4. CHEMICAL KINETICS

The branch of Chemistry that deals with the rate of chemical reaction, factors affecting the rate and the mechanism of a reaction is called **Chemical Kinetics**.

Rate of a chemical reaction

The rate of a chemical reaction is the change in concentration of any one of the reactant or product in unit time. Or, it is the rate of decrease in concentration of any one of the reactant or the rate of increase in concentration of any one of the product.

For a chemical reaction, if Δx is the change in concentration of a reactant or a product in a time Δt, the rate of reaction (r) = $\Delta x / \Delta t$.

For a hypothetical reaction R → P, the rate of reaction can be expressed by decrease in concentration of reactants or by increase in concentration of products.

i.e., Rate of reaction = Rate of disappearance of R

$$r = \frac{\text{Decrease in concentration of R}}{\text{Time taken}}$$

Or, $r = \dfrac{-\Delta[R]}{\Delta t}$ [Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity].

Or, Rate of reaction = Rate of appearance (formation) of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}}$$

i.e., $r = \dfrac{\Delta[P]}{\Delta t}$

The above rate expressions are also called Average rate.

Units of Rate of reaction

If concentration is expressed in moles/L and time is in second, the unit of rate of reaction is mol/L/s. In general the dimension of rate of reaction is Concentration/Time. For gaseous reactions, the concentration is replaced by partial pressure and so the unit of rate of reaction is atm/s.

Instantaneous Rate of a reaction

The rate of a reaction at a particular instant of time is called Instantaneous Rate of a reaction. Or, it is the rate of a reaction when the time interval approaches zero.

i.e., Instantaneous Rate of a reaction = $\lim\limits_{\Delta t \to 0} \dfrac{\Delta x}{\Delta t} = \dfrac{dx}{dt}$

For the reaction, R→ P, the Instantaneous Rate is given by, $r_{inst} = -\dfrac{d[R]}{dt} = \dfrac{d[P]}{dt}$

For the reaction, $2N_2O_5 \to 4NO_2 + O_2$, $r_{inst} = -\frac{1}{2}\dfrac{d[N_2O_5]}{dt} = \frac{1}{4}\dfrac{d[NO_2]}{dt} = \dfrac{d[O_2]}{dt}$

For the reaction, $H_2 + I_2 \to 2HI$, $r_{inst} = -\dfrac{d[H_2]}{dt} = -\dfrac{d[I_2]}{dt} = \frac{1}{2}\dfrac{d[HI]}{dt}$

And $r_{av.} = -\dfrac{\Delta[H_2]}{\Delta t} = -\dfrac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\dfrac{\Delta[HI]}{\Delta t}$

Determination of Instantaneous Rate of a reaction

Instantaneous Rate of a reaction can be determined graphically. First conduct the chemical reaction and find out the concentration of reactants or product at a regular interval of time. Then plot a graph between concentration along y-axis and time along x-axis.

In order to determine the Instantaneous Rate at a particular time, mark the point on the graph at that time and draw a tangent at the point. The slope of this tangent gives the instantaneous rate at that time.
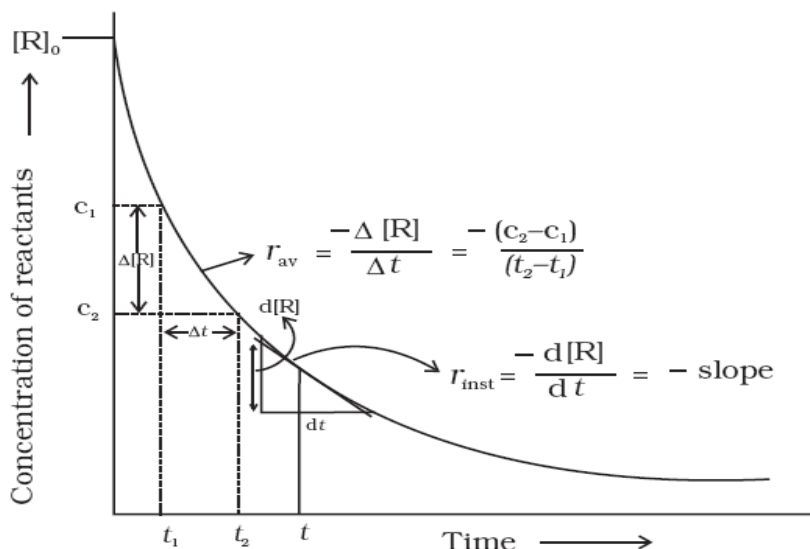
For a general reaction $aA + bB \rightarrow cC + dD$, the rate is given by

$$r_{inst} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Factors affecting rate of a reaction

The important factors which affect the rate of a chemical reaction are:
1. Nature of the reactants
2. Concentration of the reactants
3. Temperature
4. Pressure (for gaseous reaction only)
5. Effect of catalyst
6. Influence of radiation

Dependence of Rate of reaction on concentration

It is found experimentally that Rate of reaction is directly proportional to the concentration of reactants. Thus for a general reaction, $aA + bB \rightarrow cC + dD$,

Rate α $[A]^x[B]^y$

Or, $r = k[A]^x[B]^y$ (where x and y may or may not be equal to a and b)

This expression is known as **rate law or rate equation**. Thus rate law is a "mathematical equation relating the rate of a chemical reaction and concentration of reactants, in which each concentration term is raised to a power which may or may not be equal to the stoichiometric coefficients in the balanced chemical equation."

In the above equation 'k' is a constant called *rate constant or velocity constant or specific reaction rate of the reaction*. It is defined as the rate of the reaction when the concentration of each of the reactants is unity.

Order of reaction

Order is the sum of the powers of the concentration terms of the reactants in the rate law. It is an experimental quantity. It can have the values 0,1,2,3,...... or a fraction. It is applicable to both elementary and complex reactions.

For a general reaction, $aA + bB \rightarrow cC + dD$; $r = k[A]^x[B]^y$, Order of the reaction = x + y

If the order of a reaction is zero, it is called zero order reaction, if it is one, it is called first order reaction, if it is two, it is called second order reaction and so on.

Molecularity of a reaction

It is *the total number of reacting species collides simultaneously in a chemical reaction*. It is a theoretical quantity. It cannot be zero or fractional. It can have values 1,2,3 etc. it is applicable only to elementary reactions.
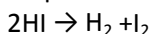
If the molecularity of a reaction is 1, it is called unimolecular reaction.

e.g. Decomposition of ammonium nitrite

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$
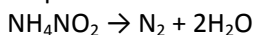
If the molecularity of a reaction is 2, it is called bimolecular reaction.

e.g. Decomposition of Hydrogen Iodide

$$2HI \rightarrow H_2 + I_2$$

## Differences between Order and Molecularity of a reaction

|	Order	Molecularity
1.	It is the sum of the powers of the concentration terms in the rate law expression	It is the total number of reactant species collide simultaneously in a chemical reaction
2.	It is an experimental quantity	It is a theoretical quantity
3.	It can be zero or fractional	It cannot be zero or fractional
4.	It is applicable to both elementary and complex reactions	It is applicable only to elementary reactions

Elementary and complex reactions

A reaction that takes place in a single step is called elementary reaction. While a reaction that occurs in more than one step is called a complex reaction. In a complex reaction one of the steps is slower than the other steps and this step is called the Rate determining step. The overall rate of the reaction is controlled by this slowest step. The sequence of steps by which a chemical reaction occurs is called the mechanism of the reaction.

Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in alkaline medium.

$$2H_2O_2 \xrightarrow[\text{Alkaline Medium}]{I^-} 2H_2O + O_2$$
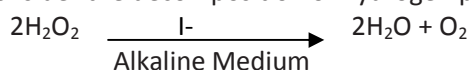
The rate equation for this reaction is found to be $r = -\dfrac{d[H_2O_2]}{dt}$

This reaction is first order with respect to both H_2O_2 and I^-. This reaction takes place in two steps

(1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

(2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$
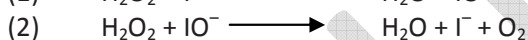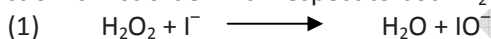
Here the first step is slower than the second. So it is the rate determining step (rds).

Unit of Rate constant

Different ordered reactions have different units for k.

For an nth order reaction $nA \longrightarrow$ products, rate = $k[A]^n$

Therefore, $k = \dfrac{rate}{[Concentration]^n}$

Unit of $k = \dfrac{mol/L/sec}{(mol/L)^n} = (mol/L)^{1-n} s^{-1}$

The units of rate constant for different ordered reactions are:

| Reaction	Order	Unit of rate constant
Zero order reaction	0	$Mol\, L^{-1}s^{-1}$
First order reaction	1	s^{-1}
Second order reaction	2	$Mol^{-1}L\, s^{-1}$

Integrated Rate law Equations

These are equations relating the rate of a reaction and concentration of reactants. Different ordered reactions have different integrated rate law equations.

1. Integrated Rate law Equation for a Zero Order Reaction

Zero order reactions are reactions in which the rate of reaction is independent of concentration of the reactants. Consider a zero order

$$R \longrightarrow P$$
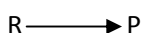
The rate expression for the above reaction is $r = -\dfrac{d[R]}{dt}$ ……………… (1)

Rate law for the above reaction is $\qquad$ r= k$[R]^0$ = k ………………… (2)

From equations (1) & (2), we can write $-\dfrac{d[R]}{dt} = k$

The above equation is known as *differential rate equation for a zero order reaction*.

Or, d[R] = $-$ k.dt

On integrating the above equation we get,

$\qquad$ [R] = $-$kt +C $\qquad$ ………………… (3)

Where C is the constant of integration. To evaluate the value of C, consider the initial conditions. i.e., when t=0, [R] = $[R]_0$

Substitute these values in eqn. (3)

$\qquad$ $[R]_0$ = $-$ k x0 + C

$\qquad$ Or, C = $-$ $[R]_0$

Substituting in equation (3), we get

$\qquad$ [R] = $-$ kt $-$ $[R]_0$ …………. (4)

$\qquad$ Or, $[R]_0$ - [R] = kt

$\qquad$ Or, k= $\dfrac{[R]_0 - [R]}{t}$ $\qquad$ ………………… (5)

This equation is of the form of a straight line, y = mx + c. So if we plot [R] against t, we get a straight line with slope = $-$k and intercept equal to $[R]_0$.
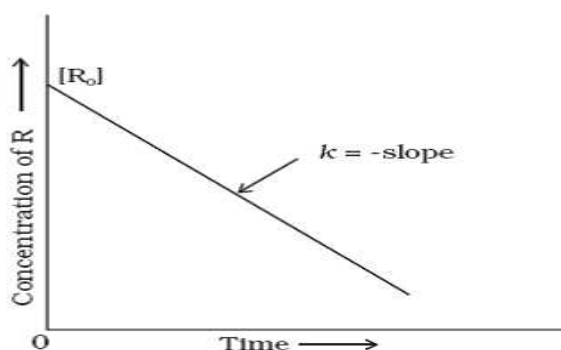
Example for zero order reaction is the decomposition of gaseous ammonia on a hot platinum surface at high pressure.

$\qquad$ $N_2 + H_2 \longrightarrow 2\,NH_3$

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions does not change the rate of the reaction. So it becomes a zero order reaction.

Another e.g. is the thermal decomposition of HI on gold surface.

2. Integrated Rate law Equation for a First order reaction

Here the rate of the reaction is proportional to the concentration of the reactant.

Consider a first order reaction, R$\longrightarrow$ P

The rate expression for the above reaction is r= $-\dfrac{d[R]}{dt}$ ……………. (1)

Rate law for the above reaction is $\qquad$ r = k[R] $\qquad$ ………………… (2)

From equations (1) & (2), we can write $-\dfrac{d[R]}{dt} = k[R]$ …………………… (3)

The above equation is known as *differential rate equation for a 1st order reaction*.

Or, $\qquad$ $-$ d[R] = k.dt

$$\overline{[R]}$$

On integrating the above equation we get,

$$- \ln[R] = kt + C \quad \text{.....................} (3)$$

Where 'C' is the constant of integration. To evaluate the value of C, consider the initial conditions.

i.e., when t=0, $[R] = [R]_0$

Substitute these values in eqn. (3)

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

$$\text{Or, } C = - \ln[R]_0$$

Substituting in equation (3), we get

$$- \ln[R] = kt - \ln[R]_0 \quad \text{.............} (4)$$

$$\text{Or, } \quad \ln[R]_0 - \ln[R] = kt$$

$$\text{Or, } \quad \ln[R]_0/[R] = kt \quad \text{.................} (5)$$

$$K = \frac{1}{t} \frac{\ln [R]_0}{[R]} \quad \text{.....................} (6)$$

On changing the base we get

$$\boxed{k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}} \quad \text{....................} (7)$$

This equation is known as *integrated rate equation for a first order reaction*.

From eqn. (4), $-\ln[R] = kt - \ln[R]_0$

On changing the sign we get $\ln[R] = -kt + \ln[R]_0$

This equation is of the form y = mx + c, equation for a straight line. So if we plot a graph between ln[R] against time, t we get straight line graph as follows:
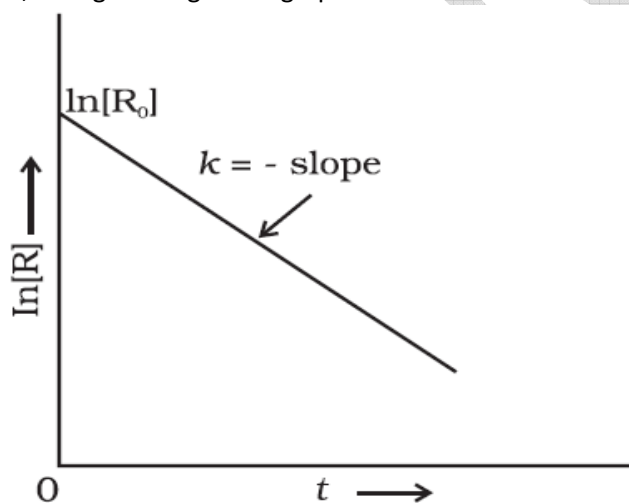
From the eqn. (5) $\ln[R]_0/[R] = kt$

$$\text{Or, } \quad 2.303 \log[R]_0/[R] = kt$$

$$\text{Or, } \quad \log[R]_0/[R] = kt/ 2.303$$

So if we plot a graph between $\log[R]_0/[R]$ against 't', we get a straight line graph as shown above.

Examples for 1st order reactions are:

1. Hydrogenation of ethene: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$; $r = k[C_2H_4]$
2. All natural and artificial radioactive decay

Half life of a reaction ($t_{1/2}$)

The half-life of a reaction is the time taken for concentration of a reactant is reduced to one half of its initial concentration. Or, it is the time taken for half of a reaction to complete. It is represented as $t_{1/2}$.

1. Half life of a zero order reaction

For a zero order reaction, the integrated rate law is: $k = \dfrac{[R]_0 - [R]}{t}$

When $t = t_{1/2}$, $[R] = \frac{1}{2}[R]_0$
On substituting these values in the above equation,

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

or, $\boxed{t_{1/2} = \dfrac{[R]_0}{2k}}$

i.e. half life of a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

2. Half life of a first order reaction

For a first order reaction, $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$

When $t = t_{1/2}$, $[R] = [R]_0/2$
Substitute these values in the above equation

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

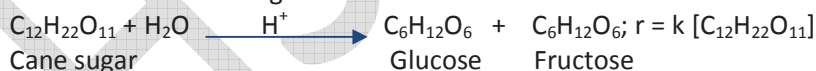Or, $t_{1/2} = \dfrac{2.303}{k} \log 2 = \dfrac{2.303 \times 0.3010}{k}$

Or, $\boxed{t_{1/2} = \dfrac{0.693}{k}}$

Thus for a first order reaction, half-life period is constant. i.e., it is independent of initial concentration of the reacting species.

Pseudo first order reaction

These are reactions which appear to follow higher order but actually follow first order kinetics. In these reactions the concentration of one of the reactants is large excess and so its change in concentration does not affect the rate of the reaction.

e.g. 1. Hydrolysis of ester (ethyl acetate)
$CH_3COOC_2H_5 + H_2O \xrightarrow{\ H^+\ } CH_3COOH + C_2H_5OH$; $r = k[CH_3COOC_2H_5]$
Here the concentration of water does not change during the reaction.
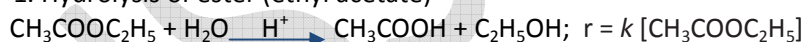
2. Inversion of cane sugar
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\ H^+\ } C_6H_{12}O_6 + C_6H_{12}O_6$; $r = k[C_{12}H_{22}O_{11}]$
Cane sugar   Glucose   Fructose

Rate of reaction and Temperature

Most of the chemical reactions are accelerated by increase in temperature. It has been found that for a chemical reaction, when the temperature is increased by 10°, the rate of the reaction and the rate constant is nearly doubled. The ratio of the rate constants of a reaction at two temperatures differing by 10^0 is called temperature coefficient.

i.e., Temperature coefficient = $\dfrac{\text{Rate constant of the reaction at }(T + 10)K}{\text{Rate constant of the reaction at } T\ K}$

The temperature dependence of the rate of a chemical reaction can be accurately explained by **Arrhenius equation**. The equation is:

$$k = A\, e^{-E_a/RT} \quad \text{..................................... (1)}$$

Where *A* is a constant called the Arrhenius parameter or the frequency factor or the pre-exponential factor. It is constant for a particular reaction. *R* is the universal gas constant and *E*a is activation energy measured in joules/mole (J mol $^{-1}$).

According to Arrhenius, a chemical reaction occurs by the collision of reactant molecules. All the molecular collisions are not effective. For effective collision, the colliding molecules should have a minimum kinetic energy called **activation energy**. When such molecules collide, an unstable intermediate called **activated complex** is formed, which decomposes to form products.

For e.g. the reaction between H_2 and I_2 to form HI takes place in the following steps.
$$H_2 + I_2 \rightarrow 2HI$$

Intermediate
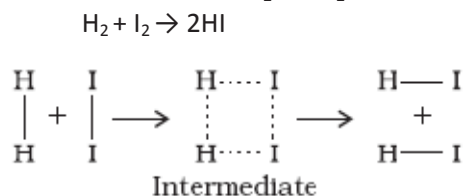
If we plot a graph between potential energy and the progress of reaction, we get the following graph.
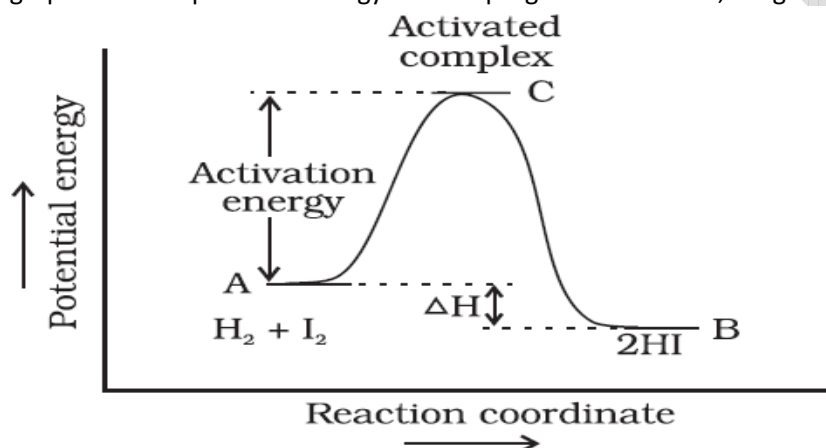
Reaction coordinate represents the profile of energy change when reactants change into products.

In a chemical reaction, all the molecules in the reacting species do not have the same kinetic energy. Ludwig Boltzmann and James Clark Maxwell calculated the distribution of kinetic energy among molecules. They plotted a graph between the fraction of molecules with a given kinetic energy against kinetic energy. This plot is known as Maxwell- Boltzmann distribution curve of molecular energies.

Maxwell-Boltzmann Distribution curve

Distribution curves at 2 different temperatures
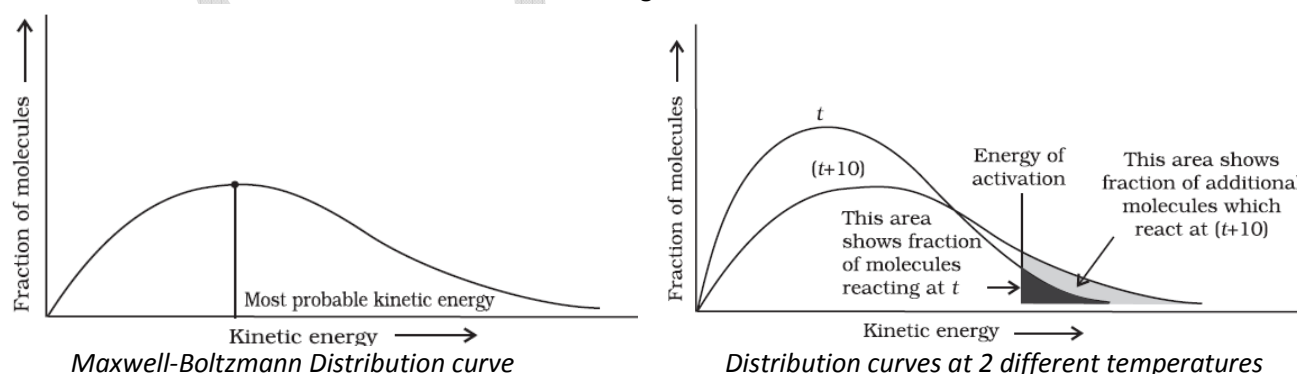
The peak of the curve corresponds to the ***most probable kinetic energy***. It is the kinetic energy possessed by maximum fraction of molecules.

When the temperature is raised, the maximum of the curve moves to the higher energy value and the curve spreads to the right. That is the fraction of molecules with activation energy increases (almost doubled).

At normal temperature the fraction of molecules having energy equal to or greater than activation energy is very low. As the temperature increases, the fraction of molecules having energy equal to or greater than activation energy increases and hence the rate of reaction also increases.

In the Arrhenius equation the factor e -Ea /RT corresponds to the fraction of molecules that have   kinetic energy greater than Ea.

Taking logarithm on both sides of equation (1), we get

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

This equation is of the form y = mx + c, equation for a straight line. So if we plot a graph between ln k against 1/T, we get a straight line with slope = – Ea/R and the y-intercept ln A
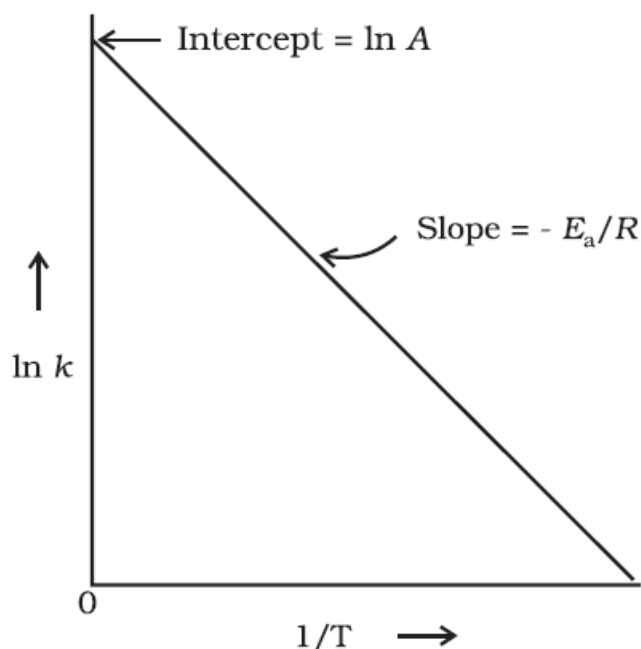
If k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2, then

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad \text{.................. (2)} \quad \text{and}$$

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \qquad \text{.................. (3)}$$

Equation (2) – (3) gives,

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

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

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

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

From this equation we can calculate the value of activation energy (E_a), by knowing all other values.

Effect of Catalyst

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change. 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 an intermediate complex. This is unstable and decomposes to yield products and the catalyst.
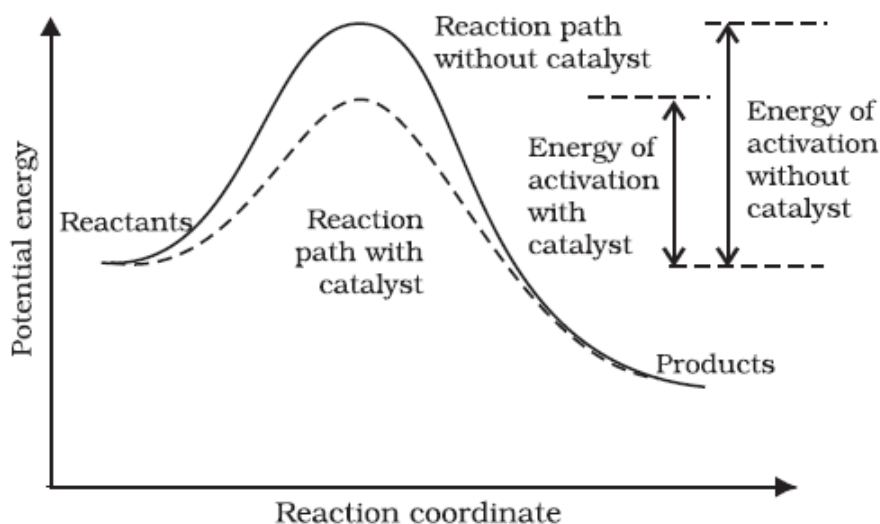
A catalyst increases the rate of a chemical reaction by providing an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products.

The important characteristics of a catalyst are:

1. A small amount of the catalyst can catalyse a large amount of reactants.
2. A catalyst does not alter Gibbs energy, ΔG of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
3. A catalyst does not change the equilibrium constant of a reaction, but it helps to attain the equilibrium faster by increasing the rate of both forward as well as the backward reactions.

Collision Theory

This theory was developed by Max Trautz and William Lewis. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is occurred 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).*

Another factor which affects the rate of chemical reactions is activation energy. For a bimolecular elementary reaction

$$A + B \rightarrow Products$$

Rate of reaction can be expressed as

Rate (r) = $Z_{AB} e^{-Ea/RT}$

Where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than Ea. Comparing with Arrhenius equation, we can see that A is related to collision frequency.

A third factor which affects the rate of a chemical reaction is the proper orientation. To account for this, a factor P called the *probability or steric factor* is introduced. So the above equation becomes:

Rate (r) = $PZ_{AB} e^{-Ea/RT}$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

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