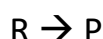


# Chemical Kinetics

- Branch of chemistry which deals with the study of chemical reactions, their rates and mechanisms is known as chemical kinetics.
- Chemical kinetics is derived from a Greek word **kinesis**; which means movement.
- Chemical kinetics helps us to determine the speed of a chemical reaction and describes us the conditions by which the reaction rates can be altered.
- The rate of reaction is affected by concentration, catalyst, temperature and pressure.

## Rate of reaction –

- The change in concentration of a reactant or the concentration of a product in unit time is known as rate of reaction.
- It can be described as:
  1. The rate of decrease in concentration of any one of the reactants, or
  2. The rate of increase in concentration of any one of the products.
- Let us consider a hypothetical reaction, assuming that volume of the system remains constant.



- Here 1 mole of the reactant R gives 1 mole of product P.
- 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:

$$\Delta t = t_2 - t_1$$

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

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

Here the square brackets used to express molar concentration.

- Rate of disappearance of R =  $\frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t}$
- Rate of appearance of P =  $\frac{\text{Increase in concentration of P}}{\text{Time Taken}} = +\frac{\Delta[P]}{\Delta t}$

➤ **Average rate of reaction ( $r_{av}$ )** –

Average rate of a reaction depends upon the change in the concentration of reactants or products and the time taken for that change to occur.

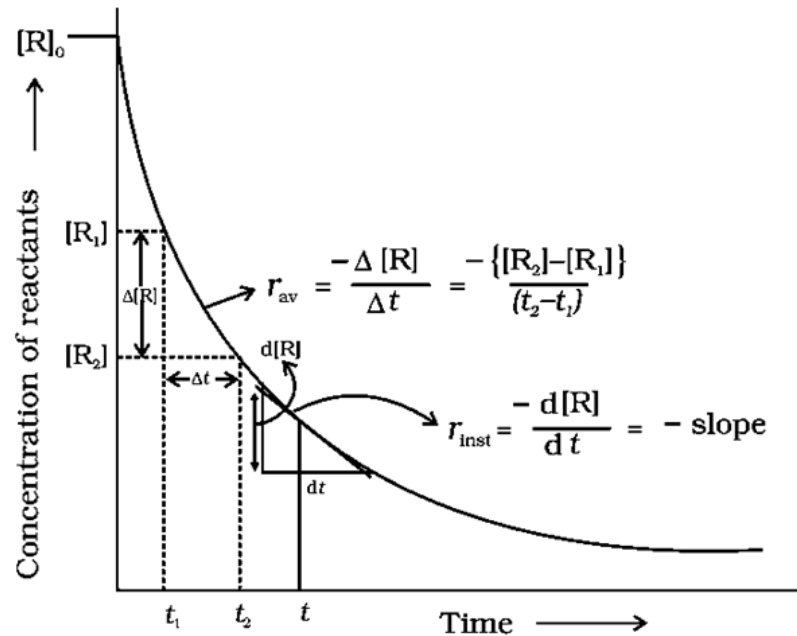


Figure: Instantaneous rate of reaction

➤ Instantaneous rate ( $r_{inst}$ ) - The rate at a particular moment of time is known as instantaneous rate.

$$r_{av} = - \frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

$$\text{As } \Delta t \rightarrow 0 \quad r_{inst} = - \frac{d[R]}{dt} = \frac{d[P]}{dt}$$

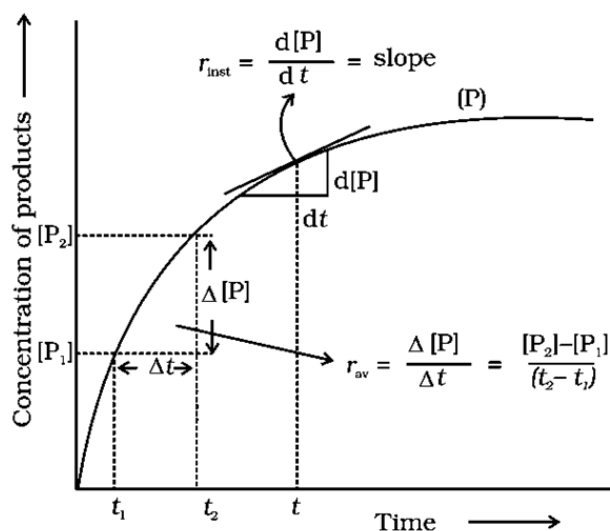


Figure: Average rate of reaction

**Unit of rate of a reaction** – The unit of rate of a chemical reaction is as follows-

$$\text{Rate of chemical reaction} = \frac{\Delta[\text{reactant}]}{t} = \frac{\text{Concentration}}{\text{time}} = \frac{\text{mol L}^{-1}}{\text{sec}}$$

➤ Unit of rate of chemical reaction =  $\text{mol L}^{-1} \text{s}^{-1}$

Example: Calculate the average rate of reaction for this reaction:



During different time intervals

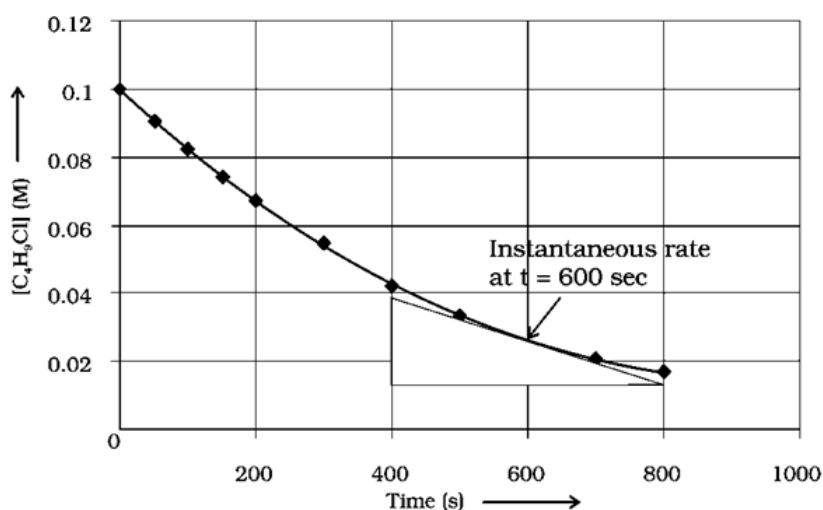
t (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ ( $\text{mol L}^{-1}$ )
0	0.100
50	0.0905
100	0.0820
150	0.0741
200	0.0671
300	0.0549
400	0.0439
700	0.0210
800	0.017

First determine the difference in concentration over different intervals of time then calculate the average rate by dividing  $\Delta[\text{R}]$  by  $\Delta t$ .

**Table: Average rates of Hydrolysis of butyl chloride**

$[C_4H_9Cl]_{t_1}$ (mol L <sup>-1</sup> )	$[C_4H_9Cl]_{t_2}$ (mol L <sup>-1</sup> )	$t_1$ (sec)	$t_2$ (sec)	$r_{av} \times 10^4 \text{ L}^{-1} \text{ s}^{-1}$ $= [C_4H_9Cl]_{t_2} - [C_4H_9Cl]_{t_1}/(t_2-t_1)$
0.100	0.0905	0	50	1.90
0.0905	0.0820	50	100	1.70
0.0820	0.0741	100	150	1.58
0.0741	0.0671	150	200	1.40
0.0671	0.0549	200	300	1.22
0.0549	0.0439	300	400	1.10
0.0439	0.0335	400	700	1.04
0.0210	0.017	700	800	0.4

According to the table the average rate ranges from  $1.90 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$  to  $0.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .



**Figure: Instantaneous rate of hydrolysis of butyl chloride**

$r_{inst}$  can be determined by graph. If a tangent drawn at time  $t$  on either of the curves for concentration of R and P versus time  $t$  and slope can be calculated. So  $r_{inst}$  at 600 second for example:

$$r_{inst} \text{ at } 600\text{s} = - \frac{0.0165 - 0.037}{(800 - 400) \text{ s}} \text{ mol L}^{-1} = 5.12 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{At } t = 250\text{s} \quad r_{inst} = 1.22 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$t = 350\text{s} \quad r_{inst} = 1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$t = 450\text{s} \quad r_{inst} = 6.4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

## Factors affecting rate of reaction –

### Concentration-

- At a given temperature the rate of reaction depends upon the concentration of one or more reactants and products.
- The representation of rate of reaction in terms of concentration of the reactants is known as rate law.

### Rate expression and rate constant-

- The rate of reaction decrease with the decrease in the concentration of reactants with time. So we can say that:

**Rate of reaction  $\propto$  concentration of reactants**

In a chemical reaction:



Here a, b, c, and d are the stoichiometric coefficients of the reactants and products.

The rate expression for this reaction is

$$\text{Rate} \propto [A]^x [B]^y$$

Here x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.

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

$$-\frac{d[R]}{dt} = k [A]^x [B]^y$$

Here k is a proportionality constant known as rate constant.

$$\text{Unit of rate constant (k)} = \frac{\text{Rate}}{[A]^x [B]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n} \quad (\text{Here } [A] = [B])$$

- The SI unit of k for different reaction order are as follows:

**Table: units of rate constant**

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$

**Rate Law** – It is the expression in which reaction rate is expressed in terms of molar concentration of reactants with each term raised to some power which may or may not be equal as the stoichiometric coefficient of the reacting species in a balanced chemical reaction.

**Order of a reaction** – In the rate law expression the sum of powers of the concentration of the reactants is called the order of that chemical reaction. In the rate equation

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

$$\text{Overall order of reaction} = x + y$$

- Order of a reaction is an experimental quantity.
- Order of a reaction can be 0, 1, 2, 3 and a fraction.
- If the value of order of reaction is zero; it means the rate of reaction is independent of the concentration of reactants.
- Order is applicable to both elementary and complex reactions.
- For complex reaction order of reaction is calculated by slowest i.e. rate determining step.

**Example:** Calculate the overall order of a reaction which has the rate expression

(a)  $\text{Rate} = k [\text{A}]^{1/2} [\text{B}]^{3/2}$

(b)  $\text{Rate} = k [\text{A}]^{3/2} [\text{B}]^{-1}$

**Solution:**

(a)  $\text{Rate} = k [\text{A}]^x [\text{B}]^y$

Order = x + y

So order =  $1/2 + 3/2 = 2$ , i.e. second order

(b) Order =  $3/2 + (-1) = 1/2$ , i.e. half order.

Elementary reactions: Reactions taking place in one step are known as elementary reactions.

Complex reactions: A sequence of elementary reactions gives us the products; the reactions are called complex reactions.

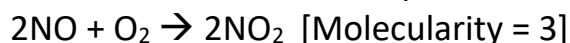
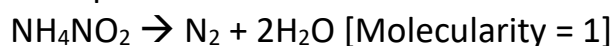
### Molecularity of a reaction-

➤ The number of reacting species i.e. atoms, ions or molecules taking part in elementary reaction, which collide simultaneously in order to bring about a chemical reaction is known as Molecularity of a reaction.

➤ It cannot be a fractional value or zero.

➤ Molecularity is applicable only for complex reactions.

➤ Examples:

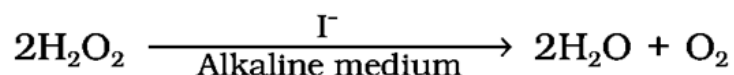


### Rate determining step –

➤ The overall rate of the reaction is controlled by the slowest step in a reaction which is known as rate determining step.

➤ When reaction takes place in several steps then we have to find the rate determining step.

➤ Let's consider decomposition of  $\text{H}_2\text{O}_2$  catalyzed by iodide ion in alkaline medium.

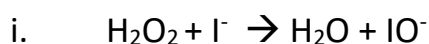


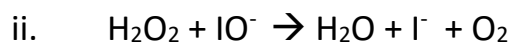
➤ The rate equation for this reaction is as follows:

$$\text{Rate} = -\frac{d[\text{H}_2\text{O}_2]}{dt} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$

➤ The order of reaction is first with respect to both  $\text{H}_2\text{O}_2$  and  $\text{I}^-$ .

➤ This reaction takes place in two steps:

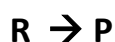




- Here  $\text{IO}^-$  is intermediate species. First step is slow so it is rate determining step.

### Integrated Rate Equations:

- The concentration dependence of a rate is called differential rate equation. By the integration of differential rate equation we can give relation between rate constant and concentration at different times.
- The integrated rate equations are different for the reactions of different reaction orders.
- **Zero Order Reactions-**
- Zero order reaction means the rate of reaction is directly proportional to the zero power of the concentration of the reactants.



$$\text{Rate} = \frac{-d[\text{R}]}{dt} = k [\text{R}]^0$$

Any quantity raised to power zero is unity, so

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

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

On integrating both sides:  $[\text{R}] = -k t + I$

Here  $I$  = Constant of integration

At  $t=0$ ; the concentration of reactant

$$R = [\text{R}]_0$$

Here  $[\text{R}]_0$  = initial concentration of reactant

On substitution the value of  $[\text{R}]_0$

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

$$[\text{R}]_0 = I$$

By substituting the value of  $I$



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

Comparing above reaction with straight line equation  $y = mx+c$   
If we plot a graph of  $[R]$  versus  $t$ , we get a straight line.

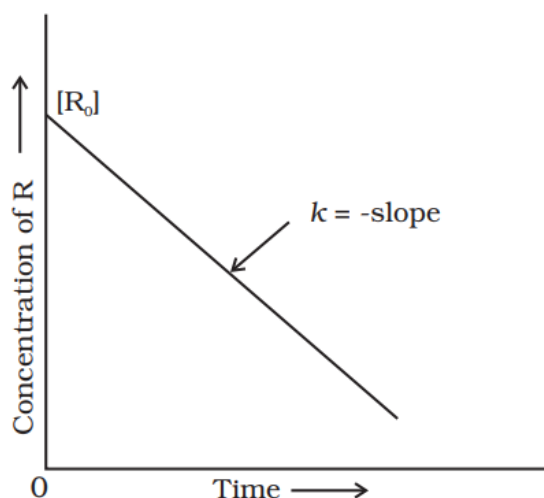


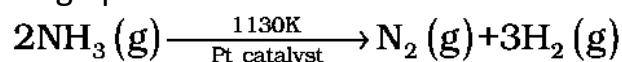
Figure: Variation in the concentration versus time plot for a Zero order reaction

Slope =  $-k$

Intercept =  $[R]_0$

$$\text{Rate constant } (k) = \frac{[R]_0 - [R]}{T}$$

**Example:** decomposition of ammonia gas on a hot Pt surface is a zero order reaction at high pressure.

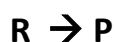


$$\text{Rate} = k [\text{NH}_3]^0 = k$$

In this reaction Pt metal is used as a catalyst. At high pressure metal surface gets saturated with gas molecules. If we change the reaction condition, it is unable to alter the amount of ammonia on the surface of the catalyst, thus rate of reaction is independent of the concentration of ammonia.

➤ **First order reactions –**

➤ The rate of reaction is directly proportional to the first power of the concentration of the reactant R.



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

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

- By integrating above equation

$$\ln [R] = -kt + I$$

Here I = constant of integration

- When  $t=0$ ,  $R = [R]_0$

Here  $[R]_0$  = initial concentration of the reactant

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

- On substituting the value of I

$$\ln [R] = -kt + \ln [R]_0$$

- Rearranging this equation

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

Or

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]}$$

At time  $t_1$

$$*\ln [R]_1 = -kt_1 + * \ln [R]_0$$

At time  $t_2$

$$\ln [R]_2 = -kt_2 + \ln [R]_0$$

Here  $[R]_1$  and  $[R]_2$  are the concentrations of the reactants at time  $t_1$  and  $t_2$  respectively.

Subtracting above equations:

$$\ln [R]_1 - \ln [R]_2 = -kt_1 - (-kt_2)$$

$$\frac{\ln [R]_1}{[R]_2} = k (t_2 - t_1)$$

$$K = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2}$$

This equation  $\ln[R] = -kt + \ln[R]_0$  can be written as:

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

Taking anti log both sides

$$[R] = [R]_0 e^{-kt}$$

Comparing this equation with  $y = mx+c$

Slope = -k

Intercept =  $\ln[R]_0$

The rate constant for first order reaction  $(k) = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

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

If we plot graph between  $\log [R]_0/[R]$  versus t

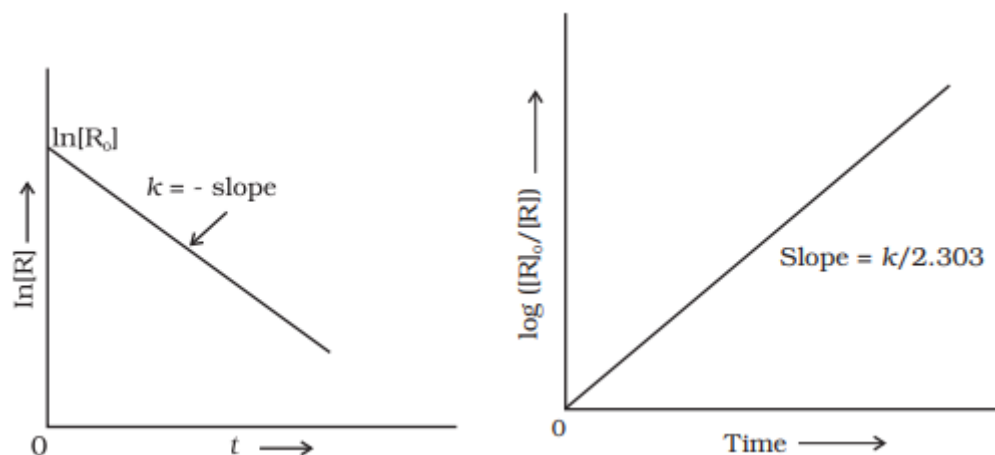


Figure: A plot between  $\ln[R]$  and t Figure: plot of  $\log[R]_0/[R]$  versus time for first order reaction



### Half-life of a reaction –

- The half-life of a reaction is the time in which concentration of a reactant is reduced to half of its initial concentration.
- It is denoted by  $t_{1/2}$ .
- **For a zero order reaction**, rate constant is

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

At  $t = t_{1/2}$

$$[R] = \frac{1}{2} [R]_0$$

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

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

➤ For first order reaction, rate constant is

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

At  $t_{1/2}$

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

The above reaction becomes

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

$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

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

➤ For first order reaction half-life period is constant. It is independent of initial concentration of the reacting species.

➤ **Example:** A first order reaction is found to have a rate constant,  $k = 5.5 \times 10^{-14} \text{ s}^{-1}$ . Find the half-life of the reaction.

**Solution:** Half-life for a first order reaction is:

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

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14}} = 1.26 \times 10^{13} \text{ s}$$

➤ **Example:** Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life of the reaction.

**Solution:** when reaction is completed 99.9%

$$[R]_n = [R]_0 - 0.999[R]_0$$

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

$$= \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t} \log 10^3$$

$$t = 6.909/k$$

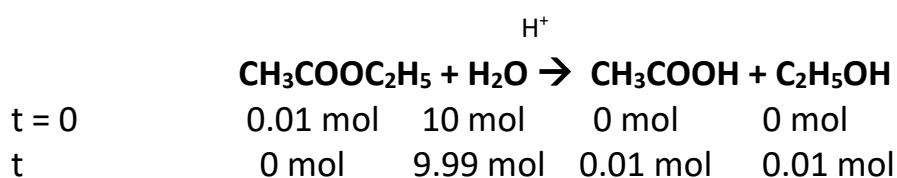
$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Table: Integrated rate laws for the reaction of zero and first order

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of $k$
0	R → P	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	[R] vs $t$	$[R]_0/2k$	conc time <sup>-1</sup> or mol L <sup>-1</sup> s <sup>-1</sup>
1	R → P	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs $t$	$\ln 2/k$	time <sup>-1</sup> or s <sup>-1</sup>

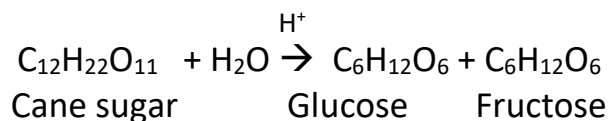
### Pseudo first order reaction-

- Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water.
- In reality, it is a second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction. But water is taken in excess for hydrolysis; so concentration of water is not altered much during the reaction. Thus, the rate of reaction is affected by concentration of ethyl acetate only.
- For example, during the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of H<sub>2</sub>O, amounts of the reactants and products at the beginning ( $t = 0$ ) and completion ( $t$ ) of the reaction are given below:



Here the concentration of H<sub>2</sub>O not altered during the reaction. So reaction behaves as first order reaction. This type of reaction is known as pseudo first order reaction.

- Another of example of pseudo first order reaction is inversion of cane sugar.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

### Temperature dependence of the rate of a reaction

- The temperature dependence of the rate of a chemical reaction is described by Arrhenius equation.

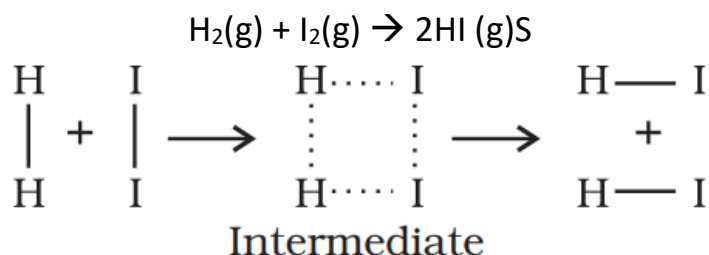
$$K = A e^{-E_a/RT}$$

Here A = Frequency factor

R = gas constant

$E_a$  = Activation energy ( $\text{J mol}^{-1}$ )

- For a simple chemical reaction:



**Figure: formation of HI through intermediate**

- According to Arrhenius when a molecule of hydrogen collides with a molecule of iodine formation of an unstable intermediate take place. This intermediate break into two molecules of hydrogen iodide.
- The energy required to form this intermediate is known as activation energy ( $E_a$ ) and this intermediate is known as activated complex.
- Activation energy can be calculated by a graph which is plotted between potential energy and reaction coordinate.

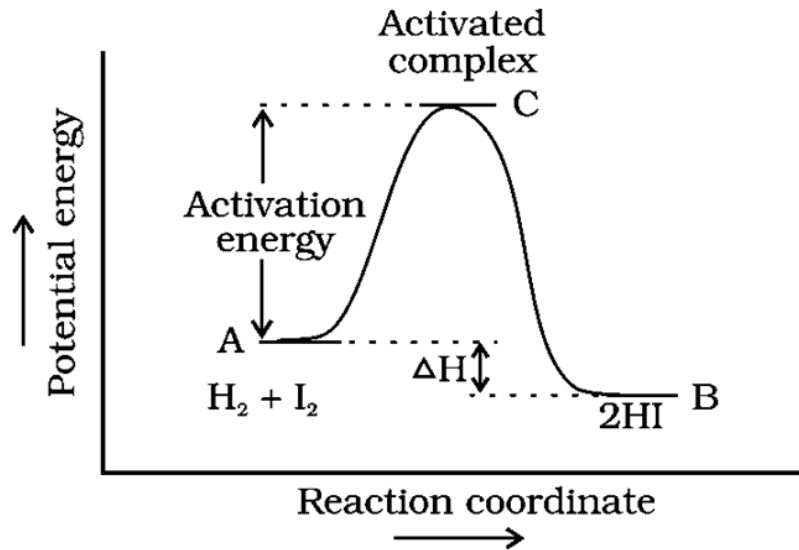


Figure: A plot of potential energy versus reaction coordinate

- Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behavior of large number of molecules.
- According to them, the distribution of kinetic energy explained by plotting the fraction of molecules ( $N_E/N_T$ ) with a given kinetic energy ( $E$ ) vs kinetic energy.

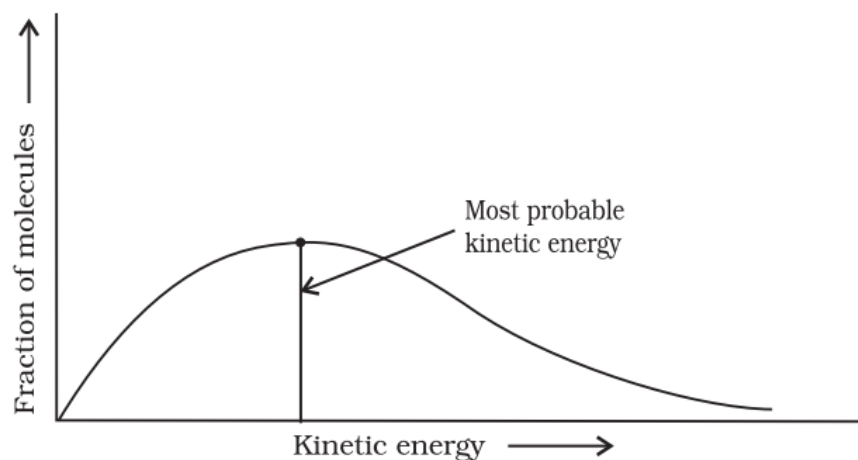
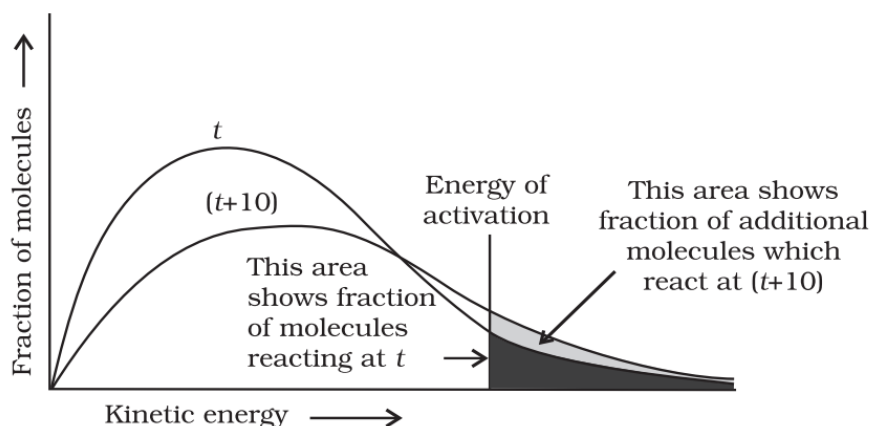


Figure: Distribution curve

- Here,  $N_E$  is the number of molecules with energy  $E$  and  $N_T$  is total number of molecules.
- The peak of the curve is known as most probable kinetic energy. This is kinetic energy of maximum fraction of molecules.
- As we raise the temperature the maximum of the curve moves towards higher energy value.



**Figure: Distribution curve showing temperature dependence or rate of reaction**

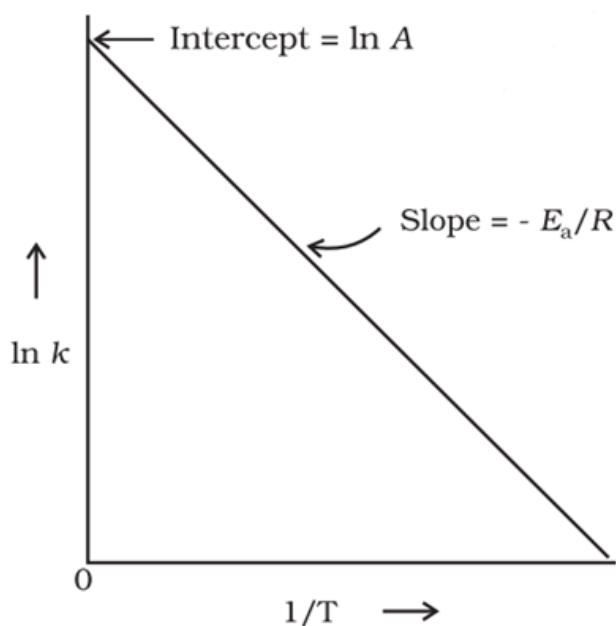
- Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than  $E_a$ .
- In the curve at  $(t + 10)$ , the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.
- In Arrhenius equation :

$$k = A e^{-E_a/RT}$$

If we take log both side

$$\ln k = - \frac{E_a}{RT} + \ln A$$

According to this line the plot of  $\ln k$  versus  $1/T$  gives a straight line.



**Figure: A plot between  $\ln k$  and  $1/T$**

- Slope =  $-\frac{E_a}{R}$



- Intercept =  $\ln A$
- At temperature  $T_1$   

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$
- At temperature  $T_2$
- $\ln k_2 = -\frac{E_a}{RT_2} + \ln A$
- $k_1$  and  $k_2$  are the values of rate constants at temperatures  $T_1$  and  $T_2$  respectively.
- Subtracting both equation:

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

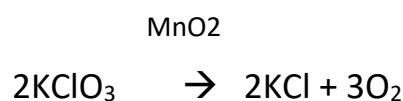
$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

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

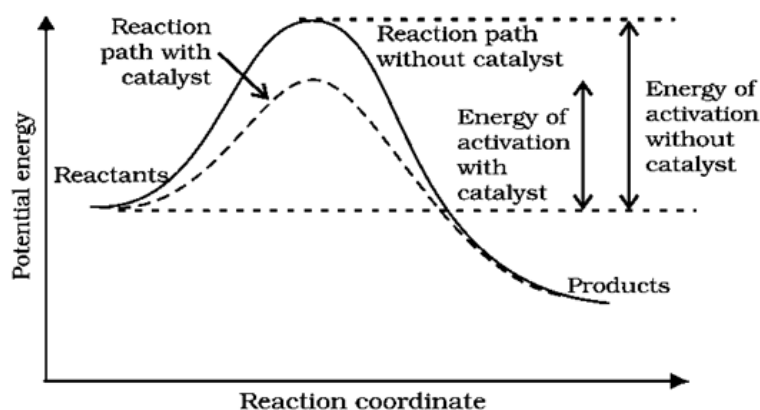
## Effect of Catalyst

- A catalyst is a substance which increases the rate of a reaction without participating in the reaction.
- For example  $\text{MnO}_2$  catalyses' the following reaction:



- The word catalyst should not be used when the added substance reduces the rate of reaction.
- The substance is then called inhibitor. The action of the catalyst can be explained by intermediate complex theory.
- According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex.
- This has a transitory existence and decomposes to yield products and the catalyst.

- Catalyst provides alternative pathway by reducing the activation energy.



**Figure: Effect of catalyst on activation energy**

### Collision theory of chemical reactions

- In 1916 -18 Max Trautz and William Lewis propounded a greater insight into the energetic and mechanistic aspects of reactions, which is based on kinetic theory of gases.
- According to this theory, the reactant molecules are assumed as hard spheres and reaction is postulated to occur when molecules collide with each other.
- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (**Z**).
- For a bimolecular elementary reaction:



$$\text{Rate of reaction} = Z_{AB} e^{-E_a/RT}$$

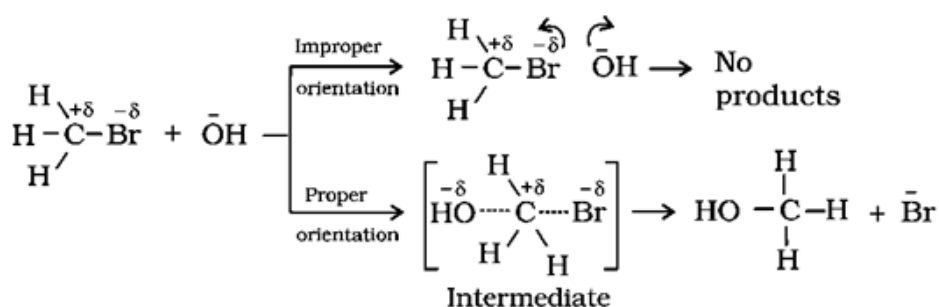
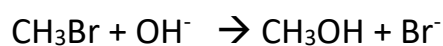
Here  $Z_{AB}$  = collision frequency of reactants A and B

$e^{-E_a/RT}$  = Fraction of molecules with energies equal to or greater than  $E_a$

- **Effective collisions –**

The collisions in which molecules collide with sufficient kinetic energy and proper orientation, which facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

- For example - Formation of methanol from bromoethane depends upon the orientation of reactant molecules.



**Figure: Diagram showing molecules having proper and improper orientation**

- The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.
- $\text{Rate} = P Z_{AB} e^{-E_a/RT}$   
Here  $P$  = probability or steric factor
- In collision theory  $E_a$  and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.