

Chemical Kinetics

Rate of Reaction :- change in concentration of reactant or product per unit time divided by their corresponding co-efficient given in balance chemical Rx



$$\text{Rate of } R_x = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}, \text{ Unit} = \frac{\text{mole} \cdot \text{sec}}{\text{litre}}$$

$$\rightarrow \text{Rate of disappearance of A} = \frac{\text{Decrease in conc}^n \text{ of A}}{\text{Time taken}} = -\frac{d[A]}{dt}$$

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

$$\rightarrow \text{Rate of disappearance of B} = \frac{\text{Decrease in conc}^n \text{ of B}}{\text{Time taken}} = -\frac{d[B]}{dt}$$

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

$$\rightarrow \text{Rate of Appearance of C} = \frac{\text{Increase in conc}^n \text{ of C}}{\text{time taken}} = \frac{d[C]}{dt}$$

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

$$\rightarrow \text{Rate of appearance of D} = \frac{\text{Increase in conc}^n \text{ of D}}{\text{Time taken}} = \frac{d[D]}{dt}$$

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

Classification of ROR = ① Average rate of Rx ② Instantaneous rate of reaction

① **Average Rate of Reaction** :- The rate which measure over a long interval of time.

$$\text{mathematically : } \left. \begin{array}{l} (-) \frac{[A]_2 - [A]_1}{t_2 - t_1} \quad \text{or} \quad - \frac{\Delta[A]}{t} \quad : \text{ wrt to A} \\ (+) \frac{[B]_2 - [B]_1}{t_2 - t_1} \quad \text{or} \quad + \frac{\Delta[B]}{t} \quad : \text{ wrt to B} \end{array} \right\} \begin{array}{l} \text{For the Rx} \\ A \longrightarrow B \end{array}$$

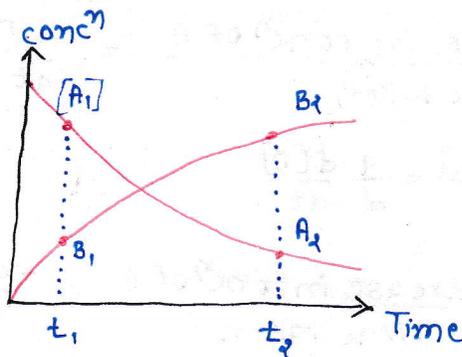
② **Instantaneous rate of Rx** :-

Rate which is measure in a very short interval of time.

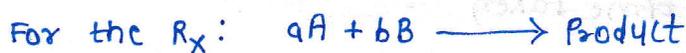
mathematically: $\lim_{t \rightarrow 0} \frac{-\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$ wrt. to A

$\lim_{t \rightarrow 0} \frac{\Delta[B]}{\Delta t} = +\frac{d[B]}{dt}$ wrt to B

graph: For a reaction $A \longrightarrow B$



Law of mass Action:- ROR is directly proportional to the concⁿ of reactant like to the power of their co-efficient given in balance chemical Reaction



$\text{ROR} \propto [A]^a [B]^b$: By the law of mass action

$r = k [A]^x [B]^y$: By the experimental data or Rate law equation

if $[A] = [B] = 1$ then $r = k$: ROR of unit concentration of reactant is called rate constant (K)

order of Reaction :

sum of power of concentration of reactant in rate law equation.

$r = k [A]^x [B]^y$

$x =$ order of rxⁿ wrt to A

$y =$ order of rxⁿ wrt to B

$x+y =$ overall order of rxⁿ

order in complex reaction:-

- Rx which complete in multi steps are called complex Rx
- slowest step is called rate determining step. because rate is determined by slowest step.

Ex: $2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$, determine order of R_x :

mechanism of r_x :

1. $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$: Fast R_x step
2. $\text{N}_2\text{O}_2 + \text{H}_2 \longrightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$: slow R_x step
3. $\text{N}_2\text{O} + \text{H}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{O}$: Fast R_x step

sol: $r = k [\text{N}_2\text{O}_2] [\text{H}_2]$

$$K_{eq} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$

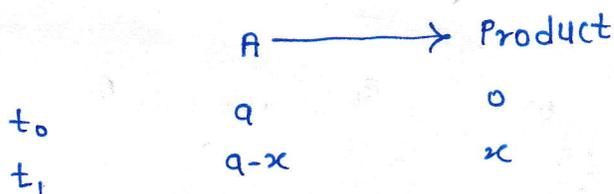
$$[\text{N}_2\text{O}_2] = K_{eq} [\text{NO}]^2$$

$$r = k \cdot K_{eq} [\text{NO}]^2 [\text{H}_2]$$

$$r = k' [\text{NO}]^2 [\text{H}_2]$$

① Zero order Reaction:-

R_x which rate is independent of the concentration of reactant.

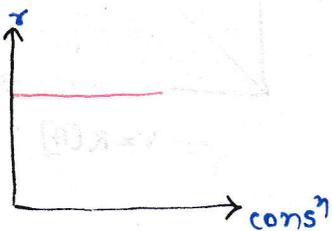


$$\text{Rate} = -\frac{d[A]}{dt} = \frac{dx}{dt} = k[A]^0 = k \implies \boxed{r = k}$$

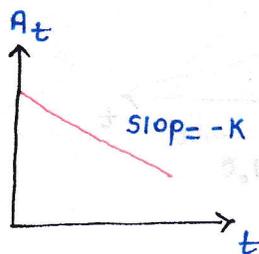
• Rate of R_x is equal to rate constant : $[A]_0 - [A]_t = kt$

$$A_t = A_0 - kt$$

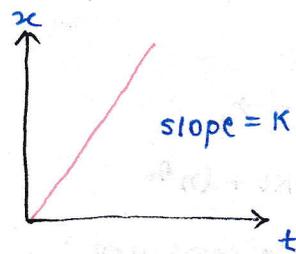
• Graphs:



$$: r = k$$



$$A_t = A_0 - kt$$



$$x = kt$$

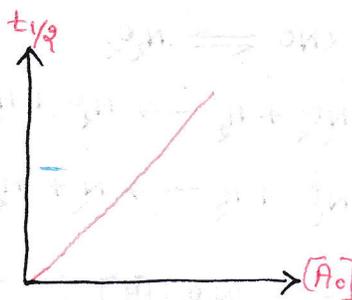
Unit of rate constant: $r = k$ unit of $r =$ unit of $k = \frac{\text{mole}}{\text{litre}} \cdot \text{sec}$

Half life: time in which half of the initial amount is consumed.

$$A_t = \frac{A_0}{2}$$

$$t_{1/2} = \frac{A_0}{2k} \Rightarrow t_{1/2} \propto A_0$$

$$: T \uparrow \quad k \uparrow \quad t_{1/2} \downarrow$$



Time For completion of Reaction: $t_{100\%} = \frac{A_0}{k}$ when $A_t = 0$

② First order Reaction:- R_x which rate is directly proportional to concentration of reactant.



$$t_0 : a \qquad \qquad \qquad 0$$

$$t_1 : a-x \qquad \qquad \qquad x$$

Differential rate equation

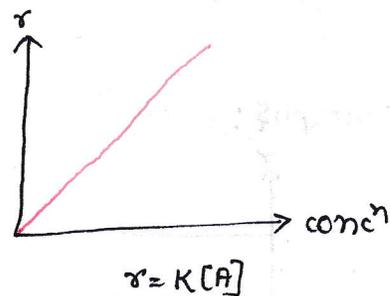
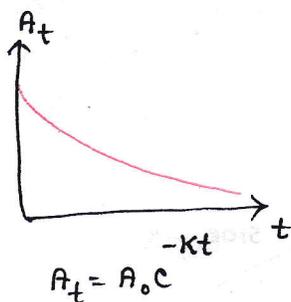
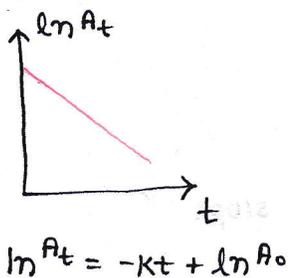
$$r = -\frac{d[A]}{dt} = \frac{dx}{dt} = k \cdot (a-x)$$

$$\ln A_0 - \ln A_t = kt \quad \text{or} \quad \ln A_t = -kt + \ln A_0$$

$$A_t = A_0 e^{-kt}$$

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A_t]}$$

Graphs:

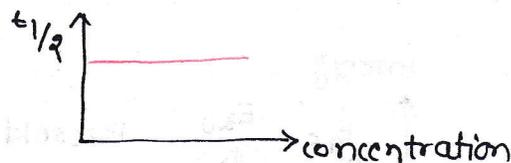


Unit of rate constant:

$$r = k[A] \quad : \quad k = \frac{r}{A} = \frac{\text{mol/Lsec}}{\text{mol/Lit}} = \text{sec}^{-1}$$

Half life: $t_{1/2} = \frac{a}{k}$

$$t_{1/2} = \frac{0.693}{k} \quad : \quad T \uparrow \quad k \uparrow \quad t_{1/2} \downarrow$$



Factor affecting rate of reaction:

1. Effect of concentration of reactant
2. Effect of pressure
3. Effect of catalyst
4. Effect of Activation energy and temp.

1. Effect of concentration of Reactant :- $\text{conc}^n \uparrow \rightarrow \text{Reacting molecules} \uparrow \rightarrow \text{collision} \uparrow \rightarrow \text{ROR} \uparrow$

collision :- Three necessary condition For a rxⁿ to Form a product.

Theory.

- collision : Necessary but not sufficient
- Proper orientation: Necessary but not sufficient
- Threshold Energy : minimum Energy to required For a rxⁿ to give Product

effective collision: collision with sufficient energy and proper orientation.

$$\text{ROR} \propto \text{effective collision}$$

2. Effect of pressure: $p \uparrow \quad v \downarrow \quad c \uparrow \Rightarrow \text{ROR} \uparrow$

3. Effect of catalyst:

⊕ catalyst : increase the ROR, $E_a \downarrow \rightarrow \text{ROR} \uparrow$

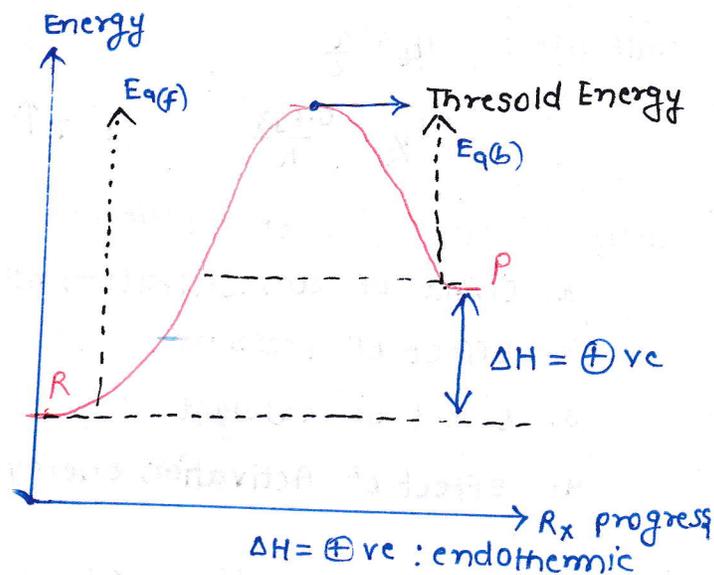
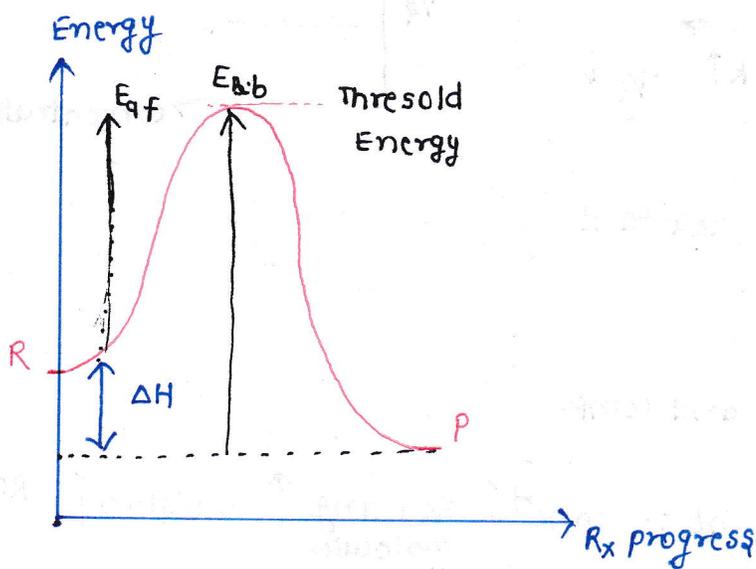
⊖ catalyst : decreases the ROR, $E_a \uparrow \rightarrow \text{ROR} \downarrow$

4. Effect of Activation energy and Temperature:

Activation energy: Additional energy given to reactant molecules to take Part in chemical Rx

OR

: Difference of threshold energy and internal energy is called Activation energy.

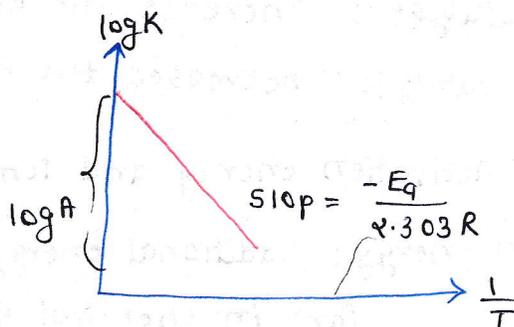


$$\Delta H = E_a(f) - E_a(b)$$

Reaction b/w Rate constant and temperature $\Rightarrow K = Ae^{\frac{-E_a}{RT}}$: Arrhenius eqⁿ

- K = rate constant
- A = Arrhenius constant or frequency / Pre exponential Factor
- e = exponent
- E_a = Activation energy
- R = gas constant
- T = Temperature

$$\log K = \frac{-E_a}{2.303 R \cdot T} + \log A$$



At $T \rightarrow \infty$ then $K = A$

At $E_a \rightarrow 0$ then $K = A$

} unit of K = unit of A

$T \uparrow \quad K \uparrow \quad \text{ROR} \uparrow$

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

(u) Temp. coefficient :- Ratio of K at two different temp. differ by 10°C

$$u = \frac{K_{T+10}}{K_T} \approx 2 \text{ to } 3 \quad \text{OR} \quad \frac{r_2}{r_1} = \frac{K_2}{K_1} = (u)^{\Delta T/10}$$