

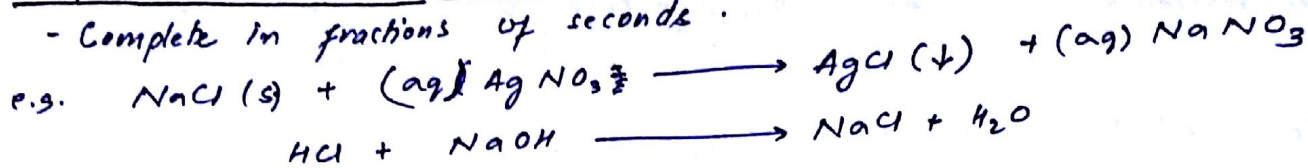
## Chemical Kinetics

→ Deals with rate of  $rk^{ns}$ , various factors influencing the rate and also mechanism of  $rk^{ns}$ .

### Ⓐ CLASSIFICATION OF $rk^{ns}$ :

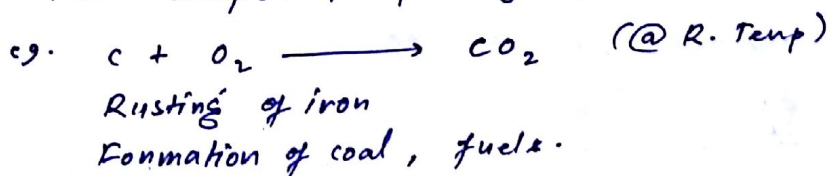
(a) Very Fast  $rk^{ns}$  (or) Instantaneous  $rk^{ns}$ :

- Complete in fractions of seconds.



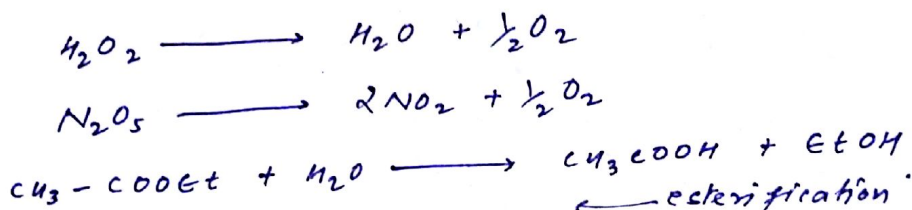
(b) Very Slow  $rk^{ns}$ :

- For completion, very large period of time is required.



(c) Moderate  $rk^{ns}$ :

- For completion, few min. (or) few hours are required.



### Ⓑ RATE OF REACTION:

The change in conc. in unit time is called rate of  $rk^{ns}$ .

$$\text{Rate of } rk^{ns} = \frac{\text{change in conc.}}{\text{time taken.}}$$

For a  $rk^{ns}$ , Reactants  $\longrightarrow$  Products.

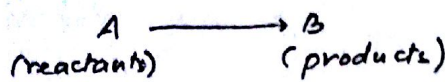
$$R.O.R = \frac{\left( \text{Dec. in conc. of } \overset{\text{React.}}{\text{Prod.}} \text{ (or) Inc. in conc. of } \underset{\text{Prod.}}{\text{React.}} \right)}{\text{(Time Period)}}$$

Units:  $M \text{ time}^{-1}$  (or)  $\frac{\text{mol L}^{-1} \text{ time}^{-1}}{\text{time}^{-1}: \text{sec}^{-1} \text{ (or) minute}^{-1}}$

$$1L = 10^3 \text{ mL} = 10^3 \text{ cm}^3 = (10^{-1} \text{ m})^3 = 1 \text{ dm}^3$$

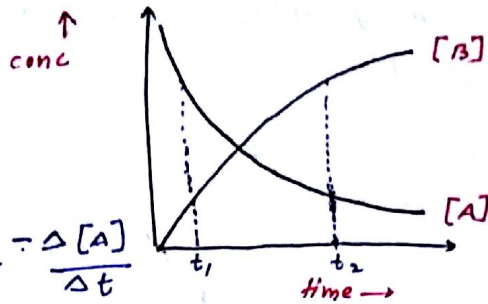
$$\therefore \boxed{1 \text{ dm}^3 = 1L}$$

→ for a  $rk^n$ :



change in rate =  $\frac{\Delta x}{\Delta t}$

for reactants:  $-\left[\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}\right] = -\frac{\Delta[A]}{\Delta t}$



for products:  $\left[\frac{[B]_{t_2} - [B]_{t_1}}{t_2 - t_1}\right] = +\frac{\Delta[B]}{\Delta t}$

# Instantaneous Rate of Reaction.

- Measured for very small interval i.e.  $\Delta t \rightarrow 0$

- For a  $rk^n$ :  $\lim_{\Delta t \rightarrow 0} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$

for reactants:  $\lim_{\Delta t \rightarrow 0} -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$  (Rate of consumption or rate of disappearance of A)

for products:  $\lim_{\Delta t \rightarrow 0} \frac{\Delta[B]}{\Delta t} = \frac{d[B]}{dt}$  (Rate of appearance of B)

\* The instantaneous rate of  $rk^n$  is equal to slope of tangent @ that time, in the graph of conc. (M) and time.

# For a  $rk^n$ :

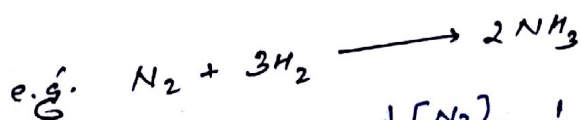


For reactants:  $-\frac{d[A]}{dt} = \frac{a}{t} \Rightarrow \frac{1}{a} \cdot -\frac{d[A]}{dt} = \frac{1}{t}$

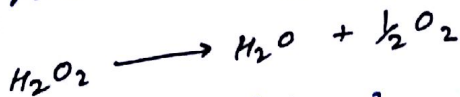
$-\frac{d[B]}{dt} = \frac{b}{t} \Rightarrow \frac{1}{b} \cdot -\frac{d[B]}{dt} = \frac{1}{t}$

For products:  $\frac{1}{c} \frac{d[C]}{dt} = \frac{1}{t}$ ,  $\frac{1}{d} \frac{d[D]}{dt} = \frac{1}{t}$

Rate Expression:  $\frac{1}{a} \left(-\frac{d[A]}{dt}\right) = \frac{1}{b} \left(-\frac{d[B]}{dt}\right) = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$  (\*) v. Imp.



$\therefore \text{rate} = -\frac{d[N_2]}{dt} = \frac{1}{3} \left[-\frac{d[H_2]}{dt}\right] = \frac{1}{2} \frac{d[NH_3]}{dt}$



$\therefore \text{rate} = -\frac{d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = 2 \frac{d[O_2]}{dt}$



## # Various Terms for the rate of reaction

\* Rate of the reaction =  $\frac{dx}{dt} = \frac{d\left(\frac{n}{V}\right)}$

@ const. V' Rate =  $\frac{1}{V} \cdot \frac{d}{dt} \left(\frac{w}{GMW}\right) = \frac{1}{V} \cdot \frac{1}{GMW} \cdot \frac{dw}{dt}$

∴ For a particular substance,  $\text{Rate} = \frac{1}{V \cdot GMW} \cdot \frac{dw}{dt}$

\* For gaseous rxn:  $PV = nRT$   
 $\left(\frac{n}{V} = \frac{P}{RT}\right)$

∴ Rate =  $\frac{d}{dt} \left(\frac{P}{RT}\right)$

@ const. temperature,  $\text{Rate} = \frac{1}{RT} \frac{dP}{dt}$

Note: In any rxn, rate of formation of products and rate of consumption may (or) may not be equal but rate of the rxn w.r.t. any reactant and product is always same.  
i.e.  $\left(\text{Rate} = \frac{1}{a} \left(-\frac{d[A]}{dt}\right) = \frac{1}{b} \left(\frac{d[B]}{dt}\right) \dots\right)$

### Problems:

1. For a rxn,  $mA \rightarrow nB$   
if  $\log_8 \left(-\frac{d[A]}{dt}\right) = \log \left(\frac{d[B]}{dt}\right) + 0.3010$ , then find the value of  $\frac{m}{n}$ .

Sol<sup>n</sup>

⇒  $\log \left(-\frac{d[A]}{dt}\right) = \log \left(\frac{d[B]}{dt}\right) + \log(2)$

⇒  $-\frac{d[A]}{dt} = 2 \frac{d[B]}{dt}$

also,  $\frac{1}{m} \cdot -\frac{d[A]}{dt} = \frac{1}{n} \frac{d[B]}{dt}$

∴  $\frac{m}{n} = 2$  Ans.

For a rxn:  $N_2 + 3H_2 \rightarrow 2NH_3$ , rate of formation of  $NH_3$  is  $2.4 \times 10^{-3}$  M/min. Calculate the rate of consumption of reactants and rate  $rk^{\text{th}}$ .

Sol<sup>n</sup>  

$$\frac{d[NH_3]}{dt} = 2.4 \times 10^{-3} \text{ M/min}$$

Rate =  $\frac{1}{2} \frac{d[NH_3]}{dt} = 1.2 \times 10^{-3} \text{ M/min}$  } Ans.  
 (from Rate expression)

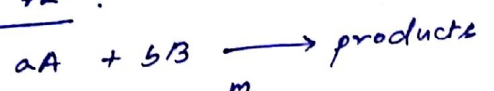
Also,  $-\frac{d[N_2]}{dt} = 1.2 \times 10^{-3} = -\frac{1}{3} \frac{d[H_2]}{dt}$

$$\left. \begin{aligned} \frac{d[H_2]}{dt} &= -3.6 \times 10^{-3} \text{ M/min} \\ \frac{d[N_2]}{dt} &= -1.2 \times 10^{-3} \text{ M/min} \end{aligned} \right\} \text{ Ans.}$$

# Rate Equation (or) Rate Law:

The equation which gives exact relationship b/w rate of the rxn and conc. of reactants is called Rate Equation (or) Rate Law.

For a rxn:



$$\left[ \begin{aligned} \text{Rate} &\propto [A]^m \\ \text{Rate} &\propto [B]^n \end{aligned} \right. \rightarrow m, n \text{ are the partial orders of } Rk^{\text{th}}, \text{ may (or) may not be equal to } a, b.$$

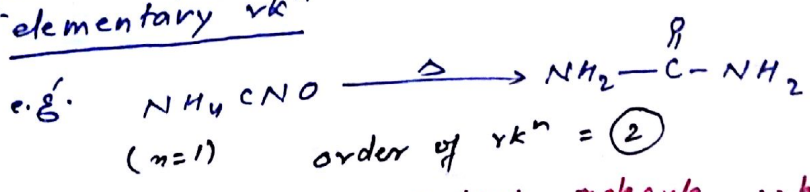
$$\text{Rate} \propto [A]^m [B]^n$$

$$\therefore \text{Rate} = k [A]^m [B]^n$$

Note: (Total order of reaction = sum of powers of conc. terms in Rate Reaction (m+n))

Order of Reaction may be integer, may be -ve, zero (or) any fractional value.

- It's determined by experimental results.
- It's independent of stoichiometric representation of rxn<sup>no</sup> - except "elementary rxn"

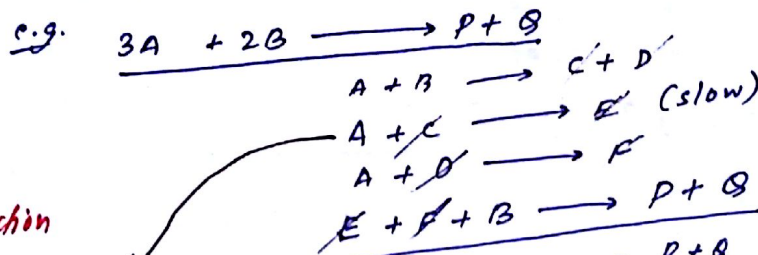
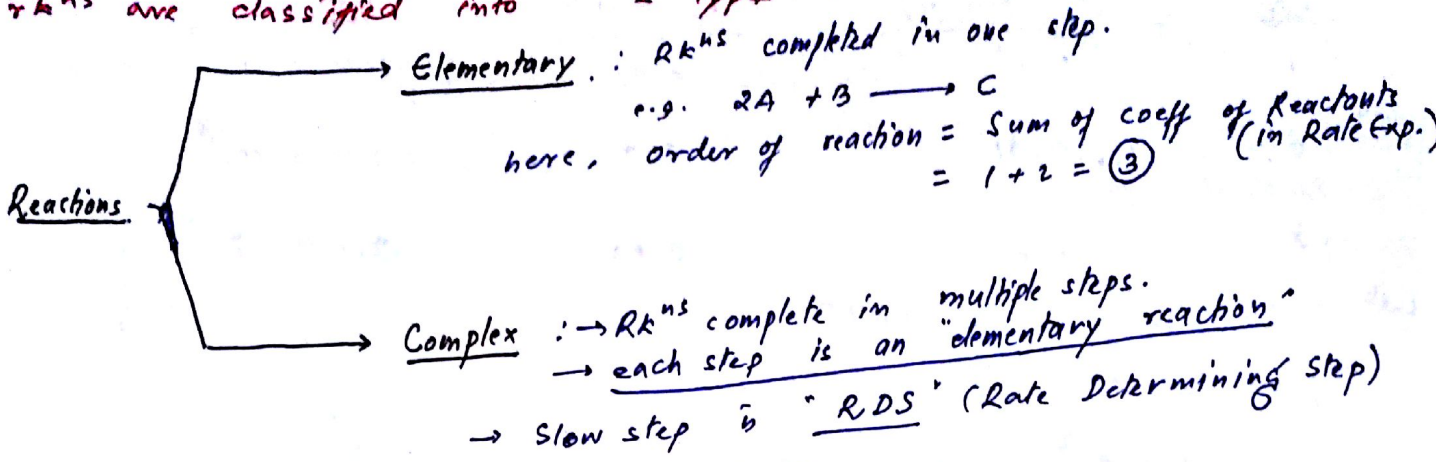


- Order of rxn is the no. of reactant molecule whose conc. determines the rate of the reaction.



### III TYPES OF REACTION

On the basis of no. of steps involved in a particular rxn, rxns are classified into 2 types:-



Here, rate in complex reaction =  $k [A][C]$

Note: "Intermediates" shouldn't be present. (Rate law)

### \* Molecularity of the Reaction

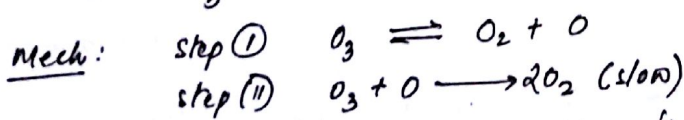
The total no. of reactant molecules present in slowest step of the reaction (RDS) is known as the molecularity of the reaction.

$\rightarrow$  If no. of molecules = 1  $\rightarrow$  Unimolecular  
 = 2  $\rightarrow$  Bimolecular

e.g.  $S_N1$ , Rate =  $k [R-X]$   
 e.g.  $S_N2$ , Rate =  $k [R-X] [Nu^-]$

### Problems:

1. For the following rxn,



then write "Rate law" for the given rxn?

Soln From s(I):  $k = \frac{[O_2][O]}{[O_3]} \therefore [O] = \frac{k [O_3]}{[O_2]}$

From s(II): Rate =  $k [O_3][O]$   
 $= k [O_3] \frac{k [O_3]}{[O_2]} = k [O_3]^2 [O_2]^{-1}$

Order of reaction =  $2 - 1 = 1$  Ans

on the basis of following products, find order of rxn, rate const. given data.

S.N.	[A] (mol/L)	[B] (mol/L)	Rate
1	0.01	0.01	$1.2 \times 10^{-3}$
2	0.01	0.02	$2.4 \times 10^{-3}$
3	0.02	0.02	$9.6 \times 10^{-3}$

Sol<sup>n</sup>

$$\text{Let Rate} = k [A]^m [B]^n$$

from (1) and (2) :-

$$\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k}{k} \left( \frac{0.01}{0.01} \right)^m \left( \frac{0.02}{0.01} \right)^n$$

$$\Rightarrow 2 = 2^n \Rightarrow \boxed{n = 1}$$

from (2) and (3) :-

$$\frac{9.6}{2.4} = \left( \frac{0.02}{0.01} \right)^m \left( \frac{0.02}{0.02} \right)^n$$

$$4 = 2^m \Rightarrow \boxed{m = 2}$$

$$\therefore \text{Rate} = k [A]^2 [B]^1$$

$$\text{Order of rxn} = 2 + 1 = 3 \text{ Ans}$$

for rate const. k :-

$$1.2 \times 10^{-3} = k (0.01)^2 (0.01)^1$$

$$\Rightarrow k = \frac{1.2 \times 10^{-3}}{10^{-6}} = 1.2 \times 10^3 \text{ Ans}$$

3. For a rxn  $A + B \rightarrow \text{Products}$ , Rate increases 2.25 times, when conc. [A] increases 1.5 times, when conc. of A & B increases 2.5 times, there is no change in rate of reaction. Then order of reaction?

Sol<sup>n</sup> Let Rate =  $k [A]^m [B]^n$

$$\text{Case (i)}: 2.25 = (1.5)^m$$

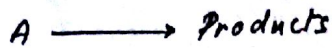
$$m = 2$$

$$\text{Case (ii)}: 1 = (2.5)^2 (2.5)^n \Rightarrow n = -2$$

$$\therefore \text{Order} = 2 - 2 = 0 \text{ Ans}$$



## Some Expressions



→ Initial concentration of the reactant  
[ @  $t=0$  ]  
(starting)

$$C_0 \text{ (or) } a \text{ (or) } [A]_0$$

→ conc. of Reactant consumed (or) Reacted  
[ @  $t=t$  ]

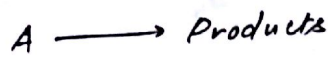
$$x \text{ (or) } C_0 - C$$

→ Conc. of Reactant Remaining  
[ @ time =  $t$  ]

$$(a-x) \text{ (or) } C \text{ (or) } [A]_t$$

## Zero Order Reaction

For a zero order reaction,



$$\text{Rate} = \frac{dx}{dt} = -\frac{d[A]}{dt} = k_0 [A]^0$$

$$\frac{dx}{dt} = k_0 (a-x)^0$$

$$-d[A] = k_0 dt$$

$$\Rightarrow -\int_a^{a-x} d[A] = \int_0^t k_0 dt$$

$$\Rightarrow a - (a-x) = k_0 t = x$$

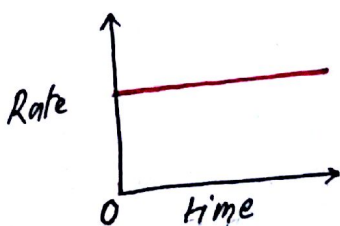
∴ Rate Constant for zero order :-

$$k_0 = \frac{a - (a-x)}{t} = \frac{x}{t}$$

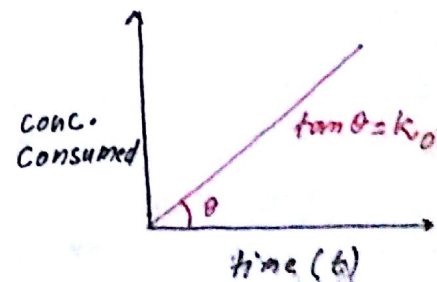
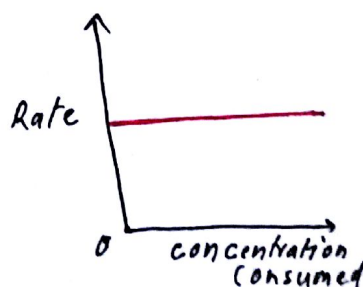
→ for a zero order react<sup>n</sup>, units of rate is equal to rate const.

Since, rate =  $\frac{dx}{dt} = k_0$

→ Rate is independent of time and conc. of Reactant.



(and)



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

The time required to consume or complete half of the initial conc. of the reactant is called half-life.

→ for a zero order  $rk^n$  :-  
initial conc. =  $a$

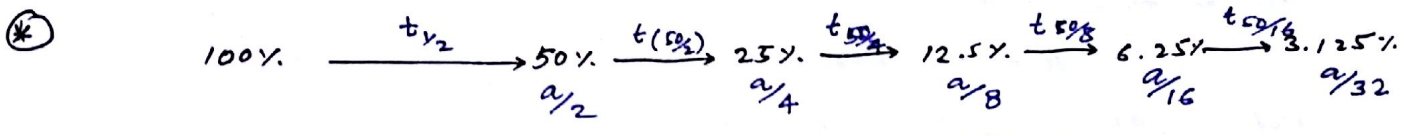
(For a particular  $rk^n$ ,  
Rate const. is same)

@  $t_{1/2}$  conc. =  $a/2$

$k_0 = \frac{x}{t} \Rightarrow t = \frac{x}{k_0}$

$t_{50\%}$  or  $t_{1/2} = \frac{a}{2k_0}$

→ Half-life of zero order  $rk^n$  is  $\propto$  initial conc. of  $rk^n$   
( $t_{1/2} \propto a$ )



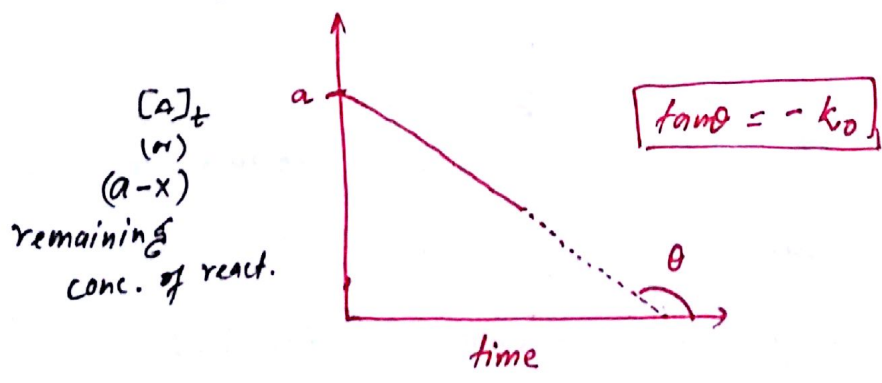
∴ time required to complete 75% of reaction:

$t_{75\%} = t_{(50\%)} + t_{50} = \frac{t}{2} + t = \frac{3t}{2} = \frac{3}{2}(t_{1/2})$

\*  $t_{100\%} = 2(t_{1/2}) = 2(\text{H.F.L})$   
Half life.

For Zero - Order Reaction

$k_0 = \frac{a - (a-x)}{t} \Rightarrow (a-x) = -k_0t + a$





Q1. If half-life of zero-order rxn is 20 min, Calc. time required to complete 87.5% of rxn, (Note: for a particular react, rate const is same)

$$50\% \longrightarrow 20 \text{ min}$$

$$87.5\% \longrightarrow \frac{20}{50} \times 87.5 = 35 \text{ min} \underline{\underline{Ans}}$$

also,  $k_0 = \frac{x}{t}$

$$(k_0)_{50\%} = (k_0)_{87.5\%}$$

(since,  $k_0$  is same for a particular rxn)

$$\frac{50}{t_{50\%}} = \frac{87.5}{t_{87.5\%}}$$

$$t_{87.5\%} = 87.5 \times \frac{20}{50} = 35 \text{ min} \underline{\underline{Ans}}$$

Q2. For a zero-order rxn, initial conc. of rxn is 0.01 M, After 10 min, the conc. of reactant remaining is 0.008 M. Calculate  $t_{1/2}$ .

Soln

$$a = 0.01 \text{ M}$$

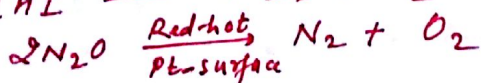
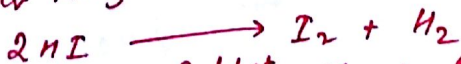
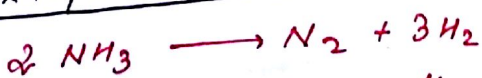
$$t_{10 \text{ min}} \Rightarrow a - x = 0.008 \text{ M}$$

$$0.01 - 0.008 = x = \text{consumed reactant} = 0.002$$

again,  $0.002 \longrightarrow 10 \text{ min}$

$$(1. \text{ half}) 0.005 \longrightarrow \frac{10}{0.002} \times 0.005 = 25 \text{ min} \underline{\underline{Ans}}$$

Examples for zero order Rxn



## 1st Order Reaction



$$\text{rate} = \frac{dx}{dt} = -\frac{d[A]}{dt} = k, [A]$$

$$\frac{dx}{dt} = 'k, (a-x)' \quad \text{or} \quad \frac{dx}{dt} = k [A] \quad \text{or} \quad -\frac{d[A]}{dt} = k, [A]$$

↳ Diff. forms

$$\text{Now, } -\frac{d[A]}{dt} = k [A]$$

$$\Rightarrow \int_a^x \frac{d[A]}{[A]} = \int_0^t k dt$$

$$\Rightarrow \ln\left(\frac{a}{a-x}\right) = kt$$

$$\begin{aligned} \Rightarrow k &= \frac{1}{t} \ln\left(\frac{a}{a-x}\right) \\ &= \frac{1}{t} \ln\left(\frac{c_0}{c}\right) \\ &= \frac{1}{t} \ln\left(\frac{[A]_0}{[A]_t}\right) \\ &= \frac{2.303}{t} \cdot \log_{10}\left(\frac{a}{a-x}\right) \end{aligned}$$

Also,

$$\begin{aligned} k &= \frac{1}{t} \ln\left(\frac{c_0}{c}\right) \\ \Rightarrow -kt &= \ln\left(\frac{c}{c_0}\right) \\ \Rightarrow c &= c_0 e^{-kt} = a-x \end{aligned}$$

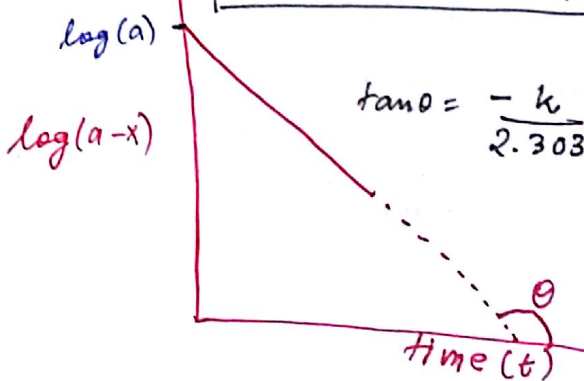
$$\text{Also, } k = \frac{1}{t} \ln\left(\frac{a}{a-x}\right)$$

$$\Rightarrow -kt = \ln\left(\frac{a-x}{a}\right)$$

$$\Rightarrow a-x = a e^{-kt}$$

$$\Rightarrow x = a(1 - e^{-kt})$$

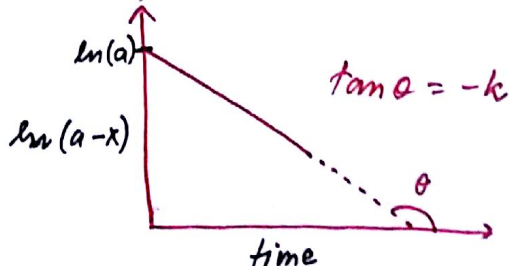
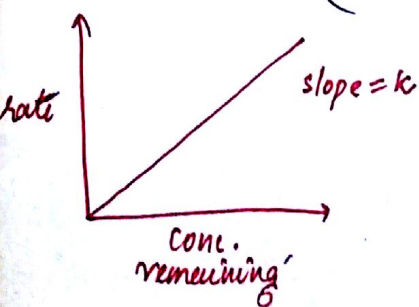
$$\log(a-x) = \log a - \frac{kt}{2.303}$$



→ For a First Order Reaction,

(i) Rate of reaction depends upon conc. of reaction.

$$\left(\frac{dx}{dt} = k[A]_t\right)$$



$$kt = \ln(a) - \ln(a-x)$$

$$\Rightarrow \ln(a-x) = -kt + \ln(a)$$