

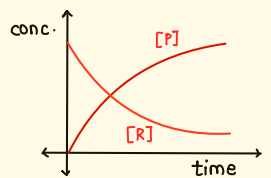
CHEMICAL KINETICS SHORT NOTES

Rate of Reaction

Rate = $\frac{\text{Change in conc. or pressure}}{\text{Time taken}}$

Unit = $\text{mol L}^{-1} \text{time}^{-1}$ or atm time^{-1}

Note = Rate of Reaction can never be -ve



Reactant $\rightarrow$ Product

Molecularity

- Can be an integer (1, 2 or 3) but it cannot be zero or negative or fractional.
- Elementary reaction, molecularity is equal to its order.
- Complex reaction molecularity of each step of mechanism is defined separately.
- Maximum value of molecularity or order is 3.

Average rate of Reaction

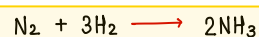
$$\text{Rate} = \frac{-\Delta C}{\Delta t} \quad \text{Rate} = \frac{\Delta C}{\Delta t}$$

(Reactant) (Product)

Instantaneous Rate of Reaction

$$\text{Rate} = -\frac{d[R]}{dt} \quad \text{Rate} = \frac{d[P]}{dt}$$

(Reactant) (Product)



$$\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{3dt} = +\frac{d[\text{NH}_3]}{2dt}$$

Differential Rate Law

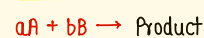
$$\text{Rate of disappearance} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt}$$

(Reactant)

$$\text{Rate of appearance} = +\frac{d[\text{NH}_3]}{dt}$$

(Product)

Rate law



$$\text{Rate} \propto [A]^x [B]^y$$

$$\text{Rate} = k[A]^x [B]^y$$

k = Rate constant or specific reaction rate

For effective collision:

- Reacting molecules must possess a minimum amount of energy.
- Proper orientation of collision.

Order of Reaction

x = order of reaction wrt A

y = order of reaction wrt B

x + y = Overall order.

Note:

- Order is an experimental quantity
- Order of rxn may be zero, +ve, -ve or fractional.

Unit of rate constant (k)

$$k = \left(\frac{\text{mol}}{\text{L}}\right)^{1-n} \text{Time}^{-1} \quad k = (\text{atm})^{1-n} \text{Time}^{-1}$$

- Zero order n=0
- First order n=1

$$k = \left(\frac{\text{mol}}{\text{L}}\right)^1 \text{sec}^{-1} \quad k = \text{sec}^{-1}$$

Elementary Reactions

- Completes in single step.
 - Rate law equal to stoichiometric coefficients of reactions.
- Note:
- Zero order reactions can never be elementary
 - For elementary reactions, Fractional order is not possible.

Zero order reactions (n=0)

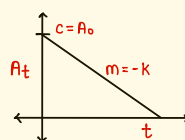
$$A_t = A_0 - kt \quad \text{Integrated Rate Law}$$

$$\text{Rate} = k$$

A₀ = Initial conc.

A_t = conc. left after time 't'

k = Rate constant



Half life ($t_{1/2}$ or $t_{50\%}$)

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

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

Completion time ($t_{100\%}$)

$$A_t = 0$$

$$t_{100\%} = \frac{A_0}{k}$$

Collision theory:

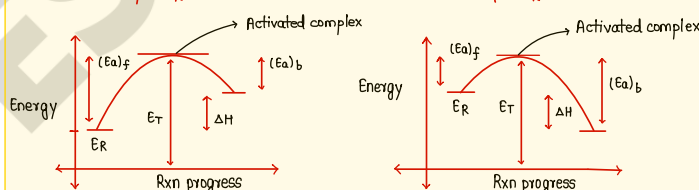
- For a reaction to occur there must be collisions in between reacting molecules.
- Total number of collisions per second in unit volume is called collision frequency.
- Small fraction of collisions are capable of converting reactants into products called effective collisions.

Energy Condition:

$$\Delta H = E_p - E_R$$

$\Delta H = +ve$
Endothermic
Energy absorbed
 $E_p > E_R$

$\Delta H = -ve$
Exothermic
Energy released
 $E_p < E_R$



$$\Delta H = (E_a)_f - (E_a)_b$$

(E_a)_f = Activation energy forward

(E_a)_b = Activation energy backward.

E_T = Threshold energy

Arrhenius equation:

A = Arrhenius constant

E_a = Activation energy

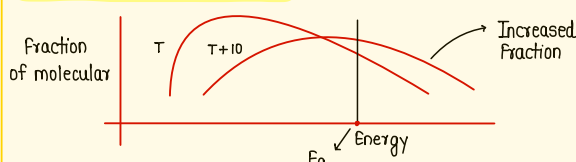
R = Universal gas constant.

T = Temperature (Kelvin)

$$k = Ae^{-E_a/RT}$$

$$T \uparrow = k \uparrow = \text{Rate} \uparrow$$

Maxwell Distribution curve:



Half Life:

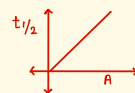
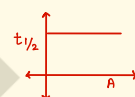
$$\text{Zero order} \therefore t_{1/2} = \frac{A_0}{2k} \Rightarrow t_{1/2} \propto A_0$$

$$\text{First order} \therefore t_{1/2} = \frac{\ln 2}{k} \Rightarrow t_{1/2} \propto A^0$$

$$\text{Second order} \therefore t_{1/2} \propto A^{-1}$$

$$\therefore n^{\text{th}} \text{ order reaction } t_{1/2} \propto A^{1-n}$$

$$\rightarrow \text{After } n \text{ half life} = \frac{A_0}{2^n}$$



First order reaction (n=1)

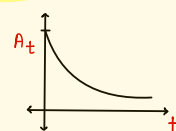
$$A_t = A_0 e^{-kt}$$

$$k = \frac{1}{t} \ln \frac{A_0}{A_t}$$

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

Half life:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad \text{Independent of } A_0$$



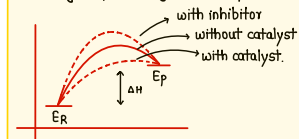
Pseudo first order reactions:

Elementary bimolecular reactions in which one of the reactant is in excess. These reactions appear to be of 2nd order but follow 1st order kinetics.

$$\text{Rate} = k_1[A]^1 \rightarrow \text{Order} = 1$$

Catalyst

Substance which can alter rate of rxn without having any change in composition

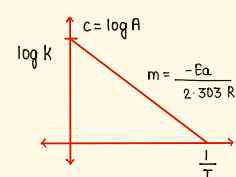


Temperature coefficient (μ)

$$\mu = \frac{k_{T+10} - k_T}{k_T} \approx 2 \text{ to } 3$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln k = \frac{-E_a}{2.303 RT} + \log A$$



$$a) \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$b) \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

