Chemical Kinetics

Rate of Reac^n :- $ROR = k[A]^x[B]^y$

k — depends on T
    — depends on E_a

Overall order is $\Rightarrow x + y$ (non-re)

** Rate law can't be predicted by merely looking into the balanced eq^n.

Unit of $k = [mol\ L^{-1}]^{1-n} sec^{-1}$, where n is the order of reac^n.

order and Molecularity

* Order → depends on experimental conditions (always determined experimentally)
    → It can be fractional, 0, 1, 2, 3

* Molecularity → it is always in whole numbers

Order	Molecularity
(i) Determined experimentally	(i) Can be determined using balanced chemical equ^n
(ii) Applicable to any type of reac^n	(ii) Applicable only for elementary rxn
(iii) It can be 0 and even a fraction	(iii) It is only a positive integer.

Elementary Rxn

$ROR = k[A]^a[B]^b$

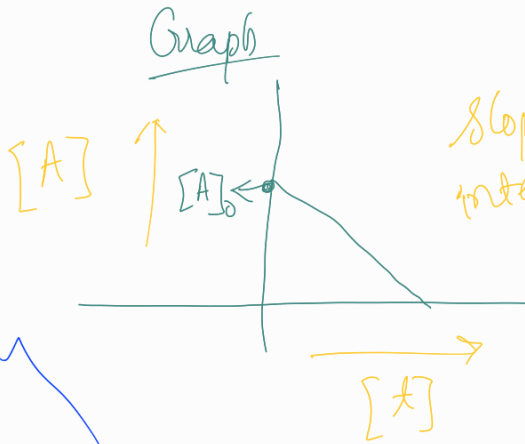Here, order = Molecularity $= a + b$.

Complex Reaction

R.D.S order is the overall order of the complex Rxn

** Zero order Rxn is always a complex Rxn.

Differential and Integral Rate Law

(a) Zero Order Rxn :→

$$\boxed{A_t = A_0 - kt}$$

Rxn which occurs on metal surfaces, NH_4 on platinum surfaces, Thermal decomposition of HI on gold surface

Graph

[A] ↑ $[A_0]$ → [t]

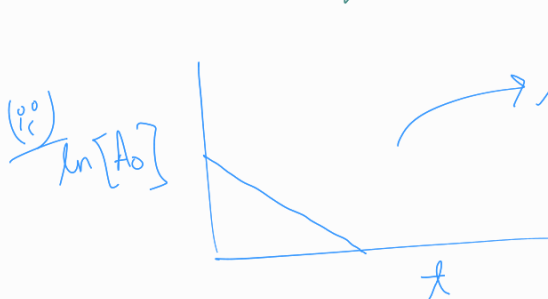Slope $(m) = -k$
intercept $(c) = [A_0]$

First Order Rxn :-

$$kt = 2.303 \log\left(\frac{A_0}{A}\right)$$

Here, slope $(m) = \dfrac{k}{2.303}$

⊛ Natural Radioactive decay of unstable nuclei are 1st order $-R_A \dfrac{}{n}$

Graphs

(i) $\log\left(\dfrac{A_0}{A}\right)$ → t

(ii) $\ln[A_0]$ → t

$$\ln[A] = \ln[A_0] - kt$$

Slope $(m) = -k$
intercept $(c) = \ln[A_0]$

(iii) $[A]$ ↑ $[A_0]$ → t
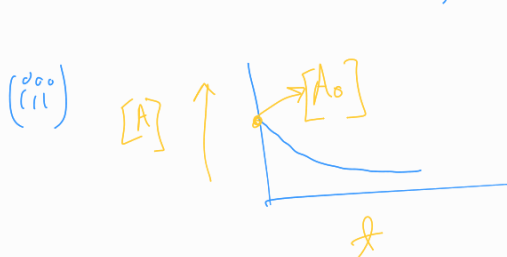
$$[A] = [A_0] e^{-k/t}$$

Theoretically infinite time is required for completion of 1st order rxn.

Half life ($T_{1/2}$)

(a) For zero order Rxn :-

$$T_{1/2} = \frac{A_0}{2K}$$
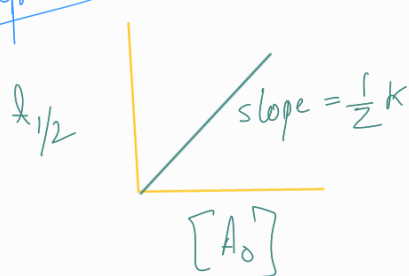
(b) For 1st order :-

$$T_{1/2} = \frac{\ln 2}{K}$$

⊛ Independent of initial concentration.
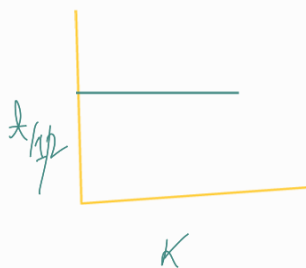
$$t_{x\%} = \frac{1}{K} \ln\left(\frac{a}{a-x}\right)$$

⊛ for n^{th} order of rxn,
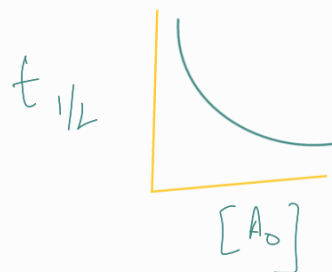
half life $\boxed{, T_{1/2} = (A_0)^{(1-n)}}$

Graphs

slope $= \frac{1}{2}K$

[A_0]

zero order

K

1st order

$t_{1/2}$

[A_0]

2nd order

Some Important Results/formulae

(a) $$\log\left(\frac{V_0}{V_t}\right) = \frac{Kt}{2.303}$$

(b) $$K = \frac{1}{t} \ln\left(\frac{P_1}{2P_1 - P_2}\right)$$

(c) $$\log\left(\frac{V_0 - V_\infty}{V_t - V_\infty}\right) = \frac{Kt}{2.303}$$

Temperature Coefficient

$$T.C = \left(\frac{R_{T+10}}{R_T}\right) = \frac{K_{T+10}}{K_T}$$

for most of the rxn,

$T.C = 2 \text{ or } 3$

$T = 25°C$ $T+10 = 35°C$

Collision Theory

$$\text{Rate} = PZ_{AB}\, e^{-\frac{E_a}{RT}}$$

Collision

- Effective (Products formed)
- Ineffective (no product formed)

$$\boxed{\Delta H_{rxn} = E_{af} - E_{ab}}$$

Arrehnius Equation

(i) $\quad K = Ae^{-E_a/RT}$

(ii) $\quad \log\left(\dfrac{K_2}{K_1}\right) = \dfrac{E_a}{2.303\,R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Series and Parallel Reactions

(i) Parallel Reactions (Formula's)

$$A \longrightarrow \begin{cases} \xrightarrow{K_1} B \\ \xrightarrow{K_2} C \end{cases}$$

(i) $\quad (K_1 + K_2) = K = \dfrac{1}{t}\, 2.303 \log\left[\dfrac{A_0}{A_t}\right]$

(ii) $\quad t_{1/2} = \dfrac{\ln 2}{K_1 + K_2}$

(iii) $\quad \dfrac{[B]}{[C]} = \dfrac{K_1}{K_2}$

(iv) $\quad E_a = \dfrac{E_{a_1} K_1 + E_{a_2} K_2}{K_1 + K_2}$

(ii) Series Connection

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

then after a time 't' concentration of A, B, C are $[A]\ [B]$ and $[C]$ as well $[A_0] = [A] + [B] + [C]$.

Formula's

(i) Max^m Conc. of $[B] = [A_0] \left(\dfrac{K_2}{K_1} \right)^{\frac{K_2}{K_1 - K_2}}$

(ii) Time max^m required for max^m amount of $B \rightarrow$

$$ T = \dfrac{1}{K_1 - K_2} \, \ln \left(\dfrac{K_1}{K_2} \right) $$