for the frequency of collisions, the necessity for the proper orientation in effective collisions, and all factors other than activation energy that are significant in effective collisions.

Taking logarithms of both sides, the equation (4.6) becomes:

$$\log k = \left( \frac{-E_a}{2.303 R} \right) \frac{1}{T} + \log A \quad \dots(4.7)$$

The above equations show that reactions with larger activation energies have smaller values of  $k$  and are, therefore, slower. The equation also shows that, for a given value of activation energy, as the temperature increases, the value of rate constant increases. This indicates that the reaction is faster, because at higher temperatures more molecules can collide effectively.

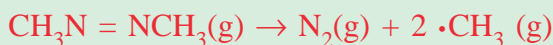
Equation (4.7) is the equation for a straight line. The value of  $E_a$  can be found from the slope of a plot of  $\log k$  versus  $1/T$ ,  $E_a = -2.303 R \times \text{slope}$ . Also, by combining the equations for the values of  $k$  at two different temperatures  $T_1$  and  $T_2$  for the same reaction, a relationship is obtained that allows for the calculation of  $E_a$ :

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots(4.8)$$

Alternatively, if  $E_a$  and three of the four values  $k_1$ ,  $k_2$ ,  $T_1$ , and  $T_2$  are known, the fourth can be found. In using the Arrhenius equation, the energy is customarily expressed in joules, temperature must be in kelvin, and  $R$  is 8.314 J/ (K mol).

### Example 4.5

The thermal decomposition of  $\text{CH}_3\text{N}=\text{NCH}_3$  in the gas phase to give nitrogen and methyl radicals



has an activation energy of  $2.14 \times 10^5 \text{ J/mol}$ , at 600 K, at the given temperature,  $k = 1.99 \times 10^8 \text{ s}^{-1}$ . Does the reaction rate double with a ten-degree rise in temperature hold for this reaction?

#### Solution:

To answer the question, we must calculate  $k$  at 610 K, using the appropriate form of the Arrhenius equation. The knowns are  $E_a$  and  $k_1$  at  $T_1 = 600 \text{ K}$ , and  $T_2 = 610 \text{ K}$ . The unknown is  $k_2$  at 610 K.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left( \frac{k_2}{1.99 \times 10^8 \text{ s}^{-1}} \right) = \left( \frac{2.14 \times 10^5 \text{ J/mol}}{2.303 \times 8.314 \text{ J/(K mol)}} \right) \left( \frac{610 \text{ K} - 600 \text{ K}}{610 \text{ K} \times 600 \text{ K}} \right)$$

Taking antilogarithms of both sides gives:

$$\frac{k_2}{1.99 \times 10^8 \text{ s}^{-1}} = 2.0$$

Therefore,  $k_2 = (2.0) (1.99 \times 10^8 \text{ s}^{-1}) = 4.0 \times 10^8 \text{ s}^{-1}$

Comparison of  $k_1$  with  $k_2$  shows that, for this reaction, the rate constant is doubled by a ten-degree rise in temperature. (This is not always the case.)

### Exercise 4.7

- Given that  $E_a$  for the hydrolysis of sucrose is  $108 \times 10^3 \text{ kJ/mol}$ , compare the rate constant of this reaction at  $37^\circ\text{C}$  ( $T_1$ ) with the rate constant of the same reaction at  $27^\circ\text{C}$  ( $T_2$ ).
- Calculate the rate constant for the above reaction at  $47^\circ\text{C}$  and compare it to the rate constant at  $37^\circ\text{C}$ .
- Plot a graph of  $\log k$  versus  $1/T$  to calculate the activation energy.

## 4.3.2 Concentration-Time Equation (Integrated Rate Law)

### Activity 4.7



Form a group and discuss each of the following questions.

1. How do you explain the concentration dependence of rate of reactions?
2. What is the mathematical expression for describing order of a reaction?
3. How do you distinguish between zero-order, first-order, and second-order reaction?

A rate law tells us how the rate of reaction depends on the concentration of the reactants at a particular moment. But, often we would like to have a mathematical relationship that shows how a reactant concentration changes over a period of time. A rate law can be transformed into a mathematical relationship between concentration and time using calculus. Therefore, an integrated law relates concentration to reaction time.

### 1. Zero Order Reaction

A zero-order reaction is a reaction whose rate of reaction does not depend on the reactant concentration. For the general reaction



the zero order rate law is written as the equation

$$r = -\frac{\Delta[A]}{\Delta t} \quad \dots(4.9)$$

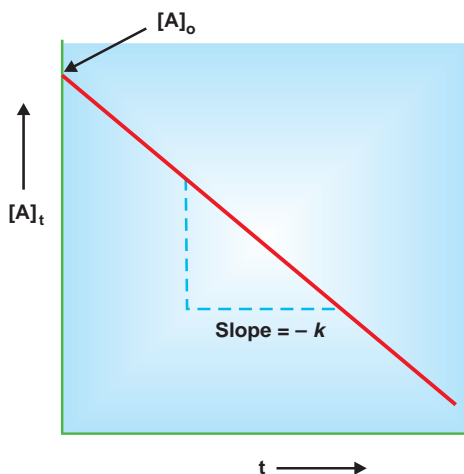
Using calculus, it can be shown from equation (4.9) that

$$[A]_t = -kt + [A]_0 \quad \dots(4.10)$$

where  $[A]$  is concentration of  $A$  at  $t = t$ ;  $[A]_0$  is the concentration of  $A$  is at  $t = 0$ . Now, zero-order reactions can be written as follows:

$$\boxed{[A]_t = -kt + [A]_0} \quad \dots \text{Integrated rate equation for } 0^{\text{th}} \text{ order reaction} \quad \dots(4.11)$$

This is a linear equation with the form of  $y = mx + b$ . For a zero-order reaction, a plot of  $[A]$  versus-time is a straight line, whose slope is  $-k$ .



**Figure 4.8** A plot of  $[A]$  versus  $t$  for a zero-order reaction.

### Example 4.6

The decomposition of HI into hydrogen and iodine on a gold surface is zero-order in HI. The rate constant for the reaction is  $0.050 \text{ M s}^{-1}$ . If you begin with a  $0.500 \text{ M}$  concentration of HI, what is the concentration of HI after 5 seconds?

**Solution:**

Use the integrated rate

$$[\text{HI}] = [\text{HI}]_0 - kt$$

The initial concentration is  $[\text{A}]_0 = 0.500 \text{ M}$ , and the reaction runs for 5 seconds.

$$[\text{HI}] = 0.500 \text{ M} - 0.050 \text{ M s}^{-1} \times 5 \text{ s} = 0.250 \text{ M}$$

## 2. First-Order Reactions

A first-order reaction is a reaction whose rate of reaction depends on the reactant concentration raised to the first power. In a first-order of the type



the rate is

$$r = \frac{\Delta[\text{A}]}{\Delta t} \quad \dots(4.12)$$

$$r = k [\text{A}] \quad \dots(4.13)$$

To obtain the units of  $k$  for this rate law, we write

$$k = \frac{r}{[\text{A}]} = \frac{\text{M/s}}{\text{M}} = 1/\text{s} \quad \text{or} \quad \text{s}^{-1}$$

Combining equations (4.12) and (4.13) for the rate, we get

$$-\frac{\Delta[A]}{\Delta t} = k[A] \quad \dots(4.14)$$

Using calculus, it can be shown from equation (4.14) that

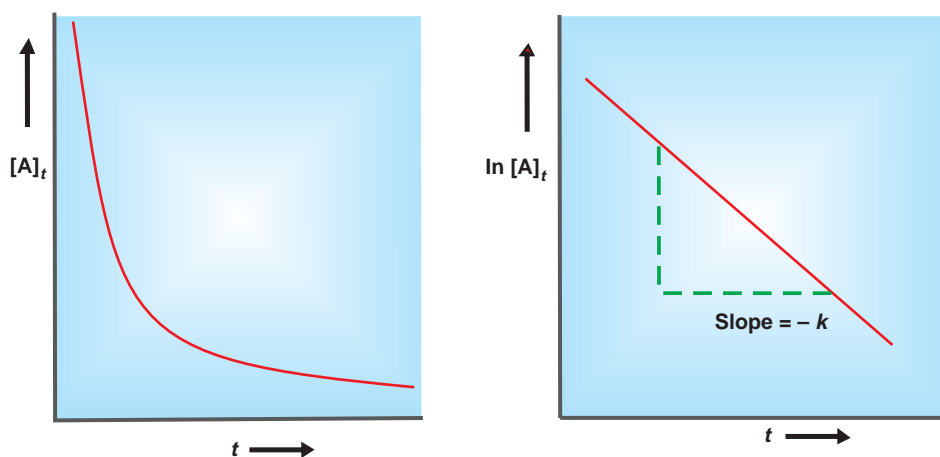
$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \dots(4.15)$$

where  $\ln$  is the natural logarithm, and  $[A]_0$  and  $[A]$  are the concentrations of A at times  $t = 0$  and  $t = t$ , respectively. It should be understood that  $t = 0$  need not correspond to the beginning of the experiment. It can be any time at which we choose to start monitoring the change in the concentration of A,

Equation (4.15) can be rearranged as follows:

$$\boxed{\ln [A]_t = -kt + \ln [A]_0} \quad \dots \text{Integrated rate equation for 1}^{\text{st}} \text{ order reaction: } \dots(4.16)$$

Equation (4.16) has the form of the linear equation  $y = mx + b$ , in which  $m$  is the slope of the line that is the graph of the equation. Thus, a plot of  $\ln [A]$  versus  $t$  gives a straight line with a slope of  $k$  (or  $m$ ). This graphical analysis allows us to calculate the rate constant  $k$ . Figure 4.9 shows the characteristics of first-order reactions.



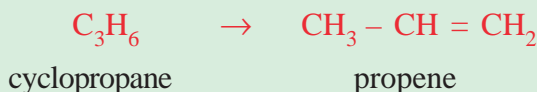
**Figure 4.9** Plot for a reaction that is first-order with respect to A, first-order overall.

**Note!** The observation that plot of  $\ln[A]$  versus time is a straight line confirms that the reaction is first-order in A and first-order overall, *i.e.*,  $\text{Rate} = k[A]$ . The slope is equal to  $-k$ .

In the following example, we apply equation (4.16) to a reaction.

### Example 4.7

The conversion of cyclopropane in the gas phase is a first-order reaction with a rate constant of  $6.7 \times 10^{-4} \text{ s}^{-1}$  at  $500^\circ\text{C}$ .



- If the initial concentration of cyclopropane is 0.25 M, what is the concentration after 8.8 minutes?
- How long does it take for the concentration of cyclopropane to decrease from 0.25 M to 0.15 M?
- How long does it take to convert 74 % of the starting material?

#### Solution :

- Applying equation (4.16),

$$\ln \frac{[A]_0}{[A]} = kt$$

Solving the equation, we obtain

$$\ln \frac{0.25 \text{ M}}{[A]} = 0.354$$

$$\frac{0.25 \text{ M}}{[A]} = e^{0.354} = 1.42$$

$$[A] = 0.18 \text{ M}$$

- Again using equation (4.16), we have

$$\ln \frac{0.25 \text{ M}}{0.15 \text{ M}} = (6.7 \times 10^{-4} \text{ s}^{-1}) t$$

$$t = 7.6 \times 10^2 \text{ s}$$

$$= 13 \text{ minutes}$$

- c In a calculation of this type, we do not need to know the actual concentration of the starting material. If 74% of the starting material has reacted, the amount left after time  $t$  is (100% – 74%), or 26%. Thus,  $[A]/[A]_0 = 26/100 = 0.26$ . From equation (13.3), we write

$$\begin{aligned} t &= \frac{1}{k} \ln \frac{[A]_0}{[A]} \\ &= \frac{1}{6.7 \times 10^{-4} \text{ s}^{-1}} \ln \frac{1.0 \text{ M}}{0.26 \text{ M}} \\ &= 2.0 \times 10^3 \text{ s} \\ &= 33 \text{ minutes} \end{aligned}$$

### 3. Second-Order Reactions

A **second order reaction** is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. The simpler type of reaction involves one kind of reactant molecule



where

$$r = -\frac{\Delta[A]}{\Delta t} \quad \dots(4.17)$$

From the rate law

$$r = k[A]^a \quad \dots(4.18)$$

As before, we can determine the units of  $k$  by writing

$$k = \frac{r}{[A]^a} = \frac{\text{M/s}}{\text{M}^2} = \text{M}^{-1} \text{ s}^{-1} \quad \dots(4.19)$$

For simplicity, we will consider a second order reaction with a rate law of the following type:



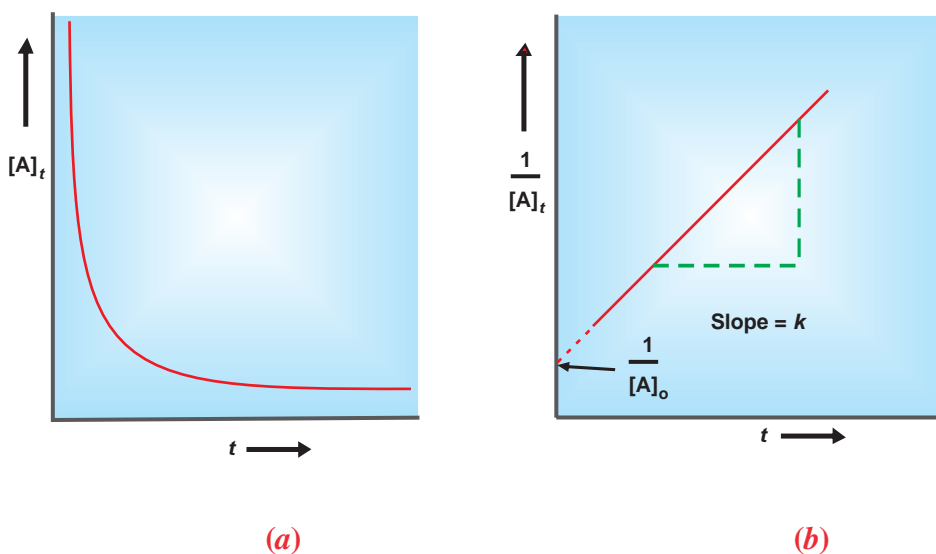


$$r = k[A]^2$$

By using calculus, we can obtain the expression

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \dots \text{Integrated rate equation for 2}^{\text{nd}} \text{ order reaction } \dots(4.20)$$

The graph of  $\frac{1}{[A]}$  versus time gives a straight line with a slope of  $k$  as shown in Figure 4.10.



**Figure 4.10** Plots for a reaction that is second-order with respect to A and overall a second-order reaction.

Another type of second-order reaction is



and the rate equation is given by

$$r = k[A][B] \dots(4.21)$$

where the reaction is first-order in A and first-order in B. Thus, this reaction has an overall reaction order of 2.

The corresponding integrated rate equation for such type of second order-reaction is too complex for our discussion and beyond the scope of this text book.

### Example 4.8

Nitrosyl chloride,  $\text{NOCl}$ , decomposes slowly to  $\text{NO}$  and  $\text{Cl}_2$  as shown in the equation below.



$$r = k[\text{NOCl}]^2$$

The rate constant,  $k$  equals  $0.020 \text{ L mol}^{-1} \text{ s}^{-1}$  at a certain temperature. If the initial concentration  $0.050 \text{ M}$ , what will the concentration be after 30 minutes?

**Solution:**

$$[\text{NOCl}] = 0.050 \text{ M} \quad k = 0.020 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$[\text{NOCl}]_t = ? \text{ M} \quad t = 30 \text{ min} = 1800 \text{ s}$$

The integrated rate equation for this reaction is given by:

$$\begin{aligned} \frac{1}{[\text{NOCl}]_t} &= kt + \frac{1}{[\text{NOCl}]_0} \\ &= (0.020 \text{ L mol}^{-1} \text{ s}^{-1})(1800 \text{ s}) + \frac{1}{0.050 \text{ mol}^{-1}} \\ &= 50 \text{ L mol}^{-1} \\ \therefore [\text{NOCl}]_t &= 0.018 \text{ L mol}^{-1} = 0.018 \text{ M} \end{aligned}$$

### 4.3.3 The Half-life of a Reaction

#### Activity 4.8



Form a group and do as directed:

1. Plot a graph that shows the time dependence of concentration of reactant for the 1<sup>st</sup> order reaction.
2. On the graph show the time when the concentration of a reactant is decreased by half of its initial amount. What do you call this situation?

Discuss the results and share your ideas with the rest of the class.

The half life of a reaction is defined as the time required for the concentration of a reactant to decrease to half of its initial concentration. This means that half-life is the time it takes for the concentration of A to fall from  $[\text{A}]_0$  to  $\frac{1}{2}[\text{A}]_0$ , i.e  $[\text{A}] = \frac{1}{2}[\text{A}]_0$ . The half-life of a reaction is designated by the symbol,  $t_{\frac{1}{2}}$ .

The mathematical expression for the half-life of a first-order reaction is determined by substituting  $t = t_{1/2}$  and  $[A] = \frac{1}{2}[A]_0$  in equation

$$\log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303}$$

This gives us

$$\ln \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{kt_{1/2}}{2.303} \quad \text{or} \quad \ln 2 = kt_{1/2} \quad \dots(4.23)$$

And solving for  $t_{1/2}$  gives,  $\frac{\ln 2}{k} = \frac{0.693}{k}$ .

From the relation, it can be noted that, for a first-order reaction, the half-life is independent of the initial concentration of A,  $[A]_0$ .

For second-order reactions, half-life depends on the initial concentration,  $[A]_0$ , and the rate constant,  $k$ . For a second-order reaction, the half-life expression is given by the equation

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \Rightarrow \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2} \quad \dots(4.24)$$

Rearranging and solving for  $t_{1/2}$ , we get the expression,

$$t_{1/2} = \frac{1}{k[A]_0} \quad \dots(4.25)$$

Summary of equations for 1<sup>st</sup> and 2<sup>nd</sup> order reactions is given in Table 4.4.

**Table 4.4 Summary of the kinetics of first-order and second order reactions**

Order	Rate equation	Concentration-time equations	Half-life
1 <sup>st</sup>	rate = $k[A]$	$\ln \frac{[A]_0}{[A]} = kt$	$\frac{0.693}{k}$
2 <sup>nd</sup>	rate = $k[A]^2$	$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$	$\frac{1}{k[A]_0}$

### Example 4.9

The decomposition of  $N_2O_5$  in  $CCl_4$  at 45 °C is first order reaction with  $k = 6.32 \times 10^{-4} \text{ s}^{-1}$ . If the initial concentration of  $N_2O_5$ , is 0.40 mol/L:

- a Calculate  $t_{1/2}$ .  
 b Find the concentration of  $\text{N}_2\text{O}_5$  remaining after  $t_{1/2}$ .

**Solution:**

$$\text{a } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.32 \times 10^{-4} \text{ s}^{-1}} = 1097 \text{ s}$$

- b The equation relating time and concentration for a first-order reaction is used with  $[\text{N}_2\text{O}_5]_0 = 0.40 \text{ mol/L}$  and  $t = 1097 \text{ s}$  to find  $[\text{N}_2\text{O}_5]$ .

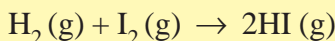
$$\begin{aligned} \ln[\text{N}_2\text{O}_5] &= -kt + \ln[\text{N}_2\text{O}_5]_0 \\ &= (-6.32 \times 10^{-4} \text{ s}^{-1})(1097 \text{ s}) + \ln(0.40) \\ &= (-0.693) + (-0.9163) = -1.6096 \end{aligned}$$

Taking the inverse of the natural logarithms of both sides gives the concentration of  $\text{N}_2\text{O}_5$  remaining after 1.0 hour,

$$[\text{N}_2\text{O}_5] = 0.1996 \text{ mol/L} \cong 0.20 \text{ mol/L.}$$

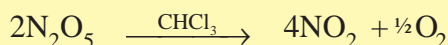
**Exercise 4.8**

- If a certain first-order reaction has a half-life of 30.0 minutes,
  - Calculate the rate constant for this reaction.
  - How much time is required for this reaction to be 35% complete?
- The rate constant for the formation of hydrogen iodide from the elements,



is  $2.7 \times 10^{-4} \text{ L}/(\text{mol}\cdot\text{s})$  at 600 K and  $3.5 \times 10^{-3} \text{ L}/(\text{mol}\cdot\text{s})$  at 650 K.

- Find the activation energy  $E_a$ .
  - Calculate the rate constant at 700 K.
- The rate constant for the decomposition of  $\text{N}_2\text{O}_5$  in chloroform,



was measured at two different temperatures,  $T_1 = 25^\circ\text{C}$ ,  $k_1 = 5.54 \times 10^{-5} \text{ s}^{-1}$  and  $T_2 = 67^\circ\text{C}$ ,  $k_2 = 9.30 \times 10^{-3} \text{ s}^{-1}$ . Find the activation energy for this reaction.

## 4.4 REACTION MECHANISM

*At the end of this section, you should be able to:*

- explain reaction mechanism;
- explain the molecularity of a reaction;
- explain what is meant by rate determining step;
- give specific examples to illustrate rate determining step;
- explain the relationship between the reaction path way and the rate law; and
- use rate equation to suggest possible reaction mechanism for a reaction.

An overall balanced chemical equation does not give any information about how a reaction actually takes place. In many cases, it merely represents the sum of several elementary steps, or elementary reactions, a series of simple reactions that represents the progress of the overall reaction at the molecular level. The term for the sequence of elementary steps that leads to product formation is **reaction mechanism**. The reaction mechanism is comparable to the simplest description you might give of the route of a trip you plan to take. The overall chemical equation specifies only the origin and destination, while the reaction mechanism describes the stopovers also.

As an example of a reaction mechanism, let us consider the reaction between nitric oxide and oxygen:



We know that the products are not formed directly from the collision of two **NO** molecules with an **O<sub>2</sub>** molecule, because **N<sub>2</sub>O<sub>2</sub>** is detected during the course of the reaction. Let us assume that the reaction actually takes place via two elementary steps as follows:



In the first elementary step, two **NO** molecules collide to form a **N<sub>2</sub>O<sub>2</sub>** molecule. This event is followed by the reaction between **N<sub>2</sub>O<sub>2</sub>** and **O<sub>2</sub>** to give two molecules of **NO<sub>2</sub>**. The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:



Species such as  $\text{N}_2\text{O}_2$  are called **intermediates** because they appear in the mechanism of the reaction (that is, the elementary steps) but not in the overall balanced equation.

### 4.4.1 Molecularity of an Elementary Reaction

#### Activity 4.9



Form a group and try to identify the number of molecular species involved in each of the following reactions:

1.  $\text{A} \rightarrow \text{products}$
2.  $\text{A} + \text{A} \rightarrow \text{products}$
3.  $\text{A} + \text{B} \rightarrow \text{products}$
4.  $\text{A} + \text{A} + \text{B} \rightarrow \text{products}$
5.  $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$ .

Share your findings with the rest of the class.

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction. It is the number of reactant molecules taking part in a single step of the reaction.

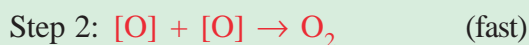
#### Example 4.10

- |   |   |                |
|---|---|----------------|
| a | $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$                       | (Unimolecular) |
| b | $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$                            | (Bimolecular)  |
| c | $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$                        | (Termolecular) |
| d | $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$               | (Bimolecular)  |
| e | $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$                          | (Termolecular) |
| f | $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{FeCl}_2$ | (Termolecular) |

In the reaction that involve sequence of steps rate is determined by the slowest step.

**Example 4.11**

Decomposition of  $\text{H}_2\text{O}_2$  takes place in the following two steps:



The slowest step is rate-determining. Thus, from **step 1**, reaction appears to be unimolecular.

It may be noted that molecularity is a theoretical concept and it cannot be zero, negative, fractional, infinite and imaginary.

**Exercise 4.9**

- Give the meanings of each of the following terms:
  - Elementary steps
  - Unimolecular reaction
  - Bimolecular reaction
  - Termolecular reaction
- Determine the molecularity of the following reactions:
  - $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
  - $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$
  - $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$

**4.4.2 Rate-Determining Step****Activity 4.10**

Form a group and discuss each of the following questions. After the discussion, share your ideas with the rest of the class.

- What do you think a rate determining step is?
- Why do chemists want to know the rate determining step?

In a multi-step reaction, all the elementary reactions do not necessarily proceed at equal rates. One of them might be very rapid, moderate or very slow. The reactants can be converted to products only as fast as they can complete the slowest step. The slowest step in the sequence of steps leading to the formation of products is called the rate-determining step. In other words, the slowest step in the mechanism determines the overall rate of the reaction.

Because the rate-determining step limits the rate of the overall reaction, its rate law represents the rate law for the overall reaction. For example, the reaction of  $\text{NO}_2$  with  $\text{F}_2$  is given by the equation:



The experimentally determined rate law is:  $\text{Rate} = k[\text{NO}_2][\text{F}_2]$ , the proposed reaction mechanism is:



Let us check whether the proposed mechanism agrees with the experimental rate law or not. First, the sum of these reaction steps must give the overall balanced equation:



Overall equation:



So, the first requirement is satisfied. The formation of  $\cdot\text{F}$  in the first step occurs more slowly than its reaction with  $\text{NO}_2$  to form  $\text{NO}_2\text{F}$  in the second step. Thus, the rate of formation of  $\text{NO}_2\text{F}$  in the second step is controlled by the rate of formation of  $\cdot\text{F}$  in the first step. The overall rate cannot be faster than that of the slowest step.

**Overall rate = the rate of the slowest step**

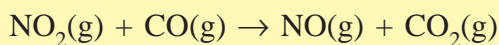
The rate law agrees with experimentally determined rate law. So, the proposed mechanism is acceptable because it satisfies both requirements.



## Exercise 4.10

Answer each of the following questions.

1. Describe the term molecularity of a reaction.
2. How do you identify the rate determining step for a reaction that involves more than one step?
3. The reaction



can be thought of as occurring in two elementary steps:

- a  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$  (slow step)
- b  $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$  (fast step)

Identify the rate determining step and determine the molecularity of this reaction.

## Unit Summary

- *Chemical kinetics is the study of the rates and mechanisms of chemical reactions.*
- *A chemical reaction occurs when atoms, molecules or ions undergo effective collisions.*
- *The larger the activation energy, the slower a chemical reaction and vice versa.*
- *In general, reaction rates increase with temperature, because higher temperature increases both the frequency of collisions and the number of molecules possessing enough energy to undergo effective collision.*
- *A chemical equation represents an elementary reaction only if the reaction in the equation represents the actual atoms, molecules or ions that must interact for the reaction to occur.*
- *Elementary reactions that are bimolecular (the most common) have two*

*reactant species, while unimolecular reactions have only one and termolecular reactions have three.*

- *Reaction rate is expressed as the change in concentration of a reactant or product, per unit time.*
- *Both reaction rates and rate equations must be determined experimentally, often by gathering data on the variation of concentration over time.*
- *Rate equations often take the form of*

$$\text{Rate} = k[A]^m[B]^n[C]^p$$

*where the sum of  $m$ ,  $n$ ,  $p$ , is the overall reaction order. The order of a specific reactant is given by  $m$ , or  $n$ , or  $p$ , and the exponents in a rate equation are often 1, 2 or 3, but may also be fractions or negative numbers.*

- *Rates of first-order and second-order reactions are dependent upon the concentrations of one or two reactants, respectively. In contrast, rates of zero-order reactions are independent of reactant concentrations.*
- *The half-life of a first order reaction is independent of the initial reactant concentration, whereas half-life of second order reaction depends on the initial reactant concentration.*
- *Reaction rates are influenced by the concentrations of reactants, temperature, catalysts and the degree of contact between reactants (surface area).*
- *Reaction rates and rate constants vary with temperature.*
- *The Arrhenius equation gives the relationships among the temperature, the rate constant and the activation energy for a given reaction, either for an elementary reaction or an overall reaction.*
- *In a heterogeneous reaction, the reactants are in different phases and the rates of such reactions are limited by the amount of the contact between reactants.*
- *Catalysts increase the rates of chemical reactions but can be recovered unchanged at the end of a reaction.*

## Check List

### Key terms of the unit

- |   |   |
|---|---|
| <ul style="list-style-type: none"> <li>• Average rate</li> <li>• Bimolecular</li> <li>• Catalyst</li> <li>• Collision theory</li> <li>• Concentration-time equation</li> <li>• Elementary reaction</li> <li>• Energy profiles of exothermic and endothermic reactions</li> <li>• Half-life of a reaction</li> <li>• Instantaneous rate</li> </ul> | <ul style="list-style-type: none"> <li>• Molecularity</li> <li>• Order of reaction</li> <li>• Rate constant</li> <li>• Rate equation or rate law</li> <li>• Rate of reaction</li> <li>• Rate-determining step</li> <li>• Reaction mechanism</li> <li>• Surface area</li> <li>• Termolecular</li> <li>• Transition-state theory</li> <li>• Unimolecular</li> </ul> |
|---|---|

## REVIEW EXERCISE

### Part I: Multiple Choices

1. The rate constant for the decomposition of gaseous  $\text{CH}_3\text{CHF}_2$



is  $7.9 \times 10^{-7} \text{ s}^{-1}$  at  $429^\circ\text{C}$  and  $1.7 \times 10^{-4} \text{ s}^{-1}$  at  $522^\circ\text{C}$ . The activation energy for this reaction is:

- |   |   |
|---|---|
| <p>a <math>340 \times 10^{-5} \text{ s}^{-1}</math></p> <p>b <math>270 \text{ kJ mol}^{-1}</math></p> | <p>c <math>135 \text{ kJ mol}^{-1}</math></p> <p>d None</p> |
|---|---|
2. Which of the following is not the concern of chemical kinetics?
- a study of "how fast?" a chemical reaction goes to completion.
  - b study of the individual steps in a chemical reaction.
  - c study of "how far?" a chemical reaction goes to completion.
  - d none of the above.

3. The short-lived combination of reacting atoms, molecules, or ions that is intermediate between reactants and products is:
- a transition state
  - b activated complex
  - c intermediate
  - d B and C
  - e A and B
4. Which of the following is false about activation energy,  $E_a$ ?
- a It is the minimum energy that reactants must have for a reaction to occur.
  - b It is the difference in energy between the transition state and the reactants.
  - c It is always negative.
  - d None of the above.
5. The correct expression for a second-order reaction is
- a rate =  $2k[A]$
  - b rate =  $k[A]^2$
  - c rate =  $k[A][B]$
  - d both b and c
6. Which of the following is true about the factors influencing rate of reaction?
- a As surface area of reactants decreases, the rate of a reaction decreases.
  - b As concentration of a reactant increases, the rate of the reaction increases except for zero-order reactions.
  - c As temperature increases, the rate of reaction decreases.
  - d A catalyst always speeds up the rate of a reaction.
7. Which of the following does not affect the rate of chemical reactions?
- a temperature
  - b concentration
  - c catalyst
  - d none
8. According to the transition state theory, reactants must \_\_\_\_\_ in order to form product(s).
- a collide
  - b go over an energy barrier
  - c have lower free energy than the products
  - d be catalyzed

9. The rate of a chemical reaction, that is independent of concentration is:
- a 2<sup>nd</sup> order
  - b 1<sup>st</sup> order
  - c 0<sup>th</sup> order
  - d None
10. Formation of an activated complex is explained by:
- a molecular kinetic theory
  - b valence-bond theory
  - c transition-state theory
  - d collision theory
11. Consider the following reaction mechanism:
- First step:  $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$  (fast)
- Second step:  $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$  (slow)
- Third step:  $\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2$  (fast)
- Which step is the rate-determining step?
- a First step
  - b Second step
  - c Third step
  - d All of these
12. Which of the following statements is correct?
- a Reactions with high activation energies are fast.
  - b Collisions between reactant particles with insufficient energies succeed in forming products.
  - c A catalyst can decrease the rate of a chemical reaction by changing the pathway of activation energy.
  - d All of the above.
13. Which of the following is false?
- a The smaller the activation energy, the slower a reaction tends to be.
  - b In general, reaction rates increase with increase in temperature.
  - c The heat of reaction is the difference between the energy of the products and the energy of the reactants.
  - d All of the above.
14. A typical pathway for a chemical reaction that includes several simple steps is:
- a elementary reactions
  - b activation energy
  - c an intermediate reaction
  - d none of the above



19. A first-order reaction,  $B \rightarrow P$ , has a half-life of 100 s, whatever the quantity of substance  $B$  involved in a particular reaction. Which of the following is true?
- a The reaction goes to completion in 200 s
  - b The quantity remaining after 200 s is half of what remains after 100 s.
  - c 100 s is required for the reaction to begin.
  - d Nothing can be said about the reaction.
20. Which of the following is true?
- a Rate depends on the manner in which molecules collide with each other.
  - b Rate is inversely proportional to frequency of collision.
  - c As a very rough approximation, we find a  $10^\circ\text{C}$  temperature increase, decreases the rate by half.
  - d None.
21. The rate at a given specific time is:
- a average rate
  - b instantaneous rate
  - c rate of a reaction
  - d formal rate
22. If we double the concentration of a reactant, the rate increase by four times, the reaction is:
- a second-order
  - b zero-order
  - c first-order
  - d none
23. Substances that slow down a reaction are:
- a Promoters
  - b Positive catalysts
  - c inhibitors
  - d none

### Part II: Answer the following questions briefly

24. For the reaction between gaseous chlorine and nitric oxide,



it is found that doubling the concentration of both reactants increases the rate by a factor of eight, but doubling the chlorine concentration only doubles the rate.

- a What is the order of the reaction with respect to  $\text{NO}$ ?
- b What is the order of the reaction with respect to  $\text{Cl}_2$ ?

- c What is the overall order of the reaction?
25. Distinguish between the order and the molecularity of a reaction.
26. Explain the differences between endothermic and exothermic reactions.
27. What are pseudo unimolecular reactions? Write an example of such a reaction.
28. What are clock reactions?
29. The concentration of A during a reaction of the type:  $A + 2B \rightarrow \text{products}$ , changes according to the data in the table.

Time/min	[A]/mol dm <sup>-3</sup>
1	0.317
5	0.229
10	0.169
15	0.130
25	0.091
40	0.062

Based on the information given in the above table, calculate the average rate of reaction and plot a graph of rate of reaction versus time.