# 3.  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 reactants or products in unit time. Or, it is the rate of decrease in concentration of any one of the reactants or the rate of increase in concentration of any one of the products.

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

For a hypothetical reaction R $\longrightarrow$ P, the rate of reaction can be expressed by rate of decrease in concentration of reactant or by rate of increase in concentration of product.

i.e. Rate of reaction (r) =  Rate of disappearance of R

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

Or,           r $= -\frac{\Delta[R]}{\Delta t}$  [Since, concentration of reactant decreases with time,  Δ[R] is negative. But rate of reaction cannot be negative. So in order to make it positive, it is multiplied with –1].

Also, rate of reaction = Rate of appearance (formation) of P

i.e. r $= \frac{\text{Increase in concentration of P}}{\text{Time taken}}$

Or, r $= \frac{\Delta[P]}{\Delta t}$

The above rate expressions are also called Average rate of reaction.

For a gaseous reaction, at constant temperature, concentration is directly proportional to the partial pressure. Hence the rate of reaction can also be expressed as the rate of change in partial pressure of the reactant or product.

## Units of rate of reaction

If concentration is expressed in mol L$^{-1}$ and time is in second, the **unit of rate of reaction is mol L$^{-1}$ s$^{-1}$**. In general the dimension of rate of reaction is concentration time$^{-1}$. For gaseous reaction, the concentration is replaced by partial pressure and so the unit of rate of reaction is atm s$^{-1}$.

## 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. for the smallest time interval).

i.e., Instantaneous rate of a reaction $= \lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$

For the reaction, R $\longrightarrow$ P, the instantaneous rate is given by, $r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$

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

For the reaction, 5 Br$^-$ (aq) + BrO$_3$ $^-$ (aq) + 6 H$^+$ (aq) $\longrightarrow$ 3 Br$_2$ (aq) + 3 H$_2$O (l)

$r_{inst} = -\frac{1}{5}\frac{d[Br^-]}{dt} = -\frac{d[BrO_3^-]}{dt} = -\frac{1}{6}\frac{d[[H]^+]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt} = \frac{1}{3}\frac{d[H_2O]}{dt}$

For a general reaction aA + bB $\longrightarrow$ cC + dD, the instantaneous rate is given by:

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

**Determination of Instantaneous rate of a reaction**

Instantaneous rate of a reaction can be determined graphically. For this first conduct the chemical reaction and find out the concentration of any one of the reactants or products 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.
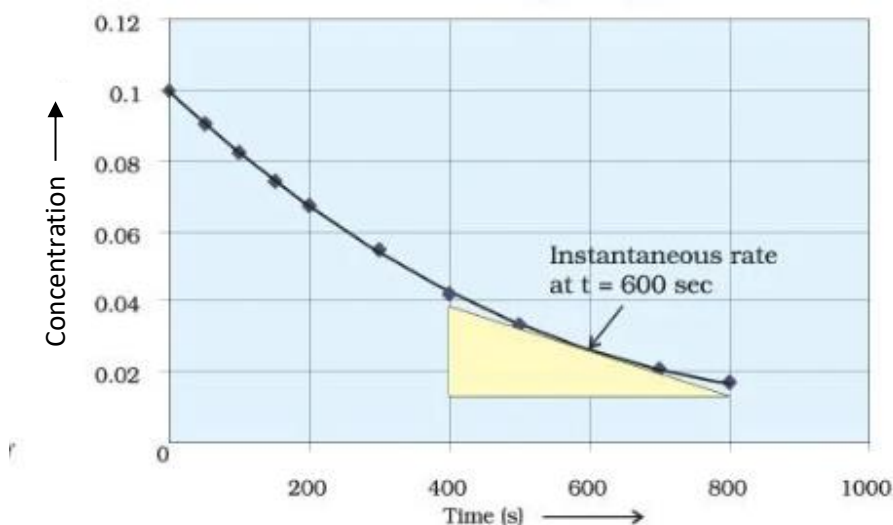


## Factors affecting rate of a reaction

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. Catalyst
6. Radiation or light

**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, $aA + bB \longrightarrow cC + dD$,

Rate $\alpha$ $[A]^x[B]^y$

Or,    $r = k[A]^x[B]^y$ (where x and y may or may not be equal to the stoichiometric coefficients 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.* It is defined as the rate of the reaction when the concentration of each of the reactants is unity.

## Order of reaction (n)

*Order of a reaction 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, $aA + bB \longrightarrow cC + dD$; $r = k[A]^x[B]^y$

Here 'x' is the order with respect to the reactant A, 'y' is the order with respect to B and (x + y) is the overall order of the reaction.

If the order of a reaction is zero, it is called zero order reaction.

E.g.: Decomposition of ammonia at the surface of platinum at high pressure.

If the order of a reaction is one, it is called first order reaction.

E.g. Decomposition of hydrogen peroxide.

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

E.g. for fractional order reactions are:

Decomposition of acetaldehyde: $CH_3\text{-}CHO \longrightarrow CH_4 + CO$; $r = k[CH_3\text{-}CHO]^{3/2}$

Chlorination of chloroform:      $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$; $r = k[CHCl_3][Cl_2]^{1/2}$

## Molecularity of a reaction

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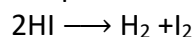
If the molecularity of a reaction is 1, it is called unimolecular reaction.

e.g. Decomposition of ammonium nitrite

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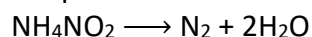
If the molecularity of a reaction is 2, it is called bimolecular reaction.

e.g. Decomposition of Hydrogen Iodide

$2HI \longrightarrow H_2 + I_2$

## 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 steps is called a complex reaction. In a complex reaction one of the steps is slower than the other steps. The overall rate of the reaction is controlled by this step and this step is called the rate determining step (rds). 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.

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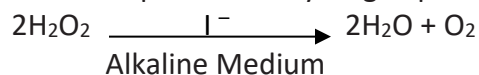
The rate equation for this reaction is found to be $r = -\dfrac{d[H_2O_2]}{dt} = k[H_2O_2][I^-]$

This reaction is first order with respect to both $H_2O_2$ and $I^-$. The reaction takes place in two steps and its mechanism can be written as:

(1)      $H_2O_2 + I^- \xrightarrow{\quad Slow/rds \quad} H_2O + IO^-$

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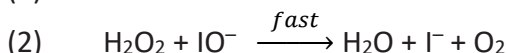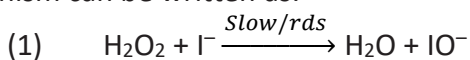
Here the first step is slower than the second. So it is the rate determining step (rds).

## Unit of Rate constant

Different ordered reactions have different units for k.

For an $n^{th}$ order reaction n A $\longrightarrow$ products, rate = $k[A]^n$

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

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

The units of rate constant for different ordered reactions are:

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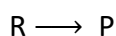
The rate expression for the above reaction is $r = -\dfrac{d[R]}{dt}$ .................. (1)

Rate law for the above reaction is $r = k[R]^0 = k$ .................. (2) [Since $[R]^0 = 1$]

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

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

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

On integrating the above equation we get,

$[R] = -kt + C$ ..................... (3)

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

Substitute these values in eqn. (3)

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

Or, $C = [R]_0$

Substituting 'C' in equation (3), we get

$[R] = -kt + [R]_0$ ............. (4)

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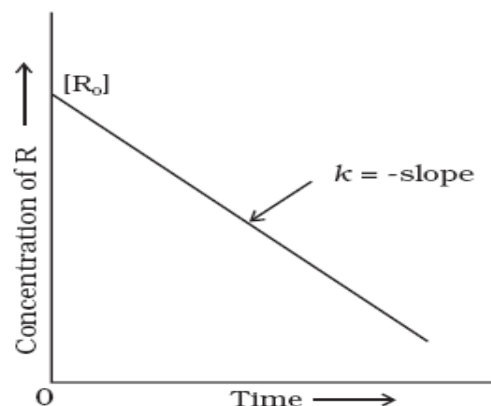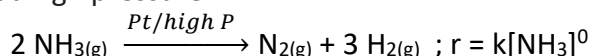
Or, $k = \dfrac{[R]_0 - [R]}{t}$ ............. (5)

Equation (4) is of the form y = mx + c, equation for a straight line.

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.

$2\ NH_{3(g)} \xrightarrow{Pt/high\ P} N_{2(g)} + 3\ H_{2(g)}$ ; $r = k[NH_3]^0$

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 pressure does not change the rate of the reaction. Hence it becomes a zero order reaction.

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

$$2HI(g) \xrightarrow{Au/high\ P} H_2(g) + I_2(g); \quad r = k[HI]^0$$
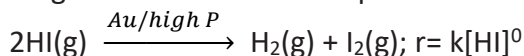
### 2. Integrated Rate Equation for a First order reaction

For a first order reaction, the rate of the reaction is proportional to the first power of 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 $r = k[R]$ .................... (2)

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

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

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

On integrating the above equation we get,

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

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

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

Substitute these values in eqn. (3)

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

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

Substituting the value of 'C' in equation (3), we get

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

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

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

$\quad$ Or, $k = \dfrac{1}{t}\ln\dfrac{[R]_0}{[R]}$ ............... (6)

On changing the base of logarithm, we get: $\mathbf{k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]}}$ .................... (7)

This equation is known as *integrated rate equation for a first order reaction*.
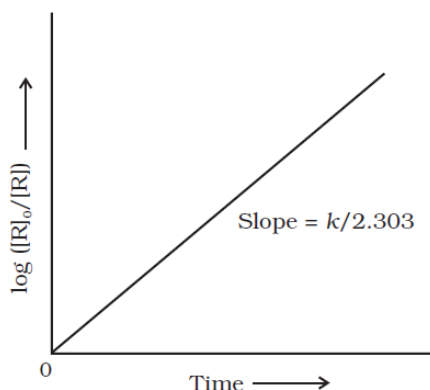
From eqn. (4), $\ln[R] = -kt + \ln[R]_0$

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) $\ln\dfrac{[R]_0}{[R]} = kt$
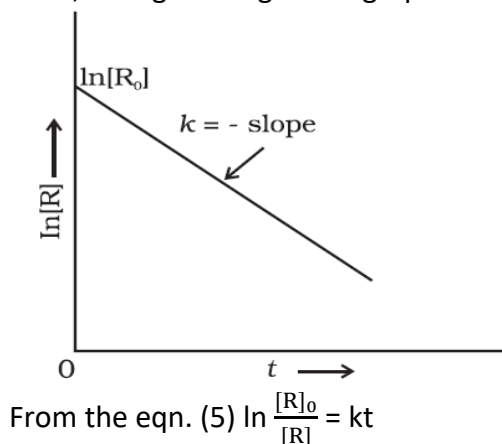
Or,   $2.303 \log \frac{[R]_0}{[R]} = kt$

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

So, if we plot a graph between $\log \frac{[R]_0}{[R]}$ against 't', we get a straight line graph as shown below:



Examples for 1st order reactions are:
1. Hydrogenation of ethene:    $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$; $r = k[C_2H_4]$
2. All natural and artificial radioactive decay.
3. Decomposition of $N_2O_5$ and $N_2O$
   $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$; $r = k [N_2O_5]$

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

The half-life of a reaction is the time taken for the concentration of a reactant is reduced to one half of its initial concentration. 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:  $k = \frac{[R]_0 - [R]}{t}$

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

On substituting these values in the above equation,

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

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

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

When $t = t_{1/2}$, $[R] = [R]_0/2$

Substitute these values in the above equation:

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

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

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

Thus *for a first order reaction, half-life period is independent of initial concentration of the reactants. Or, it is a constant.*
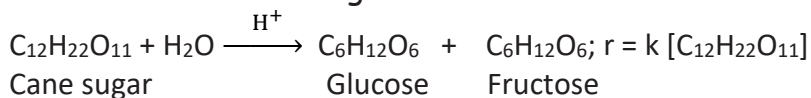
## Pseudo first order reaction

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)

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH; \quad r = k\,[CH_3COOC_2H_5]$$
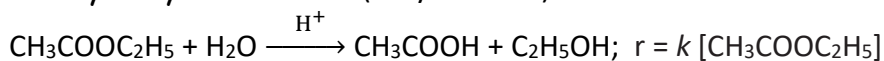
Here the concentration of water does not change during the reaction.

2. Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6; \quad r = k\,[C_{12}H_{22}O_{11}]$$

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:

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

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, $T$ is the absolute temperature and $Ea$ is activation energy measured in joules/mole (J mol$^{-1}$). [The above equation was first proposed by J H van't Hoff, but its physical justification and interpretation was given by Arrhenius.]

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.

$$H_2 + I_2 \longrightarrow 2HI$$
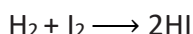


If we plot a graph between potential energy and the progress of reaction, we get the following graph. [Reaction coordinate represents the progress of reaction]

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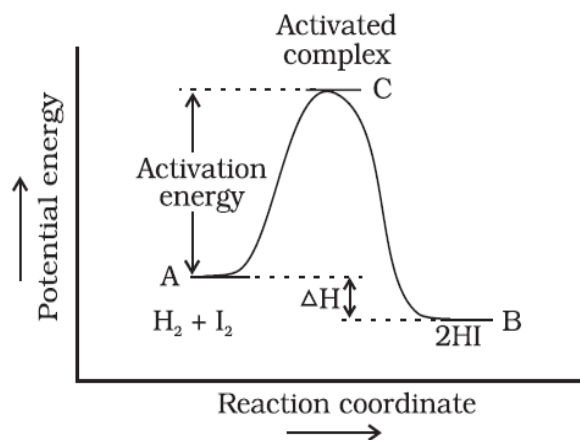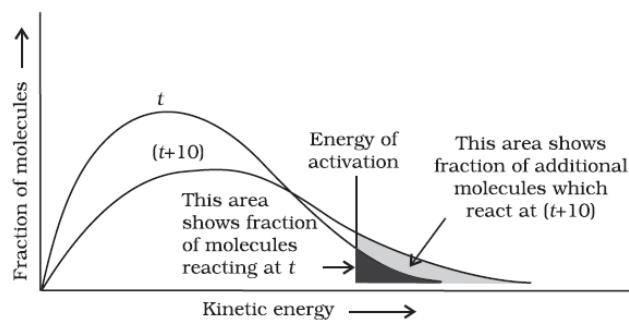
Boltzmann and James Clark Maxwell calculated the distribution of kinetic energy among molecules. They plotted a graph between the fraction of molecules with a given kinetic energy against kinetic energy. This plot is known as Maxwell- Boltzmann distribution curve of molecular energies.
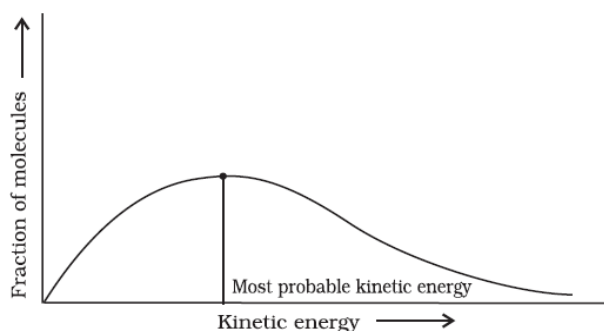


*Maxwell-Boltzmann Distribution curve*          *Distribution curves at 2 different temperatures*

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, this fraction 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*.

The logarithmic form of Arrhenius equation is: $\ln k = -\dfrac{E_a}{RT} + \ln A$

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 graph as follows:

The slope of the graph $= -\dfrac{E_a}{R}$ and the y-intercept = ln A.
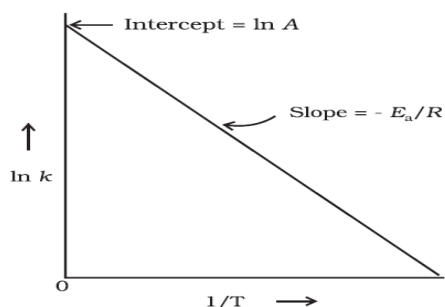


## Calculation of Activation energy by knowing the rate constants at two different temperatures

Consider a reaction R $\longrightarrow$ P. If $k_1$ is the rate constant of the reaction at temperature $T_1$ and $k_2$ is the rate constant at temperature $T_2$, then:

$$\ln k_1 = \frac{-E_a}{RT_1} + \ln A \qquad ……………. (1) \qquad \text{and}$$

$$\ln k_2 = \frac{-E_a}{RT_2} + \ln A \qquad ……………. (2)$$

Equation (2) – (1) gives,

$$\ln k_2 - \ln k_1 = \left[\frac{-E_a}{RT_2} + lnA\right] - \left[\frac{-E_a}{RT_1} + lnA\right]$$

Or, $\ln \dfrac{k_2}{k_1} = -\dfrac{E_a}{RT_2} + \dfrac{E_a}{RT_1}$

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

On changing the base of logarithm, we get:

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

Or, $\boxed{\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\,R} \left[ \dfrac{1}{T_1} - \dfrac{1}{T_2} \right]}$

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 that increases 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 combines with reactant to form an unstable intermediate complex, which decomposes to form products and the catalyst.

A catalyst increases the rate of a chemical reaction by providing an alternate path with low activation energy between reactants and products.

*[A substance that decreases the rate of a reaction is called inhibitor].*

The energy profile diagram for a reaction with catalyst and without catalyst is shown below:
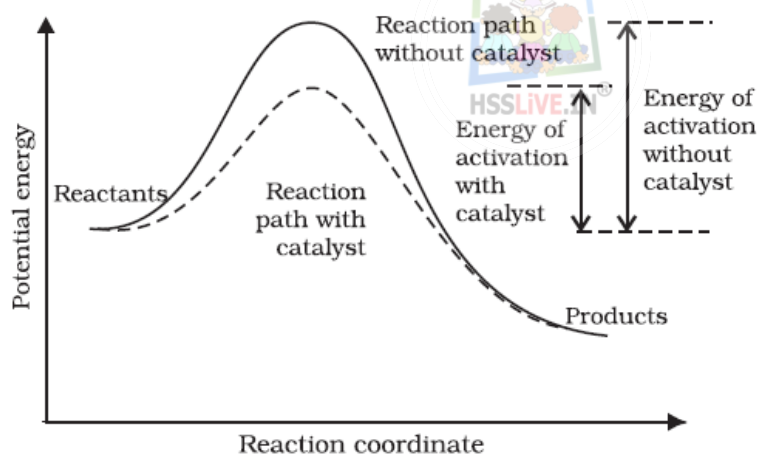


The important characteristics of a catalyst are:
1. A small amount of the catalyst can catalyse a large amount of reactants.
2. A catalyst does not change the Gibbs energy of a reaction ($\Delta_r G$). It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
3. A catalyst 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

$$A + B \longrightarrow Products$$
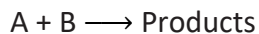
Rate of reaction can be expressed as

$$\text{Rate } (r) = Z_{AB}\, e^{-E_a/RT}$$

Where $Z_{AB}$ represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than $E_a$. 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. The proper orientation of reactant molecules lead to bond formation. While, improper orientation makes them bounce back and no products are formed. To account for this, *probability or steric factor* (P) is introduced. So the above equation becomes:

$$\textbf{Rate } (r) = \textbf{P.}Z_{AB.}\, e^{-E_a/RT}$$

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.