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 on the dependence of reaction rate on nature and concentration of reactants, surface area of solid reactants, temperature of the 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 rate laws and order of reactions from data on initial concentrations and reaction rates;*
- *apply concentration - time equation (integrated rate law) to find amount of the product at ant time of the reaction process;*
- *appreciate the importance of chemical kinetics in industry and in living organisms;*

MAIN CONTENTS

4.1 Rate of Reaction
- 4.1.1 Determination of rate of reaction
- 4.1.2 Factors that influence reaction rates

4.2 Theories of Reaction Rates
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4.3 Rate Equation or Rate law
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4.3.2 Concentration– Time equation (Integrated Rate Law)
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4.4.2 Rate determining step

INTRODUCTION

This unit is organized into four sections. The first part is concerned with rate of reaction, with emphasis on how to determine it and factors that influence rate of reaction. The second section deals with theories of reaction rates based on collision theory and transition-state theory. The third part deals with rate equation or rate law, which includes order of reaction, rate constant, concentration-time equation and half-life of a reaction. The fourth section deals with reaction mechanism, which includes the molecularity of elementary reactions and the rate-determining step.

Some chemical reactions proceed quickly, while others require days, months or even years to change into products. These differences depend primarily on the differences in the chemical nature of the reacting substances. 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 occur in decades and the brake down of plastics on earth takes more than hundred years. On the contrary, combustion of gasoline or the explosion of gunpowder occurs in a few seconds.

Chemical kinetics is the area of chemistry concerned with the speed, or rate, at which a reaction occurs and the mechanisms it follows. The word *kinetic* suggests movement or change. Chemical kinetics explains how *fast* a reaction proceeds to the product side. However, it does not give information on how *far* the reaction proceeds to the right, which is the study of chemical equilibrium.

4.1 RATE OF REACTION

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

- define chemical kinetics and 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 reaction rate from a 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 (for gases) affect rate of reaction, by giving examples;
- explain activation energy;
- define catalyst and distinguish between homogeneous and heterogeneous catalysis;
- 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.

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 $\mathbf{H_2}$ and $\mathbf{I_2}$ can combine to produce it. The chemical equation representing the formation of HI from this reaction of hydrogen and iodine is represented as:

$$H_2\,(g) + I_2\,(g) \quad \rightarrow \quad 2HI\,(g)$$

The rate of *appearance* of HI in the above reaction is defined as the rate of reaction from left to right. The rate of *disappearance* of HI is defined as the rate of reaction from left to right, which can be represented as:

$$2HI\,(g) \quad \rightarrow \quad H_2\,(g) + I_2\,(g$$

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

$$\mathbf{A \rightarrow B}$$

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

$$\boldsymbol{r} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_f - [A]_i}{\Delta t}$$

where $\boldsymbol{r}$ is rate of reaction, **A** is a reactant, **B** is a product, $\mathbf{[A]_i}$ and $\mathbf{[A]_f}$ are initial and final concentration of **A** respectively, $\Delta\mathbf{[A]}$ is change in concentration of **A** and $\Delta\boldsymbol{t}$ is the change in time.

Note that concentration is usually expressed in mole per litre.

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

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

$$r = \frac{\Delta[B]}{\Delta t} = \frac{[B]_f - [B]_i}{\Delta t}$$

where **[B]** is the concentration of a product in moles per litre, mol L^{-1}. For a given product, the final concentration of **B**, $[B]_f$, is greater than its initial concentration $[B]_i$. 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 any sign to the rate expression when rate is calculated using product concentration.

We have seen that, for stoichiometrically simple reactions of the type **A** → **B**, the rate of reaction can be expressed either in terms of the decrease in reactant concentration over time, $-\Delta[A]/\Delta t$, 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

$$2A \rightarrow B$$

For every 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:

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

For the general reaction equation: $a\,A + b\,B \rightarrow c\,C + d\,D$; the rate of the reaction is given by:

$$r = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[c]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

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

a. I^- (aq) + OCl^- (aq) → Cl^- (aq) + OI^- (aq)

b. 3 O_2 (g) → 2 O_3 (g)

c. 4 NH_3 (g) + 5 O_2(g) → 4 NO (g) + 6 H_2O (g)

Solution:

a. Since all of the stoichiometric coefficients are equal,

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

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

$$r = -\frac{1}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[O_3]}{\Delta t}$$

c. In this reaction

$$r = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

2. The balanced equation for the reaction of nitric oxide with hydrogen is:

2 NO (g) + 2 H_2 (g) → N_2(g) + 2 H_2O (g)

If the rate of disappearance of NO is 5.0×10^{-5} mol $L^{-1}s^{-1}$, what is the rate of formation of N_2?

Solution:

The rate of formation of N_2 is also the rate of the whole reaction because its coefficient is 1.

$$r = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \tfrac{1}{2}(5.0 \times 10^{-5}\ \text{mol}\ L^{-1}s^{-1}) = 2.5 \times 10^{-5}\ \text{mol}\ L^{-1}s^{-1}$$

3. Use the given information to fill the table for the reaction:

N_2O_5 (g) → 2 NO_2 (g) + ½ O_2

Time, min	$[N_2O_5]$, M	$[NO_2]$, M	$[O_2]$, M	Rate of reaction, M/s
0	1.24×10^{-2}	0	0	0
10	0.92×10^{-2}	___	___	___
20	0.68×10^{-2}	___	___	___
30	0.50×10^{-2}	___	___	___
50	0.28×10^{-2}	___	___	___
60	___	**2.08×10^{-2}**	___	___

Solution:

Rate = $-\Delta [N_2O_5] / \Delta t = \Delta [NO_2] / 2\Delta t = 2\,\Delta [O_2] / \Delta t$

For the same interval of time, $-\Delta [N_2O_5] = \Delta [NO_2] / 2 = 2\,\Delta[O_2]$.

a) Between 0 & 10 minutes:

$-\Delta [N_2O_5] = -(0.92 - 1.24) \times 10^{-2}\,M = 0.32 \times 10^{-2}\,M$. Therefore,

$\Delta [NO_2] = 2 \times 0.32 \times 10^{-2}\,M = \textit{0.64 x } 10^{-2}\,\textit{M}$.

$\Delta [O_2] = \frac{1}{2} (0.32 \times 10^{-2}\,M) = \textit{0.16 x } 10^{-2}\,\textit{M}$.

Rate of the reaction = $(0.32 \times 10^{-2} M)/10$ min **or** $(0.64 \times 10^{-2}\,M) / (2 \times 10$ min) **or**

($2 \times 0.16 \times 10^{-2}\,M) / 10$ min = $\textit{3.20 x } 10^{-4}\,\textit{M /min}$.

b) Between 10 & 20 minutes:

$-\Delta [N_2O_5] = -(0.68 - 0.92) \times 10^{-2}\,M = \textit{0.24 x } 10^{-2}\,\textit{M}$. Similarly,

$\Delta [NO_2] = 2 \times 0.24 \times 10^{-2}\,M = 0.48 \times 10^{-2}\,M$. Total concentration of NO_2 at this time, is therefore, $(0.64 + 0.48) \times 10^{-2}\,M = \textit{1.12 x } 10^{-2}\,\textit{M}$.

$\Delta [O_2] = \frac{1}{2} (0.24 \times 10^{-2}\,M) = 0.12 \times 10^{-2}\,M$. Total concentration of O_2 at t = 20 minutes is $(0.16 + 0.12) \times 10^{-2}\,M = \textit{0.28 x } 10^{-2}\,\textit{M}$.

Rate of the reaction = $(0.24 \times 10^{-2}\,M) / 10$ min = $\textit{2.4 x } 10^{-4}\,\textit{M /min}$.

Solving for the respective concentrations and rates, we get the following table.

Time, min	$[N_2O_5]$, M	$[NO_2]$, M	$[O_2]$, M	Rate of reaction, M/ min
0	1.24×10^{-2}	0	0	0
10	0.92×10^{-2}	0.64×10^{-2}	0.16×10^{-2}	3.20×10^{-4}
20	0.68×10^{-2}	1.12×10^{-2}	0.28×10^{-2}	2.40×10^{-4}
30	0.50×10^{-2}	1.48×10^{-2}	0.37×10^{-2}	1.80×10^{-4}
50	0.28×10^{-2}	1.92×10^{-2}	0.48×10^{-2}	$\mathbf{1.10 \times 10^{-4}}$
60	0.20×10^{-2}	$\mathbf{2.08 \times 10^{-2}}$	0.52×10^{-2}	0.80×10^{-4}

Note that concentration of the reactant and rate of the reaction decrease while concentrations of products increase with time. Note also that the rate in the *fifth* raw is for the time duration between 30 and 50 minutes, i.e. Δ t = 20 min!

Exercise 4.1

1. (Choose) In the reaction 2 W + X → 3Y + 2 Z, the concentration –change for the same duration of time (Δt) can be expressed as

A. Δ [W] = 2 Δ[X] B. −Δ [X] = 3 Δ [Y] C. Δ [Z] = Δ [Y] /3

D. Δ [W] /2 = Δ [Y] /3 E. −Δ [W] = Δ [Y] /3 F. -Δ [W] = Δ [Z]

2. For the reaction: 4 NH_3 (g) + 5 O_2 (g) → 4 NO (g) + 6 H_2O (g), the rate of disappearance of NH_3 is 2.0 x 10^{-2} M /min. What is the rate (at the same time) of

(a) Disappearance of O_2? (b) Formation of H_2O and (c) the reaction?

3. Does a fast reaction produce good product? Explain!

4.1.1 Determination of Rate of Reaction

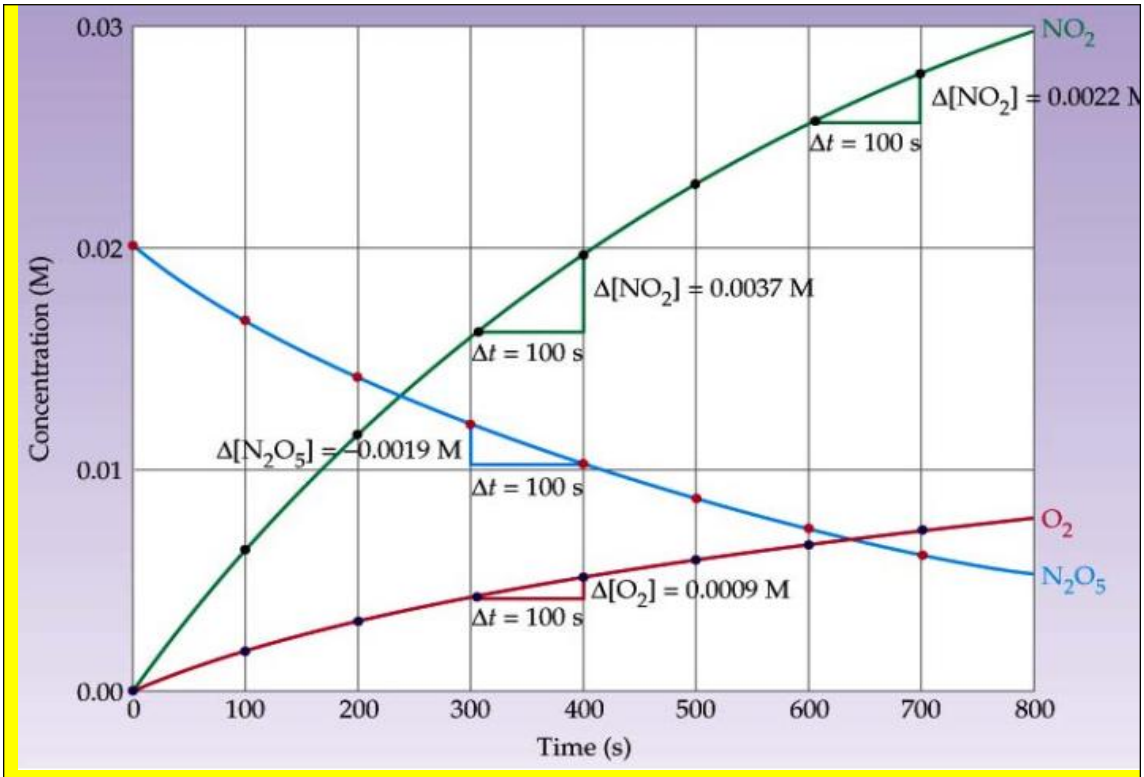
There are different ways in which reactions are monitored. These include change of colour, volume of gas evolved, amount of precipitate formed and loss or gain of mass. Graph of change in concentration of a reactant or product over a period of time can be used to estimate the average rate of the reaction in that period by looking at the slope of the curve. To do so, one has to plot concentration versus time graph as given in the following example.

Example 4.2

Consider the decomposition of N_2O_5 to give NO_2 and O_2:

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Time (s)	$[N_2O_5]$ M	$[NO_2]$ M	$[O_2]$ M
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070



1. From the graph looking at t = 300 to 400 s

$$\text{Rate of formation of } O_2 = \frac{0.0009M}{100s} = 9 \times 10^{-6} Ms^{-1}$$

$$\text{Rate of formation of } NO_2 = \frac{0.0037M}{100s} = 3.7 \times 10^{-5} Ms^{-1}$$

$$\text{Rate of disappearance of } N_2O_5 = \frac{0.001M}{100s} = 1.9 \times 10^{-5} Ms^{-}$$

According to the observed results, the one with higher coefficient in the balanced equation proceeds faster than the others. Each result represents the slope of the curve at the given interval for the species involved.

To calculate the rate of the reaction at the given interval, one must account for the *stoichiometry of the equation.*

Rate of the reaction = Rate of O_2 = 1/4 (rate of NO_2) = 1/2 (rate of N_2O_5).

$$\text{Rate in terms of } O_2 = \left(\frac{0.0009M}{100s}\right) = 9.0 \times 10^{-6} Ms^{-1}$$

$$\text{Rate in terms of } NO_2 = \frac{1}{4}\left(\frac{0.0037M}{100s}\right) = 9.2 \times 10^{-6} Ms^{-1}$$

$$\text{Rate in terms of } N_2O_5 = \frac{1}{2}\left(\frac{0.001M}{100s}\right) = 9.5 \times 10^{-6} Ms^{-}$$

These values are almost the same accounting with small experimental errors.

2. The rate of the reaction for the first 200 s

$$\text{Rate in terms of } O_2 = \left(\frac{0.0029\text{M}}{200\text{ s}}\right) = 1.45 \times 10^{-5}\ \text{Ms}^{-1}$$

$$\text{Rate in terms of } NO_2 = \frac{1}{4}\left(\frac{0.0115\text{M}}{200\text{ s}}\right) = 1.44 \times 10^{-5}\text{Ms}^{-1}$$

$$\text{Rate in terms of } N_2O_5 = \frac{1}{2}\left(\frac{0.0058\text{M}}{200\text{s}}\right) = 1.45 \times 10^{-5}\text{Ms}^{-1}$$

These figures show that the rate of the reaction is 1.45 x 10^{-5} Ms^{-1} in the first 200 seconds.

3. Looking for the rate of the reaction between t = 600 to 700 s

$$\text{Rate in terms of } O_2 = \left(\frac{0.0006\text{M}}{100\text{s}}\right) = 6.0 \times 10^{-6}\ \text{Ms}^{-1}$$

$$\text{Rate in terms of } NO_2 = \frac{1}{4}\left(\frac{0.0022\text{M}}{100\text{s}}\right) = 5.5 \times 10^{-6}\text{Ms}^{-1}$$

$$\text{Rate in terms of } N_2O_5 = \frac{1}{2}\left(\frac{0.0011\text{M}}{100\text{s}}\right) = 5.5 \times 10^{-6}\text{Ms}^{-1}$$

From the above three results, we can conclude that rate of a reaction can be evaluated from either one of the reactants or products. Furthermore, rate of a reaction is faster at the beginning and becomes slower and slower as time passes.

Exercise 4.2

1. Consider the dimerization of ethene to butene according to the following equation.

$$2C_2H_4\ (g) \rightarrow C_4H_8\ (g)$$

From the experimental data given below, plot a graph for the consumption of ethene, C_2H_4, versus time.

(a) Calculate the rate of the reaction between the time intervals 10 s to30 s.

(b) Estimate the rate of the reaction between 40s and 60s.

Time; s	0	10	20	40	60	100
$[C_2H_4]$ mol /L	0.88	0.62	0.48	0.33	0.25	0.17

2. The following data were collected for the reaction between powdered calcium carbonate and hydrochloric acid.

$$CaCO_3\ (s) + HCl\ (aq) \rightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (\ell)$$

Volume of CO_2/cm^3	0	20	35	47	56	64	69	73	77	80
Time, s	0	10	20	30	40	50	60	70	80	100

(a) Plot the above result on a graph paper as volume versus time.

(b) At which time interval is the reaction most rapid?

(c) What is the rate of reaction between 40 and 50 seconds?

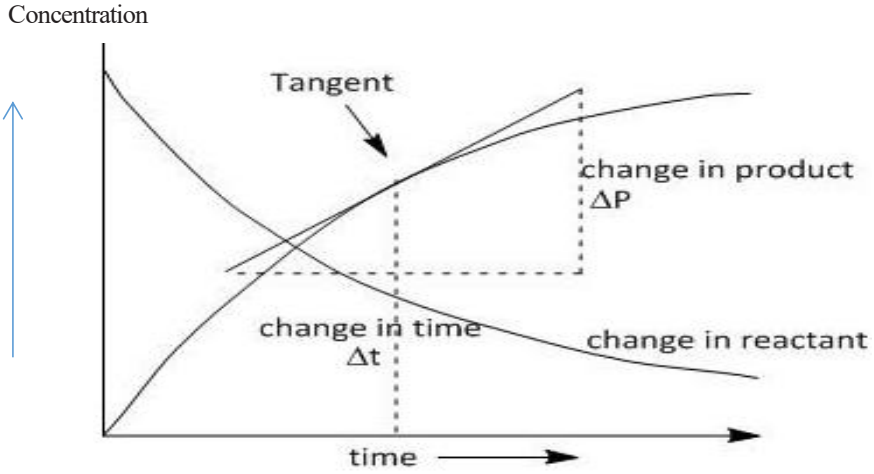
(d) What volume of gas has formed at 15 seconds?

(e) How long did it take for $40cm^3$ of carbon dioxide to be formed?

(f) Why does the rate of reaction gradually slow down?

Instantaneous rate of reaction is defined as the rate of a reaction at a specified 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.



The concentration of products increases and that of reactants decreases with time as it is observed in the above plot. Thus, a negative slope is obtained in plotting the change in concentration of reactant and a positive slope with the change in concentration of product with time. The slope of the *tangent line* indicates the instantaneous rate at that particular time.

Experiment 4.1

Measuring Rate of Reaction

Objective: To measure the rate of reaction between $CaCO_3$ and dilute HCl

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

Chemicals: 2 M HCl solution and marble chips/$CaCO_3$.

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 $CaCO_3$ in a clean 100mL conical flask.
3. Add 40mL of 2 M 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.

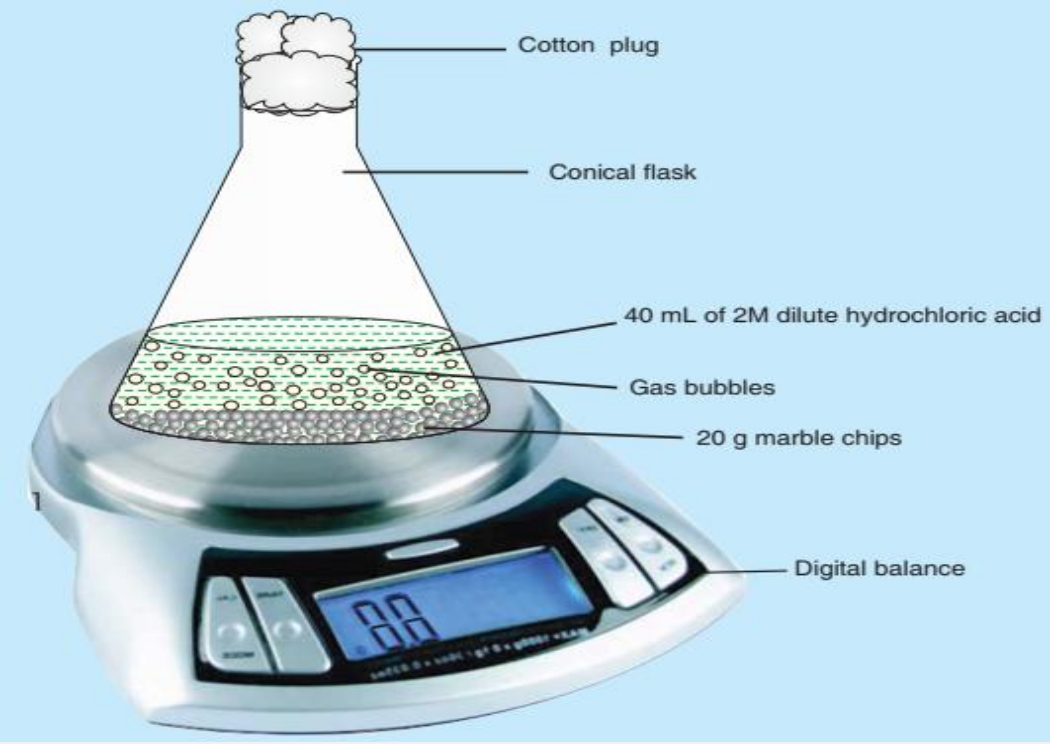


Figure 4.1 Laboratory set up for the measurement of rate of reaction

Observation and analysis:

1. Use the following table to record your observation.

Time (minutes)	0	1	2	3	4	5	6	7	8	9	10
Mass (g)											

Plot a graph of time (minutes) on the horizontal axis and mass 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. Almost horizontal at the end of the reaction?

5. Predict:

a. The average rate of the reaction in the whole time interval.

b. The instantaneous rate of reaction at 2 minutes.

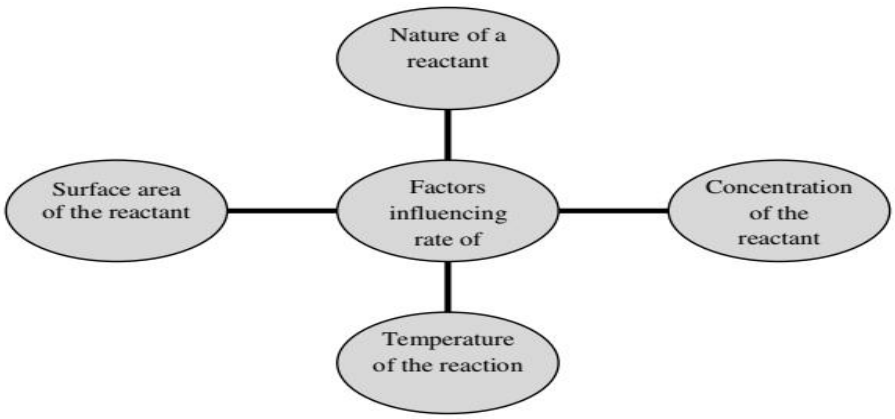
6. What is the use of the cotton plug?

7. Can we find the rate of this reaction by collecting and measuring the amount /volume of CO_2 evolved?

8. Sketch a graph of the expected result by plotting volume of CO_2 evolved vs time.

4.1.2 Factors Influencing Reaction Rates

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* results in changes of reaction rate.



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 5mL of 2M HCl to the first test tubes. Observe and record your result. Repeat the same procedure with the second test tube. Be sure to wear your safety goggles and gloves.

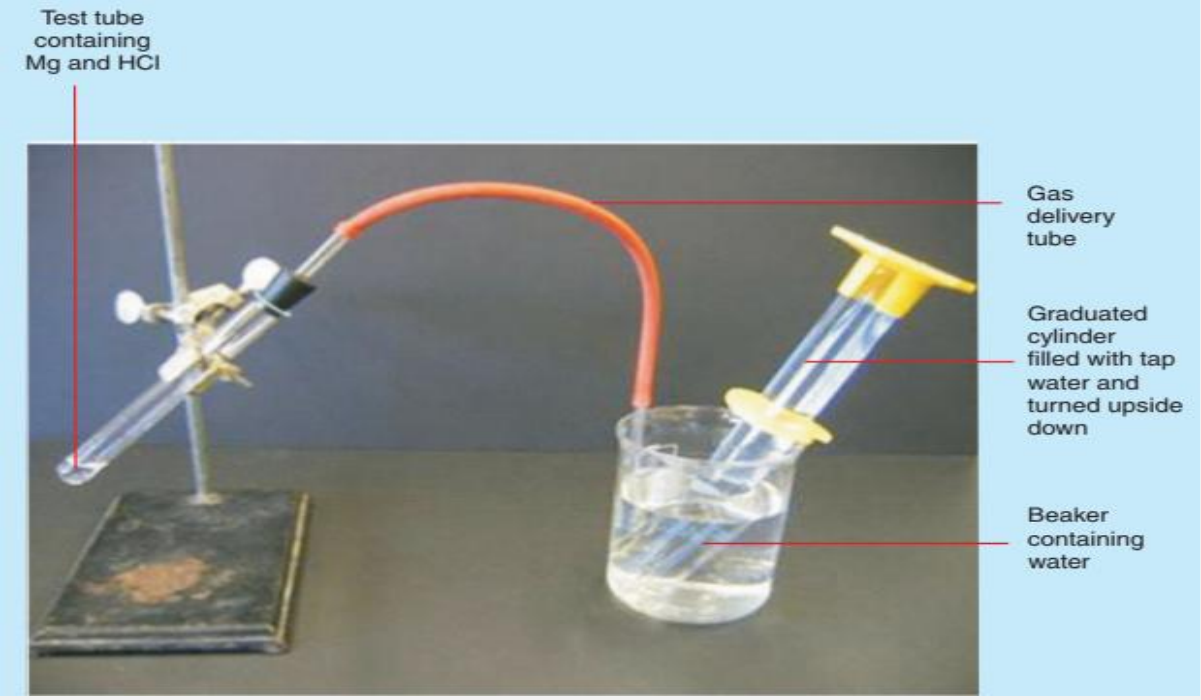


Figure 4.2 Reaction of magnesium with HCl

Observation and analysis:

1. Which of the metals, copper or magnesium, reacts faster? Why?
2. Write the balanced chemical equation for the reaction of copper and magnesium with HCl.
3. 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?
4. What do you learn from this experiment?

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,

$$H_3O^+ (aq) + OH^- (aq) \rightarrow 2H_2O (\ell)$$

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

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Similarly, precipitation reactions, which involve ions in solution are also faster.

$$NaCl (aq) + AgNO_3 (aq) \rightarrow AgCl (s) + NaNO_3 (aq)$$

Other examples are given below.

$Na\ (s) + H_2O\ (\ell) \rightarrow NaOH\ (s) + \frac{1}{2} H_2\ (g)$ …… very fast

$K\ (s) + H_2O\ (\ell) \rightarrow KOH\ (s) + \frac{1}{2} H_2\ (g)$ …….. very fast, catches fire

$Cu\ (s) + H_2O\ (\ell) \rightarrow$ no reaction

$Mg\ (s) + H_2O\ (g) \rightarrow$ slow 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: Reading balance, 100mL conical flask, stopwatch, cotton wool.

Chemicals: Cube chalk, powered chalk and 2M HCl solution

Procedure: Repeat Experiment 4.1 but use 20 g of small cubical chalk and then powdered chalk in place of marble chips. Record the rate of evolution of gas.

Observation and analysis:

1. Compare the rate curve, average rate and reaction rate at 2 minutes with that of Experiment 4.1. Explain your observation.
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 expected to be easier to dissolve in dilute HCl: large pieces 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.

$$3Fe\ (s) + 4H_2O\ (g) \rightarrow Fe_3O_4\ (s) + 4H_2\ (g)$$

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.

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, 100mL conical flask, stopwatch, cotton wool

Chemicals: 1 M HCl, 2 M dilute solutions and marble chips ($CaCO_3$).

Procedure:

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

Observation 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 HCl? Explain.
   b. 1M HCl is replaced with 0.5 M HCl? Explain.
4. Sketch a graph for each of 0.5 M, 1 M, 2 M and 4 M HCl against time on the same graph sheet.

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 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.

(i) Phosphorus + Air → phosphorus pent oxide; Rate (i) = **x**

(ii) Phosphorus + Oxygen → phosphorus pent oxide; Rate (ii) = 5**x**, this is because oxygen in air comprises 21 %.

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.

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 thio sulfate and hydrochloric acid

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

Chemicals: 0.5 M HCl solution, 0.1 M $Na_2S_2O_3$ solution, pieces of ice.

Procedure:

1. Take 25 mL of 0.1 M $Na_2S_2O_3$ 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°C [by keeping them in an ice bath as shown in Figure 4.3 (a)].
   Set (*ii*) at room temperature. Set (*iii*) at 40°C (by heating the solution in a water bath).
3. Put a cross sign on a white cardboard and place a clean dry 100 mL beaker on 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 °C versus time in minutes.

Observation 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 an equation for the reaction.
2. Under which condition of temperature does the cross take:
   a. the shortest time to disappear, and
   b. the longest time to disappear?
3. Draw a conclusion about the relationship between the average reaction rate and temperature.

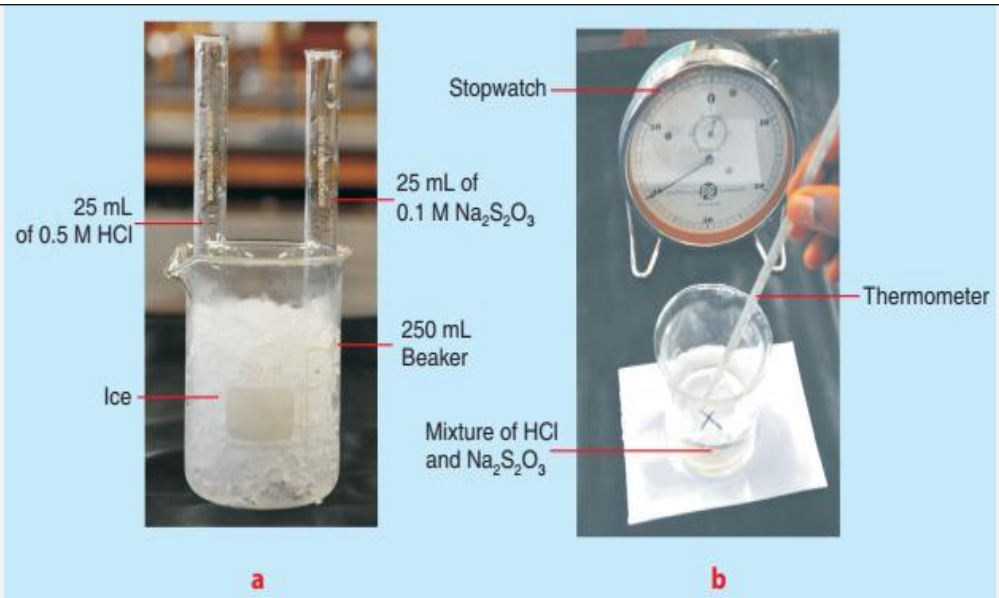


Figure 4.3: Laboratory setup for the study of the effect of temperature on reaction of $Na_2S_2O_3$ and HCl

Temperature usually has a major effect on 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 a chemical reaction. This is because as the temperature of the 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 food is kept in a refrigerator to slow down the rate of its decomposition; and

b during heart surgery, the body of a 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. Consider the following reactions as examples.

At 200°C, $NH_4NO_3\ (s) \rightarrow N_2O\ (g) + 2H_2O\ (g)$

At even higher temperature,

$$2NH_4NO_3\ (s) \rightarrow N_2\ (g) + O_2\ (g) + 4H_2O\ (g)$$

v) *Presence of a Catalyst*

Experiment 4.6

Effect of Catalyst on Rate of Reaction

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

Apparatus: Conical flask, gas syringe, delivery tube.

Chemicals: 0.5% by volume H_2O_2 solution, MnO_2.

Procedure:

1. Set-up the apparatus as shown in Figure 4.4. Set the volume of the gas syringe at 0mL. Add 25.0mL of 0.1 M H_2O_2 solution, but without manganese (IV) oxide, 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 in the presence of 1.0 g of MnO_2.

Observation and analysis:

1. Identify the gas evolved and write a balanced chemical equation for the reaction.
2. Under which condition does the gas syringe contain more gas at any one time? Give an explanation for this observation.
3. Describe the appearance of MnO_2 before and after the reaction.
4. Sketch graphs of volume of gas on the vertical axis and time on the horizontal axis for two different sets of readings. Which set of reading were faster? Why?
5. Draw conclusion about the reaction rate:
   a. in the presence of a catalyst;
   b. in the absence of a catalyst.

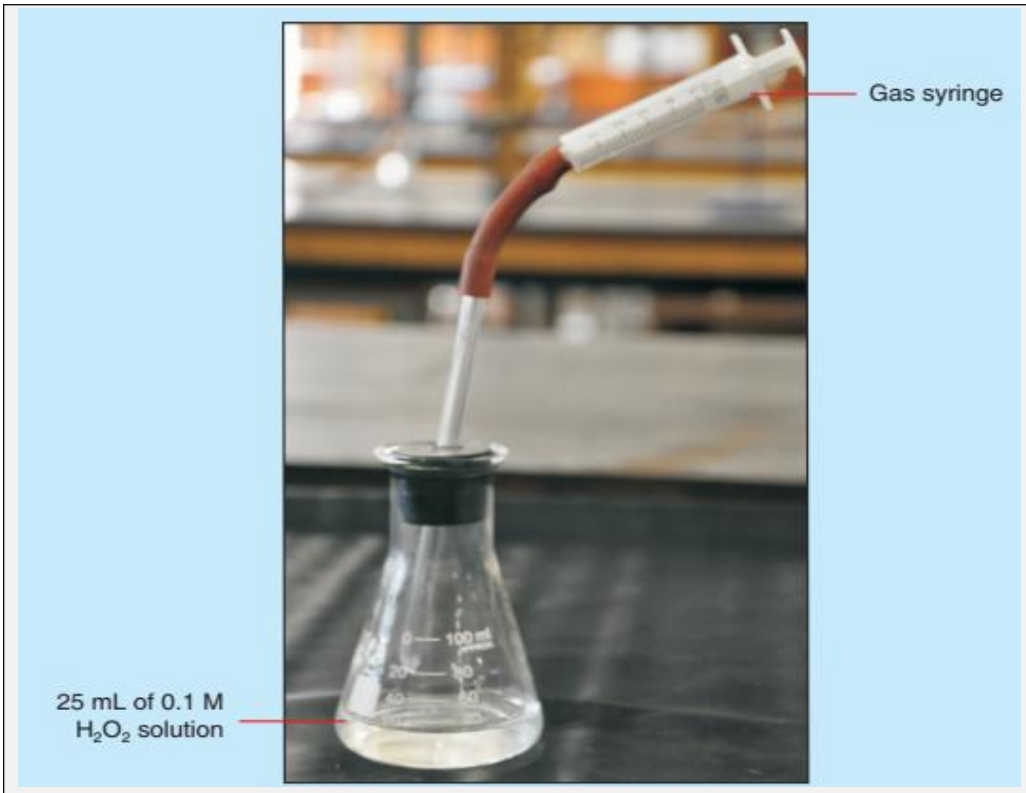


Figure 4.4 Investigating the effect of manganese (IV) oxide on hydrogen peroxide

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 intermediate 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. The effect of catalysts on the rate of chemical reaction is illustrated in Figure4.5.

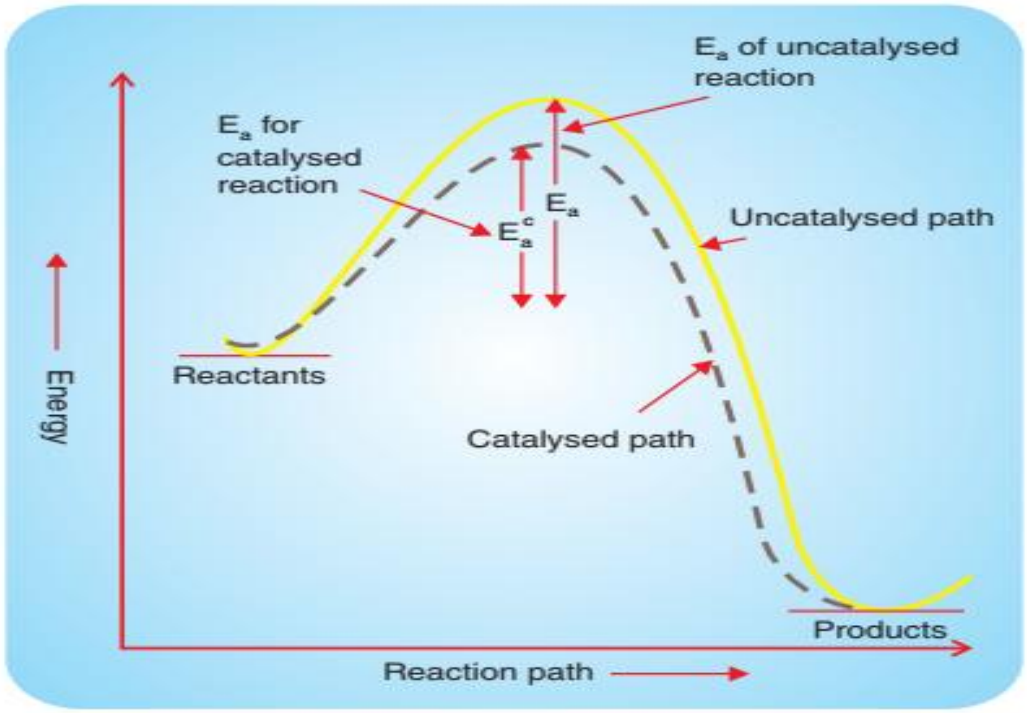


Figure 4.5 Comparison of activation energies of catalyzed and un- catalyzed reaction

Chemical catalysts can be either positive or negative. Positive Catalyst increases the rate of reaction by providing a path of lower activation energy, E_a.

Example (1): $2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$; V_2O_5 (s) as catalyst.

Negative catalyst or inhibitor decreases the rate of reaction by choosing a mechanism with higher activation energy, Ea.

Example (2): $OCl^-\ (aq) + I^-\ (aq) \rightarrow OI^-\ (aq) + Cl^-\ (aq)$; OH^- (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: $CO\ (g) + 3H_2\ (g) \rightarrow CH_4\ (g) + H_2O\ (g)$; Ni (s) is used as catalyst.

$CO\ (g) + H_2\ (g) \rightarrow HCHO\ (g)$; 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 4.3

1. Explain what happens to the rate of reaction when temperature increases.
2. What is the relationship between temperature and reaction time of a chemical reaction?
3. Explain the effect of surface area on the rate of reaction.
4. An exothermic reaction ($\Delta H < 0$) has activation energy, Ea = 45 kJ /mol. What is the activation energy of the same reaction in the reverse direction?
5. 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 materials 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;
- 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.

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).

$$Rate\ \alpha \frac{Number\ of\ collisions}{Second}$$

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 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, and they must collide with sufficient energy to break or rearrange bonds. In order to react, the colliding molecules must have a total kinetic energy equal to or greater than the **activation energy (Ea)**, which is the minimum amount of energy required to initiate a chemical reaction.

According to the postulates of collision theory, in order 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 activation energy.

Only collisions with proper orientation of reacting species possessing sufficient energy result in a reaction. The collision can either be linear or nonlinear (bent).

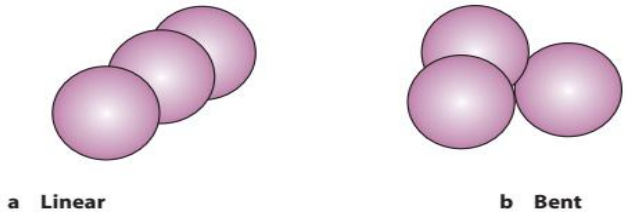


Figure 4.6 Orientation of molecules

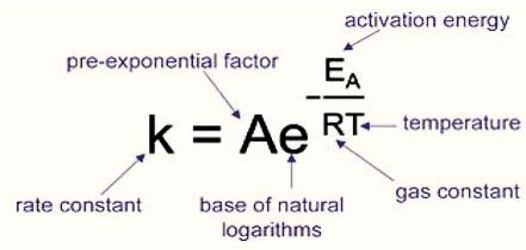
Generally, activation energy (*E*a) in linear orientation is less than that in bent orientation. Hence, orientation (a) is favoured over orientation (b).

Concentration is one of the factors that influence the rate 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 particles of reactants to collide more frequently and with greater energy. This results in an increase in reaction rate.

From experimental results, Svante Arrhenius in 1889 observed that a mathematical relationship connects activation energy, temperature, and the rate constant (or rate). This relationship is known as the Arrhenius equation given by:

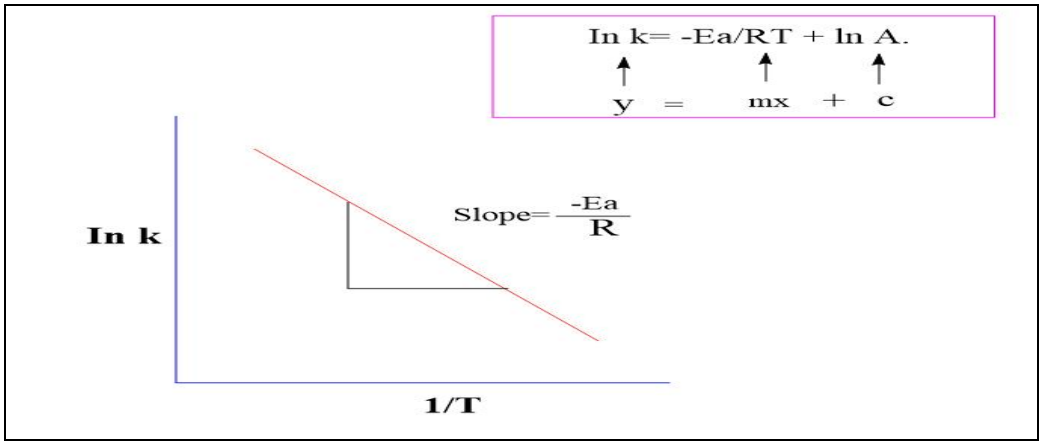


The above equation shows the fraction of collisions in an elementary reaction in which the particles have enough energy to react. The constant ***A*** corrects for the frequency of collisions, the necessity for the proper orientation in effective collisions, and all factors other than activation energy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

Taking logarithms of both sides, the equation becomes:

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

This equation shows 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.The value of Ea can be found from the slope of a plot of *ln k* versus *1/T*, and Ea = – 2.303 R × 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 Ea.

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

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 4.3

The thermal decomposition of $CH_3N{=}NCH_3$ in the gas phase to give nitrogen and methyl radicals $CH_3N{=}NCH_3\ (g) \rightarrow N_2\ (g) + 2\ {\bullet}CH_3\ (g)$ has an activation energy of 2.14×10^5 J/mol, at 600 K and at the given temperature, $k = 1.99 \times 10^8\ s^{-}$. What would be the reaction rate when there is a ten-degree rise in temperature?

Solution:

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

$$\log\frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{T_1 - T_2}{T_2T_1}\right)$$

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

Taking antilogarithms of both sides gives:

$$\frac{K_2}{1.99\ x\ 10^8 s^{-}1} = 2.0$$

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

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

Exercise 4.4

1. The activation energy for a reaction is 34.0 kJ/mol while its rate constant at 47^0C is 4.5 x $10^{-3}\ s^{-1}$. Calculate the rate constant at 127 °C.
2. Given that *E*a for the hydrolysis of sucrose is 108×10^3 J / mol,

(a) Compare the rate constant of this reaction at 37°C (T_1) with the rate constant of the same reaction at 27°C (T_2).

(b) Calculate the rate constant for the above reaction at 47°C and compare it to the rate constant at 37°C.

(c) Sketch a graph of log k versus $1/T$ to calculate (prove) the activation energy.

4.2.2 Transition State Theory

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:

$$\mathbf{A_2 + B_2 \rightarrow 2\ AB}$$

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 activation energy, *Ea*, 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 to the product conditions, particles must climb the barrier.

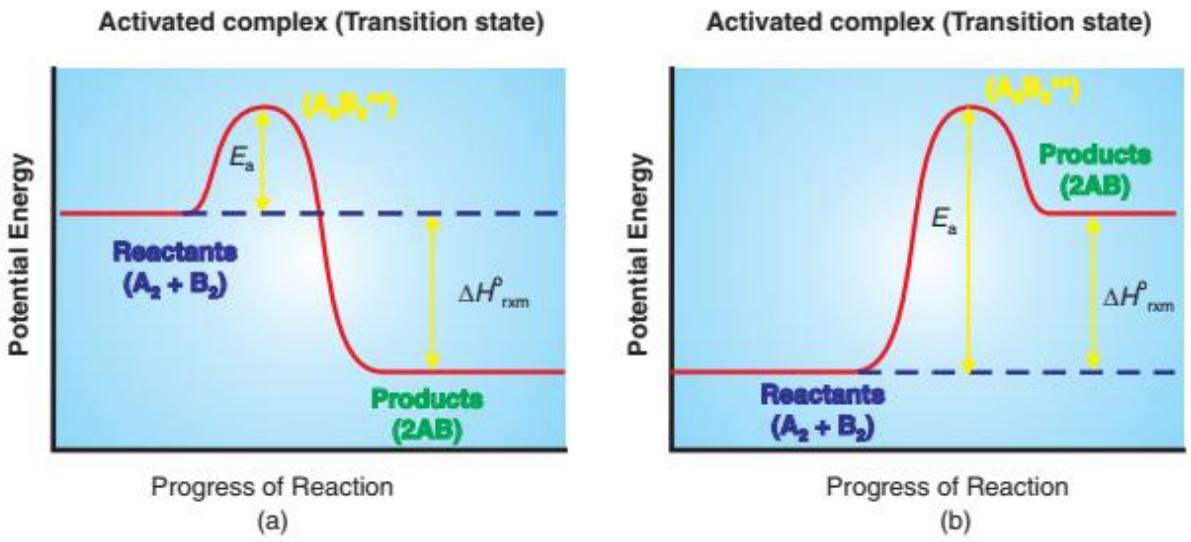


Figure 4.7 Reaction energy diagrams for a) exothermic and b) endothermic reactions

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

$$A_2 + B_2 \rightarrow A_2B_2^{\ddagger} \rightarrow 2AB$$

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

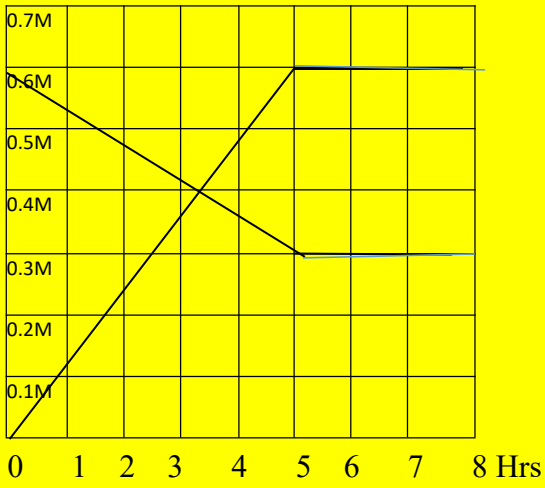
As shown in Figure 4.7, the activated complex corresponds to the peak of the energy barrier. According to transition-state theory, the rate of reaction depends on the rate at which reactants can climb to the top of the barrier and form an activated complex. On the other hand, the activation energy, E_a, 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 enthalpy of reaction is less than zero $\Delta H^o < 0$.

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

Exercise 4.5

1. The progress of the reversible reaction for A ⇆ **n** B is plotted below.



(a) Find the value of n.

(b) Which one proceeds faster: decomposition of A or production of B?

(c) What is the average rate of the reaction?

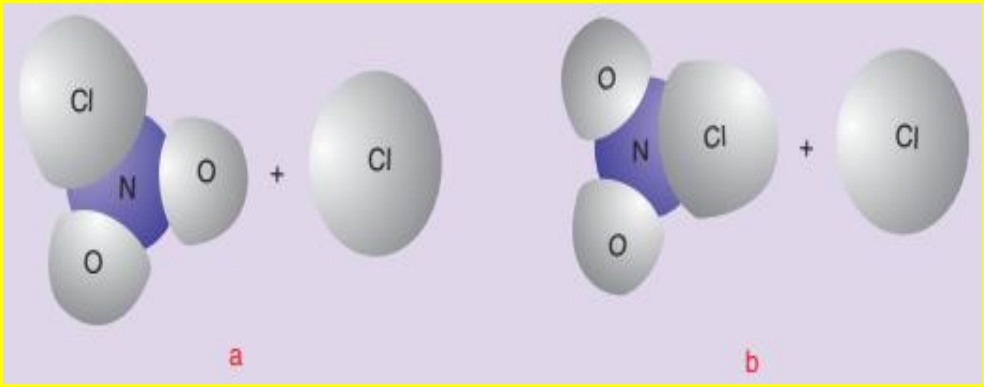
2. Describe transition-state theory.

3. How does a catalyst affect the rate of a reaction?

4. Discuss the relationship between collision and rate of a chemical reaction.

5. Consider the following reaction

$NO_2Cl + Cl \rightarrow NO_2 + Cl_2$



Which of the above collisions might be successful (a or b) to form the product?

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

4.3.1. Order of Reaction and Rate Constant

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,

$$A \rightarrow B$$

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

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

where [A] expresses its concentration (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 determined only *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 the reaction is the sum of the powers to which all concentrations are raised in the rate law expression. For the general reaction.

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

we can write the rate law expression as:

$$r = k\,[A]^x\,[B]^y$$

The reaction is x^{th} order in A, y^{th} order in B, and $(x + y)^{th}$ 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 temperature.

Consider a reaction with the rate equation,

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

The reaction with the rate equation above is described as "second-order in A" and "first-order

in B." The overall order is described as a third-order reaction, because the sum of the exponents on [A] and [B] is 3.

Table 4.1 Rate equation and reaction order for simple reaction

Rate equation	Overall reaction order
$k\,[A]^o$	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

Method of initial rates

The **method of initial rates** is a common technique for deriving rate laws. As the name implies, the method involves measuring rate at the beginning of the reaction. Here, 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 of the reactants and it 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,

$$A \rightarrow \text{products}$$

is under study. The data are inspected to find how the initial rate varies with the initial concentration of A, $[A]_o$. The objective is to find the value of the exponent in the rate equation, $\text{rate} = k\,[A]^m$, where m is the order of the reaction. For a first-order reaction, $m = 1$, and the rate varies directly with $[A]_o$. If $[A]_o$ is doubled, the rate is doubled; if $[A]_o$ is tripled, the rate is tripled; and so on (see Table 4.2). For a second-order reaction, $m = 2$ and the rate is increased by a factor of 2^2, or 4, if $[A]_o$ 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 4.2 Change in initial rate with change in $[A]_o$ for rate = k $[A]^m$

Order of reaction	If $[A]_o$ is doubled	If $[A]_o$ is tripled
Zero (m = 0)	Rate remains unchanged, 2^o	Rate remains unchanged 3^o
1st order (m = 1)	Rate is doubled, 2^1	Rate is tripled, 3^1
2nd order (m = 2)	Rate is quadruple, 2^2	Rate increases 9 times, 3^2
3rd order (m = 3)	Rate increases 8-fold, 2^3	Rate increases 27 times, 3^3

Example 4.4

1. The reaction between nitric oxide with ozone; NO (g) + O_3 (g) ⟶ NO_2 (g) + O_2 (g) was studied by varying the initial concentration of the reactants and finding the initial reaction rates. The following data were results of such a study.

Trial	[NO] mol/L	[O_3] mol/L	Δ[NO_2]/ Δt , mol/L.s
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
3	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}

a. What is the order with respect to each reactant and overall?

b. What is the value of the rate constant?

Solution

From the reaction equation, a generic rate law; rate = k $[NO]^m$ $[O]^n$ can be formulated.

The values of the reaction orders m and n, and rate constant k are determined from the experimental data.

The value of m is determined from the data in which [NO] varies and [O_3] is constant. In trials 2 and 3, [NO] varies while [O_3] remains constant. When [NO] doubles, the rate also doubles. Thus, the rate is directly proportional to [NO], and m in the rate law is equal to 1.

The value of n is determined from data in which [O_3] varies, and [NO] is constant. In trials 1 and 2, [NO] is constant and [O_3] varies. When [O_3] doubles the rate also doubles.The reaction rate changes in direct proportion to the change in [O_3]. Thus, the rate is directly proportional to [O_3], and n is equal to 1. The rate law is therefore, rate = k [NO][O_3], 2nd order overall.

The value of k is determined from any one set of the entries. For instance, taking the data from trial 1 and its corresponding rate value:

$$k = \frac{\text{rate}}{[NO][O_3]} = \frac{6.60 \times 10^{-5}\text{mol/L. s}}{(1.00 \times 10^{-6}\text{mol/L})(3.00 \times 10^{-6}\text{mol/L})}$$

$= 2.20 \times 10^{7}$ L/mol. s (or $M^{-1}s^{-1}$)

2. For a reaction whose rate equation is: Rate = k $[X]^{m}$ $[Y]^{n}$, the following experimental data were obtained at constant temperature.

Trial	[X] (M)	[Y] (M)	Rate (M /s)
1	6.0×10^{-2}	2.0×10^{-3}	3.0×10^{-6}
2	1.2×10^{-1}	2.0×10^{-3}	1.2×10^{-5}
3	6.0×10^{-2}	4.0×10^{-3}	6.0×10^{-6}

(a) Find the order with respect to each reactant and write the rate equation.

(b) Find the rate constant with its units at the same temperature.

(c) What will be the rate when [X] = 6.0×10^{-3} M and [Y] = 4.0×10^{-4} M?

Solution

(a) Compare the data of Trials 1 and 2, where the concentration of Y is constant.

Rate of 2 /rate of 1 = 4 = $(1.20 \times 10^{-1}\ M / 6.0 \times 10^{-2})^{m}$ and m = 2.

Compare the data of Trials 1 and 3, where the concentration of X is constant.

Rate of 3 / rate of 1 = 2 = $(4.0\ M / 2.0\ M)^{n}$ and n = 1. The reaction is 2nd order with respect to X and 1st order with respect to Y and the overall order is m + n = 3. Rate = k $[X]^{2}$ [Y].

(b) To evaluate the rate constant, any one of the three trials can be used.

Rate of 1 = 3.0×10^{-6} M /s = k $(6.0 \times 10^{-2}\ M)^{2}$ $(2.0 \times 10^{-3}\ M)$, from which the rate constant, k, for the third –order kinetics is 0.42 $M^{-2} s^{-1}$.

(c) Rate = 0.42 $M^{-2} s^{-1}$ $(6.0 \times 10^{-3}\ M)^{2} \times (4.0 \times 10^{-4}\ M) = 6.0 \times 10^{-9}$ M /s.

4.3.2 Concentration-Time Equation (Integrated / Instantaneous Rate Law)

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.

Zero - order reaction

A zero-order reaction is a reaction whose rate is independent of change in concentration of the reactant. For the general reaction

$$A \rightarrow \text{Product}$$

the zero order rate law is written as:

$$r = -\frac{\Delta[A]}{\Delta t} = k[A]^o = k$$

The unit of the rate constant in zero order kinetics is, therefore, M/s. Since $\Delta[A] = - k \Delta t$, integrating between the time 0 and t corresponding to concentration $[A]_o$ to $[A]_t$ produces a working equation of:

$$[A]_t = -kt + [A]_o$$

where $[A]_t$ is concentration of A at $t = t$; $[A]_o$ is the concentration of A is at $t = 0$.

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

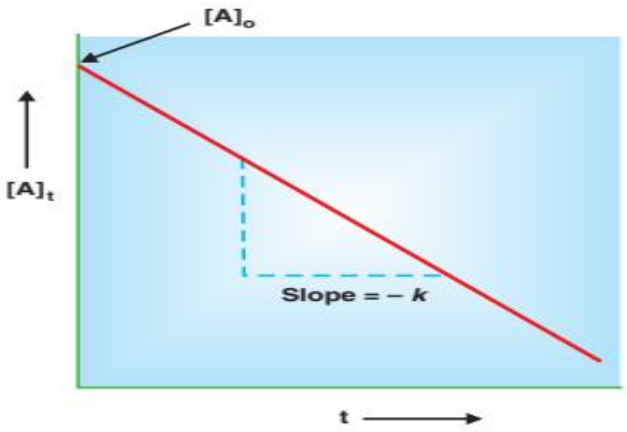


Figure 4.8 A plot of [A] versus t for a zero-order reaction

Example 4.5

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 M s^{-1}. If you begin with a 0.500 M concentration of HI, what is the concentration of HI after 5 seconds?

Solution:

Use the integrated rate law:

$[HI] = [HI]_0 - kt$

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

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

First-order reactions

A first-order reaction is a reaction whose rate depends on the reactant concentration raised to

the first power. In a first-order of the type

$$A \rightarrow Product$$

the rate is: $r = -\frac{\Delta[A]}{\Delta t} = k\,[A]$

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

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

Based on the rate equation, we have:

$$-\frac{\Delta[A]}{\Delta t} = k\,[A], \quad \text{or} \quad \Delta[A] / [A] = -\,k\,\Delta t$$

Using calculus, we get

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

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.

The above equation can be rearranged as follows

$$\ln[A]_t = -kt_0 + \ln[A]_0$$

This has the form of the linear equation $y = mx + b$, in which m is the slope of the graph of the equation. Thus, a plot of ln [A] versus t gives a linear line with a slop of $-k$. Since ln x = 2.303 log x, the equation can be further presented as: $log\,\frac{[A]_t}{[A]_o} = \frac{-kt}{2.303}$

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

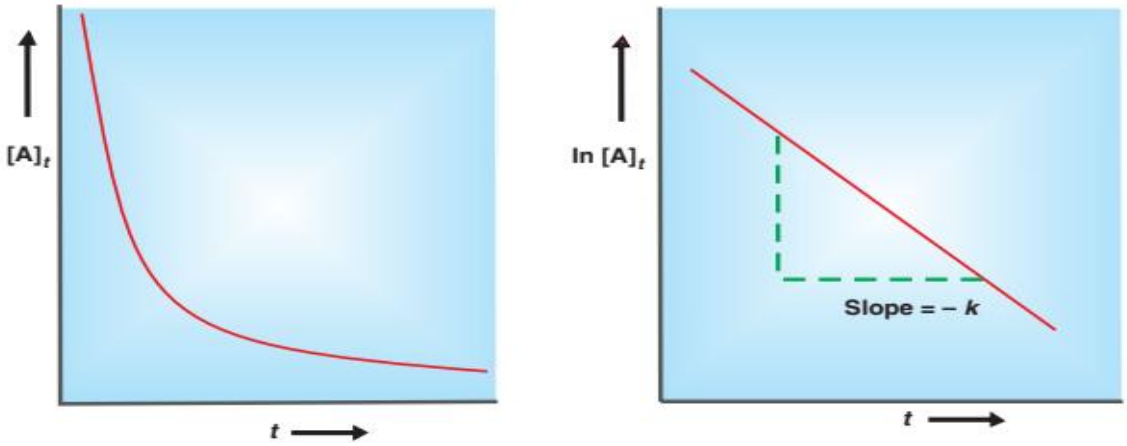


Figure 4.9 Plot for a first-order reaction

Example 4.6

1. The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of 6.7×10^{-4} s^{-1} at 500°C.

$$C_3H_6 \rightarrow CH_3 - CH = CH_2$$

a If the initial concentration of cyclopropane is 0.25 M, what is the concentration of the product after 8.8 minutes?

b How long does it take for the concentration of cyclo propane to decrease from 0.25 M to 0.15M?

c How long does it take to convert 74 % of the starting material?

Solution

a. $\ln \frac{[A]_0}{[A]_{8.8\ min}} = kt$

Solving the equation, we obtain

$$\ln \frac{0.25M}{[A]_{8.8\ min}} = 0.354$$

$$\frac{0.25M}{[A]_{8.8}} = e^{0.354} = 1.42$$

$$[A]_{8.8\ min} = 0.18M$$

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

$t = 7.6 \times 10^2$ s = 13 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, $[A]/[A]_o = 26/100 = 0.26$.

$$t = \frac{1}{K} ln \frac{[A]_0}{[A]} = \frac{1}{6.7 \times 10^{-4} s^{-1}} ln \frac{1.0M}{0.26M}$$

$= 2.0 \times 10^3$ s = 33 minutes

2.The conversion of cyclo propane to propene (the same reaction above but at a different temperature) in the gas phase has rate constant, k, equal to 2.31×10^{-3} per second at 300°C.

a. If the initial concentration of cyclo propane is 0.40 M, what is the concentration each of the reactant and the product after 10 minutes from the start of the reaction?

b. What is the rate of the above reaction at the beginning and after 10 minutes?

c. How long will it take for the initial concentration to drop to 0.04 M?

d. How long will it take for the initial concentration to decrease by 87.5 %?

Solution

The unit of the given rate constant reveals that the reaction is first –order.

(a) For a first order kinetics, $\ln([A]_o/[A]) = kt = 2.31 \times 10^{-3} s^{-1} \times 600$ s = 1.386

Since $[A]_o = 0.40$ M, it follows that $e^{1.386} = 0.40$ M / [A] and the concentration of cyclopropane, [A], after 10 minutes is 0.10 M. The concentration of the product, i.e. propene is 0.40 M – 0.10 M = 0.30 M.

(b) Initial rate = $2.31 \times 10^{-3} s^{-1} \times 0.40$ M = 9.24×10^{-4} M /s.

After 10 minutes, rate = $2.31 \times 10^{-3} s^{-1} \times 0.10$ M = 2.31×10^{-4} M /s

(c) $\ln(0.40/0.04) = 2.31 \times 10^{-3} s^{-1} \times \mathbf{t}$ and t = 1000 s.

(d) When the concentration decreases by 87.5 %, there remains 12.5 % or 0.05 M of cyclo propane and 0.35 M of propene as a product. The time for this condition can be calculated in any of the following two methods.

$\ln(100/12.5) = 2.31 \times 10^{-3} s^{-1} \times \mathbf{t}$, or $\ln(0.40/0.05) = 2.31 \times 10^{-3} s^{-1} \times \mathbf{t}$. In both cases, t = 900 s.

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

$$2\ A \rightarrow \text{Product}$$

$$r = -\frac{\Delta[A]}{\Delta t} = k\,[A]^2$$

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

$$k = \frac{r}{[A]^2} = \frac{M/s}{[M^2} = M^{-1}s^{-1}$$

By using calculus, the integrated law gives:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

The graph of $\frac{1}{[A]}$ versus time gives a linear line with a slope of *k*.

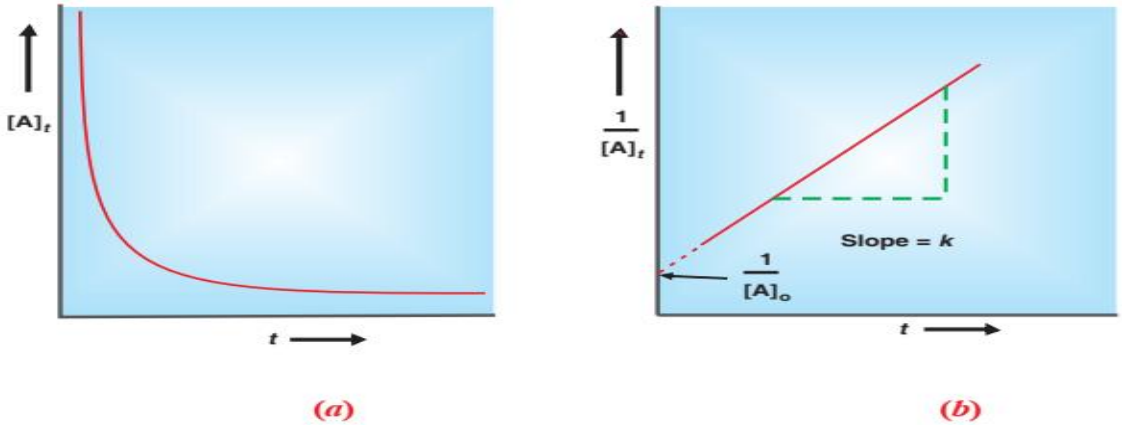


Figure 4.10 Plots for a second-order reaction

Another type of second-order reaction is

$$A + B \rightarrow \text{product}$$

and the rate equation is given by

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

where the reaction is first-order in each of A and 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 4.7

The reaction 2 NOBr (*g*) → 2 NO (*g*) + Br_2 (*g*) is a second order reaction with respect to NOBr; $k = 0.810\ M^{-1}s^{-1}$ at 10°C.

If $[NOBr]_o = 7.5 \times 10^{-3}$M, how much NOBr will be left after a reaction time of 10 minutes?

Solution:

One can solve for the amount of NOBr after 10 minutes by substituting the given data into the integrated rate law for a second-order reaction.

$$\frac{1}{[NOBr]_t} = kt + \frac{1}{[NOBr]_0}$$

$$\frac{1}{[NOBr]_t} = (0.810\ M^{-1}s^{-1}) \times (600\ s) + \frac{1}{7.5 \times 10^{-3} M}$$

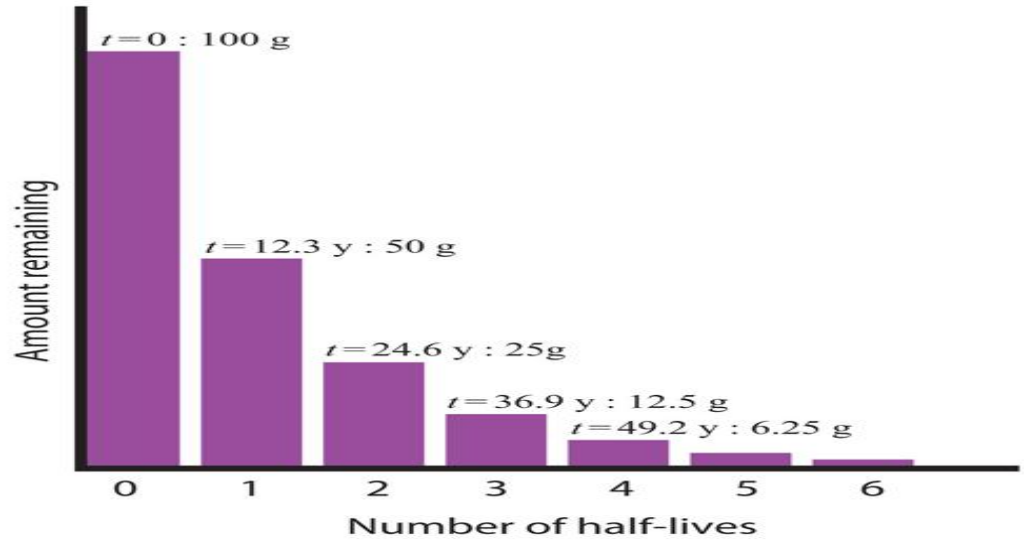
$$\frac{1}{[NOBr]_t} = 6.19 \times 10^{2} M^{-1}$$

$$[NOBr]_t = 1.6 \times 10^{-3} M$$

4.3.3 The Half-life of a Reaction

The half- life time 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 $[A]_o$ to $\frac{1}{2}[A]_o$, *i.e* $[A] = \frac{1}{2}[A]_o$. The half-life of a reaction is designated by the symbol, $t_{1/2}$.

Consider the following example. Suppose we have 100.0 g of tritium (a radioactive isotope of hydrogen). It has a half-life time of 12.3 years. After 12.3 years, half of the sample will have decayed from hydrogen-3 to helium-3 by emitting a beta particle, so that only 50.0 g of the original tritium remains. After another 12.3 years making a total of 24.6 years another half of the remaining tritium will have decayed, leaving 25.0 g of tritium. After another 12.3 years, now a total of 36.9 years another half of the remaining tritium will have decayed, leaving 12.5g.



or

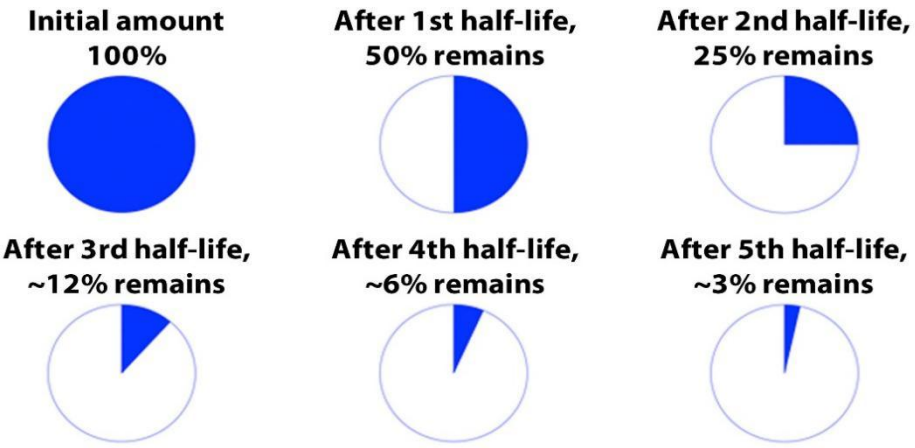


Figure 4.11: Radioactive Decay

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 the equation

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

This gives us

$$\ln \frac{[A]_0}{\frac{1}{2}[A]_0} = k\, t_{1/2} \quad \text{or } \ln 2 = k\, t_{1/2}$$

And solving for $t_{1/2}$ gives

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

It can be noted from the equation that the half-life time of a first-order reaction is independent of the initial concentration of A, $[A]_0$.

For a second-order reaction, the half-life expression is given by the equation

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt \Rightarrow \frac{1}{\frac{1}{2}[A]_o} - \frac{1}{[A]_o} = kt_{\frac{1}{2}}$$

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

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Therefore, the half-life time of a second-order reaction depends inversely on the initial concentration, $[A]_0$, and the rate constant, k.

For zero-order kinetics, the half-life time can be derived in the same manner as:

$$t_{1/2} = [A]_0 / 2k$$

Table 4.3 Summary for the kinetics of zero-, first- and second order reactions

Order	Rate equation	Concentration-time equation	Half-life time
Zero	Rate = k	$[A]_0 - [A] = k\,t$	$[A]_0 /2k$
First	Rate = k[A]	$\ln([A]_0/[A]) = k\,t$	0.693 / k
Second	Rate = $k[A]^2$	$1/[A] = 1/[A]_0 + k\,t$	$1/k[A]_0$

Example 4.8

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

a. Calculate $t_{½}$.

b. Find the concentration of N_2O_5 remaining after $t_{½}$

Solution:

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

b. $ln\,[N_2O_5] = -Kt + ln\,[N_2O_5]_0$

$= (-6.32\,x\,10^{-4}s^{-})(1097\,s) + \ln(0.40)$

$= (-0.693) + (-0.9163) = -1.6096$

Taking the inverse of the natural logarithms of both sides gives the concentration of N_2O_5 remaining after 1.0 hour as:

$[N_2O_5] = 0.1996$ mol/L ≅ 0.20 mol/L.

2.In the aqueous reaction: B (aq) → Products, the concentration of B falls from 1.0 M to 0.50 M in 280 seconds. How long will it take for the initial concentration of B to fall to 0.25 M, if the reaction is:

i) zero –order, **ii**) first –order, and **iii**) second –order, in B?

Solution:

Given: $[B]_o$= 1.0 M, $t_{½}$ = 280 s.

i) Zero –order kinetics: $[B]_o - [B] = k_0 t$, and $k_0 = 1/2t_{½} = 1/560$ M /s.

Therefore, (1.0 – 0.25) M = (1 /560 M /s) t, and t = 420 s. = ($3t_{½}$ /2). This means, the fall in concentration with time is 1.0 M (280 s) 0.50 M (140 s) 0.25 M.

ii) First –order kinetics: $k_1 = 0.693/t_{½} = 0.693/280$ s = 2.475 x 10^{-3} s^{-1}. Therefore, 2.303 log (1.0/ 0.25) = 2.475 x 10^{-3} s^{-1} x t, and t = 560 s = $2t_{1/2}$.

It is obvious that the half –life time of a first –order reaction is constant. Therefore, the time it takes for the reaction to drop from 1.0 M to 0.25 M is two half –lives.

1.0 M (280 s) 0.50 M (280 *s*) 0.25 M; total time = 560 s.

iii) Second –order kinetics: $k_2 = 1.0/(280 \text{ s} \times 1.0 \text{ M}) = 1/280$ M^{-1} s^{-1}.

Therefore, (1.0 /0.25 M) – (1.0 /1.0 M) = t (1 /280) M^{-1} s^{-1}, and t = 840 s = $3t_{1/2}$.

This means, 1.0 M (280 s) 0.50 M (560 s) 0.25 M, total time = 840 s.

Exercise 4.8

1. If a certain first-order reaction has a half-life of 30.0 minutes,

a. Calculate the rate constant for this reaction.

b. How much time is required for this reaction to be 35% complete?

2. For the reaction 2X + Y → Z, the following kinetic data applies.

Expt.	[X]	[Y]	Δ[Z] /Δt
i	4.0	1.0	A
ii	4.0	4.0	2A
iii	1.0	4.0	A

Find the rate law expression (equation).

3. A substance X may decompose by either a first –order or a second –order kinetics. If both have the same half –life time for the same initial concentration X_o, then

(a) what is the ratio of the first –order rate to that of the second –order rate ($Rate_1$ /$Rate_2$) initially?

(b) What is the ratio of first –order to second –order rate at half –life time above?

4. In several experiments on the kinetics of X + Y → Products, the rate doubled on doubling the initial concentration of Y, keeping the concentration of X constant. On

doubling the initial concentration of both X and Y at the same temperature, the rate increased by a factor of 8. What is the rate law / equation?

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. It 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, let us consider the reaction between nitric oxide and oxygen:

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

During this reaction, a substance of formula N_2O_2 was detected in the process. Hence, the product NO_2 is not formed directly from the collision of two NO molecules with an O_2 molecule. Let us assume that the reaction actually takes place via two elementary steps as follows:

$$2NO\ (g) \rightarrow N_2O_2\ (g)$$

$$N_2O_2\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

In the first elementary step, two NO molecules collide to form a N_2O_2 molecule. This event is followed by the reaction between N_2O_2 and O_2 to give two molecules of NO_2. The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:

Elementary step: $NO + NO \rightarrow N_2O_2$

Elementary step: $N_2O_2 + O_2 \rightarrow 2NO_2$

Overall reaction: $2NO + O_2 \rightarrow 2NO_2$

Species such as N_2O_2 are called intermediates because they appear in the mechanism of the reaction (that is, in elementary steps) but not in the overall balanced equation.

4.4.1 Molecularity of an Elementary Reaction

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. It may be noted that molecularity is a theoretical concept and it cannot be zero, negative, fractional, infinite and imaginary because it involves a certain number of particles.

Table 4.4: Common types of elementary reactions

Elementary reaction	Molecularity
A → products	Uni- molecular
2A → products	Bi- molecular
A+B → products	Bi- molecular
2A+B → products	Ter- molecular
A+B+C → products	Ter- molecular

4.4.2 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 one 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 NO_2 with F_2 is given by the equation:

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

The experimentally determined rate law is: Rate = $K[NO_2][F_2]$, that is first order with respect to each reactant and second order over all. The proposed reaction mechanism is:

$NO_2 + F_2 \xrightarrow{k_1} NO_2F + \cdot F$ slow

$NO_2 + \cdot F \xrightarrow{k_2} NO_2F$ fast

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:

$NO_2 + F_2 \rightarrow NO_2F + \cdot F$

$NO_2 + \cdot F \rightarrow NO_2F$

Overall equation: $2NO_2 + F_2 \rightarrow 2NO_2F$

So, the first requirement is satisfied. The formation of •F in the first step occurs slower than its reaction with NO_2 to form NO_2F in the second step. Thus, the rate of formation of NO_2F in the second step is controlled by the rate of formation of •F in the first step. The overall rate cannot be faster than that of the slowest step.

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

Example 4.8

Di nitrogen pent oxide, N_2O_5, decomposes in first –order kinetics as follows.

$2\ N_2O_5\ (g) \leftrightarrows 4\ NO_2\ (g) + O_2\ (g)$

Explain if the following mechanism is consistent with the above reaction.

(i) $N_2O_5 \leftrightarrows NO_2 + NO_3$ (fast equilibrium)

(ii) $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$, rate constant = k_2

(iii) $NO_3 + NO \rightarrow 2\ NO_2$, rate constant = k_3 $k_2 << k_3$

Solution

It is necessary to check if the three elementary reactions (steps) add –up to give the overall balanced equation. If the fast equilibrium equation, Step (i), is multiplied by 2 and added to the remaining two equations, we obtain the final balanced equation.

It is given that the second step is the slowest and hence the rate determining step.

$$\text{Rate} = k_2\ [NO_2]\ [NO_3]$$

However, NO_3 does not appear in the reaction equation. It is one of the intermediates. Hence, it is necessary to re –express the predicted rate law so as to eliminate this intermediate. For this purpose, we make use of Step (i).

$K_{equilibrium} = [NO_2]\ [NO_3] / [N_2O_5]$ and $[NO_3] = K_{equilibrium}\ [N_2O_5] / [NO_2]$

Rate = k_2 [NO_2] K $_{equilibrium}$ [N_2O_5] / [NO_2], which gives Rate = k_2 K $_{equilibrium}$ [N_2O_5]. Since the product of two constants gives another constant, Rate = K [N_2O_5]. The final rate equation together with Step (ii), i.e. the slowest step, proves that the above reaction is first order and bi-molecular.

Exercise 4.9

1. Determine the molecularity of the following elementary reactions:
   a. $NH_4NO_2 \rightarrow N_2 + 2H_2O$
   b. $O_3 + NO \rightarrow NO_2 + O_2$
   c. $2\,NO + O_2 \rightarrow 2\,NO_2$
2. What is the difference between
   a. Order and molecularity?
   b. Catalyst and intermediate?
3. The reaction $NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$ is thought to occur by the following mechanism: the experimentally rate low is Rate = $k[NO_2]^2$

   Step 1: $NO_2\,(g) + NO_2\,(g) \rightarrow NO_3\,(g) + NO\,(g)$ Slow

   Step 2: $NO_3\,(g) + CO\,(g) \rightarrow NO_2\,(g) + CO_2\,(g)$ Fast

   Check whether the proposed reaction mechanism is acceptable or not.
4. A hypothetical reaction denoted by $X_2 + Y_2 \rightarrow 2XY$, proceeds through the following mechanism.

   i) $X_2 \leftrightarrows 2X$ ... (fast) ii) $X + Y_2 \longrightarrow XY + Y$... (Slow)

   iii) $X + Y \longrightarrow XY$. What is the molecularity and overall order of the reaction?

UNIT SUMMARY

- *Chemical kinetics is the study of the rates and mechanisms of chemical reactions*
- *Chemical kinetics is developed from the law of mass action, formulated in 1864 by Peter Waage and Cato Guldberg. The law of mass action states that the speed of a chemical reaction is proportional to the amount of reactants.*
- *A chemical reaction occurs when atoms, molecules or ions undergo effective and energetic collision.*
- *Factors that affect the rate of a reaction include concentration of reactants and other species, surface area, the nature and physical state of the reactants, temperature, catalysts, pressure for gases.*
- *The larger the activation energy, the slower is 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 bi-molecular (the most common) have two reactant species, while uni-molecular reactions have only one and ter- molecular 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 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. However, overall order is always ≥ 0.*
- *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 change in reactant concentration.*

- *The half-life time of a first order reaction is independent of the initial reactant concentration, whereas half-life of second order reaction depends inversely 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 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.*
- *A positive catalyst increases the rate of a chemical reaction but can be recovered unchanged at the end of a reaction.*

Check List

Key terms of the unit

- *Average rate*
- *Bi -molecular*
- *Catalyst*
- *Collision theory*
- *Concentration - time equation*
- *Elementary reaction*
- *Energy profiles of exothermic and endothermic reactions*
- *Half -life of a reaction*
- *Instantaneous rate*
- *Order of reaction*
- *Molecularity*
- *Rate constant*
- *Rate equation or rate law*
- *Rate of a reaction*
- *Rate-determining step*
- *Reaction mechanism*
- *Surface area*
- *Ter molecular*
- *Transition state theory*
- *Uni molecular*

REVIEW EXERCISE

Part I: Multiple Choices

1. Which of the following processes is faster than the others?

A. Rusting of iron B. Transition of mono clinic sulfur to its rhombic form

C. Formation of ammonia from its elements D. Burning of sulfur in oxygen

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. Study of its spontaneity

3. For the chemical reaction $H_2 + Br_2 \rightarrow 2HBr$, what can be said of the relative rates of consumption of the reactants when compared to the formation of product?

A. HBr will be produced at half the rate that bromine is consumed.

B. HBr will be produced at the same rate that bromine is consumed.

C. Br_2 and H_2 will be consumed at different rates.

D. HBr will be produced at twice the rate that bromine is consumed

4. The proposed steps for a catalyzed reaction between X^{4+} and Z^{+} are represented below.

Step 1: $X^{4+} + Y^{2+} \rightarrow X^{3+} + Y^{3+}$

Step 2: $X^{4+} + Y^{3+} \rightarrow X^{3+} + Y^{4+}$

Step 3: $Y^{4+} + Z^{+} \rightarrow Z^{3+} + Y^{2+}$

The catalyst in this process is:

A. X^{4+} B. X^{3+} C. Y^{4+} D. Y^{2+}

5. Which of the following is false about activation energy, *Ea*?

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 a positive integer.

D. All chemical reactions require activation energy.

6. Which of the following is true about the factors influencing rate of reaction?

A. As surface area of reactants increases, the rate of the 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. The reaction between H_2 and CO to produce methanol is 2nd order with respect to H_2 and 1st order with respect to CO. What change will occur in the rate of reaction if the concentration of each reactant is doubled?

$2H_2(g) + CO(g) \rightarrow CH_3OH(g)$

A. 2-fold increase
C. 3-fold increase
B. 8-fold increase
D. 4-fold increase

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. Which of the following statements is correct?

A. Reactions with high activation energies are fast.
B. Collisions between reactant particles with any energy succeed in forming products.
C. A catalyst can decrease the rate of a chemical reaction by changing the pathway.
D. Fast reactions produce more product than slow reactions.

10. The greatest increase in the rate for the reaction between X and Z with rate $r = k\,[X][Z]^2$ will be caused by:

A. doubling the concentration of Z
C. doubling the concentration of X
B. tripling the concentration of X
D. lowering the temperature

11. 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 rough approximation, a 10°C temperature increase halves the rate.
D. Rate does not depend on concentration in zero order reaction.

12. Which of the following statements is false about order of a reaction?

A. Order of a reaction can be a fractional number.
B. Order of a reaction is an experimentally determined quantity.
C. The order of a reaction is equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
A. The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

13. Consider the Arrhenius equation given below and mark the correct option.

$$k = A\, e^{-Ea/RT}$$

A. Rate constant increases exponentially with increasing activation energy and decreasing temperature.

B. Rate constant decreases exponentially with decreasing activation energy and decreasing temperature.

C. Rate constant increases exponentially with decreasing activation energy and decreasing temperature.

D. Rate constant increases exponentially with decreasing activation energy and increasing temperature

14. Which choice matches with the integrated rate law given below?

$$1/[A]t = kt + 1/[A]o$$

A. Zero order kinetics where a plot of $1/[A]t$ versus t will be a linear line with slope = k

B. First order reaction where a plot of $1/[A]t$ versus t will be a linear line with slope = k

C. First order reaction where a plot of $1/[A]t$ versus t will be a linear line with slope = -k

D. Second order kinetics where a plot of $1/[A]t$ versus t will be a linear line with slop = k

15. For a first-order reaction of different substances Z and X

$Z \rightarrow B$, $t_{1/2} = 30.0$ min

$X \rightarrow Y$, $t_{1/2} = 60.0$ min

This means that

A. Certain number of grams of Z will react twice as fast as the same number of grams of X.

B. A certain number of grams of X will react twice as fast as the same number of grams of Z.

C. The rate constant for $Z \rightarrow B$ is lower than the rate constant of $X \rightarrow Y$.

D. 3mol of Z will react more rapidly than 3mol of X.

16. For a reaction that is first order with respect to [D] and second order with respect to [E], which of the following will result in no change to the overall reaction rate?

A. Doubling [D] and halving [E]

B. Doubling [E] and halving [D]

C. Doubling [D] and Doubling [E]

D. Increasing [D] by a factor of four and halving [E]

17. A reaction is first order with respect to [X] and second order with respect to [Y]. When both [X] and [Y] are 0.20 M, the rate of the reaction is 8.00×10^{-3} M/min. The value of the rate constant with its units is

A. 1.00 $M\ min^{-1}$

B. 2.00 $M^{-1}\ min^{-1}$

C. 1.00 $M^{-2}\ min^{-1}$

D. 2.00 $M^{-2}\ min^{-1}$

18. For the reaction given below, the following experimental rate results apply.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(g)$$

Expt.	$[BrO_3^-]_0$	$[Br^-]_0$	$[H^+]_0$	Rate
1	0.10	0.10	0.10	8×10^{-4}
2	0.20	0.20	0.10	3.2×10^{-3}
3	0.20	0.10	0.10	1.6×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Which of the following is **not** true regarding the above data?

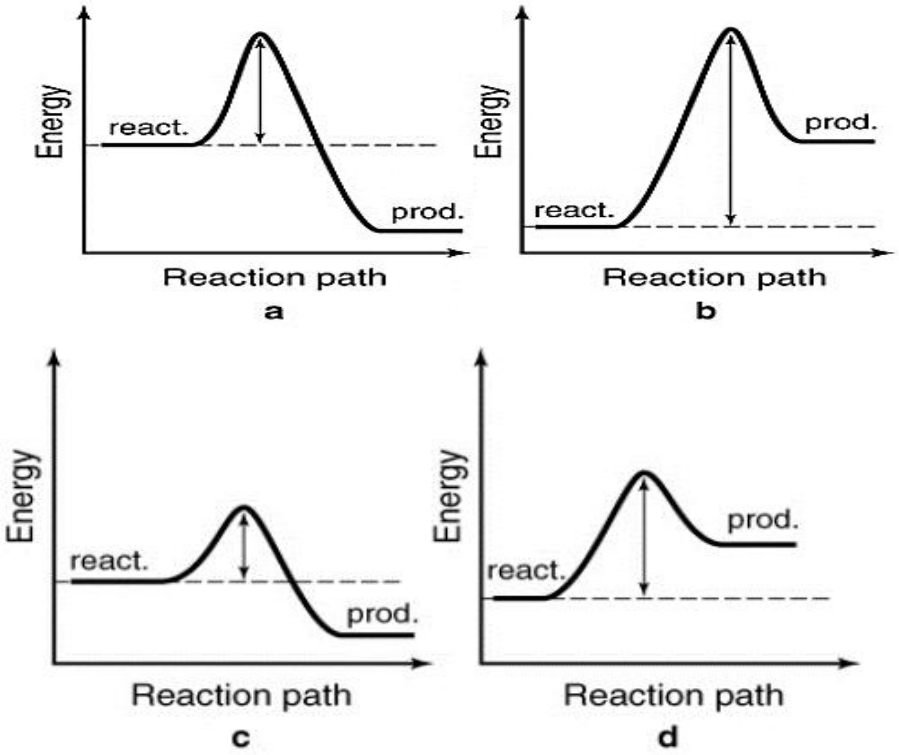
A. The reaction is first order with respect to BrO_3^- and Br^-.

B. Doubling the concentration of H^+ doubles the rate

C. Doubling concentrations of both BrO_3^- and Br^- increases the rate four times.

D. The rate of reaction depends on the initial concentrations of BrO_3^- , Br^- and H^{+1}

19. The energy profiles for four different reactions are shown. Which reaction requires the most energetic collisions to reach the transition state?



20. A sample of radioactive cadmium has a half-life of 15 days. If you have a sample that originally weighed 40 g and later weighs 2.5 g, how much time elapsed between the initial and final masses?

A. 600 days B. 100 days C. 60 days D. 45 days

21. In an experiment, a sample of $NaClO_3$ decomposed by first order kinetics in 48 min. How long would this reaction have taken if the sample had been heated 20 °C higher?

A. 6 min B. 12 min C. 16 min D. 24 min

22. The gaseous reaction $2\ X + Y \rightarrow 2\ Z$, shows a decrease in pressure from 120 torr to 100 torr in 10 minutes. The rate of appearance of Z, at the same time, is

A. 2 torr /min B. 1.0 torr /min C. 10 torr /min D. 4 torr /min

23. A reaction has rate law expression given by Rate = $k[X]^{3/2}[Y]^{-1/2}$. If initial concentrations of both X and Y are increased four times, the rate of the reaction

A. increases 16 times B. decreases four times

C. Increases two times D. increases four times

24. Which of the following reactions is faster than the others under similar conditions?

A. $H_2\ (g) + I_2\ (g) \longrightarrow 2HI\ (g)$

B. $AgNO_3\ (aq) + KI\ (aq) \longrightarrow AgI\ (s) + KNO_3\ (aq)$

C. $CH_4\ (g) + I_2\ (g) \longrightarrow CH_3I\ (g) + HI\ (g)$

D. $2KClO_3\ (s) \longrightarrow 2KCl\ (s) + 3O_2\ (g)$

Part II: Answer the following questions as indicated

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

$$2\ NO + Cl_2 \rightarrow 2\ NOCl$$

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

(i) What is the order of the reaction with respect to each of NO and Cl_2?

(ii) What is the overall order of the reaction?

26. What are pseudo uni molecular reactions? Write an example of such a reaction.

What are clock reactions?

27. The concentration of A during a reaction of the type: $A + 2B \rightarrow$ products, changes according to the data in the table.

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

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

28. For a reaction, the time required for the 10% completion is 20 minutes and 20% completion is 40 minutes, what is the order of the reactions?

29. Zero-order reaction is 25% complete in 30 seconds. What time does it take for 50% completion?

30. In first order reaction, the concentration of reactant decreases from 800 mol/dm^3 to 50mol/dm^3 in 2 x 10^4 s. find the rate constant.