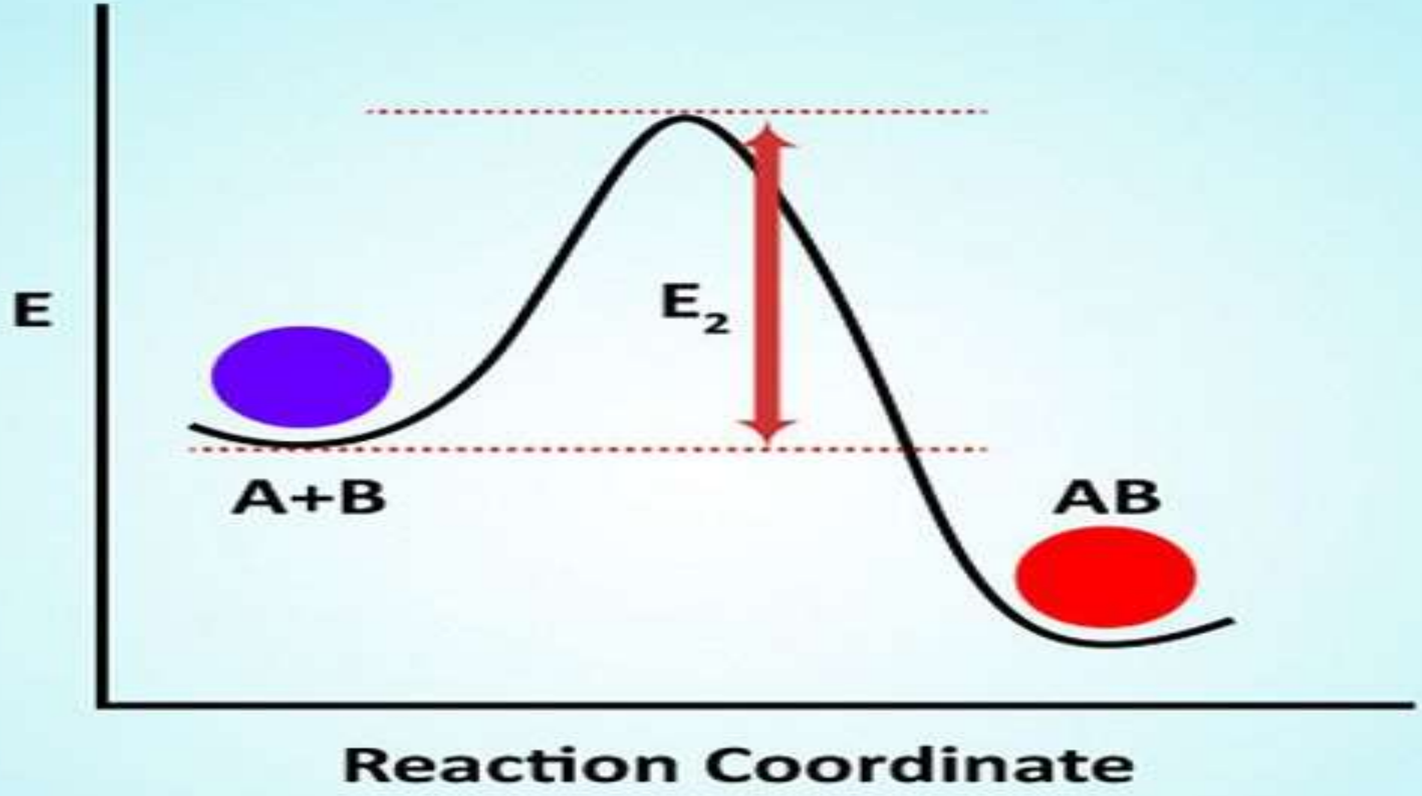
Chemical Kinetics 1



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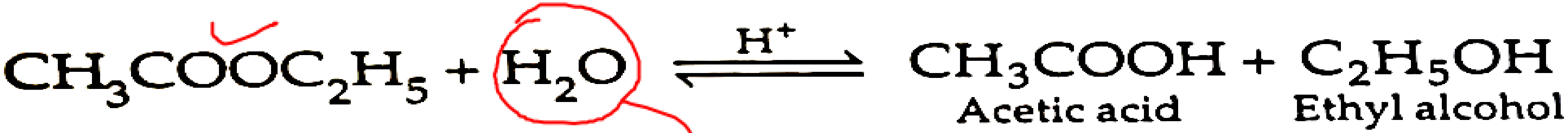
Pseudo 1st order reactions

- **The reactions which appears to be of higher order but actually follow first order are known as pseudo first order reactions**
- Consider general reaction A + B → Products
- Rate of reaction = k[A][B] if reactant B is taken in excess so that its concentration remains practically constant then

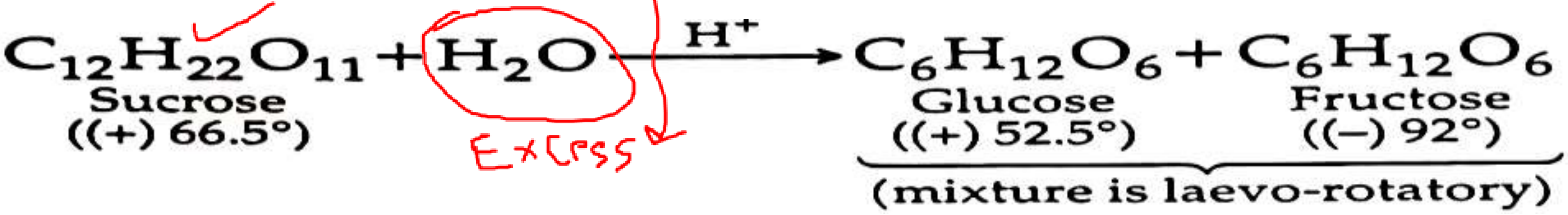
  Rate of reaction = $k_0[A]$ here $k_o = k[B]$
- Then the reaction becomes 1st order

1. Hydrolysis of Ethyl acetate



$$CH_3COOC_2H_5 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

2. Inversion of cane sugar



$$\underset{\substack{\text{Sucrose} \\ ((+)\ 66.5°)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{Glucose} \\ ((+)\ 52.5°)}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose} \\ ((-)\ 92°)}}{C_6H_{12}O_6}}_{\text{(mixture is laevo-rotatory)}}$$

Kinetics of 2^{nd} order reactions

❖ Rate depends upon two concentration terms

❑ Reactions involving one type of reactant

- Consider general reaction 2A → Products
- Rate of reaction α $[A]^2$ or $= k[A]^2$

❑ Reactions involving two different reactants

- Consider general reaction A + B → Products
- Rate of reaction α [A][B] or $=k[A][B]$

Kinetics of 2nd order reactions

❑Reactions involving one type of reactant

- Consider general reaction $2A \rightarrow$ Products

Initial conc.	a	0	
Conc. after time t	$a-x$	x	x is decrease in conc. Of A

Rate of reaction $\frac{dx}{dt} \propto (a-x)^2$ or $\boxed{\frac{dx}{dt} = k(a-x)^2}$ or $\frac{dx}{(a-x)^2} = k\,dt$

- Upon integration, we get
- $\int \frac{dx}{(a-x)^2} = \int k\,dt$
- $\frac{(a-x)-2+1}{-2+1} \int \frac{d}{dx}(a-x) = k \int dt$
- $\frac{(a-x)-1}{-1}(-1) = kt + I$
- $\frac{1}{a-x} = kt + I$ Now when t=0 then x=0 S0 $I = \frac{1}{a}$

Kinetics of 2nd order reactions

❑Reactions involving one type of reactant

- $\frac{1}{a-x} = kt + \frac{1}{a}$
- $\frac{1}{a-x} - \frac{1}{a} = kt$ **Now take LCM and Solve**
- $kt = \frac{a-(a-x)}{a(a-x)} = \frac{\cancel{a}-\cancel{a}+x}{a(a-x)} = \frac{x}{a(a-x)}$
- $K = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$

Kinetics of 2nd order reactions

❑Reactions involving one type of reactant

- Alternative form of integral rate equation

- If Initial conc. a = C_o & a-x = C_t then we can write

- $k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right] = \frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_o}\right] = \frac{1}{t}\left[\frac{C_o - Ct}{C_t C_o}\right]$

Kinetics of 2nd order reactions

❑Reactions involving two different reactants

- Consider general reaction A + B → Products

Initial conc. a b 0

Conc. after time t a-x b-x x

x is decrease in conc. Of A & B respectively

- Rate of reaction $\frac{dx}{dt}$ α (a-x)(b-x) or

$$\frac{dx}{dt} = k(a-x)(b-x) \quad \text{(differential rate equation)}$$

- or $\frac{dx}{(a-x)(b-x)}$ = k dt ……………………………1
- Now resolve in to partial fractions and integrate
- $\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$ ……………………….2

Kinetics of 2nd order reactions

❑Reactions involving two different reactants

- $\frac{1}{\cancel{(a-x)(b-x)}} = \frac{(b-x)A + (a-x)B}{\cancel{(a-x)(b-x)}}$
- Or $(b-x)A + (a-x)B = 1$
- Now when x = a then $A = \frac{1}{(b-a)}$ and when x = b then $B = \frac{1}{(a-b)}$
- Now put these values of A & B in equation 2, we get
- $\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)} = \frac{1}{(b-a)(a-x)} + \frac{1}{(a-b)(b-x)}$ ……………………….3

Kinetics of 2nd order reactions

- Now from equation 3 & 1
- or $\frac{dx}{(b-a)(a-x)} + \frac{dx}{(a-b)(b-x)}$ = k dt ……………………………4 Now integrate
- $\int \frac{dx}{(b-a)(a-x)} + \int \frac{dx}{(a-b)(b-x)} = k \int dt$
- $\frac{1}{(b-a)} \int \frac{dx}{(a-x)} + \frac{1}{(a-b)} \int \frac{dx}{(b-x)} = k \int dt$
- $\frac{1}{(b-a)} \ln(a-x) \frac{d}{dx}(a-x) + \frac{1}{(a-b)} \ln(b-x) \frac{d}{dx}(b-x) = kt + I$

Kinetics of 2nd order reactions

- $-\frac{1}{(b-a)}\ln(a\text{-}x) - \frac{1}{(a-b)}\ln(b\text{-}x) = kt + I$

- $\frac{1}{(a-b)}\ln(a\text{-}x) - \frac{1}{(a-b)}\ln(b\text{-}x) = kt + I$
- $\frac{1}{(a-b)}[\ln(a\text{-}x) - \ln(b\text{-}x)] = kt + I$ or
- $\frac{1}{(a-b)}\ln\frac{(a-x)}{(b-x)} = kt + I$ …………………….5

Kinetics of 2nd order reactions

- Now at t =0 x=0 So a-x = a and b-x = b
- And I = $\frac{1}{(a-b)} \ln \frac{a}{b}$ ……………………………6

From equations 5 & 6

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

Kinetics of 2nd order reactions

- $\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}+\ln\frac{b}{a}\right]= kt$ or
- $\frac{1}{(a-b)}\ln\frac{(a-x)b}{(b-x)a}= kt$ or $kt = \frac{1}{(a-b)}\ln\frac{(a-x)b}{(b-x)a}$
- $k = \frac{1}{(a-b)t}\ln\frac{(a-x)b}{(b-x)a}$ or $K = \frac{2.303}{(a-b)t}\log\frac{(a-x)b}{(b-x)a}$
- **Alternatively**

$$K = \frac{1}{(C_A^o-C_B^o)t}\ln\frac{C_AC_B^o}{C_BC_A^o} \quad \text{or} \quad K = \frac{2.303}{(C_A^o-C_B^o)t}\log\frac{C_AC_B^o}{C_BC_A^o}$$

Kinetics of 2nd order reactions

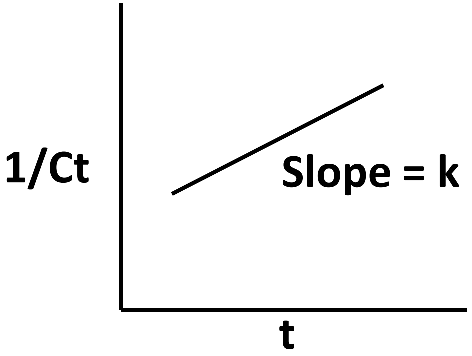
❑ Characteristics

1. Checking a reaction for second order kinetics

i. Substitution method

- The appropriate values of a, b, & x are substituted for the corresponding times in 2nd order rate equation
- If k comes out to be constant then it is said that the reaction follows second order kinetics

ii. Graphical method



- Consider equation $k = \frac{1}{t}\left[\frac{1}{Ct} - \frac{1}{Co}\right]$
- It can be rearranged as $kt = \frac{1}{Ct} - \frac{1}{Co}$ or $\frac{1}{Ct} = kt + \frac{1}{Co}$ This is equation of straight line
- Plot a graph between $\frac{1}{Ct}$ & t, if a straight line is obtained then the reaction follows 2nd order kinetics

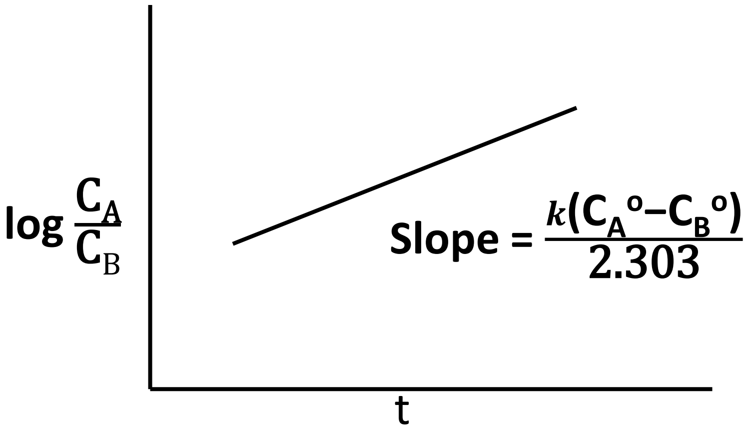
Kinetics of 2nd order reactions

☐ **Characteristics**

1. Checking a reaction for second order kinetics

ii. Graphical method contd…

- **Second equation can also be used ie** $K = \frac{2.303}{(C_A^o - C_B^o)t} \log \frac{C_A C_B^o}{C_B C_A^o}$
- **It can be rearranged as** $\frac{k(C_A^o - C_B^o)t}{2.303} = \log \frac{C_A}{C_B} + \log \frac{C_B^o}{C_A^o}$ **or =** $\log \frac{C_A}{C_B} - \log \frac{C_A^o}{C_B^o}$
- **or** $\log \frac{C_A}{C_B} = \frac{k(C_A^o - C_B^o)t}{2.303} + \log \frac{C_A^o}{C_B^o}$ **This is equation of straight line ie y = mx + c**
- **Plot a graph between** $\log \frac{C_A}{C_B}$ **& t, if a straight line is obtained then the reaction follows 2nd order kinetics**



Kinetics of 2nd order reactions

❑Characteristics

2. Half life period of reaction

- We can use the equation $K = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$
- Now when $t = t_{1/2}$ then $x = a/2$ So put the respective values and solve, we get
- $K = \frac{1}{t_{1/2}}\left[\frac{a/2}{a(a-a/2)}\right]$ or $= \frac{1}{t_{1/2}}\left[\frac{\cancel{a/2}}{a\cancel{(a/2)}}\right]$ or $= \frac{1}{t_{1/2}}\frac{1}{a}$
- So $t_{1/2} = \frac{1}{k\,a}$ or $t_{1/2} \propto \frac{1}{a}$
- Similarly other fractional lives can also be calculated

$t_{1/4}$ $x = ?$ ✓

$t_{3/4}$ $x = ?$ ✓

3. Units of second order rate constant

- $K = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] = \frac{1}{s}\ \frac{\cancel{mol/L}}{mol/L \ \times \ \cancel{mol/L}} = \frac{1}{s}\ \frac{1}{mol/L} = L\ mol^{-1}\ s^{-1}$

Kinetics of 2nd order reactions

❑Characteristics

4. If one of the reactants is taken in large excess then 2nd order rate equation changes to 1st order

- We can use the equation $K = \frac{2.303}{(a-b)t} \log \frac{(a-x)b}{(b-x)a}$ to show it.
- Now if B is in large excess then b>>>a So (a-b) = -b & (b-x) = b
- Now equation 1 can be written as
- $K = \frac{2.303}{-bt} \log \frac{(a-x)\cancel{b}}{\cancel{b}.a} = \frac{2.303}{-bt} \log \frac{(a-x)}{a} = \frac{2.303}{bt} \log \frac{a}{(a-x)}$
- $K.b = \boxed{k = \frac{2.303}{t} \log \frac{a}{(a-x)}}$ Now since B is in large excess so b is practically constant and k x b = constant

Kinetics of 2nd order reactions

❑Example

❖Saponification of ester

- $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

- Kinetics of this reaction is followed by titrating the reaction mixture against standard acid solution using phenolphthalein as an indicator after different intervals of times

- At start of reaction at t=0 the volume of acid used (V_o) α Initial conc. Of NaOH ie ‘a’
- After time t the volume of acid used(V_t) α conc. Of NaOH at time t ie ‘a-x’
- Now $a - (a-x) = \cancel{a} - \cancel{a} + x = \underset{\smile}{x}$ So $x = V_o - V_t$

Kinetics of 2^{nd} order reactions

- **Put values of x, a, a-x in the rate equation**
- **K =** $\frac{1}{t}\left[\frac{x}{a(a-x)}\right]$ **ie K =** $\frac{1}{t}\left[\frac{V_o - Vt}{V_o. Vt}\right]$ **…………………1.**

- **Put values of V_o & V_t at different values of t in equation 1 and calculate k values, If values of k come out to be constant then the reaction follows 2^{nd} order kinetics**