Chemical Kinetics

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INTRODUCTION :

Chemical Kinetics : Chemical kinetics is the study of rates of reactions, the mechanism by which the reactions proceed and the effect of temperature, pressure and concentration on the rates of reactions.

On the basis of rate, chemical reaction are broadly divided into three categories :-

(a) Very fast or instantaneous reactions : These reactions occur at a very fast rate. Generally these reactions involve ionic species and known as ionic reactions. These reactions take about 10^{-14} or 10^{-16} seconds for completion. Its rate can be measured by employing special methods. So, It is almost impossible to determine the rates of these reactions.

Examples :

$$AgNO_3 + NaCl \rightarrow \underset{\text{ppt.}}{AgCl} + NaNO_3$$

$$BaCl_2 + H_2SO_4 \rightarrow \underset{\text{ppt.}}{BaSO_4} + 2HCl$$

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NaOH} \rightarrow \underset{\text{salt}}{NaCl} + H_2O$$

(b) Moderate reaction : This type of reactions proceed with a measurable rates at normal temperature. In this a large number of bonds have to be broken in reactants molecules and a large number of new bonds have to be formed in product molecules.

* Mostly these reactions are molecular in nature.

Examples :

* Decomposition of H_2O_2

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

* Decomposition of N_2O_5

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

* Hydrolysis of ester

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

* Inversion of cane sugar in aqueous solution

* Reaction of NO with chlorine

$$NO + Cl_2 \rightarrow NOCl_2$$

* Moderate reactions are studied in chemical kinetics.

(c) Very slow reaction : These reaction proceed very slowly. They may take months together to show any measurable change at room temperature.

Examples :

- Rusting of iron
- Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.
- $CO + 2H_2 \xrightarrow{\text{at room temperature}} CH_3OH$
- The chemical reactions can be slowed down or speeded up by changing conditions under which they occur.

For example :

$CO + 2H_2 \longrightarrow CH_3OH$

The reaction can be speeded up by maintaining temperature around 400^0C, pressure about 300 atm and using a catalyst containing ZnO and Cr_2O_3.

RATE OF REACTION :

Rate of reaction defined as the change in concentration of reactant or product per unit time. It is always a positive quantity.

Rate of reaction

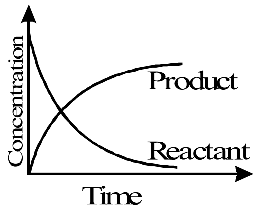
$$= \frac{\text{Total change in concentration of reactant or product}}{\text{Change in time (in second)}}$$

$$\boxed{v = \pm\frac{dc}{dt}}$$

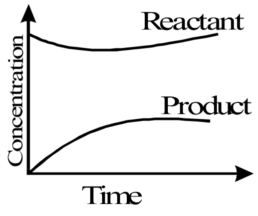
Where dc = change in concentration in a small interval dt

[+] sign is used when we refer to product concentration.

[–] sign is used when we refer to reactant concentration.



(a) For an irreversible reaction



(b) For an reversible reaction

Figure : The change in the concentrations of the reactants and products.

- **Average Rate of Reaction :** The rate of reaction over a certain measurable period of time during the course of reaction, is called as average rate of reaction. It is denoted by R.

For a reaction A → B

$$\overline{R} = \left(\frac{[A]_2 - [A]_1}{t_2 - t_1}\right) = -\frac{\Delta[A]}{\Delta t}$$

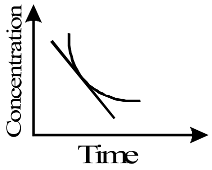
Where $[A]_1$ = Concentration of reactant A at time t_1,

$[A]_2$ = Concentration of reactant A at time t_2.

- **Instantaneous Rate of Reaction :** The rate of reaction at any particular instant during the course of reaction is called as instantaneous rate of reaction.

Mathematically ; Instantaneous rate = (Averge rate)$_{\Delta T \to}$

$$R_t = -\left(\frac{\Delta[A]}{\Delta t}\right)_{\Delta t \to 0} = \left(\frac{\Delta[B]}{\Delta t}\right)_{\Delta t \to 0}$$

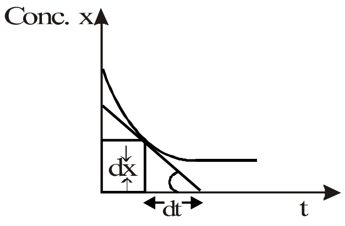


or $\boxed{R_t = -\frac{d[A]}{dt} = \frac{d[B]}{dt}}$

Hence, Slope of the tangent at any point of curve indicates instantaneous rate of reaction.

- The slope of the tangent at time t in plot of concentration with times gives rate at time t.

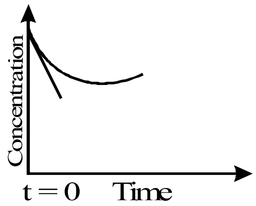
Rate of reaction = tan θ = $\frac{dx}{dt}$



- **Initial Rate :**

The slope of the tangent at t = 0 in the plot of concentration vs time gives the initial rate.

Rate of reaction = tan θ = $\frac{dx}{dt}$



* **Rate of reaction in the form of stoichiometry of a chemical reaction :**

Let us consider a reaction : $m_1A + m_2B$ + ---------→ $n_1P + n_2Q + n_3R$ + ---------

$$\text{Rate of reaction} = -\frac{1}{m_1}\frac{d[A]}{dt} = -\frac{1}{m_2}\frac{d[B]}{dt} = \frac{1}{n_1}\frac{d[P]}{dt} = \frac{1}{n_2}\frac{d[Q]}{dt}$$

* **Unit of Reaction Rate :** Unit of reaction rate = mol L^{-1} time^{-1} i.e. (mol L^{-1} s^{-1} or mol L^{-1} min^{-1} or mol L^{-1} h^{-1})

Note :

For a chemical reaction $A + B \longrightarrow P + Q$

Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of formation of P = $\frac{d[P]}{dt}$

Rate of formation of Q = $\frac{d[Q]}{dt}$

Rate Law :

According to the law of mass action, the rate of a chemical reaction is directly proportional to active masses of reactants.

$A + B \longrightarrow$ products

Rate of reaction $\propto [A][B] = K[A][B]$

where K is proportionaly constant and is called velocity constant or rate constant or specific reaction rate.

* For general reaction : $m_1A + m_2B + m_3C \longrightarrow$ products

The rate of reaction $= K[A]^{m_1}[B]^{m_2}[C]^{m_3}$

$$r = K[A]^{m_1}[B]^{m_2}[C]^{m_3}$$

* Unit of rate constant :

$$\frac{\text{concentration}}{\text{time}} = K[\text{concentration}]^{m_1+m_2+m_3}$$

Note :

$(m_1 + m_2 + m_3) = n$(order of reaction)

$$\frac{\text{mole}}{\text{litre second}} = K\left(\frac{\text{mole}}{\text{litre}}\right)^{m_1+m_2+m_3} \qquad K = \left(\frac{\text{mole}}{\text{litre}}\right)^{(1-n)} \text{second}^{-1}$$

* The rate constant is constant for a particular reaction at a particular temperature and does not depend upon the concentration of the reactants.

ORDER OF REACTION :

The order of reaction may be defined as the sum of powers of concentration (or pressure) terms involved in rate low expression.

i.e., number of molecules whose concentration determined the rate of the reaction is called order of the reaction.

Rate Law :

The mathematical expression that gives the true rate of reaction in terms of concentration of the reactants, which actually influence the rate, is called rate law.

Example :

Reaction is : $2NO_2 + F_2 \rightarrow 2NO_2F$

(nitrogen fluoride)

the expected rate expression is

rate = $K[NO_2]^2[F_2]$

but it is found experimentally that the rate of this reaction is proportional to the product of single conce ntration term of NO_2 and F_2.

Thus the experimental rate of the reaction is given by : rate = $K[NO_2][F_2]$

Rate controlling step : The slowest step of the complex reaction is called the rate controlling step.

Example : We have a reaction

$2NO_2 + F_2 \rightarrow 2NO_2F$

The mechanism of this reaction is as follows –

$NO_2 + F_2 \longrightarrow NO_2F + F$ (slow)

$NO_2 + F \longrightarrow NO_2F$ (fast)

....

$2NO_2 + F_2 \longrightarrow 2NO_2F$ (overall reaction)

* Order is a purely experimental quantity. It may be a whole number or zero or even a fraction.

* For the reaction : $aA + dB \longrightarrow \text{product}$

Experimental rate equation : $r = K[A]^m[B]^n$

Order with respect to A = m,

Order with respect to B = n

total order = m + n

* m and n may be equal to a and b.

* Reactions are classified according to the order of reaction.

(a) A reaction is said to be of first order when the one concentration term determine the rate of reaction :

Example : $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$r = K[N_2O_5]$

(b) A reaction is said to be of second order when two concentration terms determine the rate of reaction.

Example : $2N_2O \longrightarrow 2N_2 + O_2$

$r = K[N_2O]^2$

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

$r = K[CH_3COOC_2H_5][NaOH]$

(c) A reaction is said to be of third order if three concentration terms determine its rate.

Example : $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

$r = K[FeCl_3]^2[SnCl_4]$

The order of following reaction is fraction :-

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

$r = K[H_2][Br_2]^{\frac{1}{2}} \Rightarrow \text{order} = 1 + \frac{1}{2} = \frac{3}{2}$

$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

$r = K[CHCl_3][Cl_2]^{\frac{1}{2}} \Rightarrow \text{order} = 1 + \frac{1}{2} = \frac{3}{2}$

MOLECULARITY :

Molecularity is defined as the number of molecules atoms or radicals that must collide simultaneously in order for the reaction to take place.

* It is always a whole number and cannot be negative and fraction.

* Reactions are classified in terms of molecularity as unimolecular, bimolecular, termolecular depending upon the number of molecules involved in the reaction.

* The molecularity of a reaction cannot always be predicted from the stoichiometric reaction. It is obtained by compounding various elementry steps.

Example : $2H_2O_2 \longrightarrow 2H_2O + O_2$

First step $H_2O_2 \longrightarrow H_2O + O$ (slow step)

Second step $O + O \longrightarrow O_2$ (Fast step)

* The rate determining step indicates that it involves only one molecule. So the molecularity is 1.

(a) Unimolecular reaction :

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$N_2O_4 \rightleftharpoons 2NO_2$

$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

(b) Bimolecular reaction :

Saponification of ethyl acetate

$CH_3COOC_2H_5 + NaOH \rightleftharpoons CH_3COONa + C_2H_5OH$

Two molecules are involved in the reaction hence the molecularity of the reaction is 2.

$2HI \longrightarrow H_2 + I_2$ (molecularity is 2)

(c) Trimolecular reaction :

$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

The molecularity of the reaction is 3 since three molecules are involved in the reaction while the order of reaction is 2.

$2NO + O_2 \longrightarrow 2NO_2$

molecularity $\Rightarrow 3$

$H_2O_2 + 2H^+ + 2I^- \longrightarrow I_2 + 2H_2O$

molecularity $\Rightarrow 3$

	Order of reaction		Molecularity of reaction
(1)	It is the sum of the powers of concentration in terms of the reactants in the rate equation.	**(1)**	It is the number of chemical species taking part in the rate determining step.
(2)	It is empirical and must be determined experimentally.	**(2)**	It is concerned with the reaction mechanism and is a theoretical concept obtained from the balanced single step reaction
(3)	It is a whole number, zero or fraction	**(3)**	Molecularity is a whole number and never zero
(4)	It is same for the whole reaction no matter the reaction is simple or complex.	**(4)**	It represents a multistep reaction and is expressed for each step.
(5)	It refers to a reaction as a whole irrespective number of involved steps in the reaction	**(5)**	It depends upon the rate determining step in the reaction

PSEUDO-UNIMOLECULAR REACTION :

Such reactions whose order is one but the molecularity is two, are called pseudo-unimolecular reaction.

Examples :

(a) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

(b) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

(c) $C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

(d) $R–X + H_2O \longrightarrow ROH + HX$

DIFFERENT ORDER OF REACTION

(A) Zero Order Reaction :

Reaction in which the concentration of reactant do not change with time are said to be zero order reaction.

(i) Reaction : A $\longrightarrow$ Product

Example :

(a) $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$

(b) $2NH_3(g) \xrightarrow{hv} N_2(g) + 3H_2(g)$

(c) Reaction between Acetone and Bromine.

(d) Dissociation of HI on gold surface.

(e) Decomposition of gas on surface of catalyst

(ii) Differential rate equation : A $\longrightarrow$ Product

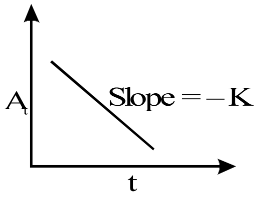
$$-\frac{d[A]}{dt} = k_0[A]^0 \quad \text{or} \quad \boxed{\frac{dx}{dt} = k_0[A]^0}$$

Where x is molar concentration of product at time 't'.

(iii) Calculation of rate constant : Let us take the reaction

$$A \longrightarrow \text{Product} \qquad -\frac{d[A]}{dt} = k[A]^0 = K$$

$$-\int_0^t d[A] = \int k\,dt \qquad -[A]_t = kt + C$$



$[A]_t = [A]_0$ on $t = 0$ $\qquad C = -[A]_0$

Put the value of C

$-[A]_t = kt - [A]_0$ $\qquad -[A]_t = [A]_0 - kt$

Note :

For zero order reaction that rate of reaction is equal to rate constant

Time for completion of reaction

$$[A]_t = [A]_0 - kt$$

For complete $\qquad [A]_t = 0$

$$k = \frac{[A]_0}{t}$$

	A $\longrightarrow$	Product
t = 0	a	0
After time t	a – x	x

$$\frac{dx}{dt} = k(a - x)^0 = k$$

$x = kt$

x = Amount of reactant that will change in product.

(iv) Unit of rate constant :

$k = \text{mol L}^{-1}\text{ s}^{-1}$ = unit of rate of reaction.

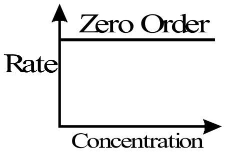
(v) Half-life period : The half life period for a zero order reaction is directly proportional to the initial concentration of the reactants.

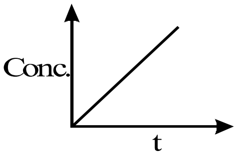
$$x = \frac{a}{2}$$

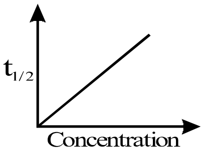
$$x = kt \quad \Rightarrow \quad \frac{a}{2} = kt$$

$$t_{1/2} = \frac{a}{2k} \quad \Rightarrow \quad t_{1/2} \propto A$$

(vi) Graphical representation :







(B) First Order Reaction :

Reaction in which that rate of reaction depends only on one concentration term of reactant.

Reaction : A $\longrightarrow$ Product.

(i) Example :

(a) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(c) $CH_3COOC_2H_5 \longrightarrow CH_3COOH + C_2H_5OH$

(d) $2Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2$

(ii) Differential rate equation :

$$-\frac{d[A]}{dt} = k[A] \quad \text{or} \quad \frac{dx}{dt} = k(a - x)$$

(iii) Calculation of Rate Constant :

Let us take the reaction.

	A $\longrightarrow$	Product
t = 0	a	0
After time t	(a – x)	x

Here, 'a' be the concentration of A at the start and (a – x) is the concentration of A after time taken t. i.e. x part of A has been changed in the product. So, the rate of reaction after time t is equal to.

$$\frac{dx}{dt} \propto (a - x) \quad \text{or} \quad \frac{dx}{dt} = k\,(a - x)$$

$$\text{or} \quad \frac{dx}{(a-x)} = k\,dt$$

Where k is specific reaction rate for the first order reaction, 'a' is initial concentration of A and x moles/litre of A has been decomposed up to the time t.

Upon integration of above equation

$$\int \frac{dx}{(a-x)} = \int k\,dt \quad \text{or} \quad -\ell n\,(a - x) = kt + C$$

$x = 0$ on $t = 0$ $\qquad C = -\ell n\, a$

Put the value of 'C'

$$-\ell n\,(a - x) = kt - \ell n\, a \qquad \text{or } kt = \ell n \left(\frac{a}{a-x}\right)$$

$$\text{or } k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

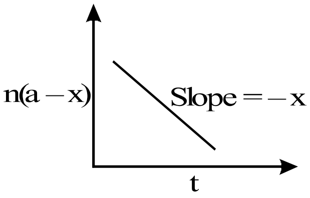
$$kt = \ell n \frac{a}{a-x} \qquad -kt = \ell n \frac{(a-x)}{a} \qquad \frac{a-x}{a} = e^{-kt}$$

$$\frac{C_t}{C_0} = e^{-kt} \qquad C_t = C_0\, e^{-kt} \quad \text{(Willhalpi equation)}$$

Here $C_0 \rightarrow$ Concentration on time t = 0, $C_t \rightarrow$ Concentration on time t

(iv) Unit of rate constant :

$k = \text{second}^{-1}$



$$kt = \ell n \frac{a}{a-x} \qquad kt = \ell n a - \ell n(a - x)$$

(v) Half-life period :

Putting a – x = a/2 and t = $t_{1/2}$ in the integrated rate equation we get

$$t_{1/2} = \frac{1}{k}\ell n\left(\frac{a}{a/2}\right) \quad \text{or} \quad t_{1/2} = \frac{\ell n2}{k}$$

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

Half-life period for first order reaction is independent from the concentration of reactant.

(vi) Time for 3/4 of the reaction ($t_{3/4}$)

Putting a – x = $\frac{a}{4}$ and t = $t_{3/4}$ in the integrated rate equation we get

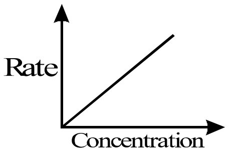
$$t_{3/4} = \frac{2.303}{k}\log 4 = \frac{1.386}{k} \qquad \boxed{\frac{t_{3/4}}{t_{1/2}} = 2}$$

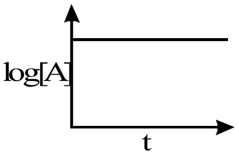
(vii) Interval formula : $\boxed{k = \frac{2.303}{t_2 - t_1}\log\frac{a - x_1}{a - x_2}}$

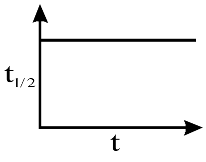
where x_1 and x_2 be the amounts decomposed up to the time t_1 and t_2 respectively.

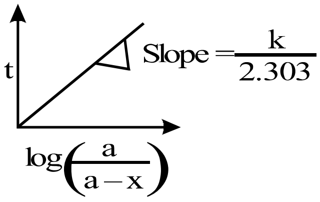
Speical Note : Time required for the completion of definite fraction of the first order reaction is independent of the initial concentration of the reactant.

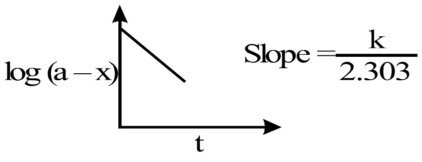
(viii) Graphical representation :











A few examples of 1st order and their formula for rate constant are as under :

(a) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_6H_{12}O_6$

$$\boxed{k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}}$$

where V_0, V_1 and V_∞ are the volumes of NaOH solution used for titrating a definite volume of the reaction mixture of zero time t and after time infinite respectively.

(b) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$;

$$\boxed{k = \frac{2.303}{t}\log\frac{r_0 - r_\infty}{r_t - r_\infty}}$$

where r_0, r_t and r_∞ are the polarimatric readings at zero time, after time t and after time infinitely respectively.

(c) $2N_2O_5 \longrightarrow 4NO_2 + O_2$ and $NH_4NO_2 \longrightarrow 2H_2O + N_2$

$$\boxed{k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}}$$

where V_t and V_∞ are the volume of O_2 or N_2 gas collected after time t and after time infinite respectively.

(d) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

$$\boxed{k = \frac{2.303}{t}\log\frac{V_0}{V_t}}$$

where V_0 and V_t are the volumes of $KMnO_4$ solution used for titrating a definite volume of the reaction mixture in the begining (at t = 0) and at time t respectively.

(C) Second Order Reaction :

Reaction whose rate depends on two concentration terms of reactant. Reactions

(i) 2A ⟶ Product (ii) A + B ⟶ Product

(i) Example :

(a) $CH_3COOCH_3 + NaOH \longrightarrow CH_3COONa + CH_3OH$

(b) $2CH_3CHO \longrightarrow 2CH_4 + 2CO$

(c) $2NO_2 \longrightarrow 2NO + O_2$

(d) $S_2O_6^{2-} + 2I^- \longrightarrow 2SO_3^{2-} + I_2$

(e) $CH_3COOH + C_2H_5OH \xrightarrow{OH^-} CH_3COOC_2H_5 + H_2O$

(ii) Differential rate equation :

(a) When A and B have equal initial concentration [say 'a' mole/litre]

$$\frac{dx}{dt} = k\,(a - x)^2$$

(b) When A & B have two different initial concentration (say 'a' & 'b' mole/litre)

$$\frac{dx}{dt} = k(a - x)\,(b - x)$$

(iii) Calculation of Rate Constant :

(a) When concentration of A and B taking same.

	A	+	$B \longrightarrow$	Product
t = 0	a		a	0
t = t	(a – x)		(a – x)	x

$$\frac{dx}{dt} = k[A]\quad[B] = k[a - x]\,[a - x]$$

$$\frac{dx}{dt} = k(a - x)^2$$

On taking the integration of above equation.

$$\int \frac{dx}{(a-x)^2} = \int k\,dt \quad \text{or} \quad \frac{1}{(a-x)} = kt + C,$$

$$\text{at } t = 0 \;;\; x = 0 \quad \Rightarrow \quad C = \frac{1}{a}$$

On putting the value of C on above equation

$$k\,t = \frac{1}{(a-x)} - \frac{1}{a} \quad \text{or} \quad \boxed{k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]}$$

(b) When concentration of A and B are different

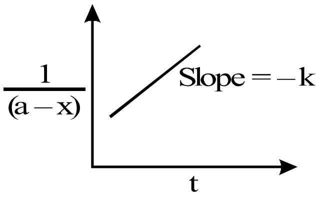
Case I : a > b

Then $\boxed{k = \frac{2.303}{t(a-b)}\log\left[\frac{b(a-x)}{a(b-x)}\right]}$

Case II : b > a

Then $\boxed{k = \frac{2.303}{t(b-a)}\log\left[\frac{a(b-x)}{b(a-x)}\right]}$

(iv) Unit of rate constant : $k = mol^{-1}\,L\,s^{-1}$



(v) Half-life period ($t_{1/2}$) :

Putting a – x = a/2 and t = $t_{1/2}$ in the integrated rate equation, we get

$$t_{1/2} = \frac{a/2}{k \times a(a - a/2)} \quad t_{1/2} = \frac{1}{ka} \quad \text{or} \quad \boxed{t_{1/2} \propto \frac{1}{a}}$$

Half-life of second order reaction is depend upon the concentraion of the reactant.

(vi) Time for 3/4th of the reaction ($t_{3/4}$) :

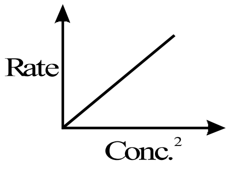
Putting $x = \frac{3}{4}a$, $a - x = \frac{a}{4}$ and $t = t_{3/4}$ in integrated rate equation.

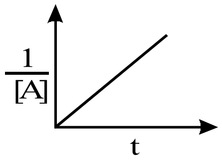
we get $t_{3/4} = \frac{3}{ka}$ or $\boxed{t_{3/4} \propto \frac{1}{a}}$

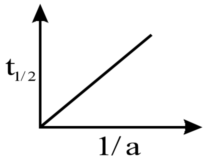
Note :

Time required for the completion of definite fraction of the second order reaction is inversely proportional to the first power of initial concentration of reactant.

(vii) Graphical representation :







(D) Third Order Reaction :

Reaction in which rate of reaction is determined by three concentration term of reactant.

Reaction :

(i) $A + B + C \longrightarrow$ Product

(ii) $A + 2B \longrightarrow$ Product

(iii) $2A + B \longrightarrow$ Product

(iv) $3A \longrightarrow$ Product

(i) Example :

(a) Reactio of nitiric oxide and chlorine

$2NO + Cl_2 \longrightarrow 2NOCl$

(b) Reaction of nitric oxide and oxygen

$2NO + O_2 \longrightarrow 2NO_2$

(c) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(ii) Differential rate equation :

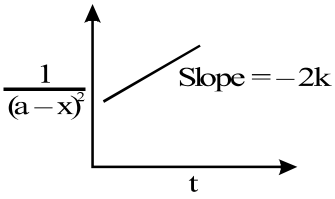
When the initial concentration of all the three reactants is same.

$$\frac{dx}{dt} = k\,(a-x)^3$$

(iii) Integrated rate equation :

$$kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

$$k = \frac{x(2a-x)}{t.2a^2(a-x)^2}$$



(iv) Half-life period : Putting $a - x = \frac{a}{2}$ and $t = t_{1/2}$ in the integrated rate equation, we get

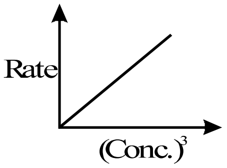
$$t_{1/2} = \frac{3}{2ka^2} \quad \text{or} \quad \boxed{t_{1/2} \propto \frac{1}{a^2}}$$

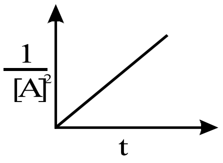
Note :

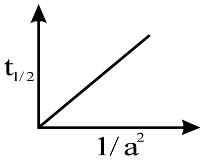
For a third order reaction, time required for the completion of definite fraction of the reaction is inversely proportional to the square of the initial concentration of the reactant.

(v) Unit of rate constant : $k = mol^{-2}\,L^2\,s^{-1}$

(vi) Graphical representation :







DETERMINATION OF ORDER OF REACTION :

(a) Integration Method : In this method known quantities of the reactants are mixed and the reaction rate is determined by analysing the reaction mixture after different intervales of time. The values so obtained are subsituted, in the kinetic equations of first, second and third order .

The equation which gives the most constant value for the K for a series of time intervales is the one corresponding to the order of reaction :

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

$$K_2 = \frac{1}{t}\left[\frac{1}{a} - \frac{1}{(a-x)}\right]; \quad K_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

* This method can be used only for simpler reactions.

(b) Half life Method :

* General expression for the half life period for a reaction of nth order is :

$$t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{K_n\, a^{n-1}(n-1)} \qquad (n \neq 1)$$

For first order	$t_{1/2} \propto a^0$	
For second order	$n = 2$	$t_{1/2} \propto 1/a$
For third order	$n = 3$	$t_{1/2} \propto 1/a^2$
In general	$t_{1/2} \propto 1/a^{n-1}$	

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

(c) Graphical Method :- If a straight line is obtained by plotting log (a–x) against $\frac{dx}{dt}$, it is a first order reaction. Similarly, if a straight line is obtained by plotting $(a-x)^2$ or $(a-x)^3$ against $\frac{dx}{dt}$, the reactions are second and third order respectively.

(d) The order of reaction can also be determined by Van't Hoff differential method :-

$$n = \frac{\log_{10}\left(\frac{dx_1}{dt}\right) - \log_{10}\left(\frac{dx_2}{dt}\right)}{\log_{10} x_1 - \log_{10} x_2}$$

Here x_1 and x_2 different initial concentrations.

THEORY OF REACTION RATES :

Important theories to explain reaction rates are :

(a) Collision theory

(b) Transition state or absolute reaction theory.

(a) **Collision Theory :** The important points of this theory are :

(i) If two molecules are to react together they must collide with each other.

(ii) The collision between all molecules do not lead to chemical reaction.

(iii) Only those collisions result in chemical reaction in which the molecules acquire energy greater than the activation energy.

* The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency and its value is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(iv) The colliding molecules must posses certain minimum energy (threshold energy) to make the collision effective.

(v) The additional energy required by the molecule to attain the threshold energy is called activation energy. It is acquired by the molecules as a result of interchange of energies during collisions.

* Thus, activation energy = Threshold energy. – Energy of colliding molecules.

(b) **Transition state theory :** The important points are:

(i) The theory is based on the fact that bond formation and bond dissociation involved in a chemical reaction must occur continuously.

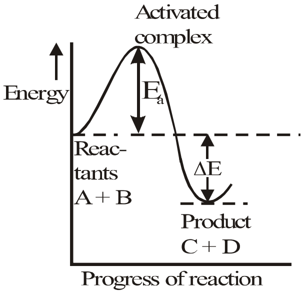
(ii) For a reaction to occur, the reactants having sufficient energy must approach each other to form activated complex.

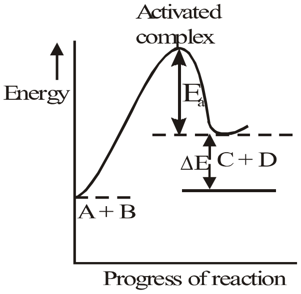
(iii) The energy of activated complex is higher than that of reactants and products.

(iv) The reactants must cross the energy barrier (activated complex formation) before converting into products.

(v) The energy barrier has energy equal to the energy of activation.

* The energy changes during exothermic and endothermic reactions versus the process of reaction are shown below -





Factors affecting Reaction rates :

(i) **Nature of reactants :**

In reactions involving higher **energy barrier**, the reactant molecules require higher energy of activation to cross the barrier and get converted into products. A smaller number of molecules possesses this higher amount of energy hence the rate of reaction is slow. In a reactions with lower energy barrier, the reactant molecules require lesser amount of activation energy to pass the barrier. Hence large number of molecules possess, this energy and the rate of reaction will be fast.

(ii) **Concentration of reactants :**

The rate of reaction increases with the increase in concentration of reactant (except zero order reactions) In the reaction $A + B \rightarrow AB$, if the concentration of A and B are doubled the rate of reaction will increase to 4 times.

(iii) **Pressure :**

For reaction involving gases an increase in pressure increases the rate of reaction by increasing the probability of collision among the molecules.

(iv) **Temperature :**

Increase in temperature in most cases increases the rate of the reaction and the rate constant.

The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two different temperature differing by 10°C.

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

Its value lies generally between 2 and 3.

When the temperature is increased, the kinetic energy $\left(\frac{3}{2}RT\right)$ of the reacting molecules increase. This shall increase the number of collisions and the rate of reaction shall increase.

* If temperature is raised from 10 to n times then the rate of reaction will increase by 2^{n-1} times.
* If temperature is raised from 0° to n times then the rate of reaction will increase by 2^{n} times.
* Arrhenius suggested an equation which describes K as a function of temperature

$$K = A\,e^{-\frac{Ea}{RT}}$$

Where K = rate constant

A = a constant (Frequency factor)

Ea = activation energy

At two temperature T_1 and T_2 taking log of Arrhenius equation

$$\log_e K_1 = \log A - \frac{E_a}{RT_1}\log_e e$$

$$\log_e K_2 = \log A - \frac{E_a}{RT_2}\log_e e$$

So, $\log_e K_1 - \log_e K_2 = E_a\left(\frac{1}{RT_2} - \frac{1}{RT_1}\right)$

$$\log\frac{K_1}{K_2} = \frac{E_a}{2.303R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

(v) Catalyst :

A catalyst is a substance which lowers the energy of activation of a reaction. The magnitude of energy barrier is reduced in presence of catalyst. Hence a greater number of reactant molecules can get over the energy barrier and as a result rate of reaction increases.

PHOTO CHEMICAL REACTION :

Reactions which occurs in presence of light are photochemical reaction i.e., reaction which do not occur in dark.

Example : **(i)** $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

(ii) Photo synthesis

(iii) Vision

* In photochemical reaction, each molecule of the reacting substance absorbs one quantum (single photon) of radiation and is activated to form the product.
* for every reaction, a certain amount of energy is required.
* Higher the intensity of light greater will be the rate of reaction.
* For these reactions, the value of ΔG may be positive or negative.
* Temperature have no significant effect.

Mechanism :

$Cl_2 + h\nu \longrightarrow Cl_2^*$ (activated molecule)

Primary step of reaction : $Cl_2^* \longrightarrow Cl + Cl$

Secondary step of reaction :

$H_2 + Cl \longrightarrow HCl + H$

$Cl_2 + H \longrightarrow HCl + Cl$

Final step of reaction : $Cl + Cl \longrightarrow Cl_2$

Quantum yield (or quantum efficiency) :

The quantum efficiency yield (ϕ) of a photochemical reaction may be expressed as

$$\phi = \frac{\text{Number of molecules reacted or product formed}}{\text{Number of photon absorbed}}$$

Application of photochemical reaction :

(i) in photography

(ii) in photo printing

(iii) in photosynthesis

(iv) in vision

(v) in electronic industries

(vi) in many polymerization reactions.

Mechanism of Reactions : The most of the reactions occur in a series of steps, some of which may be quite fast while other may be slower.

Vant Hoff proposed that whole kinetics of the reaction depends upon the rate deter mining step (the slowest step of a reaction is taken as the rate determining step)

Examples :

(i) Reaction between NO and H_2 :

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

This reaction involves 4 molecules but it has found to be third order because it occurs in the following steps:

(a) $2NO + H_2 \longrightarrow N_2 + H_2O_2$ (slow)

(b) $H_2O_2 + H_2 \longrightarrow 2H_2O$ (fast)

Thus (a) being slow is the rate determining step. The rate is given by: Rate = $K[NO]^2 [H_2]$

(ii) Reaction between $FeCl_3$ and KI :

$2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$

This reaction involves 8 molecules, but it has been found to be of third order -

(a) $FeCl_3 + 2KI \longrightarrow FeI_2 + 2KCl + Cl^-$ (slow)

(b) $2KI + 2Cl^- \longrightarrow 2KCl + I_2$ (fast)

Rate = $K [FeCl_3] [KI]^2$

This indicates that the reaction is of third order.

(iii) Reaction between H_2 and I_2:

$H_2 + I_2 \rightleftharpoons 2HI$

(a) $I_2 \longrightarrow 2I$ (fast)

(b) $H_2 + I \longrightarrow H_2I$ (fast)

(c) $H_2I + I \longrightarrow 2HI$ (slow)

(iv) Combination of NO_2 and F_2 :

$2NO_2 + F_2 \longrightarrow 2NO_2F$

(a) $NO_2 + F_2 \longrightarrow NO_2F + F$ (slow)

(b) $NO_2 + F \longrightarrow NO_2 F$ (fast)

Thus order = 2

SPECIAL POINTS

(1) Chemical kinetics predicts the rate and mechanism of chemical reaction.

(2) Rate of reaction is the rate of change of concentration of reactants and products with time.

(3) Rate of reaction depends upon nature of reactants, concentration, temperature, catalyst, surface area and radiation.

(4) Molecularity of a reaction is the total number of reacting molecules taking part in rate determining step.

(5) Order of reaction may be determined by integration, graphics or half period method.

(6) First order reaction is one in which the rate is directly proportional to the concentration of reacting substance.

(7) The additional energy required to attain threshold energy is called activation energy.

(8) Activated complex is the unstable complex formed in the transition state with effective collision.

(9) The minimum energy which the molecules should possess so that their collisions result in chemical reaction is called threshold energy.

(10) According to Arrhenius

rate of reaction $\propto K = A e^{-\frac{E_a}{RT}}$