

Chemical Kinetics



C11CH8



Learning Objectives

Upon completion of this topic, learners will:

- Discuss the Rate Laws
- Demonstrate the reaction mechanism
- Discuss Activation Energy
- Explain the concept of Collision Theory

The extent to which a reaction will proceed can be determined from **chemical equilibrium** whereas the feasibility of a chemical reaction can be predicted by thermodynamics ($\Delta G < 0$). The knowledge of **free energy** change of a reaction however gives us no idea about the rate and the factors controlling the rate of a reaction.

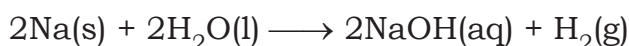
How quickly a chemical reaction occurs is a crucial factor in how the reaction affects its surroundings. Therefore, **knowing the rate of a chemical reaction is integral to understanding the reaction.**

*All these questions can be answered by the branch of chemistry known as **chemical kinetics**.*

The kinetic studies deals with the study of reaction rates or velocity or speed of a reaction. It describes the conditions by which the reaction rates can be altered. The kinetic data is used to predict the mechanism governing the reactions.

Types of Reaction Based on Rates

1. **Very fast Reactions:** These are instantaneous reaction. It is very difficult to find rate of such reactions



2. **Very slow reactions:** These reactions occur at a very slow rate and take years to complete. e.g. rusting of iron, weathering of rock.

3. **Moderately slow reactions:** Their rate is between very fast and very slow reactions.

8.1. RATE OF A CHEMICAL REACTION

The **rate of a chemical reaction** is the speed or velocity at which a reaction takes place.

It may be expressed in any of the following ways:

- (i) *The rate of decrease in concentration of any one of the reactant, or*
- (ii) *The rate of increase in concentration of any one of the product at a given temperature.*

For **example**, for a hypothetical reaction,



If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

Time required for change in conc.,

$$\Delta t = t_2 - t_1$$

Change in concentration of reactants,

$$\Delta[R] = [R]_2 - [R]_1$$

Change in concentration of products,

$$\Delta[P] = [P]_2 - [P]_1$$

Rate of disappearance of reactant R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = - \frac{\Delta[R]}{\Delta t}$$

Rate of appearance of product P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = + \frac{\Delta[P]}{\Delta t}$$

The expressions for rate in terms of reactants carry a negative sign.

Significance of Negative Sign

The negative sign in first expression does not mean that the rate is negative, rather it indicates the decrease in concentration of the reactant. As we know that with passage of time the concentrations of reactants

decrease, therefore, the change in concentration, $\Delta[R] = (\text{Final conc.} - \text{Initial conc.})$ will have a negative value. Since the rate of a reaction is a positive quantity, thus, to get a positive rate we put a -ve sign in the rate expression.

Note: The square brackets in the above expressions are used to express molar concentration.

Thus, rate of reaction = Rate of disappearance of R = Rate of appearance of P = $-\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$

Mathematical Expression for Rates of Reaction

1. Reactions Involving Same Stoichiometric Coefficients of all the Reactants and Products

Let us consider the gaseous reaction between nitrogen dioxide and carbon monoxide.



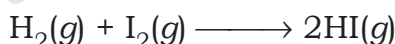
In this case, as the reactants and products appear in **same stoichiometric proportions**, therefore, the rate of the reaction may be expressed in terms of rate of disappearance of nitrogen dioxide or carbon monoxide or **alternatively**, by the rate of appearance of carbon dioxide or nitric oxide whichever may be convenient.

Thus, rate of reaction is mathematically given as,

$$= -\frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{CO}]}{\Delta t} = +\frac{\Delta[\text{CO}_2]}{\Delta t} = +\frac{\Delta[\text{NO}]}{\Delta t}$$

2. Reactions Involving Different Stoichiometric Coefficients of Reactants and Products

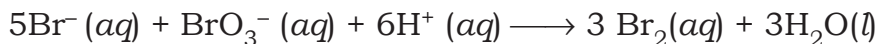
Let us take an example of simple reaction,



Now, in the present case, as the reactants (H_2 and I_2) and products (HI) have **different stoichiometric coefficients**, this means that for every mole of H_2 or I_2 reacting, we get two moles of HI. Thus, the rate of formation of HI will be twice the rate of disappearance of H_2 or I_2 . *In such cases, we divide the rate of change of concentration by the stoichiometric coefficient of reactants or products involved in the reaction.* Thus, we have

$$\begin{aligned} \text{Rate of reaction} &= -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} \\ &= +\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} \end{aligned}$$

Similarly, for the reaction,



$$\begin{aligned} \text{Rate of reaction} &= \frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{Br}_3^-]}{\Delta t} \\ &= -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} \\ &= +\frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = +\frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} \end{aligned}$$

Units of Rate of Reaction

The units of rate of reaction are units of concentration divided by units of time. As concentration of substance is expressed in mol L^{-1} and the time is expressed in **seconds (s)** or **minutes (min)** or **hours (h)** then, the units for reaction rate will be **moles litre⁻¹ sec⁻¹ ($\text{mol L}^{-1} \text{s}^{-1}$)** or **moles litre⁻¹ min⁻¹ ($\text{mol L}^{-1} \text{min}^{-1}$)** or **moles litre⁻¹ hr⁻¹ ($\text{mol L}^{-1} \text{h}^{-1}$)** respectively.

For gaseous reactions, whose concentrations are given in terms of partial pressures, the units of rate of reaction will be **atm min⁻¹** or **bar min⁻¹** or **atm s⁻¹** or **bar s⁻¹** or **atm h⁻¹** or **bar h⁻¹**.

Interconversion of units. The partial pressure can also be converted into units of concentration, *i.e.*, moles per litre, by using the following equation:

$$pV = nRT \quad \text{or} \quad p = \frac{n}{V} RT = cRT \quad \text{or} \quad c = \frac{p}{RT}$$

$$\text{Rate in terms of change in pressure} = \frac{\Delta(p)}{\Delta t}$$

If $\Delta(p)$ and Δt are known then

rate in terms of conc. units (mol L^{-1})

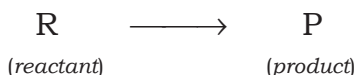
$$= \frac{\text{rate in terms of pressure units}}{RT}$$

8.2. AVERAGE RATE AND INSTANTANEOUS RATE

Average Rate

The **average rate** of a reaction is defined as the *rate of change of concentration per unit time*. It is calculated by dividing the total change

in concentration of any one of the reactant or product by the total time taken to do so. For a reaction.



Average rate

$$\begin{aligned} &= \frac{\text{Change in concentration in given time}}{\text{Time taken}} \\ \text{i.e.,} \quad &= -\frac{\Delta R}{\Delta t} \quad \text{or} \quad = +\frac{\Delta P}{\Delta t} \quad \text{or} \quad = \frac{\Delta x}{\Delta t} \end{aligned}$$

The Average rate of reaction changes with passage of time hence to know the true rate, it is expressed as instant rate.

Instantaneous Rate

The **instantaneous rate** of a reaction is defined as the *decrease in concentration of any one of the reactants or increase in concentration of any one of the product at a particular instant of time for a given temperature.*

Mathematically, the instantaneous rate may be written as,

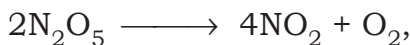
$$r_{\text{inst}} = -\frac{d[R]}{dt} \quad \text{or} \quad +\frac{d[P]}{dt} \quad \text{or} \quad = \frac{dx^*}{dt}$$

Here, dt is the infinitesimally small time interval and dx is the change in concentration of any of the species in time interval dt .

To **sum up**, the expression $-\frac{\Delta[R]}{\Delta t}$ or $\frac{\Delta[P]}{\Delta t}$ or $\frac{\Delta x}{\Delta t}$ becomes $-\frac{d[R]}{dt}$ or $\frac{d[P]}{dt}$ or $\frac{dx}{dt}$ as Δt approaches zero. The average rate approaches the instantaneous rate as Δt becomes smaller and approaches zero, *i.e.*,

$$\left(\frac{\Delta x}{\Delta t}\right)_{\Delta t \rightarrow 0} = \frac{dx}{dt}$$

For **example**, for the gaseous reaction,



the **instantaneous rate** will be expressed as,

$$r_{\text{inst}} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}.$$

Experimental Determination of Reaction Rate

The rate of a reaction is determined by measuring the concentration of any of the reactants or products after definite intervals of time. The common practice to find the change in concentration is, to withdraw a small amount of reaction mixture (2 cm^3 to 5 cm^3) at different intervals of time. The withdrawn sample is then placed in the freezing mixture of ice and sodium chloride. It is called **freezing of reaction**. The concentration at the given interval is then determined by a suitable method. On the basis of kinetic data, a graph is plotted between **concentration** and **time** (Fig. 8.1) and the rate is calculated, *i.e.*, average rate or instantaneous rate, as illustrated in next topic.

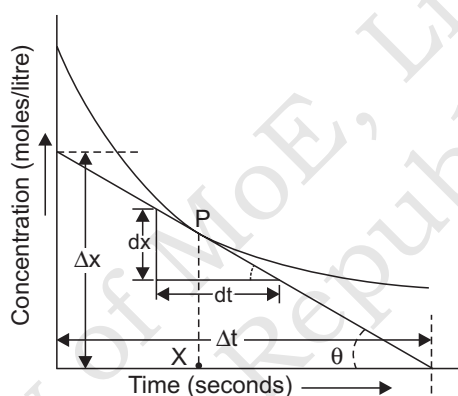
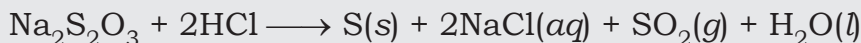


Fig. 8.1. Determination of rate of a reaction.

EXPERIMENT 1

Aim: To study the effect of concentration on the rate of reaction.

Theory: According to the **law of mass action**, *rate of a chemical reaction is directly proportional to the product of the molar concentration of the reactants*. In other words the rate of reaction increases with the increase in the concentration of the reactants. The effect of concentration of reactants on rate of a reaction can be studied easily by the reaction between sodium thiosulphate and hydrochloric acid.



The insoluble sulphur, formed during the reaction, gives a milky appearance and makes the solution opaque. Therefore, rate of the reaction can be studied by measuring the time taken to produce enough sulphur to make some mark invisible on a paper kept under the conical flask in which the reaction is carried out.

Requirements: Stop-watch, two burettes and five conical flasks (100 ml).

Materials Required: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution and 1 M HCl solution.

Procedure:

1. Wash the conical flasks with water and label them as 1, 2, 3, 4 and 5 respectively.
2. With the help of a burette, add 10, 20, 30, 40 and 50 ml of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to the flasks 1, 2, 3, 4 and respectively.
3. Now add 40, 30, 20 and 10 ml of distilled water to the flask 1, 2, 3 and 4 respectively so that volume of solution in each flask is 50 ml.
4. Take 10 ml of 1 M HCl in a test tube with the help of a burette.
5. Add 10 ml of hydrochloric acid taken in a test tube to the conical flask No. 1 containing 10 ml of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 40 ml of distilled water and start the stop-watch. When half of the hydrochloric acid solution has been added. Shake the contents of the conical flask and place it on the tile with a cross mark as shown in Fig. 8.2.
6. Go on observing from top to downwards in the flask and stop the stop-watch when the cross mark just becomes invisible. Note down the time.
7. Repeat the experiment by adding 10 ml of 1 M HCl to flasks 2, 3, 4 and 5 record the time taken in each case for the cross to become just invisible.

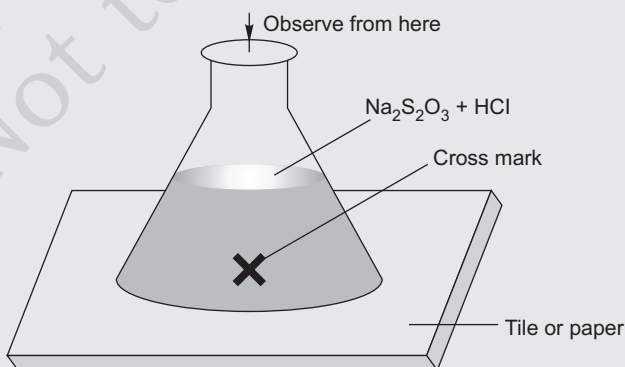


Fig. 8.2. Study of rate of reaction

Observations:

Flask No.	Volumes of $\text{Na}_2\text{S}_2\text{O}_3$ solution in ml	Volume of water in ml	Total volume of solution in ml	Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution	Volume of 1 M HCl (ml)	Time taken for cross to become just invisible (t)	$\frac{1}{t}$ (s^{-1})
1.	10	40	50	0.02 M	10s	
2.	20	30	50	0.04 M	10s	
3.	30	20	50	0.06 M	10s	
4.	40	10	50	0.08 M	10s	
5.	50	0	50	0.10 M	10s	

Plotting of graph: Plot a graph between $\frac{1}{t}$ (in seconds) and the conc. of sodium thiosulphate by taking $\frac{1}{t}$ along ordinate (vertical axis) and conc. of $\text{Na}_2\text{S}_2\text{O}_3$ along abscissa (horizontal axis). It should be a straight sloping line.

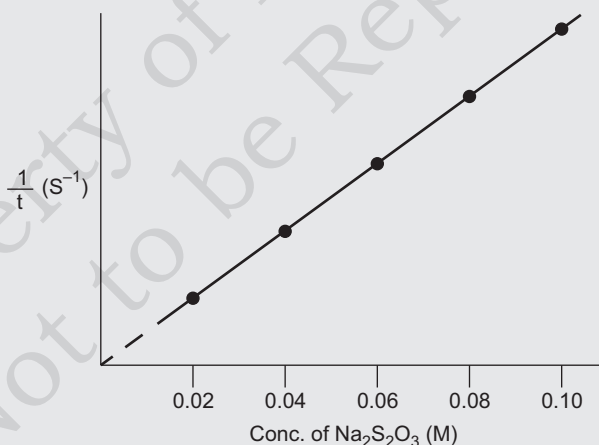


Fig. 8.3. A graph of conc. $\text{Na}_2\text{S}_2\text{O}_3$ vs $\frac{1}{t}$.

Result: From the graph, it is clear that $\frac{1}{t}$ is directly proportional to the conc. of $\text{Na}_2\text{S}_2\text{O}_3$ solution. But $\frac{1}{t}$ is a direct measure of rate of the reaction, therefore, rate of the reaction between $\text{Na}_2\text{S}_2\text{O}_3$ and HCl is directly proportional to the conc. of $\text{Na}_2\text{S}_2\text{O}_3$ solution taken. Hence,

rate of this reaction is directly proportional to the concentration of $\text{Na}_2\text{S}_2\text{O}_3$, which is one of the reactants.

Note: It may be noted that the reaction rate also increases when the amount of sodium thiosulphate is kept constant but the concentration of hydrochloric acid is increased.

Precautions:

1. The apparatus must be thoroughly clean. If the same conical flask is to be used again and again, it should be thoroughly washed with conc. HNO_3 and then with water.
2. Measure the volumes of sodium thiosulphate solution, hydrochloric acid and distilled water very accurately.
3. Use the same tile with the same cross-mark for all observation.
4. Complete the experiment at one time only so that there is not much temperature variation.
5. Start the stop-watch immediately when half of the hydrochloric acid solution has been added to sodium thiosulphate solution.
6. View the cross-mark through the reaction mixture from top to bottom from same height for all observations.

EXPERIMENT 2

Aim: To study the effect of change in temperature on the rate of reaction.

Theory: The rate of a chemical reaction depends to a great extent upon temperature. The rate of reaction increases with increase in temperature. Increase in temperature increase kinetic energy of the molecules. Therefore, the fraction of molecules having energy greater than its threshold energy increases which results in the increase in number of effective collisions per second. It has been observed that in most of the cases *for every 10°C rise in temperature, the rate of the reaction becomes almost double*. The rate of reaction between sodium thiosulphate and hydrochloric acid increase with increase in temperature.

Requirements: Conical flask (250 ml) measuring cylinders (50 ml and 5 ml), stop-watch, thermometer, tripod stand, wire-gauze and burner.

Materials Required: 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution, 1 M HCl , distilled water and conc. HNO_3 .

Procedure:

1. Take 50 ml of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution in a 100 ml conical flask and note its temperature with the help of a thermometer.

2. Add 10 ml of 1 M HCl to it and start the stop-watch immediately when half of the hydrochloric acid solution has been added.
3. Shake the contents of the flask gently and place it on the tile with a cross-mark.
4. Observe the cross-mark from the top and note the time taken for the mark to become just invisible.
5. Empty the flask and clean it thoroughly with conc. HNO_3 and then with water.
6. Take again 50 ml of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ in conical flask and heat it so that the temperature of the solution become $(T + 10^\circ)\text{C}$.
7. Remove the flask from the tripod-stand and add 10 ml of 1 M HCl to it and start the stop-watch.
8. Shake the contents gently and place it on the tile having a cross-mark.
9. Note the time taken for the mark to become just invisible.
10. Repeat the experiment at $(T + 20)^\circ\text{C}$, $(T + 30)^\circ\text{C}$ and $(T + 40)^\circ\text{C}$ temperatures and record the observations as given below.

Other examples: Volume of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution taken each time = 50 ml

Volume of 1 M HCl added each time = 10 ml.

S. No.	Temperature	Time taken for cross to become just invisible (t)	$\frac{1}{t}$
1.			
2.			
3.			
4.			
5.			

Plotting of Graph: Plot a graph by taking $\frac{1}{t}$ along the ordinate (vertical axis) and temperature along the abscissa (horizontal axis).

Result: Rate of reaction between sodium thiosulphate and hydrochloric acid increases with the increase in temperature.

Precautions: Same as in experiment 1.

8.3. FACTORS INFLUENCING RATE OF A REACTION

The rate of reactions is influenced by the following factors:

- (i) Concentration of the reactants,
- (ii) Temperature of the reactants,
- (iii) Nature of the reacting substances,
- (iv) Presence of catalyst, and
- (v) Exposure to radiations.

8.4. DEPENDENCE OF RATE ON CONCENTRATION

When a chemical reaction occurs, the reactants change over to products. It is observed that with the passage of time the concentrations of reactants decrease while those of products increase. It is graphically shown in Fig. 8.4.

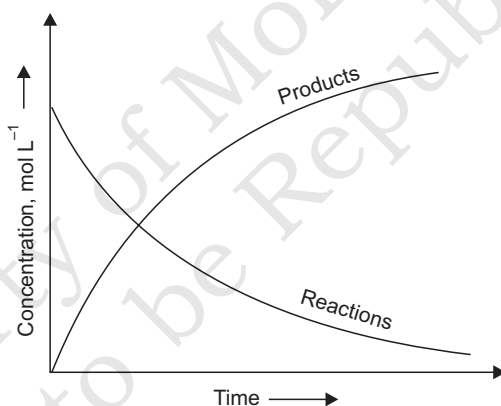


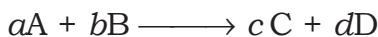
Fig. 8.4. Time dependence of the concentrations of reactants and products in a reaction.

Now, if we assume that other factors are constant then the rate of a chemical reaction decreases with the decrease in concentration of the reactants. Conversely, rates generally increase when reactant concentrations increase. For **example**, we find that a piece of wood burns at a much faster rate in oxygen than in air. It is because of higher concentration of oxygen in the former.

The representation of the rate of reaction in terms of concentration of reactants is known as **rate law**. It is also called **rate equation**.

Rate Expression and Rate Constant

Consider a general reaction



(Here, a , b , c and d are stoichiometric coefficients)

The rate equation for the reaction is

$$\begin{aligned} \text{Rate} &\propto [A]^x [B]^y \\ &= k [A]^x [B]^y \end{aligned} \quad \dots(1)$$

or

$$-\frac{d[R]}{dt} = k [A]^x [B]^y \quad \dots(2)$$

Note: x and y may or may not be equal to stoichiometric coefficients a and b .

The equation (1) is called **rate law** or **rate expression**. Thus, *rate law is the mathematical expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.*

The equation (2) is known as **differential rate equation**.

The constant k is a proportionality constant and is known as **rate constant** or **velocity constant** or **specific reaction rate**.

If the concentration of all reacting species is taken as unity then,

$$\text{rate} = k \quad [\because [A] = [B] = 1 \text{ mol L}^{-1}]$$

Hence, **rate constant** is defined as *the rate of reaction when the concentration of each reactant is taken as unity*. It is for this reason that the rate constant is also called **specific reaction rate**.

Deriving the Rate Expression from Data

There are many different ways and methods to determine the rate expression for a reaction. One experimental method that is used to determine rate laws of chemical reactions is the **method of initial reaction rate**.

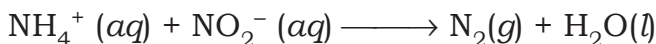
Initial Rate Method

The initial rate of a reaction is the instantaneous rate determined just after the reaction begins ($t \approx 0$).

In this method the basic idea is to determine the instantaneous rate before the initial concentrations of reactants have changed significantly. Several experiments are carried out using different initial concentrations, and the initial rate is determined for each experimental run. The results

are then compared to see how the initial rate depends on the initial concentrations. On the basis of kinetic data the rate law is determined.

Let us **illustrate** the method of initial rates using the following equation:



The general form of the rate law for this reaction is,

$$\text{rate} = - \frac{d[\text{NH}_4^+]}{dt} = k [\text{NH}_4^+]^m [\text{NO}_2^-]^n$$

On the basis of experimental studies, the following table giving initial rates is formulated from three experiments involving different concentration of reactants.

Experiment	Initial $[\text{NH}_4^+]$ (mol L ⁻¹)	Initial $[\text{NO}_2^-]$ (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

The above data is used to determine the values of the rate exponents, m and n . The strategy is to find two experiments in which only one of the initial concentrations is changing while the other is kept constant. Accordingly, we can find the dependence of the rate on the change in initial concentration.

In the given kinetic data table, in experiments 1 and 2, the initial concentration of NH_4^+ remains the same but the initial concentration of NO_2^- doubles. Using the rate expression, we get

$$\text{rate}_{\text{exp 1}} = k [0.1]^m [0.005]^n \quad \dots(i)$$

$$\text{rate}_{\text{exp 2}} = k [0.1]^m [0.010]^n \quad \dots(ii)$$

Dividing eqn. (ii) with eqn. (i)

$$\frac{\text{rate}_{\text{exp 2}}}{\text{rate}_{\text{exp 1}}} = \frac{k [1.0]^m [0.010]^n}{k [1.0]^m [0.005]^n} = \left[\frac{0.010}{0.005} \right]^n = (2)^n$$

or
$$\frac{2.70 \times 10^{-7}}{1.35 \times 10^{-7}} = (2)^n$$

or
$$2 = (2)^n. \text{ Hence } n = 1$$

In a similar manner the results of experiment 2 and 3 yield the ratio.

$$\frac{\text{rate}_{\text{exp 3}}}{\text{rate}_{\text{exp 2}}} = \frac{5.40 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{k [0.2]^m [0.01]^n}{k [0.1]^m [0.01]^n} = (2)^m$$

or $2 = 2^m$, Hence $m = 1$

Conclusion

- The value of exponents, $m = 1$ and $n = 1$
- The rate expression of the reaction is therefore

$$\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

- The differential form of this rate expression is given as

$$-\frac{d[\text{R}]}{dt} = k[\text{NH}_4^+][\text{NO}_2^-]$$

Characteristics of Rate Constant

- The value of rate constant gives an idea about the rate of a reaction, *i.e.*, greater is the value of rate constant faster is the reaction.
- Each reaction has a definite value of the rate constant at a particular temperature.
- The value of rate constant depends on the temperature *i.e.*, changes with change in temperature.
- The value of rate constant is independent of the concentration of reacting species.
- The units of rate constant depend on the order of reaction.

Difference Between Rate of Reaction and Rate Constant

The important differences between the **rate** of the reaction and **rate constant** of the reaction are being given as follows in tabular form.

<i>Rate of Reaction</i>	<i>Rate Constant of Reaction</i>
1. It is the speed at which the reactants are converted into the products at any moment of time.	1. It is constant of proportionality in the rate law expression.
2. It depends upon the concentration of reactant species at that moment of time.	2. It refers to the rate of reaction at the specific point when concentration of every reacting species is unity.
3. It generally decreases with the progress of reaction.	3. It is constant and does not depend on the progress of the reaction.

8.5. RATE LAW OR RATE EQUATION

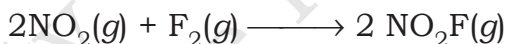
A very curious question arises here that how could we know the rate equation or rate expression of a complex reaction? Which of the steps in the mechanism can be chosen as rate determining step. It must be noted that the determination of the rate law expression of a complex reactions is not an easy task. Its determination requires.

- *Information about the number of moles of reactants consumed during the reaction.*
- *A knowledge of the intermediates produced during the reaction and how much they accumulate during the early period of reaction.*
- *The rate data to be supplemented by different techniques so that the certain elementary steps are verified to the maximum.*

In complex reactions the rate expression written on the basis of the overall balanced equation has no significance at all. The rate expression for such complex reactions can be written on the basis of the experimental evidence like detection of the presence of some short lived intermediates, etc.

Illustration

Let us consider the gaseous reaction,



- The rate expression on the basis of balanced equation is:
rate = $k [\text{NO}_2]^2 [\text{F}_2]$
- The rate expression on the basis of experimental results is:
rate = $k [\text{NO}_2] [\text{F}_2]$

“A mathematical expression written in terms of concentration of reactants, which actually influence the rate, is called Rate Law.”

8.6. ORDER OF REACTION

It is an important parameter for every chemical reaction. It is always determined experimentally and cannot be written from the balanced chemical equation.

It may be defined as, *“the sum of powers or exponents to which the concentration terms are raised in the rate law expression.”*

For a hypothetical reaction,



if the rate law expression for this reactions is,

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

- The **order** of the above reaction is equal to (**m + n**).
- The powers or exponents, *i.e.*, *m* and *n* have no relation to the stoichiometric coefficients *a* and *b* of the balanced chemical equation.
- Order of the reaction with respect to A is *m* and that with respect to B is *n*.
- If the sum of the power is equal to *one*, the reaction is called **first order reaction**.
- If the sum of the powers is **two or three**, the reaction is **second order or third order** reaction respectively.

The order of a reaction can also be zero or fractional.

First Order Reaction

First order reaction can be defined a chemical reaction in which the rate of reaction is directly proportional to the concentration of only one reactant. If the concentration of that reactant is doubled the rate of reaction is also doubled.

In other words the sum of power to which the concentration terms are raised in the rate law equation is one then reaction is first order reaction.

$$\text{Rate of reaction} = k[A]^1 \Rightarrow k[A]$$

Second Order Reaction

Second order reaction is defined as a chemical reaction which depend on either the concentration of two first order or the concentration of one second order reactant.

In other words second order reactions are those reactions where in the sum of exponent in the corresponding rate law of the chemical reaction is equal to 0.2.

The rate of second order reaction is either as

$$r = k[A]^2 \text{ or as } r = k[A] [B]$$

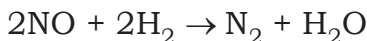
8.7. REACTION MECHANISM

Reaction mechanism is the sequence of elementary steps (reaction) by which the overall chemical reaction occurs leading to the formation of final product. Reaction mechanism is the sequential account of each

step describing details of electron movement, energies during bond dissociation and bond formation and rates of transformation of reactants and products. The first test of reaction mechanism is that it must give the experimental rate law, but it does not guarantee the correctness of rate mechanism.

Some reaction occur in two steps.

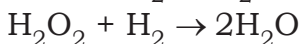
For example:



First step.



Second step.



Here the first step is intermediate step.

The product formed in first step (intermediate step) is consumed in next elementary step so that it does not appear as final product. The first being the slow step determines the rate. The rate determining step is termolecular hence the overall order of reaction is 3.

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

8.8. INTEGRATED RATE EQUATIONS

We have already learnt that the concentration dependence of rate is called **differential rate equation**. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point 't' in concentration vs time plot. This makes it difficult to determine the rate law and hence the order of the reaction. *In order to avoid this difficulty, we can integrate the differential rate equation. The integrated rate equation gives a relation between directly measured experimental quantities, i.e., concentrations at different times and the rate constant.*

For a general reaction, $a\text{A} + b\text{B} \longrightarrow \text{Products}$ the differential rate law equation is,

$$\frac{dx}{dt} = k[\text{A}]^a [\text{B}]^b$$

Zero Order Reaction

A reaction is zero order if its rate is independent of the concentration of reactants or the rate of reaction is proportional to zero power of the concentration of reactants. Consider a general zero order reaction:



For this reaction,

$$\text{Rate} = - \frac{d[R]}{dt} = k[R]^0 \quad \dots(8.1)$$

(Here, $[R]$ is the concentration of reactant and k is the rate constant of zero order reaction)

As any quantity raised to power zero is unity

$$\therefore \text{Rate} = - \frac{d[R]}{dt} = k \times 1$$

or $d[R] = - kdt$

Integrating both sides, we get

$$\int d[R] = - k \int dt$$

$$[R] = - kt + I \quad \dots(8.2)$$

where, I is the constant of integration

$$\text{At } t = 0, \quad [R] = [R]_0,$$

(where $[R]_0$ is initial concentration of reactant).

$$\text{Hence,} \quad I = [R]_0$$

Substituting this value in equation (8.2), we get

$$[R] = - kt + [R]_0 \quad \text{or} \quad kt = [R]_0 - [R]$$

or $k = \frac{1}{t} [[R]_0 - [R]] \quad \dots(8.3)$

Significance of Integrated Rate Equation

- (i) All zero order reactions obey the equation 8.3.
- (ii) The value of k can be evaluated if $[R]_0$ and $[R]$ at time t are known.
- (iii) The expression, $[R] = - kt + [R]_0$, is comparable to straight line equation, $y = mx + C$, and therefore the value of k can be evaluated by **graphical method**.

The above equation can be written as:

$$[R] = [R]_0 - kt$$

On plotting a graph of $[R]$ vs. t we get a straight line as shown in the figure below. The slope of the line is given as:

$$\text{slope} = - k$$

The intercept on the concentration axis = $[R]_0$

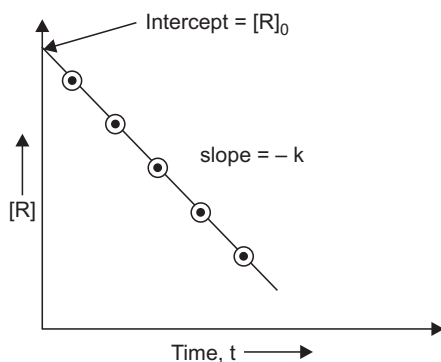


Fig. 8.5

First Order Reaction

Let us assume a simple hypothetical first order reaction as,



If the initial concentration of R is $[R]_0$, k is the rate constant and $[R]$ is conc. at time t then the differential form of this first order reaction will be

$$\frac{-d[R]}{dt} = k[R]$$

Rearranging the equation, we get

$$\frac{d[R]}{[R]} = -k dt \quad \dots(8.4)$$

On integrating equation (8.4),

$$\int \frac{d[R]}{[R]} = - \int k dt$$

We get, $\ln [R] = -k t + \text{constant} \quad \dots(8.5)$

$$\left[\text{Integral of } \frac{d[R]}{[R]} \text{ is } \ln [R] \right]$$

At $t = 0$, $[R] = [R]_0$

therefore eqn. 8.5 reduces to form

$$\ln [R]_0 = -k \times 0 + \text{constant}$$

or $\text{constant} = \ln [R]_0$

Substituting this value in Eqn. (8.5), we get

$$\ln [R] = -k t + \ln [R]_0$$

or $k t = \ln [R]_0 - \ln [R]$

$$k t = \ln \frac{[R]_0}{[R]} = \ln [R]_0 - \ln [R] \quad \dots(8.6)$$

Changing the above expression to common log ($\ln_e x = 2.303 \log_{10} x$) we get,

$$k t = 2.303 \log \frac{[R]_0}{[R]}$$

or
$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \dots(8.7)$$

Equation (8.7) is the **Integrated Rate Equation** for the first order reaction.

Physical significance of k. It represents the fraction of the reactant decomposed per unit time of constant concentration. For example, if k for a given reaction is 0.00674 s^{-1} . It means that $0.00674 \times 100 = 0.674\%$ of substance would dissociate per second provided initial concentration is kept constant.

8.9. HALF LIFE OF A REACTION

It is defined as *the time during which the concentration of the reactants is reduced to half of the initial concentration or it is the time required for the completion of half of the reaction*. It is denoted by $t_{1/2}$ or $t_{0.5}$

Half Life of Zero Order Reaction

The integrated equation for zero order reaction is;

$$[R] = [R]_0 - kt$$

Now at $t_{1/2}$,

$$[R] = \frac{[R]_0}{2}$$

$$\therefore \frac{[R]_0}{2} = [R]_0 - kt$$

or
$$kt_{1/2} = [R]_0 - \frac{[R]_0}{2} = \frac{[R]_0}{2}$$

or
$$t_{1/2} = \frac{[R]_0}{2k} \quad \dots(8.8)$$

From the eqn. 8.8 it is clear that the half life of a zero order reaction is directly proportional to initial concentration.

i.e.,

$$t_{1/2} \propto [R]_0$$

The plot of $t_{1/2}$ vs. $[R]_0$ is shown below:

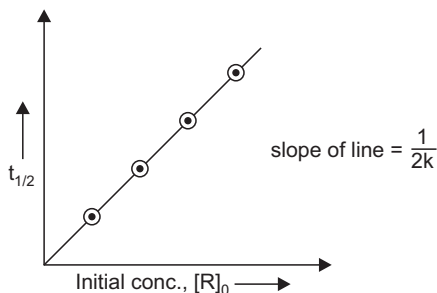


Fig. 8.6

Half Life of First Order Reaction

For first order reaction, we know that

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \text{ or } t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

when

$$t = t_{1/2} \text{ then } [R] = \frac{[R]_0}{2},$$

therefore,

$$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{0.693}{k} \quad [\because \log 2 = 0.3010]$$

The above expression does not carry conc. term hence the *half life period or half change time for first order reaction does not depend upon initial concentration of the reactants. Similarly, the time required to reduce the concentration of the reactant to any fraction of the initial concentration for the first order reaction is also independent of the initial concentration.*

Plots of Half Lives vs. Initial Concentration

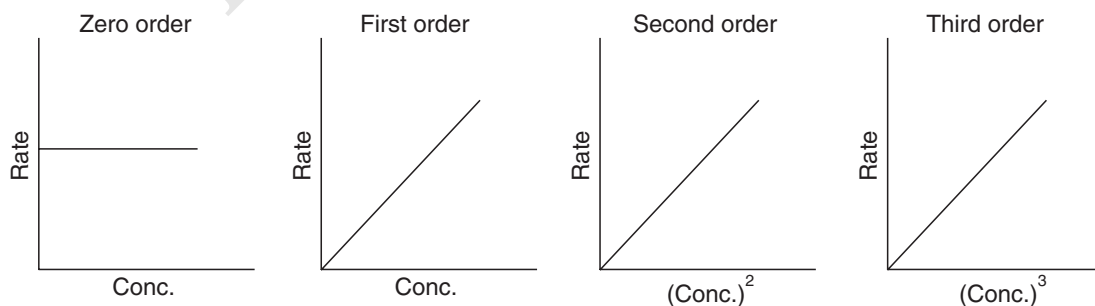


Fig. 8.7

8.10. ACTIVATION ENERGY

A reaction can occur when molecules of reactants collide with each other to form an unstable intermediate. The intermediate exists for a very short time and then breaks up to form product molecules.

The energy required to form this intermediate, called **activated complex (C)**, is known as **activation energy (E_a)**. In a given sample of gas, at a given temperature, all the molecules of the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of individual molecule with precision, Ludwig Boltzmann and James Clerk Maxwell used statistics to predict the behaviour of large number of molecules. According to them, the distribution of kinetic energy may be described by **plotting the fraction of molecules (N_E/N_T) with a given kinetic energy (E) vs kinetic energy** (Fig. 8.8).

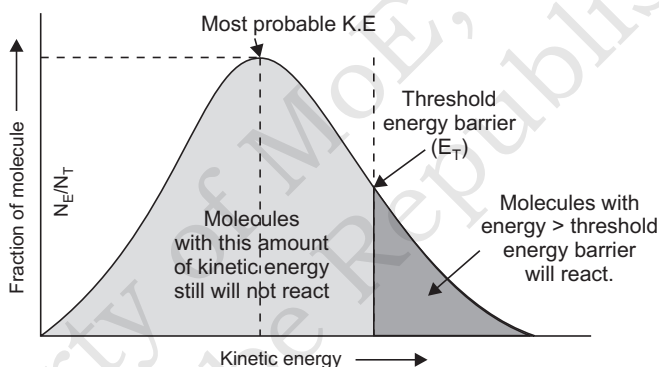


Fig. 8.8. Distribution of energies of gaseous molecules.

Here, N_E is the number of molecules with energy E and N_T is the total number of molecules.

The peak of the curve corresponds to the **most probable kinetic energy** i.e., kinetic energy of maximum fraction of molecules. Only those collisions result in the formation of products which possess energy equal to or more than the certain minimum energy called **threshold energy**. Collisions of the molecules possessing energy less than threshold energy do not form products. In between the reactants and the products there is an energy barrier which must be crossed before the reactants are converted into products. The energy required for crossing this energy barrier is called **activation energy**. It is defined as,

“The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them

to cross over the energy barrier between reactants and products is called Activation energy”.

$$\text{Activation energy} = (\text{Threshold energy}) \\ - (\text{Average energy of the reactants})$$

or

$$E_a = E_T - E_R$$

The idea of activation energy and the energy barrier involved in a reaction is represented graphically in Fig. 8.9.

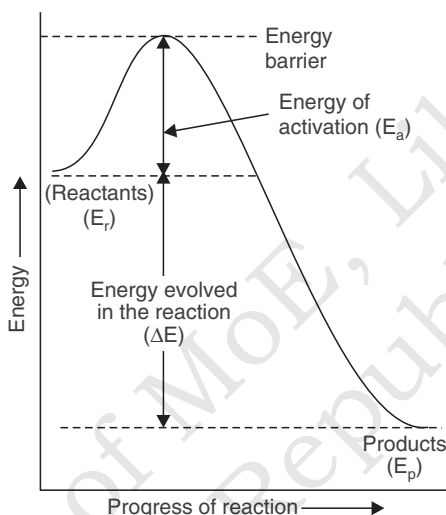


Fig. 8.9. Illustration of activation energy and energy barrier involved in a reaction.

Each reaction has a definite value of E_a and this decides the fraction of total collisions which are effective. Obviously,

- (i) if the activation energy for a reaction is low, large number of molecules can have this energy and the **fraction of effective collision, f** , will be large. Such a reaction proceeds at high rate.
- (ii) if the activation energy is high, then **f** will be small and the reaction may be quite slow.

Activated Complex or Transition State

In a chemical reaction certain bonds are broken and certain new bonds are formed. The breaking of bonds requires absorption of energy whereas the formation of bonds results in the release of energy.

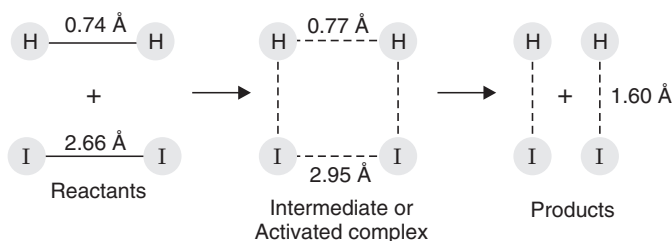


Fig. 8.10. Formation of activated complex during the reaction of H_2 and I_2 from HI .

For example, in the reaction of hydrogen with iodine to form hydrogen iodide, when a molecule of hydrogen approaches that of iodine, $\text{H}-\text{H}$ and $\text{I}-\text{I}$ bonds start breaking and $\text{H}-\text{I}$ bonds start forming. In the beginning, breaking of bonds predominates and therefore, energy of the system starts increasing till it reaches a maxima (corresponding to threshold energy). After this, the energy starts decreasing because the process of bond formation predominates and finally leads to the product hydrogen iodide. **The arrangement of atoms corresponding to energy maxima (threshold energy) is called transition state or activated complex.** In transition state, the system has partial reactant character and partial product character as shown in Fig. 8.10 and Fig. 8.11.

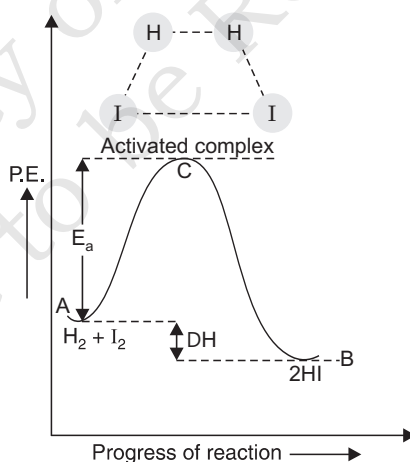


Fig. 8.11. Transition state or activated complex.

The difference between energy of the transition state and energy of the reactants is equal to activation energy.

$$E_{\text{transition state}} - E_{\text{reactants}} = E_{\text{activation}}$$

The difference of energy between reactants (E_R) and products (E_P) at constant temperature and pressure is called enthalpy of reaction *i.e.*, ΔH .

Explanation of Effect of Temperature

Let us now consider the effect of increase in temperature on the number of effective collisions (f).

When the temperature increases the kinetic energy of molecules increases (\because K.E. \propto T) therefore, the maximum of the energy distribution curve gets flattened and shifts towards higher energy value *i.e.*, shifts to right as there is now greater proportion of molecules with much higher energies. On the basis of probability consideration Fig. 8.12 is drawn to give the energy distribution curves at temperatures T_1 and T_2 (where $T_2 = T_1 + 10$). A close examination of the curves in the graph clearly reveals that the fraction of the molecules possess higher kinetic energy *i.e.*, energy greater than threshold energy, as indicated by shaded portion becomes almost double and therefore **the rate of reaction almost doubles for 10° rise of temperature.**

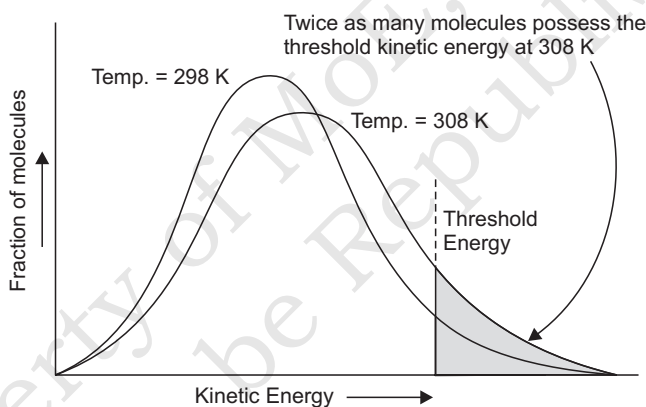


Fig. 8.12. Energy distribution at different temperatures.

Thus increase in the rate of reaction with increase in temperature is mainly due to increase in number of collisions **which are energetically** effective.

Effect of Catalyst

A catalyst is a substance that alters rate of a chemical reaction without itself being permanently chemically changed.

Never state things like “it doesn’t react, just speeds it up”.

It must take part in the reaction and it must change chemically, albeit on a temporary basis. A catalyst provides a different ‘pathway’ or mechanism that makes the bond breaking processes (or other electronic changes in the reactants) occur more readily. In general,

- A catalyst speeds up a reaction, but it must be involved 'chemically', however temporarily, in some way, and is continually changed and reformed as the reaction proceeds.
- Catalysts work by providing an alternative reaction pathway of lower activation energy.

Thus, the function of a catalyst is to lower down the activation energy i.e., greater is the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. **In the presence of a catalyst, the reaction follows a path of lower activation energy.** Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. The energy profile diagram for the catalysed and uncatalysed reactions are as shown in the Fig. 8.13. Where dotted curve represents the progress of catalysed reaction and solid curve represents the uncatalysed reaction.

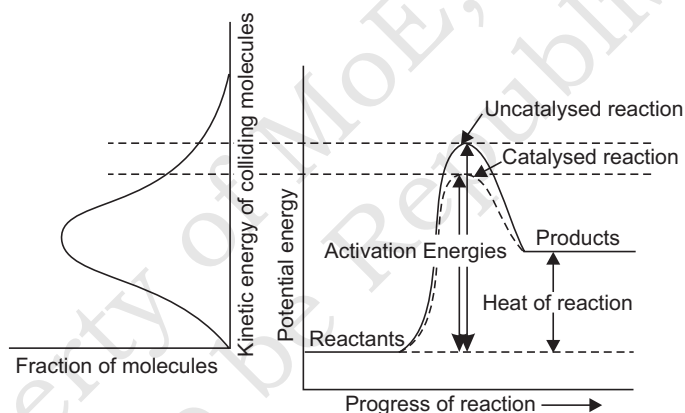
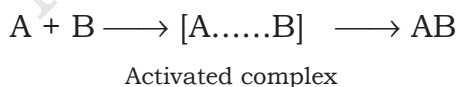


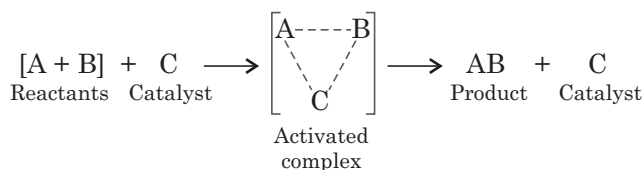
Fig. 8.13. Potential energy curves for catalysed and uncatalysed reactions.

For a general reaction of the type, $A + B \longrightarrow AB$ the course of uncatalysed and catalysed reaction may be represented as:

(a) *Uncatalysed reaction:*



(b) *Catalysed reaction:*



Though the catalyst increases the rate of the reaction, yet it does not effect the state of equilibrium in case of reversible reactions. It is because the activation energy for the forward reaction and backward reaction is reduced to the same extent.

EXPERIMENT 3

Aim: To study the effect of catalyst on the rate of reaction.

Theory: A catalyst speeds up the rate of reaction. A catalyst lowers the activation energy (the energy required to initiate the reaction) hence facilitate the reaction.

Requirements: Conical flask, delivery tube, measuring cylinder, trough, plug, $\text{H}_2\text{O}_2(l)$, catalyst (manganese (IV) oxide), lead (III) oxido, iron (III) oxide and copper (II) oxide).

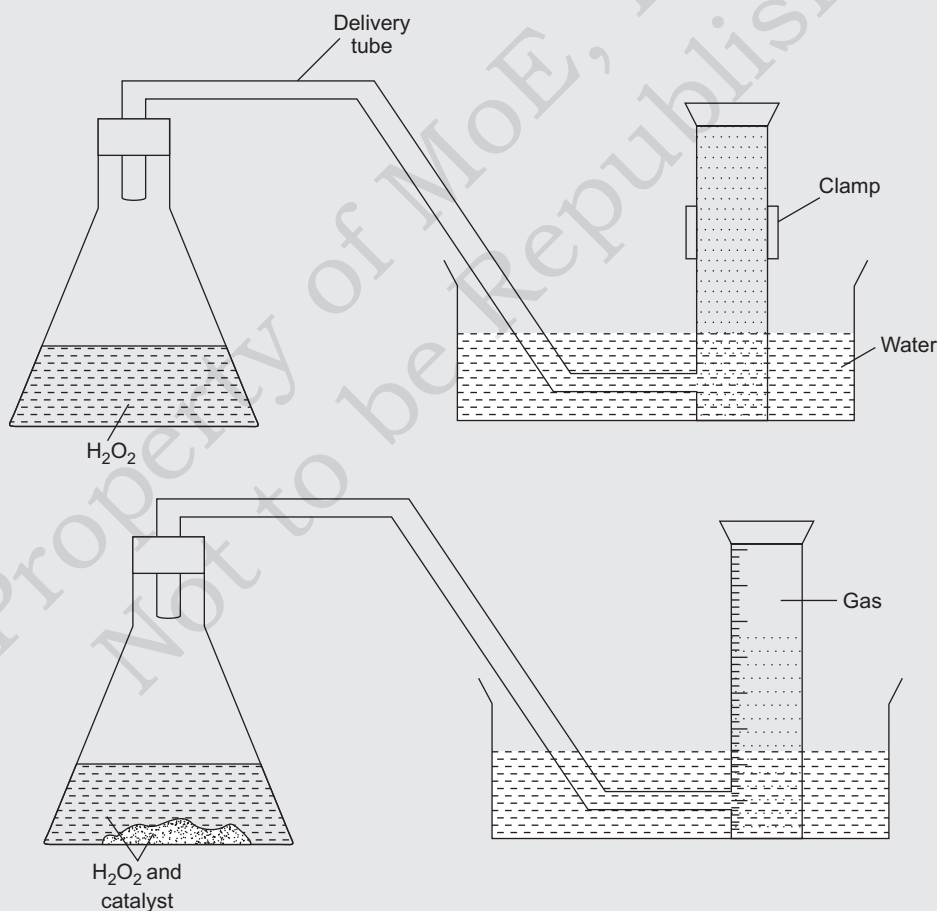


Fig. 8.14. Effect of catalyst on reaction rate

Procedure:

1. Add H_2O_2 in a conical flask.
2. Connect conical flask to a measuring cylinder put inverted in a water trough.
3. Add a catalyst in to conical flask and close the plug.
4. Measure the volume of gas produced using a fixed interval of time, in the measuring cylinder.
5. Repeat the experiment with different catalysts and compare the volume produced, hence the rate of reaction.

Precautions:

1. Plug should be tightly put on the mouth of conical flask
2. Conical flask and water trough should be put at same level.

Result:

1. Volume of gas collected after 2 minutes will be different with different catalyst.
2. Compare the data and plot the data for different catalysts on the same graph.

8.11. COLLISION THEORY OF CHEMICAL REACTIONS

Though, Arrhenius equation is applicable under a wide range of circumstances but **collision theory**, which was developed by Max Trautz and William Lewis in 1916–18, provides a greater insight into the energetic and mechanistic aspects of reactions. *It is based on kinetic theory of gases.* According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. Thus, the reaction rate shall be dependent upon:

(i) Collision frequency (Z) (ii) Effective collisions and (iii) Activation energy.

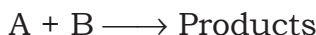
Postulates of Collision Theory

(i) A reaction occurs on collision of two molecules only if they possess a certain minimum amount of energy in excess of the normal energy of molecules.

(ii) The minimum energy which molecules must possess before collision should be equal to or greater than the activation energy.

Expression for Rate Constant of a Bimolecular Reaction

Say we have an elementary bimolecular reaction



According to collision theory the reaction takes place as a result of collisions between A and B. **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z_{AB}).** As all the collisions between A and B are not effective therefore, the rate of reaction is equal to the rate of collisions per unit volume per unit time multiplied by the fraction of collisions that have sufficient relative kinetic energy to overcome the energy barrier, *i.e.*, molecules with energies equal to or greater than E_a . Thus, the rate constant (or rate) is given as:

$k \propto$ rate of collisions or frequency of collisions ($Z_{AB}) \propto$ energy factor (given by Boltzmann factor, $e^{-E_a/RT}$)

Thus, the rate of a reaction would be mathematically expressed as:

$$\text{Rate} = Z_{AB} \cdot e^{-E_a/RT} \quad \dots(8.9)$$

The above equation predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The *reason could be that all the collisions between A and B will not lead to reaction even if the energy requirement is satisfied. It is because the colliding molecules should also have proper orientation.* In simple words all colliding molecules having sufficient energy but no proper orientation will bounce back without any reaction.

Similarly, it can be predicted that the, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 8.15. **The proper orientation of reactants molecules leads to bond formation whereas improper orientation makes them simply bounce back and no products are formed.**

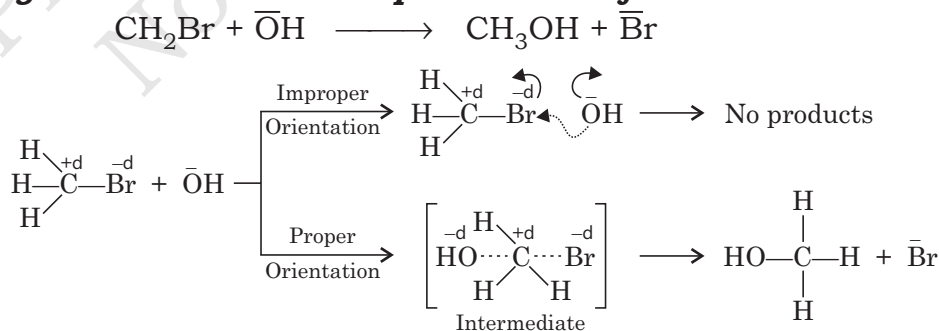


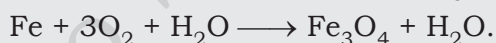
Fig. 8.15. Diagram showing molecules having proper and improper orientation.

ASSIGNMENTS/EXERCISES**1.** Describe the speed of certain natural reactions

- (a) explosions (b) food decay
(c) rusting of iron (d) ripening of fruits

Students can be explained following topics in the laboratory with the help of some example demonstration of the following natural reactions.

- (a) **Explosions:** Explosions are the conclusion reactions of explosive chemicals like TNT (Trinitrotouline). Explosive chemicals when undergo rapid oxidation with the production of large quantity of gases. The shock waves produced by expanding gases cause much damage with lots of sound and heat.
- (b) **Food decay:** The food kept for long time at a temperature range of 25–40°C smells foul and looks rotten making it unsuitable for eating. This food decay may be due to light, oxygen, heat, humidity bacterial growth, protozoa, fungi, like yeasts and moulds. Food decay can be identified by change in colour, change in texture, unpleasant odour or undesirable taste. Food can be prevented from decay by any means which stops on control the growth of germs like bacterial fungi etc. Freezing, boiling. Using preservatives (as for pickles and fish), by adding excess sugar (james, jellies, murabbas etc.) and dehydration are the ways to protect fruits from decaying.
- (c) **Rusting of Iron:** Rusting is slow oxidation that occurs on the surface of iron in the presence of oxygen and moisture resulting in the formation of plucky brown layer that accumulates on the iron surface. It results in formation of oxide (Fe_3O_4).



- (d) **Ripening of fruits:** Ripening of fruits is a process in which fruit attains more sweatiness, desirable colour and flavour and become palatable in nature. On ripening level of ethylene increases in fruits. During ripening fruit flash, softens, sugar content rises, acid level reduced because of formation of esters from organic acids. The production of ethelene in fruits causes increase in production of ethelene. So ethylene has autocatalytic effect in ripening of fruits.

SUMMARY

- **Rate of Reaction:** It is the rate of change of concentration of any of the reactant or product with time at any particular moment of time.
- **Average Rate:** The rate of reaction measured over a long time interval is called average rate. It is given as $\Delta x/\Delta t$.

- **Instantaneous Rate:** It is the rate of a reaction at a given instant of time *i.e.*, $\frac{\Delta x}{\Delta t}$ (average rate) becomes $\frac{dx}{dt}$ when Δt approaches zero.
- **Initial Rate:** The rate at the beginning of a reaction when the conc. have not changed appreciably.
- **Law of Mass Action:** The rate of a reaction is directly proportional to the product of conc. of reactants with each term raised to power number of times it is present in a balanced equation at a given temperature.
- **Rate Constant (k):** It is the rate of the reaction when the concentration of each of reacting species is unity. It is also called *velocity constant* or *specific reaction rate* of the reaction.
- **Rate Law:** The mathematical expression based on experimental fact, which describes the reaction rate in terms of concentrations of reacting species. It cannot be written from the balanced equation.
- **Integrated Rate Equation:** The differential rate equations which are integrated to give a relationship between rate constant and concentrations at different times.
- **Order of Reaction:** The sum of the exponents of the concentration terms in the experimental rate law of reaction. It can be zero, 1, 2, 3 or and any fractional value.
- **First Order Reaction:** A reaction in which the rate of reaction is directly proportional to the conc. of reacting substance, *i.e.*,
 $r = k[A]$
or $kt = 2.303 \log [A]_0/[A]$
- **Half-life Period of Reaction ($t_{1/2}$):** The time taken for the concentration of reactants to be reduced to half of their initial concentration.
- **Activation Energy (E_a):** The additional energy required by reacting species over and above their average PE to enable them to cross the energy barrier between reactants and products.
- **Catalyst:** A substance which enhances the rate of a reaction.
- **Mechanism of Reaction:** The sequence of elementary steps leading to overall stoichiometry of a reaction.
- **Threshold Energy:** The minimum energy that a reacting species must possess in order to undergo effective collisions.

- **Collision Theory:** A chemical reaction takes place due to collisions between reacting molecules. For a bimolecular reaction, $\text{Rate} = Z_{AB} \cdot e^{-E_a/RT}$. Here Z is collision frequency and $e^{-E_a/RT}$ is fraction of molecules with energy equal to or greater than E_a .



EVALUATION

I. Multiple Choice Questions

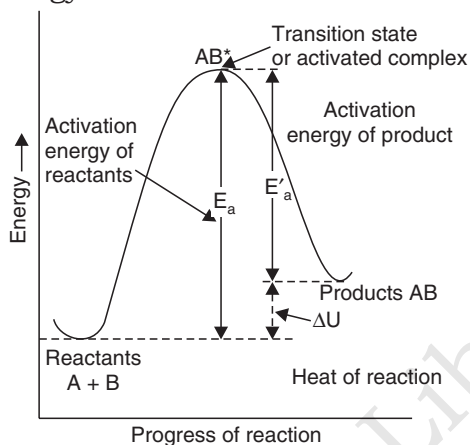
1. The rate of a chemical reaction can be expressed in
 - (a) grams per mole
 - (b) energy consumed per mole
 - (c) volume of gas per unit time
 - (d) moles formed per liter of solution
2. The addition of a catalyst to a reaction causes
 - (a) an increase in the Gibb's energy of the reaction.
 - (b) a decrease in the enthalpy of the reaction.
 - (c) a change in the activation energy of the reaction.
 - (d) an increase in the equilibrium constant of the reaction.
3. When a catalyst is added to an exothermic reaction, the heat evolved during the reaction
 - (a) increases
 - (b) decreases
 - (c) remains unchanged
 - (d) may increase or decrease
4. Which of the following factors affects the rate of heterogeneous reaction only?
 - (a) Nature of reactants
 - (b) Temperature of system
 - (c) Surface area of reactants
 - (d) Concentration of reactants
5. The addition of a catalyst to a reaction provides an alternative mechanism with
 - (a) lower activation energy and lower reaction rate
 - (b) lower activation energy and higher reaction rate
 - (c) higher activation energy and lower reaction rate
 - (d) higher activation energy and higher reaction rate
6. Collision theory states that
 - (a) all collisions lead to chemical reactions
 - (b) most collisions lead to chemical reactions
 - (c) very few reactions involves particle collisions
 - (d) effective collisions lead to chemical reactions.

7. When a lit match stick is touched to the wick of a candle, the candle begins to burn. When the match is removed, the candle continues to burn. In this reaction, the lit match stick
- acts as a catalyst
 - supplies activation energy
 - touched to wick is the rate-determining step
 - lowers the activation energy barrier
8. To have successful collisions the reactants must have
- favourable geometry only
 - sufficient heat of reaction only
 - sufficient potential energy only
 - sufficient kinetic energy and favorable geometry
9. The half-life period for a certain first order reaction is 30 minutes. How long will it take for $1/32$ of the reactant to be left behind?
- 60 minute
 - 120 minute
 - 90 minute
 - 150 minute
10. How does the addition of a catalyst increase the reaction rate of an endothermic reaction?
- It reduces the ΔH of the reaction.
 - It increase the ΔH of the reaction.
 - It reduces the required activation energy.
 - It causes the reaction to become exothermic.

II. Descriptive Questions

- Write a chemical reaction in which the units of rate and rate constant are same.
- Define order of a reaction.
- Define 'activation energy' of a reaction.
- What is the effect of adding a catalyst on activation energy (E_a) of a reaction.
- What do you understand by the rate of a chemical reaction? Name the factor on which it depends.
- Why the rate of a chemical reaction do not remain uniform throughout the reaction? Is it possible to have reactions with a uniform rate?
- A chemical reaction has zero activation energy. What is the effect of temperature on rate constant of reaction?
- How a catalyst only changes the speed of a reaction whereas a photosensitizer initiates the reaction?

9. State the role of activated complex in a reaction and state its relation with activation energy.



Potential energy diagram of an endothermic reaction

10. The rate constant of a zero order reaction is $1 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. Starting with 50 moles, calculate the time in minutes in which the concentration decreases to 10 moles.

III. Numerical Questions

1. Rate of formation of nitric oxide (NO) in the following reaction is $3.6 \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$.



Find the rate of disappearance of oxygen.

2. Calculate the overall order of the reaction which has the rate expression.
 (a) $\text{Rate} = k[\text{A}]^{1/2} [\text{B}]^{3/2}$
 (b) $\text{Rate} = k[\text{A}]^{3/2} [\text{B}]^{-1}$
3. A first order reaction has rate constant of 10^{-2} sec^{-1} . Calculate the half life period for this reaction.