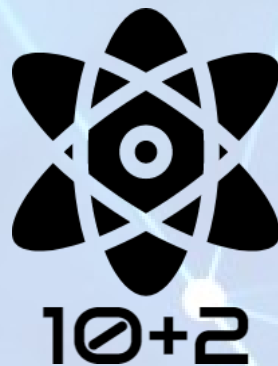


10+2 PCM NOTES

BY

JOYOSHISH SAHA

(PDF version handwritten notes of Maths, Physics and Chemistry for 10+2 competitive exams like JEE Main, WBJEE, NEST, IISER Entrance Exam, CUCET, AIPMT, JIPMER, EAMCET etc.)



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With best wishes from Joyoshish Saha

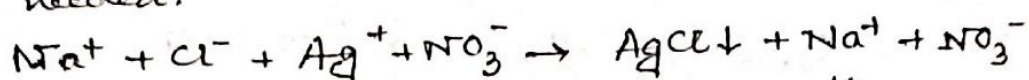
Chemical Kinetics &

1

Nuclear Chemistry.

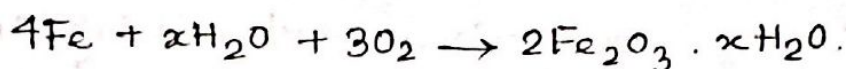
* The rate of a chemical reaction actually depends upon the strength of the bond(s) & number of bonds to be broken during the reaction.

* Reactions - i) Instantaneous reactions: such as ionic reactions. In aqueous solution, ionic compound exists as its constituent ions, so no bond breaking needed.

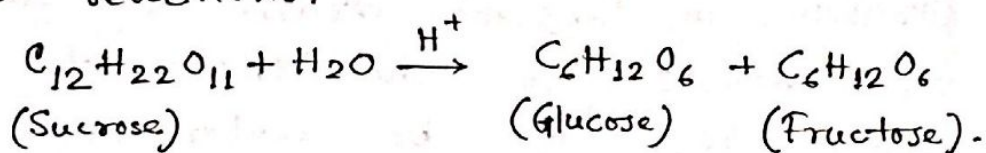


Half-life period of ionic reaction 10^{-10} s.

ii) Slow reactions: Half-life period is several years.
eg. rusting of iron.



iii) Reactions with moderate rate: Half-life period is of the order of minutes, hours, days. Such as organic reactions.



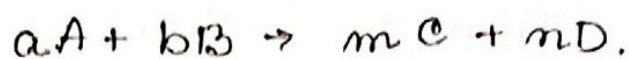
* Rates of fast reactions are determined by lasers, of late.

* Rate of reaction decreases with time, as the concentration of reactants decrease.

* Rate, $R_{\text{instantaneous}} = \pm \frac{dc}{dt}$ [c → concentration of reactants/products(+)]

Jayoshish Saha

* General reaction - observation:



Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of " " " B = $-\frac{d[B]}{dt}$

Rate of formation of C = $\frac{d[C]}{dt}$

Rate " " " D = $\frac{d[D]}{dt}$

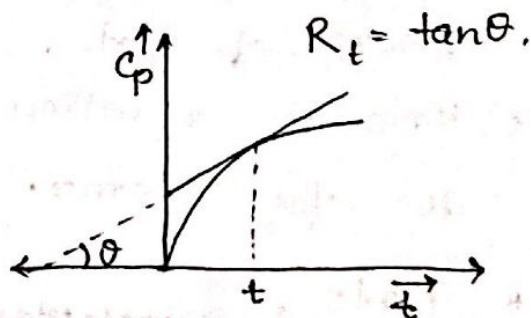
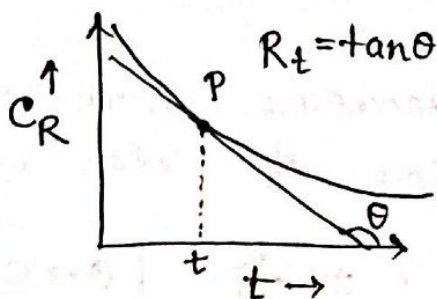
Rate of the reaction, $r =$

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{m} \frac{d[C]}{dt} = \frac{1}{n} \frac{d[D]}{dt}.$$

These are the rates per mole.

* Rate of reaction - determining methods:

- i) Concentration of any reactants/products is determined at several short time intervals.
- ii) Concentration vs time curve drawn.
- iii) Tangent drawn at a point which corresponds to the time, at which rate is to be determined.
- iv) The slope gives the rate.



- * Molecularity: The molecularity of an elementary reaction (reaction occurring in one step) is defined as the minimum number of molecules, atoms or ions of the reactant(s) required for the reaction to occur. Complex reactions don't have molecularity of their own, but of their elementary reactions. The slowest step or rate determining step of the complex reaction determine the molecularity.
- molecularity > 3 is rare.

- * Rate law expression: $aA + bB \rightarrow \text{products}$.
- $$\text{Rate} \propto [A]^a [B]^b \Rightarrow \text{Rate} = k [A]^a [B]^b$$

Experimentally, $r = k [A]^x [B]^y$ [$k \rightarrow$ rate constant].

Law of mass action is dependent upon stoichiometry of equation, whereas rate law depends as observed experimentally.

- * Order of Reaction: $r = k [A]^x [B]^y$ [rate law]
- order = $x + y$

order with respect to A, B $\rightarrow x$ & y .

1st order $\rightarrow r = k_1 C_A$ | 0 order $\rightarrow r = k_0$

2nd order $\rightarrow r = k_2 C_A^2$, $r = k_2 C_A C_B$.

3rd order $\rightarrow r = k_3 C_A^3$, $r = k_3 C_A^2 C_B$, $r = k_3 C_A C_B^2$
 $r = k_3 C_A C_B C_C \dots$

Joyoshish Saha

* Reaction Rate

- i) Changes with temperature.
- ii) At const. T, with change in concentration, rate changes.
- iii) Rate decreases with time.

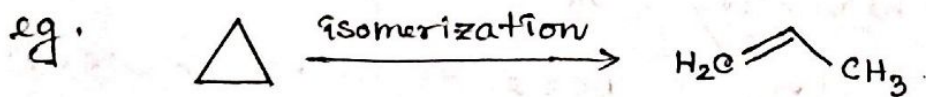
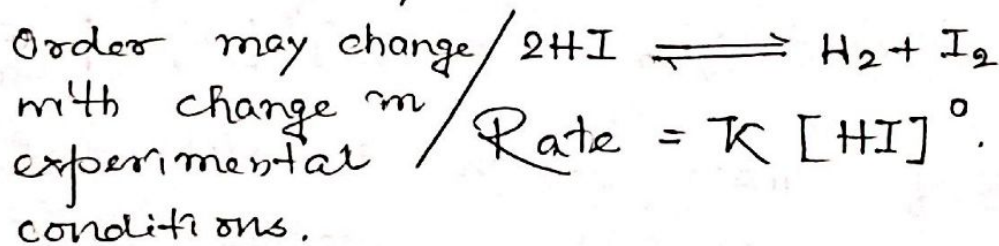
Rate-constant.

- i) Changes with temperature.
- ii) At const T, with change in conc., rate constant does not change.
- iii) No change with time.

* Order concerns with kinetics (rate law), while molecularity concerns with mechanism.

* In zero order reaction, the concentration of reactants remains constant throughout, by backward reaction.

Order may change with change in experimental conditions.



This reaction follows first order kinetics at high pressure and second order kinetics at low pressure of cyclopropane.

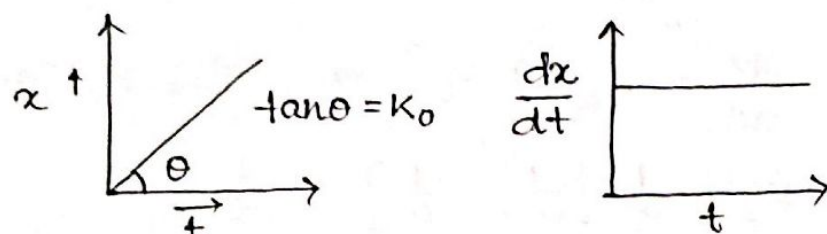
* Kinetics of Zero order reaction:

Differential Rate Equation (DRE). $\frac{dx}{dt} = k_0$

Integrated Rate Equation (IRE) $x = k_0 t$

Half-Time Period ($t_{1/2}$) $= \frac{a/2}{k_0} = \frac{a}{2k_0}$ [$a \rightarrow$ initial conc. of reactant]

Graphical Representation



Examples: Photochemical reactions, $H_2 + Cl_2 \rightarrow 2HCl$.

* Kinetics of 1st Order Reaction:

DRE. $\frac{dx}{dt} = k_1 (a - x)$

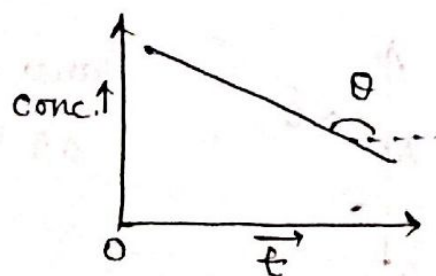
IRE. $k_1 = \frac{1}{t} \ln \frac{a}{a-x}$

$$k_1 = \frac{1}{\Delta t} \ln \frac{(a-x_1)}{(a-x_2)} = \frac{1}{\Delta t} \ln \frac{a_i}{a_f}$$

$$k_1 = \frac{1}{\Delta t} \ln \frac{R_1}{R_2} \quad [R \text{ is rate}]$$

$$[A] = [A]_0 e^{-k_1 t}$$

Graphical Representation: $\log (a-x) = \log a - \frac{k}{2.303} t$



Degree of Dissociation (DOD): $\frac{x}{a} = 1 - e^{-kt}$

Half-Life Period: $t_{1/2} = \frac{0.693}{k}$ half-time of a 1st order of reaction is a constant, independent of initial concentration of reactant.

Conc. left after n half-lives = $\left(\frac{1}{2}\right)^n [A]_0$

* Kinetics of 2nd Order Reaction:

DRE $\frac{dx}{dt} = -k_2 (a-x)^2$ or $\frac{dx}{dt} = -k_2 (a-x)(b-x)$.

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

$$k_2 = \frac{1}{\Delta t} \left[\frac{1}{a-x_2} - \frac{1}{a-x_1} \right]$$

$$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} \quad [A, B \text{ have different conc.}]$$

Pseudo 1st order reaction: If $a \gg b$,

$$a-b \approx a$$

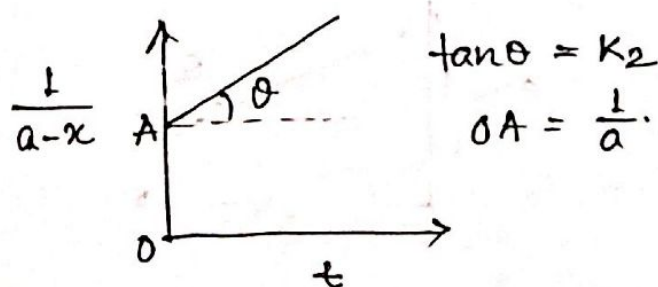
$$a-x \approx a$$

$$k_2 = \frac{1}{ta} \ln \frac{b}{b-x}$$

$$k_2' = k_2 a = \frac{1}{t} \ln \frac{b}{b-x} \quad [\text{equ}^n \text{ of 1st order}]$$

This is called pseudo 1st order reaction.

Graphical Representation: $\frac{1}{a-x} = k_2 t + \frac{1}{a}$



* n^{th} Order Reaction: $\frac{dx}{dt} = -k_n(a-x)^n$. [DRE]

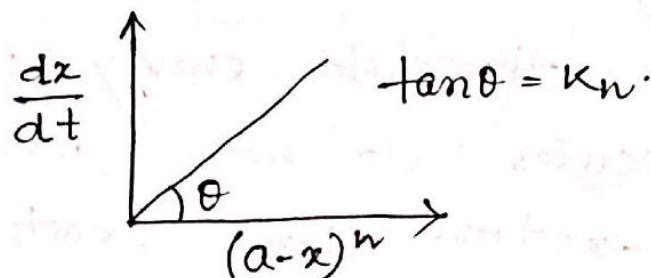
IRE $k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$

Half-life of n^{th} Order Reaction:

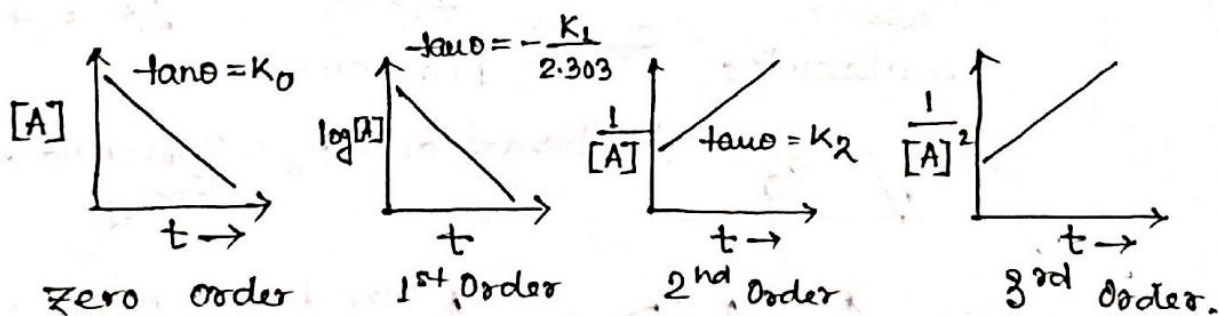
$$t_{1/2} = \frac{(2^{n-1} - 1)}{k_n (n-1) [A]_0^{n-1}} \quad \left| \quad t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \right.$$

$[n \geq 2]$

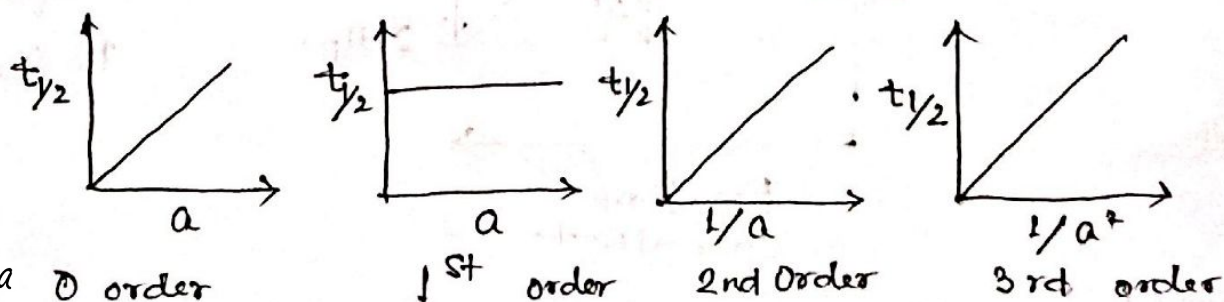
Graphical Representation: $\frac{dx}{dt} = -k_n(a-x)^n$



* Plots of Integrated Rate Equations:



* Plots of half-lives vs Initial Conc.



* Effect of Temperature on Reaction Rate:

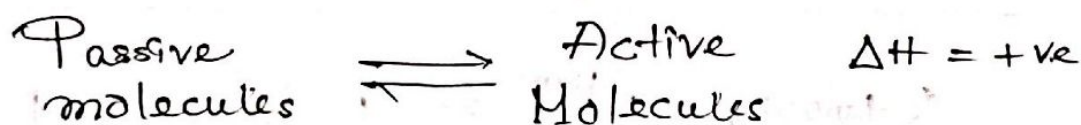
The reaction rate doubles or triples with increase of 10° rise of temperature.

Temperature coefficient: $\frac{K_{t+10}}{K_t} = \frac{K_{35^\circ}}{K_{25^\circ}} = 2 \text{ to } 3$ (nearly)

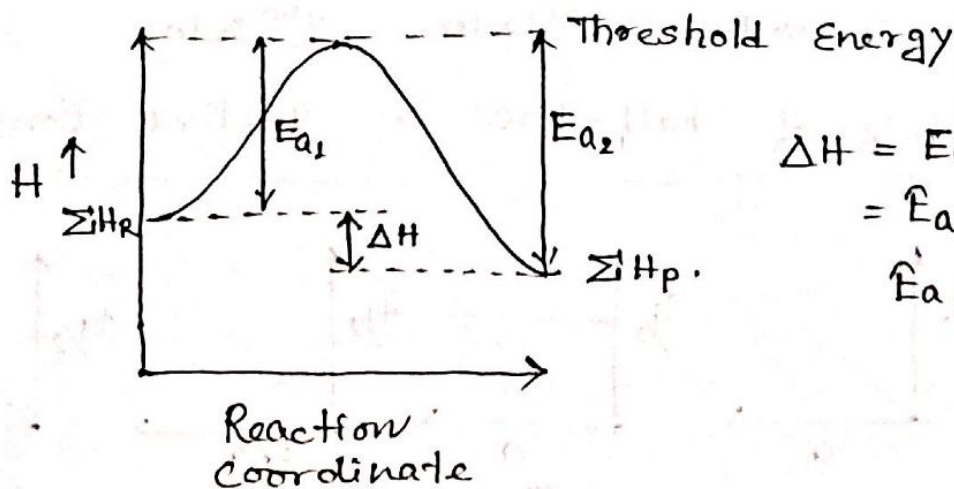
rate constant at $t^\circ\text{C} \rightarrow K_t$

and at $(t+10)^\circ\text{C} \rightarrow K_{t+10}$

With increase in temperature, the number of molecules having activation energy increases. Active molecules do have threshold energy, while passive molecules do not have. At a given temperature, there exists an equilibrium of active & passive molecules.



* Energy of Activation: $E_a = \text{Threshold Energy} - \text{Average Energy of Reactants}$



$$\begin{aligned} \Delta H &= E_{a1} - E_{a2} \\ &= E_a(\text{forward}) - E_a(\text{backward}) \end{aligned}$$

* Forward reaction exothermic, when

$$\sum H_R - \sum H_P > 0$$

* Reaction rate = collision frequency \times fraction of the total number of collision which is effective.

* Arrhenius Equation: $k = Ae^{-E_a/RT}$

$A \rightarrow$ frequency factor. $\ln k = \ln A - \frac{E_a}{RT}$

A is constant for given reaction.

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

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left\{ \frac{a_2}{a_1} \right\}^{n-1}$$

Radioactivity

1. **Binding energy (B.E.)** $\Delta E = 931.478 \times \Delta m' \text{ MeV}$ ($\Delta m'$ is mass decay)

2. **Binding energy/nucleon** = $\frac{\text{Total B.E.}}{\text{No. of nucleons}}$

3. **Rate of decay** = $K \times \text{No. of atoms at that time} = K \times N$

4. **Decay constant (K)** = $\frac{2.303}{t} \log_{10} \frac{N_0}{N}$ or $K = \frac{1}{t} \log_e \frac{N_0}{N}$

$$\text{or } \frac{N_0}{N} = e^{Kt} \quad \text{or } \frac{N}{N_0} = e^{-Kt}$$

(N_0 is no. of atoms at $t = 0$, N is no. of atoms at $t = t$)

5. **Half life ($t_{1/2}$)** = $\frac{0.693}{K}$

6. **Average life (τ)** = $\frac{1}{K} = t_{1/2} \times 1.44$

7. **Amount left after n halves** = $\frac{N_0}{2^n}$

8. **Amount decayed after n halves** = $\frac{N_0 [2^n - 1]}{2^n}$

9. **Different units of rate of decay:**

$$1 \text{ Curie} = 3.7 \times 10^{10} \text{ dps} = 3.7 \times 10^{10} \text{ Bq.} = 3.7 \times 10^4 \text{ rd} \quad (\text{SI unit is Bq. or dps})$$

10. **Radioactive equilibrium;**

$$\frac{K_A}{K_B} = \frac{N_B}{N_A} = \frac{(t_{1/2})_B}{(t_{1/2})_A} = \frac{\tau_B}{\tau_A}$$

11. **Parallel path decay :** $K_{av.} = K_{I \text{ path}} + K_{II \text{ path}}$

12. **Maximum yield of daughter element :** $t_{\max} = \frac{2.303}{K_B - K_A} \log_{10} \left[\frac{K_B}{K_A} \right]$