



University School of Automation and Robotics  
**GURU GOBIND SINGH INDRAPIRASTHA UNIVERSITY**  
East Delhi Campus, Surajmal Vihar  
Delhi - 110092



# **BS-109 Engineering chemistry-I**

## **Reaction Kinetics**

**Karan Chaudhary**

## CHEMICAL KINETICS

Rate of reaction:  $A \rightarrow P$

- at a given time, depends upon concentration of reactants.
- concentration of A keeps on falling with time.
- so, rate of reaction is given by expression:  $r_c = -\frac{dC_A}{dt} \quad \dots (1)$

- Concentration of product goes on increasing with time. Hence rate of reaction can be expressed as,  $r_c = \frac{dC_P}{dt} \quad \dots (2)$

from eq 1 and 2,

$$r_c = \frac{-dC_A}{dt} = \frac{dC_P}{dt}$$

- For another reaction,  $A + B \rightarrow L + M$

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

Rate law and the rate constant:

representation of rate of reaction in terms of molar concentration of the reactants raised to some power.

For, reaction  $A \rightarrow \text{Products}$ ,

rate of reaction given experimentally as,

$$r_c \propto [A] \quad \text{or} \quad r_c = K[A]$$

where K is rate constant or velocity constant of reaction at given temp.

If,  $[A] = 1$ , in that case  $r_c = K$ .

In general reaction,  $aA + bB + cC \rightarrow \text{Products}$ .

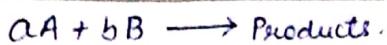
$$r_c = K[A]^a[B]^b[C]^c$$

here also, if  $[A] = [B] = [C] = 1$ , then  $r_c = K$

so, rate constant is defined as rate of reaction when concentration of each reactant is unity.

### X Order of reaction:

Sum of powers to which the concentrations terms are raised in rate law expression. For example,



$$\text{so, rate of equation (ii)} = K [A]^a [B]^b$$

∴ order of reaction will be =  $(a+b)$

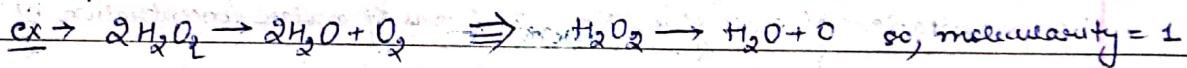
<u>Reactions</u>	<u>Expt. determined rate</u>	<u>Order</u>
(1) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	$r = K[\text{HI}]^2$	2
(2) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	$r = K[\text{H}_2][\text{I}_2]$	2
(3) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow$ $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$	$r = K[\text{CH}_3\text{COOC}_2\text{H}_5][\text{NaOH}]$	2

[Note]: order of reaction may be zero or fraction.

### X Molecularity of reaction: minimum number of molecules, atoms or ions

taking part in chemical reaction is known as molecularity. [rate determining step is involved]

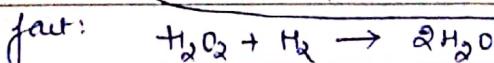
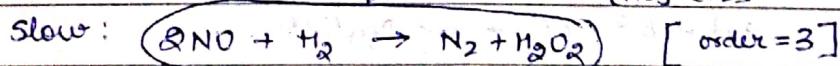
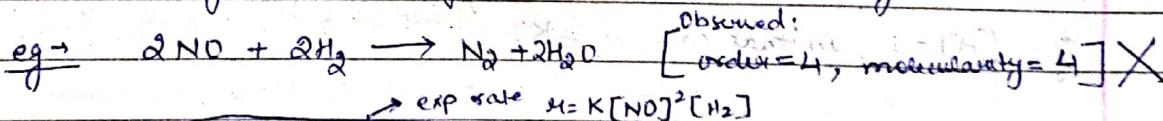
In eq (1) above, 2 HI molecules are involved. ∴ molecularity = 2.



### X Differentiate b/w order & molecularity of reaction:

→ Order: determined from experiment from rate law which is given from rate determining step.

→ molecularity: it is no. of molecules in rate determining step.



& molecularity cannot be defined in multi-step reaction. Molecularity can be given for individual elementary reactions.

so, for slow step, molecularity = 3

for fast step, molecularity = 2.

expression were

till now, relation between instantaneous reaction rates and concentration of reactants. Such relationship is called "the differential rate law". And actual rate is determined experimentally.

Units of rate constant:

(a) Zero order  $\Rightarrow \text{Rate} = \left[ -\frac{d[A]}{dt} \right] = K_0$  Unit  $\Rightarrow \text{mol dm}^{-3} \text{s}^{-1} = K_0$

(b) First order  $\Rightarrow \text{Rate} = \left[ -\frac{d[A]}{dt} \right] = K_1 [A]$  Unit of  $K_1 = \frac{1}{\text{mol dm}^{-3}} \times \frac{\text{mol dm}^{-3}}{\text{s}}$   
 $K_1 = \frac{-1}{[A]} \times \frac{d[A]}{dt}$   $K_1 = \text{s}^{-1}$

(c) Second order  $\Rightarrow \text{Rate} = -\frac{d[A]}{dt} = K_2 [A]^2$  Unit of  $K_2 = \frac{1}{(\text{mol dm}^{-3})^2} \times \frac{\text{mol dm}^{-3}}{\text{s}}$   
 $K_2 = -\frac{1}{[A]^2} \frac{d[A]}{dt}$   $K_2 = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

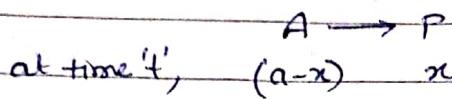
(d) Third order  $\Rightarrow \text{Rate} = -\frac{d[A]}{dt} = K_3 [A]^3$  Unit of  $K_3 \Rightarrow \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$   
 $K_3 = -\frac{1}{[A]^3} \frac{d[A]}{dt} \Rightarrow$

## # INTEGRATED RATE LAWS (time dependence of concentration)

- differential rate law gives the rate of change of extent of reaction with time.
- So except for zero-order rate law, rate of reaction will change as conc. change.
- Therefore, desirable to have expression that describes change in reactant concentration as a function of time. (i.e.: integrated rate equation)
- integrating the differential rate equations.
- Advantage: 1) predict the concentration at any time.  
2) to determine order of reaction.

(I). FIRST ORDER REACTION:  $\text{eg} \rightarrow \text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$

$$\text{differential rate law} \Rightarrow -\frac{d[A]}{dt} = \frac{d[P]}{dt} = k_1 [A]$$



$a$  = initial conc. of A

$x$  = conc. of product at time 't'

$$\frac{d[P]}{dt} = k_1 [A] \quad \text{--- (1)}$$

$$\frac{dx}{dt} = k_1 (a-x) \quad \text{--- (2)}$$

$$\frac{dx}{(a-x)} = k_1 dt \quad \text{--- (3)}$$

on integration, we have

$$\int \frac{dx}{(a-x)} = k_1 \int dt \Rightarrow -\ln(a-x) = k_1 t + z \quad \text{--- (4)}$$

where,  $z$  = integration constant.

now, at  $t=0, x=0$

$$\text{from eq (4), } -\ln(a) = z \quad \text{--- (5)}$$

put (5) in (4),

$$-\ln(a-x) = k_1 t - \ln(a)$$

$$\ln(a) - \ln(a-x) = k_1 t$$

$$\ln\left(\frac{a}{a-x}\right) = k_1 t \quad \text{--- (6)}$$

$$k_1 = \frac{1}{t} \ln\left(\frac{a}{a-x}\right) = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right) \quad \text{--- (7)}$$

Another way, we can write as:

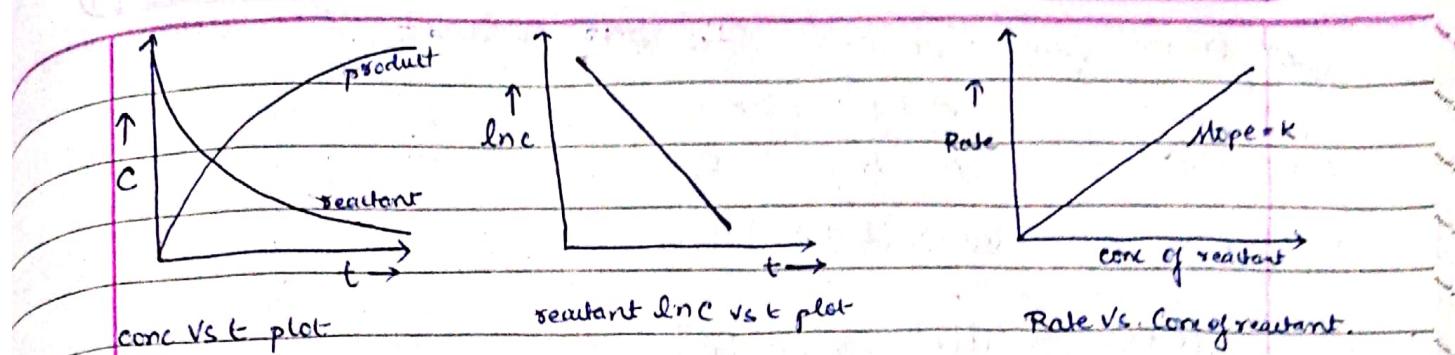
$$\ln\left(\frac{a}{a-x}\right) = k_1 t$$

$$-\ln\left(\frac{a-x}{a}\right) = k_1 t$$

$$\frac{a-x}{a} = e^{-k_1 t}$$

$$a-x = a \cdot e^{-k_1 t}$$

$$x = a - a \cdot e^{-k_1 t} = a(1 - e^{-k_1 t}) \quad \text{--- (8)}$$



# Half life of first order reaction:

from eq (7)  $t = \frac{1}{k_1} \ln \left( \frac{a}{a-x} \right)$ , and at  $t_{1/2} \Rightarrow x=a/2$

$$\begin{aligned} \text{so, } t_{1/2} &= \frac{1}{k_1} \ln \left( \frac{a}{a-a/2} \right) \\ &= \frac{1}{k_1} \cdot \ln 2 \\ &= \frac{2.303 \log 2}{k_1} = \frac{0.693}{k_1} \end{aligned}$$

$$\text{so } \boxed{t_{1/2} = \frac{0.693}{k_1}}$$

# Completion of reaction;  $x=a$

from eq (8),  $a = a(1-e^{-k_1 t})$

true is only possible, when  $t=\infty$ .

so, a first order reaction is never completed.

# at time  $t$ ,  $a = C_0$  and  $(a-x) = c$

$$k_1 = \frac{2.303}{t} \log \left( \frac{C_0}{c} \right)$$

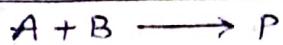
$$\frac{k_1 t}{2.303} = \log C_0 - \log c$$

$$\log c = -\frac{k_1 t}{2.303} + \log C_0$$

If we plot  $\log c$  Vs  $t$  plot

straight line, Mope will be  $-k_1 \Rightarrow \text{slope} = -\frac{k_1}{2.303}$

(II) SECOND ORDER REACTION:  $\text{eg: } 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$



$t=0$  Initial Conc.  $a \quad b \quad 0$

$t=t'$  conc.  $(a-x) \quad (b-x) \quad x$

Rate eq  $\frac{d[P]}{dt} = k_2[A][B]$

$$\frac{dx}{dt} = k_2(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = k_2 dt$$

resolving into partial fraction,

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

now,  $k_2 dt = \frac{1}{(b-a)} \left[ \frac{1}{a-x} - \frac{1}{b-x} \right] dx$

on integration,

$$k_2 \int dt = \frac{1}{(b-a)} \int \left[ \frac{1}{a-x} - \frac{1}{b-x} \right] dx$$

$$k_2 t = \frac{1}{(b-a)} \left[ \int \frac{dx}{a-x} - \int \frac{dx}{b-x} \right]$$

$$k_2 t + z = \frac{1}{(b-a)} \left[ -\ln(a-x) + \ln(b-x) \right]$$

$$k_2 t + z = \frac{1}{(b-a)} \left[ \ln \left( \frac{b-x}{a-x} \right) \right]$$

at  $t=0, z=0$

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

$$k_2 t + \frac{1}{(b-a)} \ln \left( \frac{b}{a} \right) = \frac{1}{(b-a)} \left[ \ln \left( \frac{b-x}{a-x} \right) \right]$$

$$k_2 t = \frac{1}{(b-a)} \left[ \ln \left( \frac{b-x}{a-x} \right) - \ln \left( \frac{b}{a} \right) \right]$$

$$k_2 (b-a) t = \ln \left( \frac{a(b-x)}{b(a-x)} \right)$$

$$K_2 = \frac{2 \cdot 303}{(b-a)t} \log \frac{a(b-x)}{b(a-x)}$$

**Case:** When reactants are same,



Initial conc.  $a$       0

conc at time  $t$ ,  $(a-x)$       ( $x$ )

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

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

on integration, we get

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

$$\frac{1}{(a-x)} = K_2 t + z$$

so, at  $t=0$ ,  $x=0$

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

$$\text{so, } \frac{1}{(a-x)} = K_2 t + \frac{1}{a}$$

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

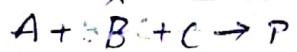
$t_{1/2}$  of reaction:

$$t_{1/2} = \frac{1}{K_2} \frac{x}{a(a-x)} \quad \text{as, at } t_{1/2} \Rightarrow x = a/2$$

$$\text{so, } t_{1/2} = \frac{1}{K_2} \frac{a/2}{a(a-a/2)} = \frac{1}{aK_2}$$

$$\therefore \text{at } a=1, \boxed{t_{1/2} = \frac{1}{K_2}}$$

(III) THIRD ORDER REACTION: eg:  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$



Initial conc      a    b    c    0

Conc at time t,  $(a-x)$   $(b-x)$   $(c-x)$   $x$

When,  $a=b=c$ , then

$$\frac{dx}{dt} = K_3(a-x)^3$$

$$\frac{dx}{(a-x)^3} = K_3 dt$$

on integration,

$$\frac{-1}{2} \times \frac{-1}{(a-x)^2} = K_3 t + z$$

$$\frac{1}{2(a-x)^2} = K_3 t + z$$

at  $t=0, x=0, z=0$ ,

$$z = \frac{1}{2a^2}, \text{ put it back in above eqn}$$

$$\frac{1}{2(a-x)^2} - \frac{1}{2a^2} = K_3 t$$

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

$$K_3 = \frac{1}{t} \frac{x(2a-x)}{2a^2(a-x)^2}$$

at  $t_{1/2}$  when  $x = a/2$

$$K_3 = \frac{1}{t_{1/2}} \frac{\frac{a}{2}(2a-\frac{a}{2})}{2a^2(a-\frac{a}{2})^2}$$

$$= \frac{1}{t_{1/2}} \frac{\frac{3a^2}{4}}{\frac{a^4}{4}} = \frac{1}{t_{1/2}} \frac{3a^2 \times 2}{4a^4}$$

$$K_3 = \frac{1}{t_{1/2}} \frac{3}{2a^2} \Rightarrow t_{1/2} = \frac{1}{K_3} \frac{3}{2a^2}$$

$\therefore t \propto \frac{1}{a^2}$ , Time required for completion of reaction is inversely proportional to square of initial concentration.

(IV) ZERO ORDER REACTION:  $\text{eg} \rightarrow \text{CH}_3\text{COCH}_3 + \text{BH}_2 \rightarrow \text{CH}_3\text{C(OCH}_3\text{)BH}_2 + \text{H}_2\text{O}$

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

When conc of A = c

$$-dc = K_0 dt$$

on integration,

$$-\int_{c_0}^c dc = \int_0^t K_0 dt$$

$$-[c - c_0] = K_0 [t - 0]$$

$$[c_0 - c = K_0 t]$$

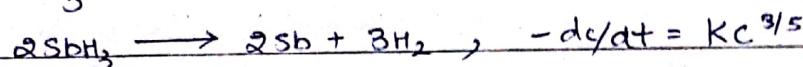
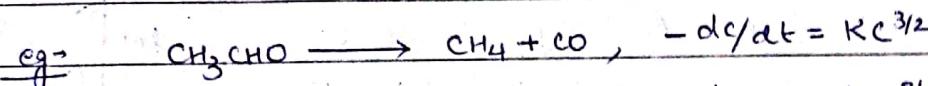
reaction is zero order w.r.t to  $\text{BH}_2$ .

since reaction velocity is not influenced by a change in conc of  $\text{BH}_2$

[when plot C vs t, get straight line having slope  $K_0$ ]

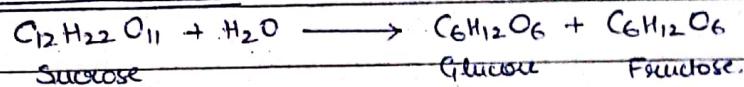
# Fractional order reaction: rate of reaction is proportional to fractional power of concentration of reactant, i.e

$$-\frac{dc}{dt} = K c^{1/n}$$



In such reaction, mechanism involves atoms or free radicals as intermediates.

# Pseudo unimolecular reaction:



What rate should be,

$$-\frac{dc}{dt} = K [\text{C}_{12}\text{H}_{22}\text{O}_{11}] [\text{H}_2\text{O}]$$

but in solution, amount of water is excessively high compared to sugar.

so  $[\text{H}_2\text{O}]$  is constant, so,

$$-\frac{dc}{dt} = K' [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

so, 
$$K' = \frac{1}{t} \ln \frac{a}{a-x}$$

Effect of temperature on reaction rate. (Arrhenius equation)

→ rate of every reaction increases with increase of temperature.

→ rate of reaction double when temperature increases by  $10^\circ$ .

On keeping concentration constant, if we increase temperature, rate of reaction will increase i.e. value of  $k$  will increase so Arrhenius proposed equation:

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

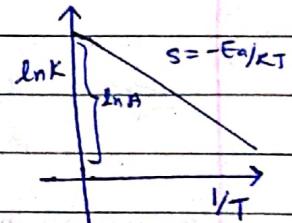
$E_a$  = Arrhenius activation energy,  $A$  = Arrhenius pre-exponential factor or frequency.  
taking log on both sides,

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{--- (2)}$$

so, plot  $\ln k$  vs.  $\frac{1}{T}$ , gives straight line & slope =  $-\frac{E_a}{R}$  & intercept =  $\ln A$ .

so, at temp  $T_1$ ,

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \quad \text{--- (3)}$$



& at temp.  $T_2$ ,

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \quad \text{--- (4)}$$

eq (3) - (4)

$$\ln \frac{K_1}{K_2} = - \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

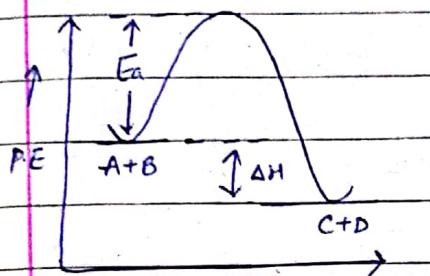
$$\log \frac{K_1}{K_2} = - \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Temperature Coeff = ratio of rate constant at two temp. differing by  $10^\circ\text{C}$

$$= \frac{K_{85^\circ\text{C}}}{K_{25^\circ\text{C}}}$$

## Energy of Activation (Ea)

Molecules of reactants taking part in chemical reaction should get activated by gaining a minimum definite amount of Energy known as activation energy (Ea). For every reaction, molecules should be gained to a state of sufficient energy, otherwise the reaction will not go.



After the reaction, this excess energy is liberated in the form of heat. When liberated energy is less than Ea, reaction is endothermic.

OR

if liberated energy is more than Ea, reaction becomes exothermic.

## # COLLISION THEORY →

(1) products are formed only when the reactant molecules come close & ~~collide~~ collide with each other.

(2) only those collisions are effective in producing products which satisfy the criteria of energy of activation and the specific orientation of molecules.

When two gases A and B react, reaction becomes possible when A & B collide. so number of collision per second ( $Z$ ) in given volume can be obtained from Kinetic theory.

$$Z_{AB} = n_A n_B \sigma_{AB}^2 \left( \frac{8\pi k_B T}{\mu} \right)^{1/2}$$

$\sigma$  → collision diameter

$\mu$  → reduced mass

$k_B$  → Boltzmann constant

number of molecules reacted in one second can be obtained from rate constant,  $k$ .

- It was observed, number of molecules reacted is always less than the number of molecules collided i.e. every collision does not give rise to reaction.
- Arrhenius proposed, molecules having Ea after collision will result in reaction.

so, according to Maxwell, at a temperature  $T$ , ratio of total number of collisions and number of collisions giving  $E_a$  to molecules is

$$e^{-E_a/RT}$$

$$\text{so, } Z' = Z \cdot e^{-E_a/RT}$$

$Z$  = total no of collision.

$Z'$  = no of collision giving  $E_a$  to molecules.

$$\delta$$

$$-\frac{dC_A}{dt} = Z'$$

ideally

rate of relative collision.

$$\text{so, } -\frac{dC_A}{dt} = K C_A C_B$$

$$\text{where, } C_A = \frac{n_A}{N_A}$$

$$-\frac{1}{N_A} \frac{dC_A}{dt} = K \frac{n_A n_B}{(N_A)^2}$$

therefore rate constant,

$$k = -\frac{N_A}{n_A n_B} \frac{dC_A}{dt}$$

$$C_B = \frac{n_B}{N_B}$$

$N$  = Avogadro No.

$$= \frac{N_A}{n_A n_B} Z'$$

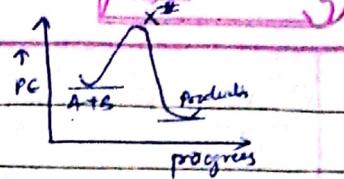
$$K = \frac{N_A}{n_A n_B} Z e^{-E_a/RT}$$

frequency factor.

For complicated gaseous molecules, rate tends to be smaller than collision theory predicts by a factor of  $10^5$ . To account for this, an additional factor "p" called probability factor or steric factor is inserted in expression of  $K$

$$K = p \frac{N_A}{n_A n_B} Z e^{-E_a/RT}$$

## ACTIVATED COMPLEX THEORY -



$X^\ddagger$  is activated complex

hence rate of reaction depends upon two factors concentration of activated complex and frequency of decomposition of activated complex.

Thus,  $\text{rate} = (\text{concentration of } A \cdot c) (\text{freq. of decomposition of } A \cdot c)$

Cone of  $A \cdot c$   $\rightarrow$  reaction is in equilibrium with  $A \cdot$  complex, so, equilibrium constant

$$K^\ddagger = \frac{[X^\ddagger]}{[A][B]}$$

$$[X^\ddagger] = K^\ddagger [A][B]$$

Freq. of decomposition of  $A \cdot c$   $\rightarrow$  since  $A \cdot c$  is in a process of decomposition, so one of its vibrational degrees of freedom will change to translational degree of freedom.

so, let  $E_{\text{vib}}$  be the average vibrational energy which results in bond breaking.

by Planck's eqn:  $E_{\text{vib}} = h\nu$

by classical mechanics,  $E_{\text{vib}} = K_B T$   $K_B$  = boltzmann's constant.

$$\text{so, } h\nu = K_B T = \left(\frac{R}{N_A}\right) T$$

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

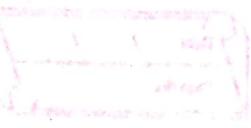
now, rate of reaction.

$$\text{rate} = K^\ddagger [A][B] \left(\frac{RT}{N_A h}\right)$$

$$= \left(\frac{K^\ddagger RT}{N_A h}\right) [A][B]$$

$$= k_2 [A][B]$$

$$k_2 = \left(\frac{RT}{N_A h}\right) K^\ddagger = \left(\frac{K_B T}{h}\right) K^\ddagger$$



as equilibrium constant is expressed in terms of  $\Delta G^\circ$

$$\Delta G^\circ = -RT \ln K$$

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

$$\& (\Delta G^\circ)^\# = (\Delta H^\circ)^\# - T(\Delta S^\circ)^\#$$

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

$$= e^{-(\Delta H^\circ)^\#/RT} e^{(\Delta S^\circ)^\#/R}$$

now,

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

taking log & diff wrt T

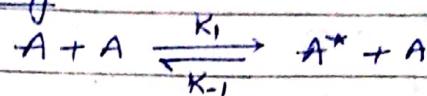
$$\frac{d \ln K_2}{dT} = \frac{(\Delta H^\circ)^\#}{RT^2} + \frac{1}{T} = \frac{(\Delta H^\circ)^\# + RT}{RT^2}$$

Arrhenius eq  $K = A e^{-E_a/RT}$ , log & diff wrt T

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

$$E_a = (\Delta H^\circ)^\# + RT$$

## Lindemann Theory:



$$K_{eq} = \frac{[A^*][A]}{[A][A]}$$



$A^*$  is energized molecule having sufficient vibrational energy to form product.

$$\text{rate of formation of } A^* = K_1[A]^2$$

$$\text{rate of decomposition of } A^* = K_2[A^*] + K_{-1}[A^*][A]$$

Now, Thus.

$$(using SSA) \quad \frac{d[A^*]}{dt} = K_1[A]^2 - K_{-1}[A^*][A] - K_2[A^*] = 0$$

$$\text{so, that } [A^*] = \frac{K_1[A]^2}{K_{-1}[A] + K_2}$$

now, rate of reaction is

$$-r_C = -\frac{d[A]}{dt} = K_2[A^*]$$

$$-r_C = \frac{K_1 K_2 [A^*]^2}{K_{-1}[A] + K_2} = \left( \frac{K_1 K_2}{K_{-1} + K_2} \right) [A]$$

now,

$$\text{at high pressure } K_{-1}[A] \gg K_2$$

$$-r_C = \frac{K_1 K_2 [A]}{K_{-1}} \Rightarrow \text{first order reaction.}$$

$$\text{at low pressure } K_{-1}[A] \ll K_2$$

$$-r_C = K_1[A]^2 \Rightarrow \text{second order reaction.}$$

Limitation of theory →

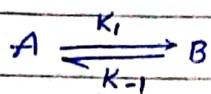
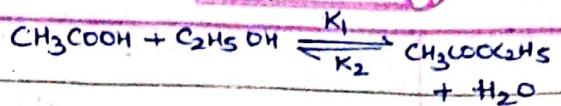
(i) energy dependence of activation & degree of freedom of molecules were neglected.

Therefore theory underestimates rate of activation.

### Complex reaction:

- such reaction occur in several steps where each step is elementary.
- molecularity of complex reaction is not defined.  
molecularity of each step is determined.
- rate is given by slowest step of complex reaction.
- There will be intermediate in reaction
- Intermediate should not appear in rate law.

Reversible reaction:



at time  $t$ ,  $(a-x)$   $(x)$

at equilibrium,  $(a-x_e)$   $(x_e)$

rate,  $\frac{dx}{dt} = K_1 [A] - K_1 [B]$

$$= K_1 (a-x) - K_1 (x)$$

at equilibrium,

$$K_{eq} = \frac{x_e}{a-x_e}$$

and rate is zero so

$$K_1 (a-x_e) = K_1 (x_e)$$

$$\boxed{\frac{K_1}{K_1} = \frac{x_e}{a-x_e} = K_{eq}}$$

so,  $K_1 = K_1 \frac{(a-x_e)}{x_e}$

so, rate  $\frac{dx}{dt} = K_1 (a-x) - K_1 \frac{x(a-x_e)}{x_e}$

$$\boxed{\frac{dx}{dt} = K_1 \frac{(x_e - x)a}{x_e}}$$

$$\frac{dx}{x_e - x} = \frac{a}{x_e} K_1 dt$$

on integration,

$$-\ln(x_e - x) = \frac{a}{x_e} (K_1 t + I)$$

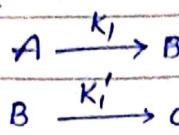
$$-\frac{x_e}{a} \ln(x_e - x) = K_1 t + I$$

at  $t=0, x=0$   $I = -\frac{x_e}{a} \ln x_e$

$$K_1 t = -\frac{x_e}{a} \ln(x_e - x) + \frac{x_e}{a} \ln x_e$$

$$\boxed{K_1 t = \frac{x_e}{a} \ln \left( \frac{x_e}{x_e - x} \right)}$$

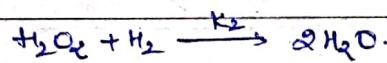
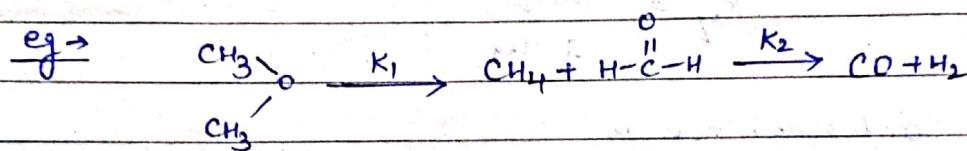
Consecutive reaction:



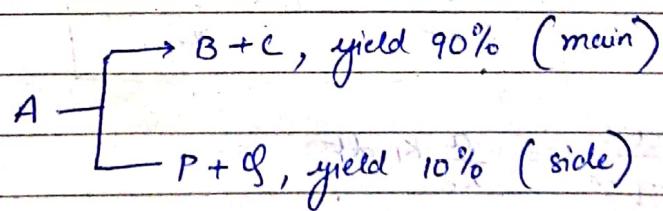
$$-\frac{d[A]}{dt} = k_1[A]$$

$$+\frac{d[B]}{dt} = k_1[A] - k'_1[B]$$

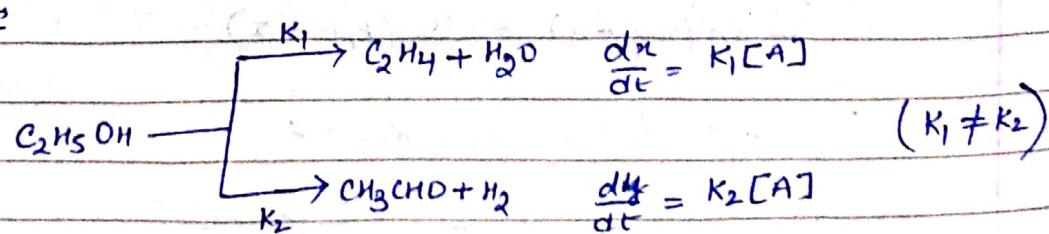
$$\frac{d[C]}{dt} = k'_1[B]$$



Parallel reaction: reactants undergo two or more independent reactions simultaneously. Each reaction gives a set of products. The reaction which give major product is called main reaction & other is side reaction.

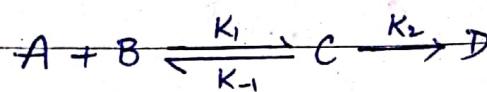


eg →



## Steady state approximation: (SSA)

In a case where reactions are investigated under such conditions that the slowest rate determining step does not exist, then one assumes SSA. for a transient i.e. short lived intermediate.



We assume that production of intermediate ( $C$ ) and consumption occur at same rate, so that rate of change of  $[C]$  with respect to time is zero.

$$\text{i.e. } \frac{d[\text{Intermediate}]}{dt} = 0$$

so, for given reaction,

so, we take  
respect of  $[C]$

$$\frac{d[C]}{dt} = K_1[A][B] - K_{-1}[C] - K_2[C] = 0$$

$$K_1[A][B] - K_{-1}[C] - K_2[C] = 0$$

$$K_1[A][B] = K_{-1}[C] + K_2[C]$$

$$K_1[A][B] = (K_{-1} + K_2)[C]$$

$$[C] = \frac{K_1[A][B]}{K_{-1} + K_2}$$

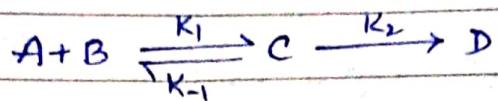
so, overall  
rate of reaction

$$\frac{d[D]}{dt} = K_2[C]$$

$$= K_2 \left( \frac{K_1[A][B]}{K_{-1} + K_2} \right)$$

### Pseudo-equilibrium Approximation:

- intermediate are supposed to be stable.
- for rate equation, we assume rate determining step exists. This step is slowest.



here we assume:

equilibrium between  $A + B$  and  $C$  has already established prior to consumption of  $C$  to produce the product  $D$ .

$$\text{equilibrium expression, } K_{eq} = \frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}}$$

$$[C] = \frac{k_1}{k_{-1}} [A][B]$$

overall rate of reaction

$$\frac{d[D]}{dt} = k_2 [C] = k_2 \frac{k_1 [A][B]}{k_{-1}}$$

$$= k_2 K_{eq} [A][B]$$

## # Methods for the determination of the order of reaction:

### 1. Substitution method (using rate equation)

$$1^{\text{st}} \text{ Order} \Rightarrow k = \frac{1}{t} \ln \frac{a}{a-x}$$

$$2^{\text{nd}} \text{ order} \Rightarrow k = \frac{1}{t} \frac{x}{a(a-x)}$$

$$3^{\text{rd}} \text{ order} \Rightarrow k = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

To determine rate, a definite amount ( $a$ ) of reactant is taken and with time change ' $t$ ', concentration changed ( $x$ ) is determined by chemical analysis or mechanically i.e.  $(a-x)$  is determined. Now placing values of ( $a$ ) &  $(a-x)$  in above equations, ' $k$ ' is determined. Now, order of reaction is determined by that equation which gives satisfactory results for ' $k$ ' value. (laborious & complicated method)

### 2. Half life method:

$$1^{\text{st}} \text{ order} = 0.693/k \text{ (fixed)}$$

$$2^{\text{nd}} \text{ order} = 1/(ak)$$

$$3^{\text{rd}} \text{ order} = 1/(a^2 k)$$

In separate sets of experiments if different concentrations are taken and  $t_{1/2}$  are measured and order can easily be determined. If  $t_{1/2}$  remains constant, it is 1<sup>st</sup> order reaction. If  $t_{1/2}$  varies inversely as the initial conc., the reaction is of 2<sup>nd</sup> order (plot  $t_{1/2}$  vs.  $1/a^2$  and give straight line). Or if we plot  $t_{1/2}$  vs  $1/a^2$  & it gives a straight line, reaction is of 3<sup>rd</sup> order.

### 3. Van't Hoff's differential method:

let order of reaction be  $n$ .

for, first set of experiment the initial concentration =  $c_1$

for, second set of experiment the initial concentration =  $c_2$

so, state equation for two experiments will be

$$R_1 = -\frac{dc_1}{dt} = kc_1^n$$

$$R_2 = -\frac{dc_2}{dt} = kc_2^n$$

Taking log on both sides

$$\log R_1 = \log k + n \log c_1$$

$$\log R_2 = \log k + n \log c_2$$

$$n = \log R_1 - \log R_2$$

$$\log c_1 - \log c_2$$

Order can be determined if  $R_1$  &  $R_2$  are known.

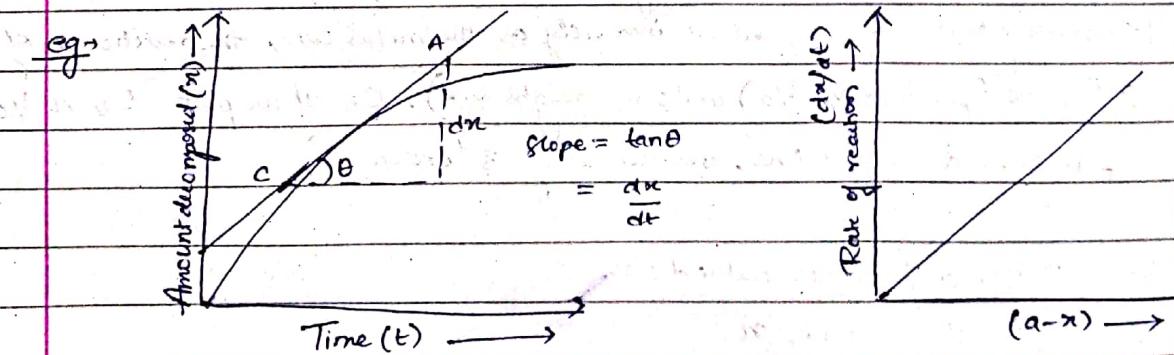
#### 4. Graphical method :

On plotting 'time' vs. 'a function of concentration', we can get order of reaction.

By plotting  $\log c$  vs.  $t$ , and get straight line reaction is of 1<sup>st</sup> order.

On plotting  $1/c$  vs.  $t$ , gives straight line, reaction is of 2<sup>nd</sup> order.

On plotting  $1/c^2$  vs.  $t$ , gives straight line, reaction is of 3<sup>rd</sup> order.



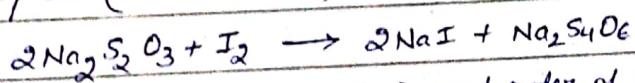
### Clock reaction (under differential method)

In case of some reaction, time taken for the colour change of reaction mixture can be used for determining initial rate. Such self indicating reactions are known as clock reactions. For example:



A reaction mixture is prepared using potassium perdisulphate and KI in a higher concentration and sodium thiosulphate in much lower concentration. A drop of starch is also present in reaction mixture. The reaction mixture is colourless in beginning and it turns blue after some time.

The time  $\Delta t$ , between the mixing of reactants and appearance of blue colour is noted. The blue colour develops due to liberation of free iodine, after sodium thiosulphate (less concentration) is consumed completely as per reaction:



Order of reaction with respect of  $\text{KI}$  ( $m$ ) and order of reaction with respect to  $\text{K}_2\text{S}_2\text{O}_8$  ( $n$ ) can be calculated by using formula:

$$\log\left(\frac{1}{\Delta t}\right) = m \log[\text{KI}] + n \log[\text{K}_2\text{S}_2\text{O}_8] + \text{constant.}$$

Plot of  $\log\left(\frac{1}{\Delta t}\right)$  vs  $\log[\text{KI}]$  is made using  $\Delta t$  values obtained by varying  $[\text{KI}]$  and keeping  $[\text{K}_2\text{S}_2\text{O}_8]$  constant. Slope of straight line gives ' $m$ '.

f.  
likewise, plot of  $\log\left(\frac{1}{\Delta t}\right)$  vs.  $\log[\text{K}_2\text{S}_2\text{O}_8]$ , by varying  $[\text{K}_2\text{S}_2\text{O}_8]$  and  $[\text{KI}]$  constant. Slope gives ' $n$ '.

Experimentally, it has been found that  $m=1$  and  $n=1$

$$\text{Hence, } -\frac{d[\text{K}_2\text{S}_2\text{O}_8]}{dt} = k [\text{KI}]^1 [\text{K}_2\text{S}_2\text{O}_8]^1$$