→ Chemical Kinetics:→

→ Introduction:→

- The word kinetics is derived from the Greek word 'kinesis' meaning movement.
- The study of chemical phenomenon can be made from two fundamental approches. The first of these, known as Thermodynamics, is a rigorous and exact method concerned with equilibrium conditions of initial and final states of chemical changes.

    The other method, known as Chemical kinetics, is less rigorous and deals with a more chemical aspect of chemical phenomenon, namely, the rate of change from initial to final state under non-equilibrium conditions.
- Chemical kinetics is the measurement of rates of reaction proceeding under given conditions of temperature, pressure and concentration.
- Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.

Example:- Thermodynamics predicts that at room temperature hydrogen and oxygen react to form water, all the reactants being essentially converted into the product. But when we actually carry out the experiment we find that the reaction takes place so slowly that it will take indefinite time.

- Chemical kinetics also describe exactly how each reaction occurs and also describe the conditions by which the reaction rates can be altered.
- Macroscopic kinetic is branch of kinetics which explains the behaviour of a very large group of molecules in thermal equilibrium.

- Microscopic kinetics is the branch of kinetics in which reacting molecules in well defined state are studied.

→ Slow and fast reactions:→

(a) Slow reactions:→

- These are the reactions which proceed slowly and their rates can be measured by conventional methods.

Example:- Inversion of cane-sugar in aqueous solution.

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

- In slow reactions a large number of bonds have to be broken in reactant molecules and a large number of new bonds have to be formed in the product molecules.

(b) Fast reactions:→

- These are the reaction which proceed fastly and their rates can not be measured by conventional methods but can be measured by special methods.

Example:- (i) Many ionic reactions such as neutralisation of acids by bases.
(ii) Reactions of biological significance.
(iii) organic substitution reactions.
(iv) Explosive reaction of oxygen with hydrogen and hydrocarbons.

- In case of simple ionic reactions, no bonds are to be broken. The reactions, therefore, are very fast.

→ Rate of reaction: →

- Rate of a reaction can be defined as the change in concentration of a reactant or product in unit time.
- To be more specific, it can be expressed in terms of:
  (i) The rate of decrease in concentration of any of the reactants, or
  (ii) The rate of increase in concentration of any of the products.

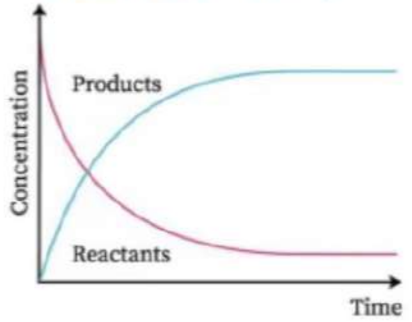


Fig:- Change in concentration of reactants & products with time

- Expressing reaction rates: →

- Consider a simple hypothetical reaction of type

$$A \longrightarrow P$$

The rate of the reaction at any given time will depend upon the concentration of the reactant A at that time. As the reaction proceeds, the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression

$$r = \frac{dx}{dt} = -\frac{dC_A}{dt} \quad — ①$$

where $-\frac{dC_A}{dt}$ = Infinitesimally small decrease in the concentration of A in an infinitesimally small intervel of time dt.

C_A = Concentration of reactant A at given instant.

✲ The minus sign in eq ①, indicates that the concentration of reactant is decreasing with time.

- The concentration of the product P goes on increasing with time. Hence, the rate of the reaction can also be expressed in terms of increase in concentration of the product. Thus

$$r = \frac{dx}{dt} = \frac{dC_P}{dt} \quad — ②$$

where $\frac{dC_P}{dt}$ = Infinitesimally small increase in the concentration of P in an infinitesimally small intervel of time dt.

C_P = Concentration of reactant P at given instant.

✱ The plus sign in eq②, indicates that the concentration of product is increasing with time.

- From eq. ① and ②

$$r = \frac{dx}{dt} = -\frac{dC_A}{dt} = \frac{dC_P}{dt} \quad — ③$$

- For a reaction of type

$$A + B \longrightarrow L + M$$

the reaction rate can be expressed as

$$r = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \frac{dC_L}{dt} = \frac{dC_M}{dt}$$

Example :-

$$Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s)$$

the reaction rate can be expressed as

$$r = -\frac{d[Hg]}{dt} = -\frac{d[Cl_2]}{dt} = \frac{d[HgCl_2]}{dt}$$

- Consider a general reaction of type

$$aA + bB \longrightarrow lL + mM$$

the reaction rate can be expressed as

$$r = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = \frac{1}{l}\frac{dC_L}{dt} = \frac{1}{m}\frac{dC_M}{dt}$$

Example:-

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

the reaction rate can be expressed as

$$r = -\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

→ Unit:→

- The unit of rate of reaction is expressed in gm moles per litre per unit time (mol litre^{-1} time^{-1}
  The time is in minutes or seconds.
- In gaseous reactions, concentration is expressed in terms of partial pressure hence the unit will be atm time^{-1}!

→ Determining reaction rates:→

- In order to determine the reaction rate curves shown in following figures are considered.
- In these curves, concentration is plotted against time t.
- The rate of reaction for an time interval is given by following expression.

$$r = -\frac{\Delta x}{dt} = \frac{\Delta x}{dt}$$

and for infinitesimal change

$$r = -\frac{dx}{dt} = \frac{dx}{dt}$$

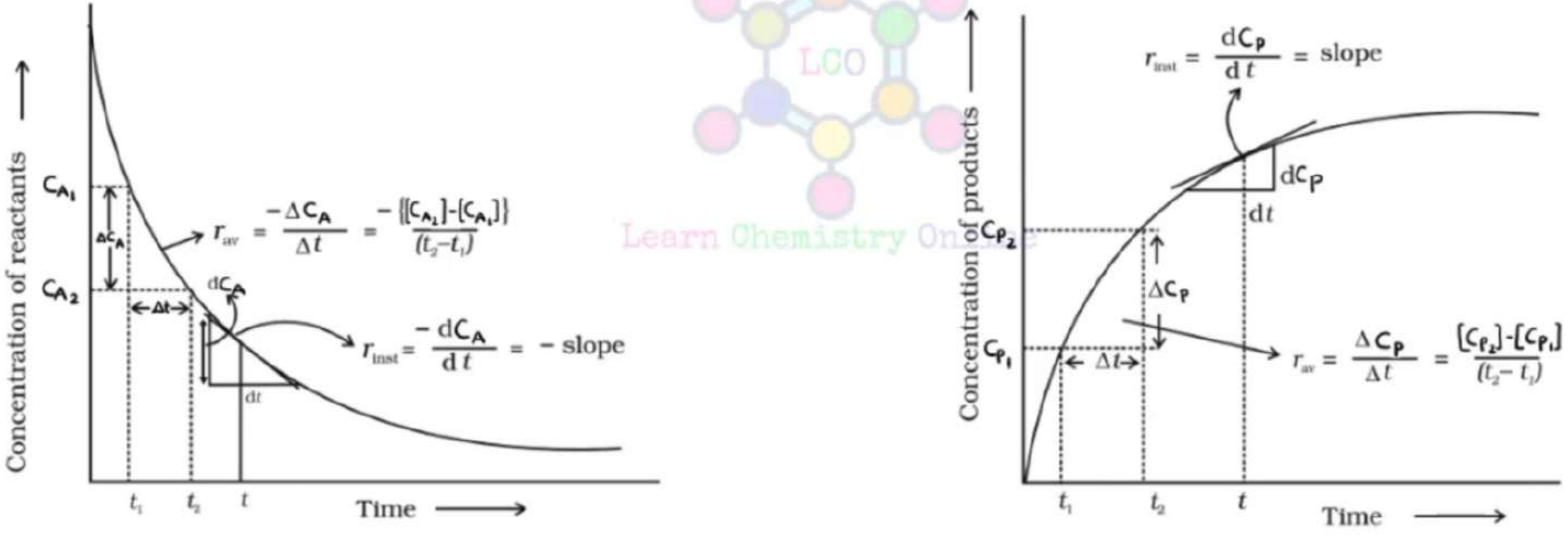


Fig:- Instantaneous and average rate of a reaction, A → P

→ Factors influencing the rate of a reaction:→

1. Concentration:→

- According to law of mass action, the rate of reaction is proportional to molar concentration of reactants.
- The rate changes with time because the concentration of reactants decrease as time passes.

Example:- Rusting of iron is enhanced during rainy season due to high concentration of water vapour in air.

2. Temperature:→

- Temperature has a striking effect on the rate of chemical reactions.
- Reaction rate negligibly slow at ordinary temperature may become appreciable and even explosive at elevated temperatures.
- As a very rough but useful rule, the rate constant is doubled for a rise in temperature of 10°C. Thus, a temperature change of 100°C may alter the rate more or less by a factor of 10^3.

Example:- In case of decomposition of HI, the rate constant increases by a factor of 1·7 for each 10°C rise in temperature.

- When logarithm of reaction rate is plotted againt $1/T$, straight light is obtained for most of the chemical reactions. The variation, therefore, can be represented by the following equation-

$$\log k = a - \frac{b}{T}$$

where k = specific reaction rate, T = Absolute temp.

a, b = Positive empirical constants.

a (Intercept), b (slope)

3. ~~Pressure~~ :→

- If the pressure of gaseous reactants is increased, there are more reactant particles for a given volume. There will be more collisions and so the reaction rate is increased.
- The higher the pressure of reactants, the faster the rate of reaction will be.

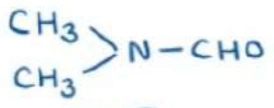
4. Solvent :→

- The nature of the solvent can also affect the reaction rates of solute particles.

Example:- A sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide.

$$CH_3COONa\,(Sol.) + HI(l) \longrightarrow CH_3COOCH_3\,(Sol) + NaI(Sol)$$

This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide than it does in methanol. Although both are organic solvents with similar dielectric constants, metanol is able to form hydrogen bond with acetate ions, wheres DMF cannot. Hydrogen bonding reduces the reactivity of oxygen atoms in the acetate ions.



DMF

Methanol Acetate ion

- Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus, the reaction rates of most reaction decrease rapidly with increasing solvent viscosity.

5. Light :→

- Not only heat energy but radiant energy may also alter the rate of certain chemical reactions.
- The term radiant energy means energy derived from x-rays, UV rays, visible and infrared rays, radiowaves etc.
- The rates of some reactions are enhanced due to absorption of photons of different energies.
- These reactions, where photons are used, are called photochemical reactions.

  Example :- Reaction between H_2 and Cl_2 to form HCl in presence of sunlight.

6. Catalyst :→

- The rates of certain reactions may be altered by the presence of certain substances in reacting system. These substances are called catalyst.

  Example :- Mangnese dioxide speeds up the rate of decomposition of potassium chlorate.

→ Concentration dependence of rates :→ (The rate law and the Rate constant or Velocity constant)

- The mathematical relation between the rate of reaction and the concentration of the reaction components is known as the rate equation or rate law expression for reaction.
- According to law of mass action, the rate of chemical reaction is directly proportional to the active concentrations of the reactants.
- Consider a general reaction of type

$$A \longrightarrow \text{Product}$$

The rate of reaction is

$$r \propto C_A \quad — ① \quad (C_A = \text{Concentration of reactant } A)$$

or $$r = kC_A \quad — ②$$

or $$-\frac{dx}{dt} = kC_A \quad — ③$$

where K = A constant which is characteristic of a reaction and is known as the rate constant or velocity constant of the reaction at given temp.

- If the concentration of reactant A is unity i.e. $C_A = 1$, then eq. ② becomes

$$r = K \quad — ④$$

Thus, at a given temperature, the rate constant or velocity constant of a reaction may be defined as the rate of reaction when the concentration of each reactant is unity.

- For a general reaction of type

$$aA + bB + cC \longrightarrow \text{Products}$$

The rate of the reaction is given by the rate-law expression

$$r = K C_A^a C_B^b C_C^c \quad - ⑤$$

- The rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e. theoritically but must be determined experimentally.

→ Units of rate constant :→

- Let us consider the general form of the reaction of the type :

$$aA + bB + \ldots\ldots \rightarrow \text{Products}$$

The rate of reaction is given by

$$r = K C_A^a C_B^b \ldots\ldots \quad - ⑥$$

$$r = \text{moles/litres/sec}$$

$$C_A = C_B = \ldots\ldots = \text{moles/litres}$$

Substituting these units in eq. ⑥

$$\frac{\text{moles}}{\text{litre}} \times \sec^{-1} = K \left(\frac{\text{moles}}{\text{litre}}\right)^a \times \left(\frac{\text{moles}}{\text{litre}}\right)^b \times \ldots\ldots$$

$$K = \left[\left(\frac{\text{litres}}{\text{moles}}\right)^{((a+b+\ldots)-1)}\right] \times \left[\sec^{-1}\right]$$

→ Molecularity of a reaction :→

- It is the sum of the number of molecules of various reactants that take part in a chemical reaction as represented by a balanced chemical reaction.

(a) Unimolecular reactions :→

- A unimolecular reaction is one in which only one molecule of reactant is involved.

Example :-

(i) $Br_2 \rightarrow 2Br$

(ii) $NH_4NO_2 \rightarrow N_2 + 2H_2O$

(b) Bimolecular reactions :→

- A bimolecular reaction is one in which two molecules of reactant are involved.

Example :- (i) Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) Hydrolysis of an ester

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

(C) Trimolecular or Termolecular reactions :→

- A termolecular reaction is one in which three molecules of reactant are involved.

Examples:-

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

(ii) $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

(iii) $2CH_3COOAg + HCOONa \rightarrow 2Ag + CO_2 + CH_3COOH + CH_3COONa$

- The probability that more than three molecules can collide and react simultanesouly is very small. Hence, reactions with molecularity more than three are very rare and slow to proceed.

It is therefore, evident that reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.

→ Order of a reaction:→

- In the study of chemical kinetics, it is not necessary that the concentrations of all the reactants taking part in a reaction can determine the rate of reaction. Therefore a new term 'order' is introduced.
- Chemical reactions are generally classified in terms of their 'order'.
- The order of reaction is given by the number of atoms or molecules whose concentrations alter during the chemical change.

or

The order of reaction is given by the total number of molecules or atoms whose concentrations determines the velocity of the reaction.

(a) Zero order reaction:→

- A reaction is said to be zero order, when its rate is independent of the concentration of the reactants.

$$r = K_0$$

(b) First order reaction:→

- It is defined as one in which one concentration term determine the rate of a reaction.

$$r = K_1 C_A$$

(c) Second order reaction:→

- It is defined as one in which two concentration terms determine the rate of a reaction.

$r = K_2 C_A^2$ (For one type of reactant) or $r = K_2 C_A C_B$ (For two types of reactants)

(d) Third order reaction:→

- It is defined as one in which three concentration terms determine the rate of a reaction.

$r = K_3 C_A^3$ (For one type of reactant)

$r = K_3 C_A^2 C_B$ (For two type of reactants)

$r = K_3 C_A C_B^2$ (For two type of reactants)

$r = K_3 C_A C_B C_C$ (For three type of reactants)

(e) General order reaction:→

- Consider a reaction of type

$$aA + bB + \dots \rightarrow \text{Products}$$

The rate of such a reaction $\propto C_A^a C_B^b \dots\dots$

or the rate of such a reaction $= K C_A^a C_B^b \dots\dots$

Then, order of such a reaction $= a + b + \dots\dots$

Therefore, the order of the reaction may be defined as "The sum of powers to which the the concentration (or pressure) terms are raised in order to determine the rate of the reaction.

- The order of a reaction is an experimental quantity. It is not necessary that the order of reaction may not always be a whole number. It can be fractional quantity also.

→ Units of rate constant :→

– The units of rate constant for a given reaction can be determined by with the help of appropriate rate equation of the reaction.

(a) Zero order reaction :→

$$\text{Rate} = -\frac{d[A]}{dt} = K_0$$

$$K_0 = \frac{\text{units of } [A]}{\text{units of } t}$$

$$K_0 = \frac{\text{mol L}^{-1}}{\text{s}} = \text{mol L}^{-1}\text{ s}^{-1}$$

(b) First order reaction :→

$$\text{Rate} = -\frac{d[A]}{dt} = K_1[A]$$

$$\text{or} \quad K_1 = -\frac{1}{[A]} \times \frac{d[A]}{dt}$$

$$K_1 = \frac{1}{\text{mol L}^{-1}} \times \frac{\text{mol L}^{-1}}{\text{s}}$$

$$K = \text{s}^{-1}$$

(C) Second order reaction:→

(i) $$\text{Rate} = -\frac{d[A]}{dt} = K_2[A]^2$$

or $$K_2 = -\frac{1}{[A]^2} \times \frac{d[A]}{dt}$$

$$K_2 = \frac{1}{(\text{mol } L^{-1})^2} \times \frac{(\text{mol } L^{-1})}{s}$$

$$K_2 = \text{mol}^{-1}\, L\, s^{-1}$$

(i) $$\text{Rate} = -\frac{d[A]}{dt} = K_2[A][B]$$

or $$K_2 = -\frac{1}{[A][B]} \times \frac{d[A]}{dt}$$

$$K_2 = \frac{1}{(\text{mol } L^{-1})^2} \times \frac{(\text{mol } L^{-1})}{s}$$

$$K_2 = \text{mol}^{-1}\, L\, s^{-1}$$

(d) Third order reaction:→

$$\text{Rate} = -\frac{d[A]}{dt} = K_3[A]^3$$

$$\text{or} \quad K_3 = -\frac{1}{[A]^3} \times \frac{d[A]}{dt}$$

$$K_3 = \frac{1}{(\text{mol L}^{-1})^3} \times \frac{\text{mol L}^{-1}}{\text{s}}$$

$$K_3 = \text{mol}^{-2}\,\text{L}^{2}\,\text{s}^{-1}$$

✱ We can also use dm^3 (cubic decimetre) instead of L (litre). [∵ $dm^3 = L$]

(e) Half order reaction:→

$$\text{Rate} = -\frac{d[A]}{dt} = K_{1/2}[A]^{1/2}$$

$$\text{or} \quad K_{1/2} = -\frac{1}{[A]^{1/2}} \times \frac{d[A]}{dt}$$

$$K_{1/2} = \frac{1}{(\text{mol L}^{-1})^{1/2}} \times \frac{\text{mol L}^{-1}}{\text{s}}$$

$$K_{1/2} = \text{mol}^{1/2}\,\text{L}^{-1/2}\,\text{s}^{-1}$$

(f) nth order reaction:→

$$K_n = \text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$$

→ Differences between order and molecularity of a reaction :→

Order of a reaction	Molecularity of a reaction
1. It is an experimentally determined quantity which is obtained from the rate for the overall reaction.	1. It is a theoretical concept which depends on the rate determining step in the reaction mechanism.
2. It possesses all sorts of values including zero.	2. It is generally not exceeding three and never zero.
3. It may be a whole number or fractional value.	3. It is always a whole number.
4. It cannot be obtained from a balanced chemical equation.	4. It is obtained from a single balanced chemical equation.
5. It does not reveal anything about the mechanism of the reaction.	5. It reveals some basic facts about reaction mechanism.
6. It is equal to the sum of the exponents of the molar concentrations of the reactants in the rate equation.	6. It is equal to the number of molecules of the reactants which are taking part in a single step chemical reaction.

→ Order and molecularity of simple reactions :→

– The reactions taking place in one step are called elemantary or simple reactions.

(i) Inversion of cane sugar :→

– This reaction is

$$\underset{\text{Cane Sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

As this reaction involves two reactants ($C_{12}H_{22}O_{11}$ and H_2O), the molecularity of the reaction is two. When its rate is determined experimentally, it has been found to observe the following rate law.

$$-\frac{d[C_{12}H_{22}O_{11}]}{dt} \propto C_{C_{12}H_{22}O_{11}}$$

As the rate of the reaction is determined by the variation of one concentration term only $[C_{12}H_{22}O_{11}]$, the order of the reaction is one. Thus, the molecularity of this reaction is two but order of the reaction is one. This is due to fact that water being present in such a large excess that its concentration does not measurably change during the chemical reaction.

(ii) Saponification of ethyl acetate :→

– This reaction is

$$CH_3COOC_2H_5 + NaOH \rightleftharpoons CH_3COONa + C_2H_5OH$$

The molecules ($CH_3COOC_2H_5$ and NaOH) are involved in this reaction and hence the molecularity of reaction is two. The rate of this reaction has been found to obey the following rate law:

$$-\frac{d[CH_3COOC_2H_5]}{dt} \propto [CH_3COOC_2H_5][NaOH]$$

Hence the order of this reaction is two.

From the above examples it is evident that the order of reaction is the number of chemical species (molecules, atoms or ions) whose concentrations affect the rate of the reaction while the molecularity of a reaction is the number of chemical species taking part in a chemical reaction.

→ Order and Molecularity of complex reactions :→

- The reactions which occur in two or more steps are called complex reactions.
- In such reactions each step has own molecularity. All these steps may proceed at the same or different rates. But the slowest step determines the order of overall reaction.

(a) The reduction of bromic acid to hydrobromic acid by hydroiodic acid :→

$$HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2 \quad — ①$$

Although this reaction involves seven molecules yet it is of the second order. This can be explained on the basis of following mechanism.

(i) $HBrO_3 + HI \longrightarrow HBrO_2 + HIO$ (slow)

(ii) $HBrO_2 + 4HI \rightarrow HBr + 2H_2O + 2I_2$ (fast)

(iii) $HIO + HI \longrightarrow H_2O + I_2$ (fast)

The first step is slow and hence the rate determining step. The reaction is of the second order. The molecularity of complex reaction ① has no significance.

The molecularities of steps (i), (ii) and (iii) are 2, 5 and 2 respectively.

(b) The oxidation of hydroiodic acid by hydrogen peroxide in aqueous solution :→

$$H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2 \quad — ②$$

Experimentally, it is of second order. This can be explained on the basis of following mechanism.

(i) $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)

(ii) $H^+ + IO^- \rightarrow HIO$ (fast)

(iii) $HIO + H^+ + I^- \rightarrow H_2O + I_2$ (fast)

The first step is slow and hence the rate determining step. The molecularities of step (i), (ii) and (iii) are 2, 2 and 3 respectively.

→ Conclusion:→

(i) The order of a complex reaction is given by the order of the slowest step in the sequence of various steps which are involved in that reaction.

(ii) The concept of molecularity of complex reaction has no significance. Each step involved in the complex reaction has its own molecularity.

→ Mathematical characteristics of simple chemical reactions :→

→ Zero order reaction :→

- Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.
- Mathematically, for a zero order reaction

$$A \longrightarrow P$$

$$r = -\frac{d[A]}{dt} = K_0[A]^0$$

$$\text{or} \quad r = -\frac{d[A]}{dt} = K_0$$

$$\text{or} \quad d[A] = -K_0 dt$$

Integrating both sides

$$[A] = -K_0 t + I \text{ --- } ①$$

where I = Integration constant

At $t = 0$

The initial concentration is $[A]_0$

Substituting these values in eq. ①

$$[A]_0 = -K_0 \times 0 + I$$

$$[A]_0 = I$$

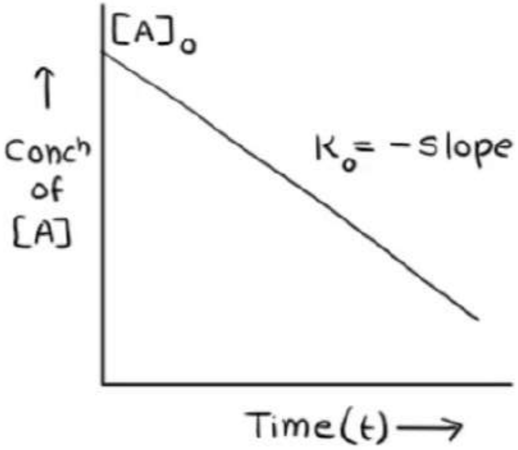
Substituting the value of I in eq. ①

$$[A] = -K_0t + [A]_0 \quad — ②$$

If concentration of reactant is plotted against time then (compare eq. ② with the straigh line equation $y = mx + c$)

$$\text{Slope} = -K_0$$

$$\text{Intercept} = [A]_0$$



On simplifying eq. ② we get the rate constant K_0

$$-K_0t = [A] - [A]_0$$

$$-K_0 = \frac{[A] - [A]_0}{t}$$

$$\text{or} \quad K_0 = \frac{[A]_0 - [A]}{t} \quad — ③$$

Eq. ③ is the integrated rate equation for zero order reaction.

✤ In such reactions, the rate may be determined by some other limiting factors such as the amount of catalyst used in catalytic reaction or the intensity of light absorbed in a photochemical reaction.

→ Examples of zero order reactions :→

(i) The reaction between acetone and bromine is found to be zero order in respect to bromine.

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

(ii) The reaction between acetone and iodine is found to be zero order in respect to iodine.

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

(iii) Decomposition of phosphine on the surface of molybdenum or tungsten at high pressure is of zero order.

$$2PH_3 \longrightarrow 2P + 3H_2$$

(iv) Decomposition of gaseous ammonia

$$2NH_3(g) \xrightarrow[\substack{\text{Pt catalyst} \\ \text{high pressure}}]{1130\,K} N_2(g) + 3H_2(g)$$

(iv) Thermal decomposition of HI on gold surface.

→ Mathematical characteristics of simple chemical reactions :→

→ First order reaction :→

- The first order reaction is that in which the rate depends upon the concentration of single reactant only.
- Consider a first order reaction

$$A \longrightarrow P$$

$$r = -\frac{d[A]}{dt} = K_1[A]$$

or

$$\frac{d[A]}{[A]} = -K_1 dt \quad — ①$$

Integrating both sides

$$\ln[A] = -K_1 t + I \quad — ②$$

where I = Integration constant

At $t = 0$

$$[A] = [A]_0$$

where $[A]_0$ = Initial concentration of reactant

Substituting these values in eq. ②

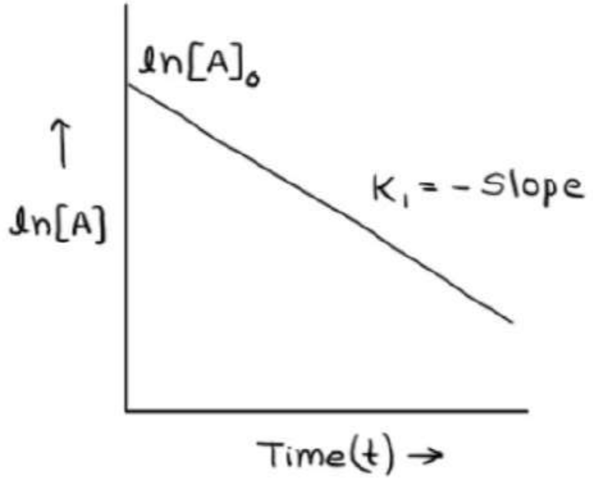
$$\ln[A]_0 = -K_1 \times 0 + I$$

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

Substituting the value of I in eq. ②

$$\ln[A] = -K_1 t + \ln[A]_0 \quad - ③$$

If ln[A] is plotted against t then (compare eq. ② with straight line equation , $y = mx + c$)



$$\text{Slope} = -K_1$$

and $\text{Intercept} = \ln[A]_0$

rearranging eq. ③

$$\ln[A] - \ln[A]_0 = -K_1 t$$

or $\ln[A]_0 - \ln[A] = K_1 t$

or $\ln\frac{[A]_0}{[A]} = K_1 t \quad — ④$

Taking antilog of both side of eq. ④

$$[A] = [A]_0 e^{-K_1 t} \quad - ⑤$$

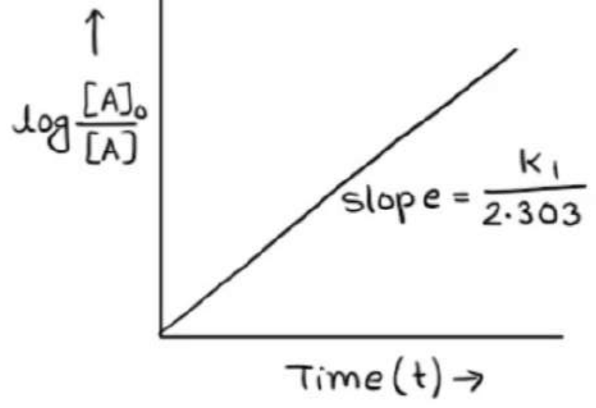
Eq. ⑤ is known as Wilhelmy's equation

rearrang eq. ④

or $K_1 = \frac{1}{t} \ln\frac{[A]_0}{[A]} \quad - ⑥$

or $K_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$ — ⑦

or $\log \frac{[A]_0}{[A]} = \frac{K_1 t}{2.303}$ — ⑧



If we plotted $\log \frac{[A]_0}{[A]}$ against t then

$$\text{slope} = \frac{K_1}{2.303}$$

or $K_1 = 2.303 \times \text{slope}$ — ⑨

suppose

		Concⁿ of A	Concⁿ of P
At	$t=0$	a	0
At	$t=t$	$a-x$	x

So $[A]_0 = a$ and $[A] = (a-x)$

At time t, eq. ⑤ becomes

$K_1 = \frac{2.303}{t} \log \frac{a}{(a-x)}$ — ⑩

At time t_1 from eq. ③

$\ln [A]_1 = -K_1 t_1 + \ln [A]_0$ — ⑪

At time t_2

$$\ln[A]_2 = -K_1 t_2 + \ln[A]_0 \quad - ⑫$$

where $[A]_1$ & $[A]_2$ = Concⁿ of reactants at time t_1 & t_2 respectively

subtracting eq. ⑫ from eq. ⑪

$$\ln[A]_1 - \ln[A]_2 = -K_1 t_1 - (-K_1 t_2)$$

or $$\ln\frac{[A]_1}{[A]_2} = K_1 t_2 - K_1 t_1$$

or $$\ln\frac{[A]_1}{[A]_2} = K_1(t_2 - t_1)$$

or $$K_1 = \frac{1}{(t_2 - t_1)} \ln\frac{[A]_1}{[A]_2} \quad - ⑬$$

or $$K_1 = \frac{2.303}{(t_2 - t_1)} \log\frac{[A]_1}{[A]_2} \quad - ⑭$$

→ Examples of first order reactions :→

1. Decomposition of di-tert-butyl peroxide

$$(CH_3)_2COOC(CH_3)_3 \rightarrow 2CH_3COCH_3 + C_2H_6$$

2. Decomposition of dinitrogenpentoxide

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

3. Decomposition of thionyl chloride

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

4. Decomposition of hydrogen peroxide

$$H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$$

5. All radioactive decay
6. Acid hydrolysis of an ester

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

7. Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightleftharpoons{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

8. Decomposition of diazonium chloride

$$C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$$

→ Mathematical characteristics of simple chemical reactions :→

→ Second order reaction :→

- The second order reaction is that in which the rate depends upon the two concentration terms of reactant.
- Such reaction can be represented as

1. Case I - When Both the Reactants are the same.
2. Case II - When the reactants are different.

1. Case I - When Both the Reactants are the same.

- In this case two molecules of the same reactant are involved in the chemical reaction.
- Consider a second order reaction

$$2A \rightarrow P$$

$$r = \frac{dx}{dt} = K_2[A]^2$$

or

$$\frac{dx}{[A]^2} = K_2 dt \quad — ①$$

Suppose

	Conc^n of A	conc^n of P
At $t = 0$	a	0
At $t = t$	$a - x$	x

At time t eq. ① becomes

$$\frac{dx}{(a-x)^2} = K_2 dt \quad — ②$$

Integrating equation ②

$$\frac{1}{(a-x)} = K_2t + I \quad — ③$$

where I is the integration constant

At $t=0,\ x=0$

substituting these values in eq. ③

$$\frac{1}{a} = K_2 \times 0 + I$$

$$\frac{1}{a} = I$$

Substituting the value of I in eq. ③

$$\frac{1}{(a-x)} = K_2t + \frac{1}{a}$$

or $$K_2t = \frac{1}{(a-x)} - \frac{1}{a}$$

or $$K_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

or $$K_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \quad — ④$$

$$\left\{\begin{matrix} \left[\frac{a-(a-x)}{a(a-x)}\right] \\ \left[\frac{a-a+x}{a(a-x)}\right] \\ \left[\frac{x}{a(a-x)}\right] \end{matrix}\right\}$$

→ Examples :→

1. Gaseous decomposition of hydrogen Iodide

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

2. Thermal dissociation of acetaldehyde

$$2\,CH_3CHO \longrightarrow 2CH_4 + 2CO$$

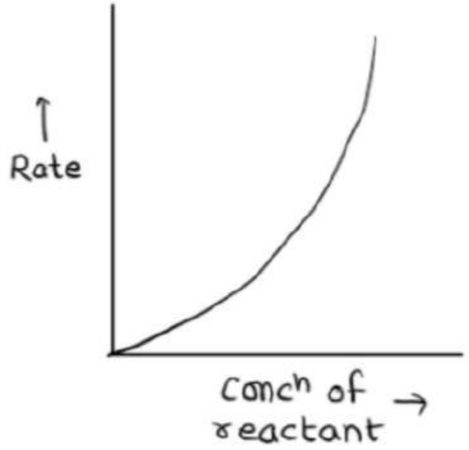


Fig : The plot of rate v/s conc^n for second order reaction

→ Mathematical characteristics of simple chemical reactions :→

→ Second order reaction :→

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1. Case I - When Both the Reactants are the same.
2. Case II - When the reactants are different.

2. Case II - When the reactants are different.

- In this case two molecules of the different reactants are involved in the chemical reaction.
- Consider a second order reaction

$$A + B \longrightarrow P$$

$$r = \frac{dx}{dt} = K_2[A][B]$$

or $$\frac{dx}{[A][B]} = K_2 dt \quad — ①$$

Suppose

	Conc^n of A	Conc^n of B	conc^n of P
At t = 0	a	b	0
At t = t	$a-x$	$b-x$	x

At time t eq. ① becomes

$$\frac{dx}{(a-x)(b-x)} = K_2 dt \quad — ②$$

Resolving into partial fraction (assuming that a>b), we have

$$\frac{1}{(a-b)}\left[\frac{dx}{(b-x)}-\frac{dx}{(a-x)}\right]=K_2dt \quad — ③ \qquad \because \frac{1}{(a-x)(b-x)}=\frac{1}{(a-b)}\left[\frac{1}{b-x}-\frac{1}{a-x}\right]$$

(Complete solution on next slide)

Integrate equation ③

$$\frac{1}{(a-b)}\left[\int\frac{dx}{(b-x)}-\int\frac{dx}{(a-x)}\right]=K_2\int dt$$

We have taken the factor 1/(a-b) outside the integral sign because this quantity is a constant.

$$\frac{1}{(a-b)}\left[-\ln(b-x)-\{-\ln(a-x)\}\right]=K_2t+I$$

or $$\frac{1}{(a-b)}\left[-\ln(b-x)+\ln(a-x)\right]=K_2t+I$$

or $$\frac{1}{(a-b)}\left[\ln(a-x)-\ln(b-x)\right]=K_2t+I$$

or $$\frac{1}{(a-b)}\ln\left(\frac{a-x}{b-x}\right)=K_2t+I \quad — ④$$

where I is the integration constant

At $t=0,\ x=0$

substitue these values in eq. ④

$$\frac{1}{(a-b)} \ln\left(\frac{a-0}{b-0}\right) = K_2 \times 0 + I$$

$$\frac{1}{(a-b)} \ln\left(\frac{a}{b}\right) = I$$

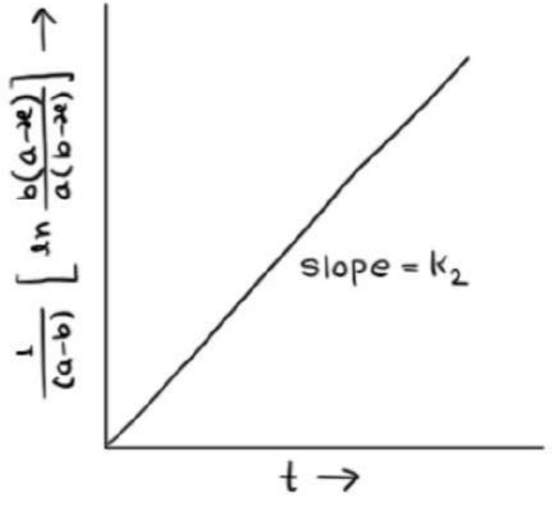
Substitute value of I in eq. ④

$$\frac{1}{(a-b)} \ln\left(\frac{a-x}{b-x}\right) = K_2 t + \frac{1}{(a-b)} \ln\left(\frac{a}{b}\right)$$

or $$\frac{1}{(a-b)} \ln\left(\frac{a-x}{b-x}\right) - \frac{1}{(a-b)} \ln\left(\frac{a}{b}\right) = K_2 t$$

or $$\frac{1}{(a-b)} \left[\ln\left(\frac{a-x}{b-x}\right) - \ln\left(\frac{a}{b}\right)\right] = K_2 t$$

or $$\frac{1}{(a-b)} \left[\ln \frac{b(a-x)}{a(b-x)}\right] = K_2 t$$



If we apply straight line equation on above equation then slope will give value of K_2

or $$K_2 = \frac{1}{(a-b)t} \left[\ln \frac{b(a-x)}{a(b-x)}\right] \quad - ⑤$$

or $$K_2 = \frac{2.303}{(a-b)t} \left[\log \frac{b(a-x)}{a(b-x)}\right] \quad - ⑥$$

Eq. ⑤ and ⑥ is known as kinetic equation for the second order reaction.

- Here we have assume that $a > b$. If we had assumed that $b > a$, then

$$k_2 = \frac{1}{(b-a)t} \ln \frac{a(b-x)}{b(a-x)} \quad - \text{⑦}$$

- It can be easily seen that neither eq. ⑤ or eq. ⑦ is applicable when the concentrations of both the reactants are same, i.e., when $a = b$.
- The rate constants of second order reactions in which the two reactants, although different, have the same initial concentration, i.e., $a = b$, are also determined with the help of equation of case - I.

→ Examples: →

1. Saponification of an ester

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

2. Reaction between persulphate and iodide

$$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$$

→ Complete solution of partial fraction:→

→ First method:→

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)} \quad - Ⓐ$$

$$\frac{1}{(a-x)(b-x)} = \frac{(b-x)A + B(a-x)}{(a-x)(b-x)}$$

$$1 = (b-x)A + B(a-x)$$

$$1 = bA - xA + Ba - Bx$$

$$1 = (bA + Ba) - xA - Bx$$

$$1 = (bA + Ba) - x(A+B)$$

Compare coefficients of x

$$1 = bA + Ba \quad — ①$$

$$A + B = 0 \quad - ②$$

or $A = -B \quad - ③$

Substitute value of A in eq. ①

$$1 = -bB + Ba$$

$$1 = B(a-b)$$

or $B = \frac{1}{(a-b)}$

Substitute value of B in eq. ③

$$A = -\frac{1}{(a-b)}$$

$\therefore$ $A = -\frac{1}{(a-b)}$ and $B = \frac{1}{(a-b)}$

Substitute value of A and B in eq. Ⓐ

$$\frac{1}{(a-x)(b-x)} = -\frac{1}{(a-b)}\frac{1}{(a-x)} + \frac{1}{(a-b)}\frac{1}{(b-x)}$$

$$= \frac{1}{(a-b)}\left[-\frac{1}{(a-x)} + \frac{1}{(b-x)}\right]$$

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]$$

→ Complete solution of partial fraction:→

→ Second method:→

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)} \quad — ①$$

$$A = \left[\frac{1}{(b-x)}\right]_{x=a} = \frac{1}{(b-a)} = -\frac{1}{(a-b)}$$

$$B = \left[\frac{1}{(a-x)}\right]_{x=b} = \frac{1}{(a-b)}$$

$\therefore$ $A = -\frac{1}{(a-b)}$ and $B = \frac{1}{(a-b)}$

substitute value of A and B in eq. ①

$$\frac{1}{(a-x)(b-x)} = -\frac{1}{(a-b)}\frac{1}{(a-x)} + \frac{1}{(a-b)}\frac{1}{(b-x)}$$

$$= \frac{1}{(a-b)}\left[-\frac{1}{(a-x)} + \frac{1}{(b-x)}\right]$$

$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right]$$

→ Pseudo order reaction:→

- The simple reactions which have different value of order and molecularity are called pseudo order reactions.

→ Pseudo unimolecular/Pseudo monomolecular reactions:→

- These reactions are not unimolecular but follow the first order equation.

→ Examples:→

1. Hydrolysis of methyl acetate:→

$$CH_3COOCH_3 + H_2O \xrightleftharpoons{H^+} CH_3COOH + CH_3OH$$

It is a pseudo-unimolecular reaction as it involves two molecules but the rate is determined by methyl acetate only and not by water because its concentration does not change appreciably due to its presence in large excess.

The progress of reaction can be measured by titrating reaction mixture with NaOH.

2. Inversion of cane sugar:→

$$\underset{\substack{\text{Cane sugar}\\ \text{(Sucrose)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

It is a pseudo-unimolecular reaction as it involves two molecules but the rate is determined by concn of sugar only and not by water because its concentration does not change appreciably due to its presence in large excess.

The progress of reaction can be measured by measuring the change in angle of rotation by means of polarimeter.

→ Half life of a reaction:→

- In order to determine the rate at which a chemical reaction may proceed, a convenient paratmeter called half life is introduced.
- It is defined as the time required for the reaction to be half completed.

OR

The half life of a reaction is the time in which the concentration of a reactant is reduced to half of its initial concentration.

- It is denoted by the symbol $t_{1/2}$.

→ Half life for zero order reaction:→

- Rate constant for zero order reaction

$$K_0 = \frac{[A]_0 - [A]}{t} \quad \text{——} ①$$

At $t_{1/2}$

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

Substitule value of [A] in eq. ①

$$K_0 = \frac{[A]_0 - \frac{[A]_0}{2}}{t_{1/2}}$$

$$K_0 = \frac{\frac{2[A]_0 - [A]_0}{2}}{t_{1/2}}$$

$$K_0 = \frac{\frac{[A]_0}{2}}{t_{1/2}}$$

$$\text{or} \quad K_0 = \frac{[A]_0}{2t_{1/2}}$$

$$\text{or} \quad t_{1/2} = \frac{[A]_0}{2K_0}$$

For zero order reaction $t_{1/2}$ is directly proportional to the initial concⁿ of the reactants and inversely proportional to the rate constant.

→ Half life of first order reaction: →

- Rate constant for first order reaction

$$K_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad — ①$$

At $t_{1/2}$ $\quad [A] = \frac{[A]_0}{2}$

Substitute value of [A] in eq. ①

$$K_1 = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{\frac{[A]_0}{2}}$$

or $\quad K_1 = \frac{2.303}{t_{1/2}} \log 2$

or $\quad t_{1/2} = \frac{2.303}{K_1} \times 0.3010 \qquad \because \log 2 = 0.3010$

or $\quad t_{1/2} = \frac{0.693}{K_1} \quad – ②$

For first order reaction $t_{1/2}$ is independent of $[A]_0$

- Rate constant for first order reaction

$$K_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad — ①$$

At $t_{1/2}$ $\qquad x = \frac{a}{2}$

Substitute value of x in eq. ①

$$K_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{(a-\frac{a}{2})}$$

$$K_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{\frac{a}{2}}$$

or $\quad K_1 = \frac{2.303}{t_{1/2}} \log 2$

or $\quad t_{1/2} = \frac{2.303}{K_1} \times 0.3010 \qquad \because \log 2 = 0.3010$

or $\quad t_{1/2} = \frac{0.693}{K_1} \quad — ②$

For first order reaction $t_{1/2}$ is independent of $[A]_0$

→ Half life of second order reaction:→

- Rate constant for second order reaction

$$K_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \quad — ①$$

At $t_{1/2}$ $\quad x = \frac{a}{2}$

Substitute value of x in eq. ①

$$K_2 = \frac{1}{t_{1/2}}\left[\frac{a/2}{a(a-\frac{a}{2})}\right]$$

or $$K_2 = \frac{1}{t_{1/2}}\left[\frac{a/2}{a(a/2)}\right]$$

or $$K_2 = \frac{1}{t_{1/2}a}$$

or $$t_{1/2} = \frac{1}{K_2 a} \quad — ②$$

For second order reaction $t_{1/2}$ is inversely proportional to the initial concentration of the reactant, thus, it does not remain constant as the reaction proceeds.

→ Determination of the order of reaction: →

- The following methods are commonly used for determining the order of a reaction.

1. Differential method
2. Method of integration
3. Method of half life period
4. Isolation method

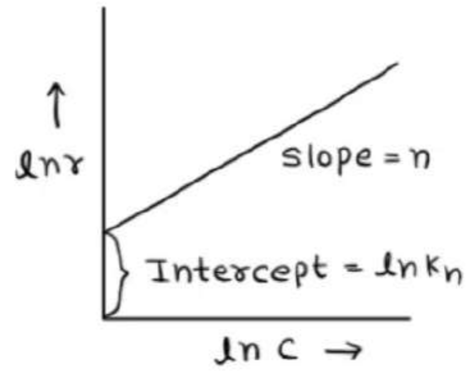
1. Differential method: →

- This method was developed by van't Hoff.
- According to this method, the rate of an nth-order reaction is given by

$$r = K_n c^n \quad — ①$$

Taking logs, we have

$$\ln r = \ln K_n + n \ln c \quad — ②$$



Thus, if a double-logarithmic plot of of rate versus concⁿ gives a straight line, then the slope gives the value of n and the intercept given ln K_n.

Also, if r_1 and r_2 are the rates at two different reactant concentrations c_1 and c_2, then

$$r_1 = -\frac{dc_1}{dt} = K_n c_1^n$$

$$r_2 = -\frac{dc_2}{dt} = K_n c_2^n$$

$$\frac{r_1}{r_2} = \frac{K_n C_1^n}{K_n C_2^n}$$

$$\frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n$$

Taking logs

$$\ln \frac{r_1}{r_2} = n \ln \frac{C_1}{C_2}$$

$$\text{or} \qquad n = \frac{\ln (r_1/r_2)}{\ln (C_1/C_2)} \quad ③$$

2. Method of integration :→

- This is also called hit and trial method.
- This method can be used either analytically or graphically.
- In the analytical method, we assume a certain order of the reaction and calculate the rate constants from the given data. The constancy of the K-values obtained suggests that assumed order is correct. If the K-values obtained are not constant, we assume a different order of the reaction and again calculate the K-values using the new rate expression and see if K is constant.
- In the graphical method, if the plot of ln c versus t is straight line, the reaction is of the first order. Similary we can use integrated expression graphically for second order and so on.

3. Method of half life period: →

- This method was suggested by Ostwald.
- The half life of nth-order reaction is

$$t_{1/2} = \frac{1}{a^{n-1}} \quad — ①$$

- If two experiments are carried out at different initial molar concentrations, then

$$(t_{1/2})_1 = \frac{1}{a_1^{n-1}} \quad \text{and} \quad (t_{1/2})_2 = \frac{1}{a_2^{n-1}}$$

$$\text{or} \quad \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{1/a_1^{n-1}}{1/a_2^{n-1}}$$

$$\text{or} \quad \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

taking log

$$\ln \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \ln \left(\frac{a_2}{a_1}\right)$$

$$\text{or} \quad \ln (t_{1/2})_1 - \ln (t_{1/2})_2 = (n-1)(\ln a_2 - \ln a_1)$$

$$\text{or} \quad n-1 = \frac{\ln (t_{1/2})_1 - \ln (t_{1/2})_2}{\ln a_2 - \ln a_1}$$

$$\text{or} \quad n = 1 + \frac{\ln (t_{1/2})_1 - \ln (t_{1/2})_2}{\ln a_2 - \ln a_1} \quad - ②$$

- The determination of half-lives of a reaction at two different initial concentrations leads to the determination of n.

4. Isolation method :→

- This method is due to Ostwald.
- In this method, all the reactants except one are taken in large quantities so that concentrations remains constant throughout this change. Thus, the order of reaction is determined with respect to the isolated reactant which is not taken in large quantity.
- The experiment is repeated by isolating each reactant in turn.
- The total order of the reaction will be given by the sum of the order of isolated reactions.
- This can be seen by considering the following general reaction.

$$n_1 A + n_2 B + n_3 C \rightarrow \text{Product}$$

Rate of reaction is given by

$$\frac{dx}{dt} = C_{A n_1} C_{B n_2} C_{C n_3}$$

First experiment → Large amount of B & C, order is determined with respect to A. Let this order be n_1 with respect to A.

Second experiment → Large amount of A & C, order is determined with respect to B. Let this order be n_2 with respect to B.

Third experiment → Large amount of A & B, order is determined with respect to C. Let this order be n_3 with respect to C.

Thus order of reaction = $n_1 + n_2 + n_3$

→ Radioactive decay as a first order phenomenon :→

- Radioactive decay is the phenomenon of spontaneous disintegration of unstable atomic nuclei to atomic nuclei to form more energetically stable atomic nuclei.
- Radioactive decay is highly exothermic, random and first order process that occurs with a small amount of mass being converted to energy.
- These reactions have been studied by recording the number of counts per second because this number is proportional to the number of atoms disintegrating per second.
- Suppose each atom of the radioactive element is having a chance λ that it decay in the next second. Thus, for a sample having N radioactive atoms, the number of disintegrations in the next second be λN.

The rate of decay is thus as follows:

$$-\frac{dN}{dt} = \lambda N \quad \text{— ①}$$

The constant λ is called decay constant. It's units are s^{-1}

or
$$\frac{dN}{N} = -\lambda dt \quad \text{— ②}$$

On integration eq. ②

$$\ln N = -\lambda t + I \quad \text{— ③}$$ I = Integration constant

At $t = 0$

$N = N_0$

Substitute these values in eq. ③

$$\ln N_0 = -\lambda \times 0 + I$$

$$\ln N_0 = I$$

Substitute the value of I in eq. ③

$$\ln N = -\lambda t + \ln N_0$$

or $$\ln N - \ln N_0 = -\lambda t$$

or $$\ln N_0 - \ln N = \lambda t$$

or $$\ln \frac{N_0}{N} = \lambda t$$

or $$\lambda = \frac{1}{t} \ln \frac{N_0}{N} \text{ — } ④$$

or $$\lambda = \frac{2.303}{t} \log \frac{N_0}{N} \text{ — } ⑤$$

→ Half life :→

At $t_{1/2}$ $\quad N = \frac{N_0}{2}$

Substitute value of N in eq. ⑤

$$\lambda = \frac{2.303}{t_{1/2}} \log \frac{N_0}{\frac{N_0}{2}}$$

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

or $\lambda = \frac{2.303}{t_{1/2}} \times 0.3010$ $\because \log 2 = 0.3010$

or $\lambda = \frac{0.693}{t_{1/2}}$

or $t_{1/2} = \frac{0.693}{\lambda}$ — ⑥

→ Experimental methods of chemical kinetics:→

1. Conductometric method:→

- The rates of ionic reactions occuring in ionising solvents such as water con be determined by measuring the conductivity of reaction mixture as a function of t.
- For dilute aqueous solutions, where ionic concentrations are almost constant, the conductivity can be regarded as a linear function of the concentration of the several ions and, therefore, to the extent of the reaction.
- This method has been used to determine the rate of hydrolysis of acid anhydrides, the saponification of ester and similar reactions.

→ Limitations:→

- This method is not applicable if the electrodes of conductivity cell (usually a platinised platinum) catalyse the reaction.
- Conductivity measurements require manual adjustment of a variable resistance and take 5 to 10 seconds for their completion. They are, therefore, not directly adapatable for measuring fast reactions.

2. Potentiometric method:→

- The half cell potential of metal electrode ($M \rightarrow M^{n+} + ne^-$) in a solution of its own ion is given by

$$E = E^\circ + \frac{RT}{nF} \log a_M$$

where :- E° = std potential of the electrode
n = Valency of ion
a_M = Activity of metal ion

- The half cell potential is thus related with the concentration of active ion and, therefore, the measurement of half cell potential can be used to study the progress of reaction.
- For example formation of complex between Fe^{+3} and F^- can be studied by measuring the potential of half cell Fe^{+2}/Fe^{+3} at various time intervals.

3. Optical methods :-

a. Polarimetry :→

- The course of a reaction involving optically active compounds may be followed by polarimetric measurement of the degree of rotation of plane-polarised light passing through the solution
- The amount of plane polarised light depends on the concentration of the optically active compounds.
- Wilhelmey applied this technique in 1950 to study the catalysed inversion of sugar.

$$\underset{\text{Sucrose }(+)}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose }(+)}{C_6H_{12}O_6} + \underset{\text{Fructose}(-)}{C_6H_{12}O_6}$$

- This technique requires expensive and specialised equipment.

b. Spectrophotometric method :→

- Ultraviolet, visible or even infrared spectra can be utilised to measure changes in the conc^{n} of reactant and products if the absorption is very strong and does not overlap the spectrum of another molecule present.
- The change in absorption in the selected wavelength range and so change in concentration is recorded.

→ Effect of temperature on rate of reaction:→

- Generally, rate of a chemical reaction increases with rise in temperature.
- In homogeneous reactions, the rate becomes doubled or tripled for each 10° rise of temperature.
- This increase in the reaction rate with temperature is expressed in the form of temperature coefficient.
- Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures separated by 10°c. The two temperatures are generally taken as 35° and 25°c.

Thus the temperature coefficient is expressed as:

$$\text{Temperature coefficient} = \frac{K_{35^\circ}}{K_{25^\circ}}$$

In general

$$\text{Temperature coefficient} = \frac{K_t + 10^\circ}{K_t}$$

where K_t = Specific rate of reaction at t°c

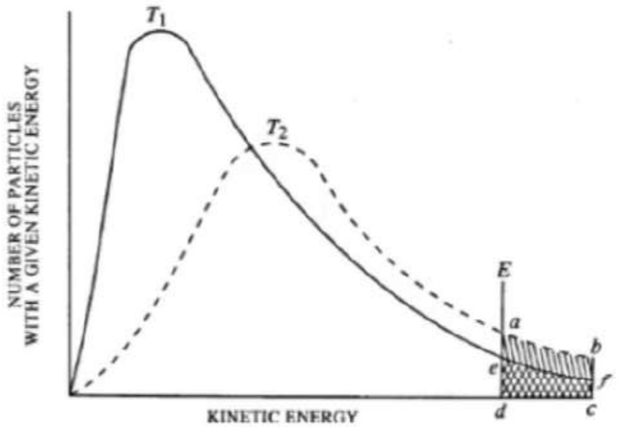
$K_t + 10^\circ$ = Specific rate of same reaction at t + 10°

- In most of the homogeneous gaseous reactions, the value of temperature coefficient lies between 2 and 3. It means that the specific reaction rate becomes two fold or three fold for every 10°c rise of temperature.
- Example :- (i) Temperature coefficient for dissociation of HI is 1.7
  (ii) Temperature coefficient for reaction between CH_3I and C_2H_5ONa is 2.9.

- The increase in rate of reaction with rise in temperature can be explained on the basis of the Collision theory.
- According to this theory, for a chemical reaction to occur, there must be collisions between the reactant molecules. However, most of the collisions taking place between the molecules are ineffective.

The important postulate of the collision theory is that only those collisions result in chemical reaction in which the colliding molecules are associated with a certain minimum energy called the threshold energy.

- Arrhenius used the Maxwell's distribution of molecular energies to explain the temperature dependence of reaction rates.
- As the temperature increases from T_1 to T_2, the energy distribution undergoes a change (figure). There is a general shift in the distribution of energies. There are more molecules on high side of kinetic energy. The number of molecules whose energies are equal or greater than threshold energy E at temperature T_1 is represented by the shaded area efcd and at temperature T_2 by the shaded area abcd.



The shaded area abcd is neary twice the shaded area efcd. This means that the number of molecules having energy equal to or greater than threshold energy becomes nearly double even with a small increase of temperature from T_1 to T_2. Consequently, the rate of reaction which depends upon the number of effective collisions, becomes almost double with a small increase of temperature.

→ Arrhenius equation:→

- Van't Hoff proved that the value of equilibrium constant varied with the temperature.
- Arrhenius extended the above suggestion of Van't Hoff and gave his own hypothesis.
- According to his hypothesis-

(i) All the molecules of a system cannot take part in the chemical reaction.

(ii) It is only a certain number of molecules which react. These reacting molecules are known as active molecules.

(iii) The molecules which do not take part in a chemical reaction are known as passive molecules.

(iv) There exists an equilibrium between passive and active molecules.

$$M(\text{passive}) \rightleftharpoons M(\text{Active})$$

(v) When the temperature is raised, the equilibrium between active and passive molecules shift towards the right. The increases the number of active molecules which are ready to take part in a reaction. Thus, the increase in reaction rate with rise in temperature is due to the increase in the number of active molecules than due to the numbe of collisions.

Thus the basic concept of Arrhenius theory is that

" The passive or non-active or non reactive molecules can become active by absorption of heat energy."

→ Derivation of Arrhenius equation: →

- Consider the following reversible reaction:

$$A + B \rightleftharpoons C + D$$

Rate of forward reaction $= K_1[A][B]$

Rate of backward reaction $= K_2[C][D]$

At equilibrium

$$K_1[A][B] = K_2[C][D]$$

or $$\frac{K_1}{K_2} = \frac{[C][D]}{[A][B]} \quad \text{or} \quad K_c = \frac{[C][D]}{[A][B]}$$

where $$K_c = \frac{K_1}{K_2} \quad — ①$$

From thermodynamics, Van't Hoff equation is

$$\frac{d\ln K_c}{dT} = \frac{\Delta E}{RT^2} \quad — ②$$

substituting value of K_c from eq. ① in ②, we get

$$\frac{d\ln K_1/K_2}{dT} = \frac{\Delta E}{RT^2}$$

or $$\frac{d\ln K_1}{dT} - \frac{d\ln K_2}{dT} = \frac{\Delta E}{RT^2} \quad — ③ \qquad (\Delta E = E_2 - E_1)$$

Van't Hoff proposed that eq. ③ can be split into two equation as follows

$$\frac{d\ln K_1}{dT} = \frac{E_1}{RT^2} + I \quad — ④$$

$$\frac{d\ln K_2}{dT} = \frac{E_2}{RT^2} + I \quad — ⑤ \quad \text{where } I = \text{Constant}$$

It was observed that I was independent of temperature. Therefore, I must be equal to zero in eq. ④ and ⑤

$$\frac{d\ln K_1}{dT} = \frac{E_1}{RT^2} \quad — ⑥$$

$$\frac{d\ln K_2}{dT} = \frac{E_2}{RT^2} \quad — ⑦$$

Equations ⑥ and ⑦ are known as Arrhenius equations.

Integrating eq. ⑥ and ⑦, we get

$$\ln K_1 = -\frac{E_1}{RT} + A \quad — ⑧$$

and $$\ln K_2 = -\frac{E_2}{RT} + A \quad — ⑨ \qquad A = \text{Constant}$$

Equations ⑧ and ⑨ can be put as

$$K_1 = A e^{-E_1/RT} \quad \text{— ⑩}$$

$$K_2 = A e^{-E_2/RT} \quad \text{— ⑪}$$

In more general

$$k = A e^{-E_a/RT} \quad \text{— ⑫}$$

Eq. ⑫ is called integrated form of Arrhenius equation. Eq. ⑬ express the temp dependence of k in terms of A and E_a. Both A and E_a are characteristics of reaction.

Where E_a is called the Arrhenius activation energy and A is called the Arrhenius pre-exponential factor.

Since the exponential factor in eq. ⑫ is dimensionless, the pre-exponential factor A has the same unit as the rate constant k. The units of k for a first order reaction are s^{-1}, which is the unit of frequency. Hence, A is also called the frequency factor. E_a and A are called the Arrhenius parameters.

Taking logs of eq. ⑫, we have

$$\ln K = \ln A - \frac{E_a}{RT} \quad \text{— ⑬}$$

If lnk is plotted against 1/T, a straight line is obtained.

$$\text{slope} = -\frac{E_a}{R} \qquad \text{and} \quad \text{Intercep} = \ln A$$

Differentiating eq. ⑬ with respect to temperature

$$\frac{d\ln K}{dT} = \frac{E_a}{RT^2} \quad — \quad ⑭$$

Integrating eq. ⑭ between the temperature limits T_1 & T_2 and K_1 & K_2 and assuming that E_a is constant over this temp. range, we obtain

$$\ln\frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

This is integrated Arrhenius equation. Thus, knowing the rate constant at two different temperatures, the energy of activation E_a can be determined.

→ Concept of activation energy :→

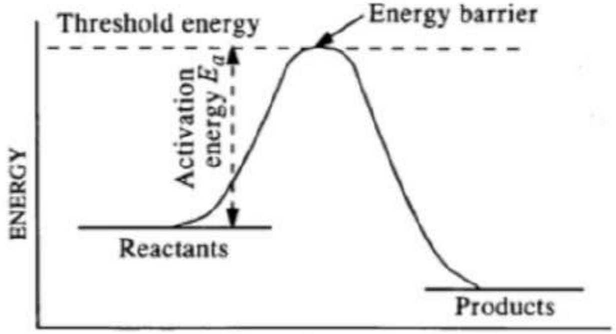
- According to the concept of activation energy, all the molecules cannot take part in the chemical reaction.
- It is only a certain number of molecules which take part. These reacting molecules are known as active molecules.
- The reactant do not pass directly to the products but must first aquire necessary energy to pass over an energy barrier known as the activated state or transition state.
- The amount of energy which the reactants must absorb to pass over this activated energy barrier is known as the activation energy.

OR

The excess energy that the reacting molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy.

Thus,

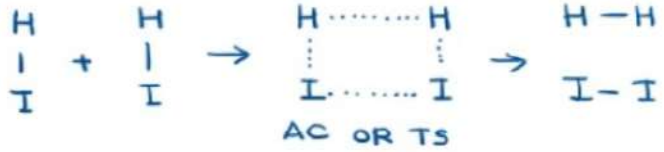
Activation energy = Threshold energy - Energy actually possessed by molecules.



The concept of energy barrier in chemical reactions

- It follows from the above discussion that there is a energy barrier placed between reactants and products. This barrier has to be crossed before reactants can yield products.
- When two molecules, having the necessary energy of activation, come together, they must form an activated complex or T.S.

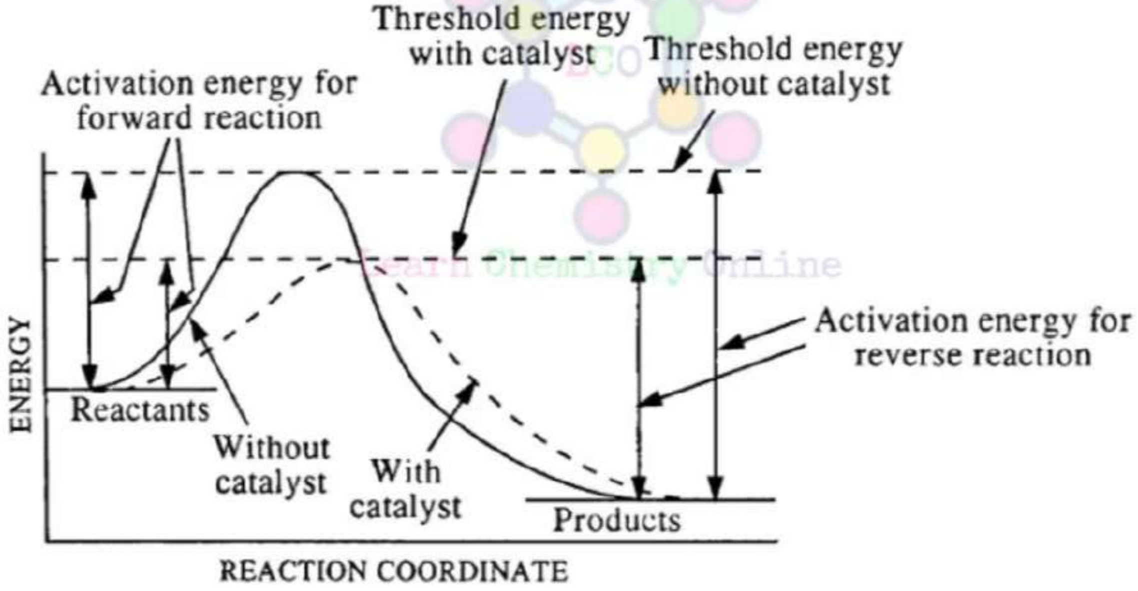
Example: -



$$\mathrm{H{-}I} + \mathrm{H{-}I} \rightarrow \mathrm{H\cdots H,\ I\cdots I} \rightarrow \mathrm{H{-}H} + \mathrm{I{-}I}$$

→ Effect of catalyst on rate of reaction:→

- A catalyst is a substance that can increase the rate of a reaction but which itself remains unchanged in amount and chemical composition at the end of the reaction.
- When a catalyst is added, a new reaction path with a lower energy barrier is provided.
- Since the energy barrier is reduced in magnitude, a large number of molecules of the reactant can get over it. This increases the rate of a reaction.
- A catalyst does not alter the position of equilibrium in a reversible reaction. It simply hasten the approach of the equilibrium by speeding up both the forward and the backward reaction.



Effect of catalyst on the rate of reaction.

→ Simple collision theory :→ (Collision theory of biomolecular gaseous reaction):→

- This theory was developed by Arrhenius and van't Hoff.
- This is the earliest theory of reaction rates.
- Since reaction between two species takes place only when they are in contact, it is suppose that reactant species must collide before they react.
- From the kinetic theory of gases, the number of bimolecular collision per second per cm^{-3} among molecules of one species is given by

$$z = 2n^2 d^2 \left(\frac{8\pi kT}{\mu}\right)^{1/2} \quad \text{— ①}$$

- For a reaction involving two different gases A and B, the rate of bimolecular collisions b/w unlike molecules is given by

$$Z_{AB} = n_A n_B (d_{av})^2 \left(\frac{8\pi kT}{\mu}\right)^{1/2} \quad \text{— ②}$$

where n_A and n_b = Number of A and B molecules

d_{av} = Average collision diameter = $\frac{d_A + d_B}{2}$

μ = Reduced mass = $\frac{m_A m_B}{m_A + m_B}$, k = Boltzmann constant

- The collision number in terms of molar masses M_A and M_B of two gases, by the expression.

$$Z_{AB} = n_A n_B (d_{av})^2 \left[\frac{(M_A+M_B)8\pi RT}{M_A M_B}\right]^{1/2} \quad \text{— ③} \qquad \{R = N_A k\}$$

- Since there are approximately 10^{29} collisions per second for 10^{19} molecules of each species, each molecules makes about 10^{10} collisions per second with the molecules of the other species. If each collision were to lead to a chemical reaction, then the whole reaction would have been completed in about 10^{-10} s. However, this predicted rate of the reaction is in complete disagreement with the experimental rate. Hence, we conclude that all collisions do not result in chemical reaction.
- In order for a reaction to occur, the energy of collision must equal to exceed the threshold energy.
- The detailed analysis of the dynamics of bimolecular collisions lead to the result that the number of collisions s^{-1} cm^{-3} between molecules A and B, when the relative kinetic energy E along the line of center is greater than the threshold energy is given by

$$Z'_{AB} = Z_{AB}\, e^{-E/RT} \quad \text{—} \ ④$$

- Assuming that Z'_{AB} gives the rate of relative collisions between A and B, we can write

$$-\frac{dn_A}{dt} = Z'_{AB}$$

or $$-\frac{dn_A}{dt} = n_A n_B (d_{av})^2 \left[\frac{(M_A+M_B)8\pi RT}{M_A M_B}\right]^{1/2} e^{-E/RT} \text{ molecules } cm^{-3}\, s^{-1} \quad \text{—} \ ⑤$$

→ Theoritical expression for the rate constant :→

- If the concentration is expressed in mol dm^{-3}, then

$$[A] = 10^3 \frac{n_A}{N_A} \quad \text{and} \quad [B] = 10^3 \frac{n_B}{N_A} \qquad N_A = \text{Avogadro's number}$$

- Hence, the rate law expression

$$-\frac{d[A]}{dt} = k_2[A][B]$$

or $$-\frac{10^3 dn_A}{N_A dt} = k_2\left(10^3 \frac{n_A}{N_A}\right)\left(10^3 \frac{n_B}{N_A}\right)$$

or $$-\frac{10^3 dn_A}{N_A dt} = k_2 \frac{10^6}{(N_A)^2} n_A n_B$$

or $$k_2 = -\frac{10^3 dn_A}{N_A dt} \times \frac{(N_A)^2}{10^6 n_A n_B}$$

or $$k_2 = -\frac{N_A}{10^3 n_A n_B} \times \frac{dn_A}{dt} \quad — ⑥$$

Using eq. ⑤ for $-\frac{dn_A}{dt}$, we have

$$k_2 = \frac{N_A}{10^3 n_A n_B} \times n_A n_B (d_{av})^2 \left[\frac{(M_A+M_B)8\pi RT}{M_A M_B}\right]^{1/2} e^{-E/RT}$$

$$k_2 = \frac{N_A (d_{av})^2}{10^3} \left[\frac{(M_A+M_B)8\pi RT}{M_A M_B}\right]^{1/2} e^{-E/RT} \quad — ⑦$$

- Comparing eq. ⑦ with the Arrhenius equation $k_2 = Ae^{-Ea/RT}$, we find that Arrhenius pre-exponential factor is given by

$$A = \frac{N_A (d_{av})^2}{10^3} \left[\frac{(M_A+M_B)8\pi RT}{M_A M_B}\right]^{1/2} \quad — ⑧$$

- The activation energy E_a in the Arrhenius equation is thus identified with the relative kinetic energy E along the line of centers of two colliding molecules which is required to cause a relation between them.
- The collision theory is applicable to simple gaseous reaction.
- For reactions between complicated molecules, the observed rate is found to be much smaller than theoretically predicted rate.

The difference is explained by the fact that the colliding molecule is treated as a hard sphere having no internal energy.

Again, the spherical model ignores the dependence of the effectiveness of a collision on the relative orientation of the colliding molecules.

Also, the activation energy treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrational motion.

For these reasons the collision theory is applicable only to reactions between very simple gaseous reactions.

- The collision theory can be generalised by introducing the so-called steric factor, p, into equation for the bimolecular rate constant in order to take account of the orientational requirement. Accordingly,

$$K_2 = pAe^{-E_a/RT} \quad — ⑨$$

- The steric factor is supposed to be equal to the fraction of molecular collisions in which the molecules A and B possess the relative orientations necessary for the reaction. However, the steric factor cannot be reliably calculated.
- Using collision theory, the Arrhenius pre-exponential factor for unlike molecules including the steric factor p is given by

$$A = (2.753 \times 10^{29})\,p(d_{av})^2 \left[\frac{T(M_A+M_B)}{M_A M_B}\right]^{1/2} \quad — ⑩$$

and for like molecules it is given by

$$A = (3.893 \times 10^{29})\,p(d_{av})^2 \left(\frac{T}{M}\right)^{1/2}$$

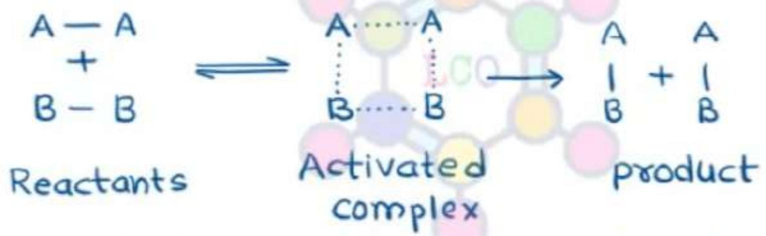
- In these equations, the molar mass is in unit of g mol^{-1} and the units of A are dm^3 mol^{-1} s^{-1}.

→ Transition state theory :→

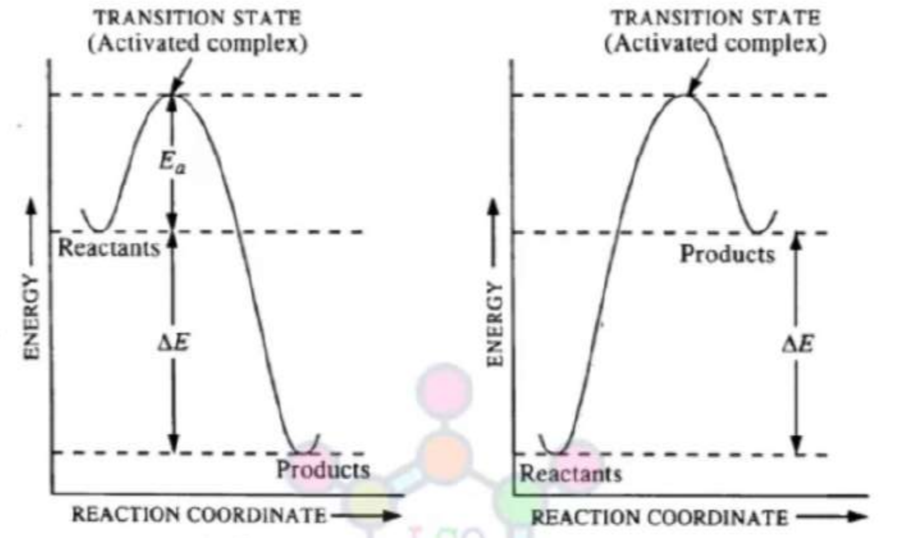
- This theory was developed by Eyring, Polanyi and Evans in 1935.
- It is known as the transition state theory (TST), or the absolute reaction rate theory (ARRT), or the activated complex theory (ACT).
- According to ACT, the bimolecular reaction between two molecules A_2 and B_2 progresses through the formation of the so-called activated complex which then decomposes to yield the product, as illustrated below:

$$A_2 + B_2 \rightleftharpoons (A_2B_2)^{\#} \longrightarrow 2\,AB$$

or



- The activated complex is a distinct chemical species in equilibrium with reactants which then decompose into products.
- The reaction coordinate is a measure of the progress of reaction.
- The activated complex is not an intermediate in the process of breaking or forming of chemical bonds.
- The activated complex is unstable because it is situated at the maximum of the potential energy barrier separating the products from the reactants.
- The difference between the energy of the activated complex and the energy of the reactants is the activation energy, E_a.



(a) Exothermic reaction (b) Endothermic reaction

The profile of energy versus reaction coordinate in ACT in the case of an exothermic and an endothermic reaction.

- For the thermodynamic formulation of the activated complex theory, consider a simple bimolecular reaction,

$$A + B \overset{K^{\#}}{\rightleftharpoons} (AB)^{\#} \xrightarrow{K_2} \text{products} \quad — ①$$

where $(AB)^{\#}$ = Activated complex

$K^{\#}$ = The equilibrium constant b/w reactants and activated complex

K_2 = Rate constant

- In $(AB)^{\#}$ one of the vibrational degrees of freedom has become a translational degree of freedom.
- From the classical mechanics energy of vibration is given by

$$E = \frac{RT}{N_A} = K_BT \quad — ② \quad \left[\because R = N_A K_B \text{ or } K_B = \frac{R}{N_A}\right]$$

K_B = Boltzmann constant

- From the quantum mechanics, energy of vibration is given by

$$E = h\nu \quad — ③$$

From eq. ② and ③

$$h\nu = \frac{RT}{N_A}$$

$$\text{or} \quad \nu = \frac{RT}{N_A h}$$

$$\text{or} \quad \nu = \frac{k_B T}{h} \quad — ④$$

- The vibrational frequency ν is the rate at which the activated complex molecules move accross the energy barrier. Thus, the rate constant k_2 can be identified with ν.
- The rate of reaction is given by

$$-\frac{d[A]}{dt} = \kappa k_2 [(AB)^{\#}] = \kappa \nu [(AB)^{\#}] = \kappa \left(\frac{k_B T}{h}\right) [(AB)^{\#}] \quad — ⑤$$

where the factor κ, called the transmission coefficient, is a measure of the probability that a molecule, once it passed over the barrier, will keep on going ahead and not return.

- The value of κ is taken to be unity; it is thus omitted from rate expression.
- The concentration of the activated complex, $[(AB)^{\#}]$, can be obtained by writing the equilibrium expression.

$$K^{\#} = \frac{[(AB)^{\#}]}{[A][B]} \quad \text{hence} \quad [(AB)^{\#}] = K^{\#}[A][B] \quad — ⑥$$

Substituting value of $[(AB)^{\#}]$ in eq. ⑤

$$-\frac{d[A]}{dt} = \left(\frac{K_B T}{h}\right) K^{\#} [A][B] \quad — ⑦$$

The rate expression for reaction 1 is given by

$$-\frac{d[A]}{dt} = K_2 [A][B] \quad — ⑧$$

From eq. ⑦ and ⑧

$$K_2 [A][B] = \left(\frac{K_B T}{h}\right) K^{\#} [A][B]$$

$$K_2 = \left(\frac{K_B T}{h}\right) K^{\#} \quad — ⑨$$

- The equilibrium constant $K^{\#}$ can be expressed in terms of $(\Delta G^{\circ})^{\#}$, called the standard Gibbs free energy of activation. Since for the activated complex, we can write

$$(\Delta G^{\circ})^{\#} = -RT \ln K^{\#}$$

or $$K^{\#} = e^{-(\Delta G^{\circ})^{\#}/RT}$$

and $$(\Delta G^{\circ})^{\#} = (\Delta H^{\circ})^{\#} - T(\Delta S^{\circ})^{\#}$$

or $$(\Delta H^{\circ})^{\#} - T(\Delta S^{\circ})^{\#} = -RT \ln K^{\#}$$

or $$K^{\#} = e^{(\Delta S^{\circ})^{\#}/R} \, e^{-(\Delta H^{\circ})^{\#}/RT} \quad — ⑩$$

Substituting value of $K^{\#}$ in eq. ⑨

$$K_2 = \left(\frac{k_B T}{h}\right) e^{(\Delta S^\circ)^{\#}/R} \, e^{-(\Delta H^\circ)^{\#}/RT} \quad — ⑪$$

Eq. ⑪ is known as Eyring equation.

where $(\Delta S^\circ)^{\#}$ = std entropy of activation

$(\Delta H^\circ)^{\#}$ = std enthalpy of activation

→ Comparision of collision theory and transition state theory :→

– According to transition state theory, rate constant is given by

$$k_2 = \left(\frac{k_B T}{h}\right) e^{(\Delta S^\circ)^\#/R} \, e^{-(\Delta H^\circ)^\#/RT} \quad — ①$$

Taking logs of both sides of eq. ① and differentiating with respect to T,

$$\frac{d\ln k_2}{dT} = \frac{(\Delta H^\circ)^\#}{RT^2} + \frac{1}{T}$$

or $$\frac{d\ln k_2}{dT} = \frac{\{(\Delta H^\circ)^\# + RT\}}{RT^2} \quad — ②$$

Also, from the Arrhenius equation,

$$\frac{d\ln k_2}{dT} = \frac{E_a}{RT^2} \quad — ③$$

Comparing eq. ② and ③

$$\frac{E_a}{RT^2} = \frac{\{(\Delta H^\circ)^\# + RT\}}{RT^2}$$

or $$E_a = (\Delta H^\circ)^\# + RT \quad — ④$$

or $$(\Delta H^\circ)^\# = E_a - RT \quad — ⑤$$

- According to Collision theory, rate constant is given by

$$K_2 = pAe^{-Ea/RT} \quad \text{——} \quad ⑥$$

Comparing equation ⑥ with eq. ①

$$pAe^{-Ea/RT} = \left(\frac{K_BT}{h}\right) e^{(\Delta S^\circ)^{\#}/R} e^{-(\Delta H^\circ)^{\#}/RT} \quad - ⑦$$

If $(\Delta H^\circ)^{\#} \approxeq E_a$, we can equate the exponential factors in eq. ⑦

$$pA = \left(\frac{K_BT}{h}\right) e^{(\Delta S^\circ)^{\#}/R}$$

→ Catalysis :→

- The word 'catalysis' was first used by Berzelius in 1936.
- Berzelius defined the catalysis as:

  " It is a phenomenon in which the presence of a foreign substance could accelerate its rate without being used up in that reaction."

- He called the foreign substance as catalyst.
- Later on, it was reported that catalyst could also retard the reaction. Thus, the definition of Berzelius was generalised. The new definition of catalyst and catalysis is:

  " Catalyst is any substance which can change the speed of reaction without being used up in that reaction and the phenomenon is known as catalysis."

- In many reactions, one of the products itself acts as a catalyst.

  Example:-

$$2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}COOH\\|\\COOH\end{matrix} \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

The speed of reaction increases as the reaction progresses. This acceleration is due to the presence of Mn^{+2} ions which get formed in the reaction. This type of phenomenon in which one of the products itself acts as a catalyst is known as auto-catalysis.

→ Characteristics of catalysed reaction :→

— The following characteristics are generally common to most of the catalytic reactions -

1. The catalyst remains unchanged in amount and chemical chemical composition at the end of the reaction.
2. Only a small quantity of catalyst is generally needed. However, in some homogeneous catalytic reactions, the rate of reaction is proportional to the concentration of the catalyst.

   For example, the rate of inversion of cane sugar catalysed by hydrogen ions varies with the concentration of the hydrogen ions present in the solution.

   In certain homogeneous reactions, the rate increases with increase in the area of the catalytic surface. This explains why the efficiency of a solid catalyst increases when it is present in a finely divided state or deposited on some inactive material such as asbestos (e.g. platinised asbestos).
3. The catalyst does not alter the position of equilibrium in a reversible reaction.
4. Catalyst does not initiate the reaction. The function of catalyst is only to speed up the reaction.
5. The catalyst is generally specific in its action.

   Manganese dioxide, for example, can catalyse the decomposition of potassium chlorate but not that of potassium perchlorate or potassium nitrate.

   Thus, manganes dioxide is specific in its action. Enzymes have also specific catalytic action.

6. The catalyst cannot alter the nature of the products of the reaction.

For examples, potassium chlorate on decomposition gives potassium chloride and oxygen whether manganese dioxide is added or not.

7. A catalyst is poisoned by certain substances. The impurities of any type, even if present in small amounts, inhibit or retard the rate of catalysed reactions to a large extent. These impurities are, therefore, called catalytic poisons.

For example, the rate of combination of sulphur dioxide and oxygen (contact process) is slowed down if some arsenic compounds are present even in traces.

8. There is particular temperature at which the efficiency of a catalyst is most marked. The temperature is known as the optimum temperature.

For example, activity of enzyme is maximum between 35° to 37°c.

9. The addition of small amounts of foreign substances which are not themselves catalytically active, sometimes increases the activity of the catalyst. Such substances are called promoters.

For example, in the manufacture of NH_3 by Haber's process, finely divided iron acts as a catalyst, while molybdenum acts as a promoter.

→ Classification of catalysis :→

- Catalysis can be divided into two classes -

(a) Homogeneous Catalysis :→

- In homogeneous catalysis, the catalyst and reactants are in the same phase.

(i) Example from gaseous phase :→

- In the manufacture of sulphuric acid, nitric oxide gas catalyses the reaction between SO_2 and O_2.

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3 \qquad \text{(Lead chamber process)}$$

- In this example, the reactants (SO_2 & O_2) and the catalyst (NO) are in gaseous phase.

(ii) Example from liquid phase :→

- The inversion of cane sugar is catalysed by a mineral acid.

$$\underset{\text{Cane sugar}}{C_{22}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

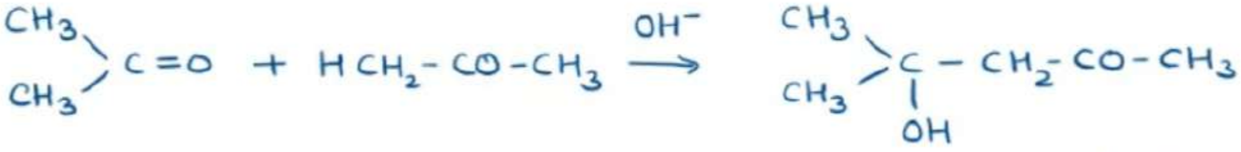
- Here the catalyst and reactants are in the liquid phase.
- The hydrolysis of an ester like methyl acetate gets catalysed by hydrogen ions:

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

- The decomposition of hydrogen peroxide is catalysed in the presence of chloride ions.

$$2H_2O_2 \xrightarrow{Cl^-} 2H_2O + O_2$$

- The conversion of acetone into diacetone alcohol is catalysed by hydroxyl ions.



Diacetone alcohol

(b) Heterogeneous catalysis:→

- In heterogeneous catalysis, the catalyst is present in a different phase than that of reactants.

(i) Heterogeneous catalysis involving solid reactants:→

- Decomposition of potassium chlorate in the presence of MnO_2 (catalyst).

$$2\ KClO_3 \xrightarrow{MnO_2} 2\ KCl + 3O_2$$

- Thus, the catalyst (MnO_2) is present as a separate phase from the solid reactant.

(ii) Heterogeneous catalysis involving liquid reactants:→

- The decomposition of hydrogen peroxide is catalysed by colloidal solution of gold & platinum.

$$2H_2O_2 \xrightarrow[Au]{Pt\ or} 2H_2O + O_2$$

Here H_2O_2 is a liquid reagent.

(ii) Heterogeneous catalysis involving gaseous reactants:→

- Combination of SO_2 and O_2 in the presence of finely divided platinum.

$$SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3$$