Chemical Kinetics :

Chemical kinetics is a section of physical chemistry which deals with the rate of reactions and the stepwise path followed by a chemical reaction.

Chemical kinetics has importance in industrial chemistry where the rates of reactions are greatly affected by the slight change in the conditions applied. It is important in biology and medicine because health represents a balance between a large number of simultaneous independent reactions and in case of illness, the rates of biologically important reactions show abnormal change.

Types of Reactions :

① **Instantaneous reactions :** Such reactions take place at once. These are also called ionic reactions. e.g.

$$BaCl_2 (aq) + H_2SO_4 (aq) \longrightarrow BaSO_4 (s) + 2HCl (aq).$$

② **Very slow reactions :** Such reactions take a long time for completion. e.g. rusting of iron.

$$Fe (s) + H_2O (g) + CO_2 (g) + \tfrac{1}{2} O_2 (g) \longrightarrow \underset{\text{(rust)}}{Fe(OH)HCO_3}.$$

③ **Moderate reactions :** These reactions neither proceed instantaneously nor very slowly. e.g. hydrolysis of ethyl acetate, dissociation of H_2O_2, etc.

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

$$2H_2O_2 \longrightarrow 2H_2O (l) + O_2 (g).$$

Rate of Reaction :

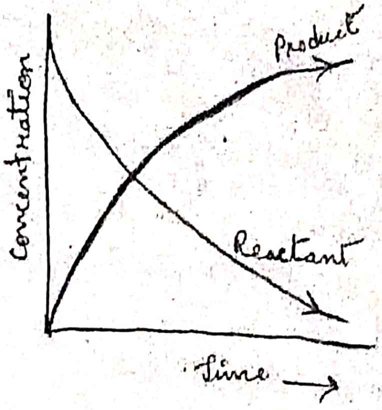
The quantity of a reactant species consumed or the quantity of a product species formed in unit time in a chemical reaction is called the rate of the reaction.

Let us consider a general reaction,

$$A \longrightarrow B.$$

Rate of reaction

$(r) = \frac{\text{Amount of A consumed}}{\text{Time taken}}$



or Rate of reaction

$r = \frac{\text{Amount of B produced}}{\text{Time taken}}$.

It can be ~~representated~~ represented as below:

$$\text{Rate of reaction} = \frac{-\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

where, $\Delta[A] = [A]_{\text{initial}} - [A]_{\text{final}}$

$\Delta t = t_2 - t_1$.

Rate of a reaction depends upon the concentration of reactant. With the passage of time, the concentration of reactant species decreases and hence, the rate of reaction goes on decreasing. ~~Therefore~~,

∴ Rate of reaction at a given moment $= \frac{dx}{dt}$.

Hence, rate of reaction may be defined as,

"The instantaneous change in concentration of a reactant or product species at a given moment of time".

Mathematical expression for rates of reaction:

① Reactions involving same stoichiometric coefficients of all reactants and products:

e.g. $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$.

$$\text{Rate of reaction} = -\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[CO]}{\Delta t} = +\frac{\Delta[NO]}{\Delta t}$$

$$= +\frac{[CO_2]}{\Delta t}$$

② Reactions involving different stoichiometric coefficients of reactants and products.

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

$$\text{Rate of reaction} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[HI]}{\Delta t}.$$

∴ For a general reaction: $aA + bB \longrightarrow cC + dD$.

Rate of reaction = ~~$\frac{1}{a}[A]$~~ $-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$

$$= +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}.$$

Units of Rate of Reaction :

① When concentration is in mol L^{-1} and time is in seconds then rate of reaction is expressed in $mol L^{-1} s^{-1}$.

② When molar concentration is expressed in terms of partial pressures, the units of reaction rate will be in atm s^{-1}

Q. In the reaction,

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g).$$

The rate of formation of NO is 3.6×10^{-3} mol $L^{-1} s^{-1}$, find the rate of disappearance of oxygen.

Solⁿ: Rate of reaction $= -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}$

$$= +\frac{1}{4}\frac{\Delta[NO]}{\Delta t} = +\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}.$$

∴ Rate of disappearance of O_2.

$$\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t}.$$

$$\Rightarrow \frac{\Delta[O_2]}{\Delta t} = \frac{5}{4}(3.6 \times 10^{-3}) mol L^{-1} s^{-1}.$$

$$= 4.5 \times 10^{-3} mol L^{-1} s^{-1}.$$ //

Factors influencing Rate of Reaction :

① **Nature of reactants:** Reaction between NO and O_2 is faster than the reaction between CO and O_2, under similar conditions of Tempʳ and concⁿ.

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g) \quad (fast).$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad (slow).$$

Since, bonds are broken in reactant molecules and new bonds are formed in chemical reactions, ~~it seems~~ the rate of a reaction ~~should~~ depends upon the type of bonds involved.

② **Effect of concentration:** greater the concentration of reactants, greater will be the inter-molecular collisions and hence, greater will be the rate of reaction. ~~eg.~~

③ **Effect of temperature:** Rise in tempʳ increases the reaction rate due to the increase in collision frequency and increase in effective collisions.

~~④ Solvent~~:

④ Effect of surface area: Increase in surface area increases rate of reaction.

⑤ Effect of catalyst: Addition of catalyst increases the rate of reaction.

⑥ Effect of light: Absortion of light may excite a reacting molecule.

Rate Equation or Rate Law:

An experimentaly determined mathematical expression, relating the molar concentration of reactants to the actual reaction rate is known as rate law.

Determination of rate law: Let us consider a general reaction.

$$nA + mB \longrightarrow \text{Products}$$

Let, $r \propto [A]^a$, where $a = n \,/\, a \neq n$.

$r \propto [B]^b$, where $b = m \,/\, b \neq m$.

$$\therefore r \propto [A]^a[B]^b \longrightarrow Ⓐ$$

The eqn Ⓐ is called the rate law for the above general reaction.

But, according to law of mass action,

$$r \propto [A]^n[B]^m.$$

Molecularity of a reaction:

It is defined as the no. of molecules or ions taking part in a collision to bring about the reaction. ~~or it is~~

Or, It is defined as the no. of reactant species included in a single step reaction.

e.g. $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ [Unimolecular].

$H_2(g) + I_2(g) \longrightarrow 2HI(g)$ [Bimolecular].

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ [Trimolecular].

Order of a Reaction:

It is defined as the sum of the exponents (powers) to which the molar concentration terms are raised in the rate law.

Let,

$$lA + mB \longrightarrow \text{Products}$$

Its rate equation is . $r = -\frac{dx}{dt} = k[A]^a[B]^b$

Here, order of reaction, $n = a+b$.

'a' and 'b' may be fractional, whole no. or zero.

Reactions of different orders :

① Zero-order reaction : These are the reactions in which the rate of reaction is independent of the concentration of all the reactants. e.g.

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g),$$

$$r = k[H_2]^0[Cl_2]^0.$$

$$\therefore n = 0+0 = 0,$$

② First order reaction : These are the reactions in which the rate of reaction is determined by the variation of one concentration term only. e.g.

$$N_2O_5(g) \longrightarrow N_2O_4(g) + \frac{1}{2}O_2(g).$$

$$r = k[N_2O_5]$$

$$\therefore n = 1.$$

③ Second order reaction : These are the reactions in which the rate of reaction is determined by variation of two concentration terms. eg.

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

$$r = k[H_2][I_2]$$

$$\therefore n = 1+1 = 2.$$

④ Third order reaction : These are the reactions in which the rate of reaction is determined by the variation of three concentration terms. eg.

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

$$r = k[NO]^2[O_2].$$

$$\therefore n = 2+1 = 3.$$

⑤ Fractional order reaction :

e.g. $CH_3CHO(l) \xrightarrow{\Delta} CH_4(g) + CO(g)$

$r = k[CH_3CHO]^{3/2}$.

$\therefore n = \frac{3}{2}$.

⑦ Pseudo first order reaction : These are the reactions in which more than one reactant molecules are involved but these are of first order e.g.

$CH_3COOC_2H_5(l) + \underset{\text{excess}}{H_2O(l)} \longrightarrow CH_3COOH(l) + C_2H_5OH(l)$.

$r = k[CH_3COOC_2H_5]$.

$\therefore n = 1$.

Mechanism of Reaction :

The sequence of steps through which a reaction is supposed to take place is called reaction mechanism.

Characteristics of an elementary step —

① It may be real or imaginary.

② It involves three or less than three reactant molecules/ions.

③ Each elementary step is represented by a balanced chemical equation.

For a reaction to occur, the mechanism must involve the one key step which is the slowest step, not necessarily the first or last step.

Integrated Rate Expressions :

Ⓘ zero order reactions (differential and Integral forms):

Here, the concentration of the reactant is so large that it remains practically constant during the course of reaction.

Let us consider a reaction,

$A \longrightarrow B$.

If x is the amount of the product formed at any instant, rate of formation of product is given by,

$$\frac{dx}{dt} = k_0(a-x)^0 = k_0 \longrightarrow (1).$$

where a = initial concn of A.

k_0 is the constant for zero order reaction.

Integrating equation (1),

$$\int dx = \int k_0\, dt \qquad [\because (a-x)^0 = 1].$$

This is a general rate equation for zero order reaction.

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

Rate of the reaction,

$$-\frac{dx}{dt} = k_0[HI]^0 = k_0.$$

Characteristics of zero order rate constant (k_0):

① Units of rate constant: $mol\ L^{-1}\ s^{-1}$ or $mol\ L^{-1}\ time^{-1}$.

③ Half life period: It is the time taken for converting the original concentration of the reactants to one half. The expression is —

when $x = \frac{a}{2} = t_{\frac{1}{2}}$, where a = initial concn.

when $t = 0$, x = amount reacted when $t = t_{\frac{1}{2}}$.

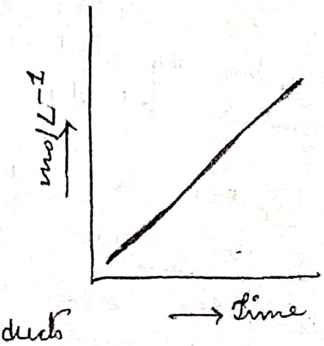
Substituting the value of x in the zero order reaction,

$$x = k_0 t.$$

$$\Rightarrow \frac{a}{2} = k_0 . t_{\frac{1}{2}}.$$

$$\boxed{\Rightarrow t_{\frac{1}{2}} = \frac{a}{2k_0}.}$$

③ Evaluation of k: A plot of x against time (t) forms a straight line passing through the origin with slope k.



Ⅱ First order reaction: A ⟶ Products

Let, the initial concentration of A be C_0 and the concentration after a time t second be C.

$$\text{Rate} = \frac{dx}{dt} = -\frac{d[A]}{dt} = k[A] \longrightarrow (1).$$

Substituting the value of concentration in equation (1), we get,

$$-\frac{dC}{dt} = kC. \Rightarrow \frac{-dc}{c} = kt.$$

Integrating, $-\int \frac{dc}{c} = k\int dt$.

$\Rightarrow -\ln c = kt + I$, where, I = constant of integration

$\longrightarrow$ (11).

when $t = 0$, $c = C_0$.

$\therefore -\ln C_0 = 0 + I$

$\Rightarrow I = -\ln C_0$.

$\therefore$ Eqn (11) $\Rightarrow -\ln c = kt - \ln C_0$.

$\Rightarrow kt = \ln C_0 - \ln C$.

$\Rightarrow kt = \ln \frac{C_0}{C}$

$\Rightarrow kt = 2.303 \log \frac{C_0}{C}$.

$$\boxed{\Rightarrow k = \frac{2.303}{t} \log \frac{C_0}{C}}$$

This is the eqn for the first order reaction. k is constant called first order rate constant.

When $C_0 = a$ and $C = a-x$.

$$\therefore \boxed{k = \frac{2.303}{t} \log \frac{a}{a-x}}$$

Characteristics of first order reactions:

① Unit of first order reaction rate constant is s^{-1} or time^{-1}.

② Half life period:

According to first order rate eqn,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

where a is the initial concentration of the reactant when $t = 0$ and $(a-x)$ is the concn at time t.

when, $t = t_{\frac{1}{2}}$, $x = \frac{a}{2}$.

$$\therefore k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{a}{a - \frac{a}{2}}.$$

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

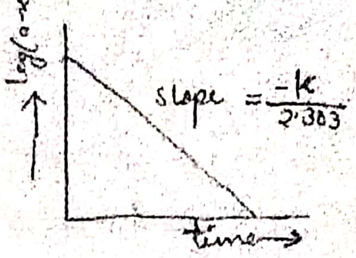
$$\Rightarrow t_{\frac{1}{2}} = \frac{2.303}{k} \cancel{\log 2} \times 0.3010 \qquad [\because \log 2 = 0.3010].$$

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

③ Evaluation of k:

We know,

$$t = \frac{2.303}{k}\log\frac{a}{a-x}.$$



~~$\Rightarrow \log a + \log(a-x) =$~~

$$\Rightarrow \log(a-x) = \frac{-kt}{2.303} + \log a.$$

This is the eq^n of a straight line $(y = mx + c)$. Thus if a graph is plotted between log(a−x) ago along y-axis and time along x-axis, a straight line is obtained where slope is $\frac{-k}{2.303}$.

Radioactive Decay as first order phenomenon:

All radioactive transformations are first order reactions. Let us consider a radioactive element A which disintegrates to form B.

$$A \longrightarrow B.$$

Let,

Initial no. of atoms of radioactive elements = N_0.

No. of atoms at any time, t = N.

~~$\therefore$ Rate = $\frac{dN}{dt}$~~

$\therefore$ Rate of disintegration at time t is,

$$-\frac{dN}{dt} \propto N$$

$$\Rightarrow -\frac{dN}{dt} = \lambda N. \longrightarrow (I).$$

where dN is the no. of atoms disintegrating in time dt. λ is disintegration constant and depends upon the nature of the radioactive element.

Now, (I) $\Rightarrow -\frac{dN}{N} = \lambda dt \longrightarrow (II)$.

If dt = 1 sec, then, $-\frac{dN}{N} = \lambda$.

Integrating eq^n (II).

$$-\int\frac{dN}{N} = \lambda\int dt.$$

$$\Rightarrow -\ln N = \lambda t + c \longrightarrow (III).$$

where c is constant of integration.

when t = 0, $N = N_0$.

$\therefore$ (III) $\Rightarrow c = -\ln N_0$.

Substituting the value of c in eq^{n} (iii).

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

$$\Rightarrow \ln \frac{N_0}{N} = \lambda t ,$$

$$\Rightarrow 2.303 \log \frac{N_0}{N} = \lambda t .$$

$$\boxed{\Rightarrow \lambda = \frac{2.303}{t} \log \frac{N_0}{N}}$$

The above relation is similar to the first order rate eq^{n}.

$$k = \frac{2.303}{t} \log \frac{a}{a-x} ,$$

where a = initial conc^{n} i.e. N_0.

$(a-x)$ = conc^{n} present at time i.e. N.

Half life ~~prio~~ period of radioactive decay :

Let $t_{\frac{1}{2}}$ be the time in which half the amount of the radioactive substance has disintegrated.

i.e. when $t = t_{\frac{1}{2}}$, $N = N_0$.

We have,

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N} .$$

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

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

$$\boxed{\Rightarrow t_{\frac{1}{2}} = \frac{0.693}{\lambda}} \qquad [\because \log 2 = 0.3010] .$$

Significance of Half life :

① It measures the radioactivity of an element.

② It measures the stability of an element.

③ It identifies a nuclide.

④ It helps to know the amount of the substance left after a particular period.

$$\text{No. of half lives, } n = \frac{\text{Total time elapsed}}{\text{Half life period}}$$

$$\text{Amount of substance left, } N = N_0 \left(\frac{1}{2^n}\right) .$$

Average life or Mean life period (T):

The reciprocal of the disintegration constant (λ) of a radio active nucleide is called average life period i.e.

$$T = \frac{1}{\lambda}.$$

$$\because \lambda = \frac{0.693}{t_{\frac{1}{2}}}$$

$$\Rightarrow \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44\, t_{\frac{1}{2}}.$$

$\therefore$ Average life period = 1.44 × Half life period.

(III) Second Order Reaction:

Case I: If the reacting substances are the same the general reaction is written as —

$$2A \longrightarrow \text{products}.$$

$\therefore$ Rate of reaction $= \frac{-d[A]}{dt} = k[A]^2$

where, k = second order rate constant.

If a is the initial concentration of A and x is the amount consumed after time t, the rate eqn becomes,

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

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

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

Integrating,

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

$$\Rightarrow \frac{(a-x)^{-1}}{-1}(-1) = kt + c.$$

where c is constant of integration

$$\text{or} \quad \frac{1}{a-x} = kt + c \quad . \longrightarrow (1).$$

Initially time, $t = 0$.

$\therefore\ x = 0$.

$\therefore$ Eqⁿ (1) $\Rightarrow \frac{1}{a} = c$.

Putting the value of c in eqⁿ(1),

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\Rightarrow kt = \frac{1}{a-x} - \frac{1}{a}$$

$$\Rightarrow kt = \frac{a-(a-x)}{a(a-x)}$$

$$\Rightarrow kt = \frac{x}{a(a-x)}.$$

$$\boxed{\Rightarrow k = \frac{1}{t}\cdot\frac{x}{a(a-x)}}$$

If initial concentration is C_0 and concⁿ $(a-x)$ at time t is C_t, then,

$$\boxed{k = \frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_0}\right]}.$$

Half life period: In time $t_{\frac{1}{2}}$, $x = \frac{a}{2}$.

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

$$\Rightarrow k = \frac{1}{t_{\frac{1}{2}}}\cdot\frac{1}{a}.$$

$$\Rightarrow \frac{1}{t_{\frac{1}{2}}} = ka.$$

$$\boxed{\Rightarrow t_{\frac{1}{2}} = \frac{1}{ka}}.$$

Case II: If the two reacting substances are different, the reaction is represented as –

$$A + B \longrightarrow \text{Products}.$$

Rate of the reaction,

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{dx}{dt} = k[A][B].$$

Let a and b be the initial concentrations of A and B respectively and x mol L⁻¹ is the amount of each reactant that would react in time, t, then at any instant of time t,

concentration of A = $(a-x)$ mol L⁻¹

concentration of B = $(b-x)$ mol L⁻¹.

∴ Rate of reaction, $\frac{dx}{dt} \propto [A][B]$

$$\frac{dx}{dt} \propto (a-x)(b-x)$$

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

where k is the rate constant.

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

The expression $\frac{1}{(a-x)(b-x)}$ can be resolved into partial fractions as,

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

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

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

If $x = a$, then, $A(b-a) = 1$.

$$\Rightarrow A = \frac{1}{b-a}.$$

when $x = b$, then, $B(a-b) = 1$.

$$\Rightarrow B = \frac{1}{a-b}.$$

$$\therefore \text{Eq}^n (1) \Rightarrow \frac{1}{(a-x)(b-x)} = \frac{1}{(b-a)(a-x)} + \frac{1}{(a-b)(b-x)}.$$

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

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

Integrating this eqⁿ, we get,

$$\frac{1}{(a-b)}\left\{\int\frac{dx}{(b-x)} - \int\frac{dx}{(a-x)}\right\} = \int k.dt.$$

$$\Rightarrow \frac{1}{(a-b)}\left[-\ln(b-x) - \{-\ln(a-x)\}\right] = kt + c.$$

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

$$\Rightarrow \frac{1}{(a-b)}\left(\ln\frac{a-x}{b-x}\right) = kt + c \longrightarrow (ii) \quad \left[c = \text{constant of integration}\right].$$

when $t = 0$, $x = 0$.

$$\text{Eq}^n\ (ii) \Rightarrow \frac{1}{a-b}\cdot\ln\frac{a}{b} = c \longrightarrow (iii).$$

Putting the value of c in eq^n (ii), we get.

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

$$\Rightarrow kt = \frac{1}{(a-b)}\ln\frac{a-x}{b-x} - \frac{1}{(a-b)}\ln\frac{a}{b}.$$

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

$$\Rightarrow kt = \frac{1}{(a-b)}\left(\ln\frac{a-x}{b-x}\times\frac{b}{a}\right)$$

$$\Rightarrow k = \frac{1}{t(a-b)}\left[\ln\frac{b(a-x)}{a(b-x)}\right].$$

$$\boxed{\Rightarrow k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}}$$

Case III: If two different reactants A and B have equal initial concentration 'a' react, the rate of the reaction is,

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

The integrated rate eq^n will be

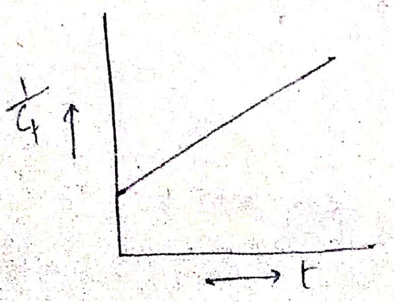
$$k = \frac{1}{t}\cdot\frac{x}{a(a-x)}.$$

Characteristics of Second order reaction:

① The second order equation can be written in the form.

$$kt = \frac{1}{C_t} - \frac{1}{C_0} \Rightarrow \frac{1}{C_t} = kt + \frac{1}{C_0}$$

It is an eq^n of straight line. If a plot is drawn between $\frac{1}{C_t}$ versus t, a straight line is obtained with slope k.



② The unit of rate constant is $conc^{-1}\,time^{-1}$. If concⁿ is in moles per litre and time is in seconds, then unit is $litre\ mol^{-1}\,s^{-1}$.

③ When one of the reactants is in large excess, the second order reaction behaves like first order.

$$k_2 = \frac{1}{t \cdot a} \ln \frac{ba}{a(b-x)} = \frac{2.303}{ta} \log \frac{ba}{a(b-x)}.$$

When a is in large excess, b and x are neglected.

$$\therefore k_2 a = k' = \frac{2.303}{t} \log \frac{b}{(b-x)}.$$

This eqⁿ is identical with the first order equation.

Imp Methods for determination of the order of a reaction:

Methods of Trial or Integration Methods:

① Method of Trial

In this method, the amounts of the reactants consumed after different intervals of time are determined by analysis. The data so obtained is substituted in the eqⁿs for the first, second and third order reactions. The eqⁿ which gives almost a constant value of k decides the order of the reaction.

We can start substituting data in the order given in the following table.

Order	0	1	2	3
Rate eqⁿ	$k = \frac{x}{t}$	$k = \frac{2.303}{t} \log \frac{a}{a-x}$	$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$	$k = \frac{1}{2t} \cdot \frac{x(2a-x)}{a^2(a-x)^2}$

2. Graphical method:

In this method, the values of x are plotted against t and rate of the reaction, $\frac{dx}{dt}$ at any time is determined from the slope, since $\frac{dx}{dt} = \tan\theta$.

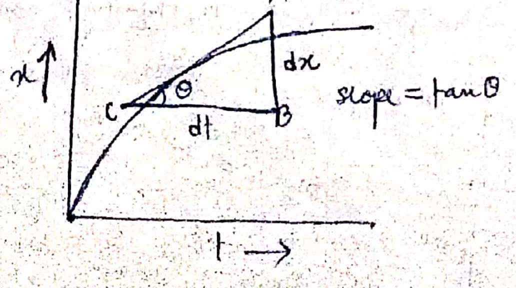


Fig: Graph of x vs t.

the various values of $\frac{dx}{dt}$ are plotted against $(a-x)$. If a straight line is obtained, the reaction is of ~~ord~~ first order. If a straight line is obtained by plotting $\frac{dx}{dt}$ versus $(a-x)^2$, it is a second order reaction. The reaction will be a third order reaction if graph between $\frac{dx}{dt}$ and $(a-x)^3$ is a straight line.

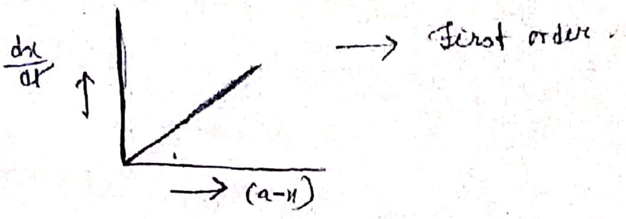


Fig. Graph of $\frac{dx}{dt}$ vs $(a-x)$.

③ Fractional change or Half change method:

Time, T_f required to complete a definite fraction of the reaction is.

ⓐ directly proportional to initial concentration for zero order reactions.

ⓑ independent of initial concentration for first order reactions i.e. $t \propto \frac{1}{a^0}$.

ⓒ inversely proportional to the initial concentration for second order reactions i.e. $t_f \propto \frac{1}{a^1}$.

ⓓ inversely proportional to the square of the initial concentration for third order reactions, ie. $t_f \propto \frac{1}{a^2}$.

In general, we can say that, $t_f \propto \frac{1}{a^{n-1}}$ where n is the order of the reaction.

If a_1 and a_2 are the initial concentrations in two different ~~too~~ experiments and t_1 and t_2 are the corresponding times for a definite fraction of the reaction to be completed, then

$$(t_f)_1 \propto \frac{1}{a_1^{n-1}} \longrightarrow ①$$

$$(t_f)_2 \propto \frac{1}{a_2^{n-1}} \longrightarrow ⑪$$

$$① \div ⑪ \Rightarrow \frac{(t_f)_1}{(t_f)_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Thus starting with two initial concentrations and finding $t_{\frac{1}{2}}$ in each case, the order of a reaction can be determined.

alternatively, if $t_{1/2}$ is the time for half change and 'a' is the initial concentration, then,

① for first order reaction, $t_{\frac{1}{2}}$ = constant.
② for second " " , $t_{\frac{1}{2}} \times a$ = "
③ " third " " , $t_{\frac{1}{2}} \times a^2$ = "
④ " nth " " , $t_{\frac{1}{2}} \times a^{n-1}$ = ".

④ Vant ~~Hoff's~~ Hoff's Differential Method:

we know that,

$$\frac{dx}{dt} = k(a-x) \quad \text{for first order reactions.}$$

$$\frac{dx}{dt} = k(a-x)^2 \quad \text{for second " "}$$

$$\frac{dx}{dt} = k(a-x)^3 \quad \text{" third " "}$$

$$\therefore \frac{dx}{dt} = k(a-x)^n \quad \text{" nth " "}$$

Putting $(a-x) = c$, the concentration at any instant, in above equation,

$$\frac{-dc}{dt} = kc^n \longrightarrow \text{(i)}$$

for two different concentrations c_1 and c_2 of the reactants,

$$-\frac{dc_1}{dt} p = kc_1^n \longrightarrow \text{(ii)}$$

$$-\frac{dc_2}{dt} = kc_2^n \longrightarrow \text{(iii)},$$

Taking logs,

$$\log\left(-\frac{dc_1}{dt}\right) = \log k + n \log c_1 \longrightarrow \text{(IV)}.$$

$$\log\left(-\frac{dc_2}{dt}\right) = \log k + n \log c_2 \longrightarrow \text{(V)}.$$

$$\text{(IV)} - \text{(V)} \Rightarrow n(\log c_1 - \log c_2) = \log\left(-\frac{dc_1}{dt}\right) - \log\left(-\frac{dc_2}{dt}\right).$$

$$\Rightarrow n = \frac{\log\left(\frac{-dc_1}{dt}\right) - \log\left(\frac{-dc_2}{dt}\right)}{\log c_1 - \log c_2} \longrightarrow \text{(VI)}.$$

Thus for determining the order of the reactions, we need the values of the rates of reaction $\frac{dc_1}{dt}$ and $\frac{dc_2}{dt}$ at two different concentrations c_1 and c_2 respectively. These can be obtained from the slopes of c vs t plots. Substitution of these values for two different initial concentrations, n can be calculated.

⑤ Ostwald's Isolation method.

This method is employed in determining the order of complicated reactions by isolating one of the reactants. This is achieved by taking all but one of the reactants in turn in a very large excess so that their active masses remain constant. Variation of concentration of this reactant only, permits a direct determination of the order of the reaction.

Concept of activation energy and Activated complex Theory:

The extra energy supplied to the reactant molecules to attain threshold energy to undergo chemical reaction is called activation energy (E_a).

E_a (Activation energy) = Threshold Energy (E_{Th}) − average kinetic energy of reacting molecules (E_R).

i.e. $E_a = E_{Th} - E_R$

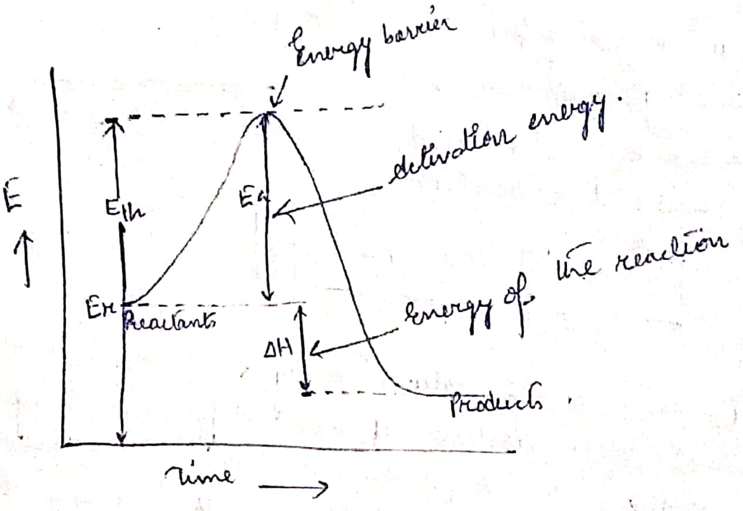


Fig: Energy level diagram.

The hump between the reactants and the products is called energy barrier.

Arrhenius Equation:

Arrhenius in 1889 gave a quantitative relationship between the temperature and the rate constant of a reaction, the called Arrhenius equation and is given by,

$$k = Ae^{-E_a/RT} \longrightarrow ①$$

E_a = activation energy

A = frequency factor and is constant.

T = absolute temperature

R = gas constant

(I). Taking log of eqn ①,

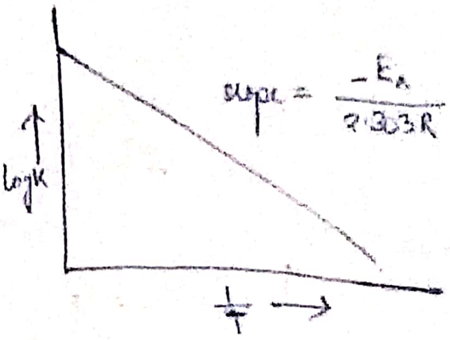
$$\ln K = \ln A + \ln e^{-E_a/RT}$$

$$\Rightarrow \ln K = \ln A + \left(-\frac{E_a}{RT}\right).$$

$$\Rightarrow 2.303 \log K = 2.303 \log A - \frac{E_a}{RT}.$$

$$\boxed{\Rightarrow \log K = \log A - \frac{E_a}{2.303RT}}$$

It is an eqn of the straight line. When log k is plotted against $\frac{1}{T}$, a straight line is obtained with slope = $\frac{-E_a}{2.303R}$.



Thus, knowing the values of R and slope, E_a can be calculated by using the relation.

$$\boxed{E_a = -2.303 \times R \times \text{slope}}.$$

(II) E_a can also be calculated by measuring the rate constant of a reaction at two different temperatures. If k_1 and k_2 are the rate constants of a reaction at temperatures T_1 and T_2 respectively, then using Arrhenius eqn,

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \longrightarrow ①$$

$$\log k_2 = \log A - \frac{E_a}{2.303RT_2} \longrightarrow ⑪.$$

$$⑪ - ① \Rightarrow \log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right].$$

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

$$\Rightarrow \log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right].$$

$$\boxed{\Rightarrow E_a = \log \frac{k_2}{k_1} \cdot \frac{2.303R\, T_1T_2}{(T_2 - T_1)}}$$

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