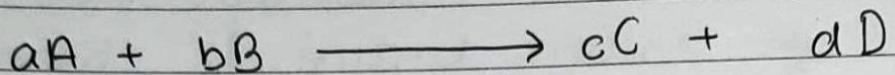


★ Chemical ★ Kinetics



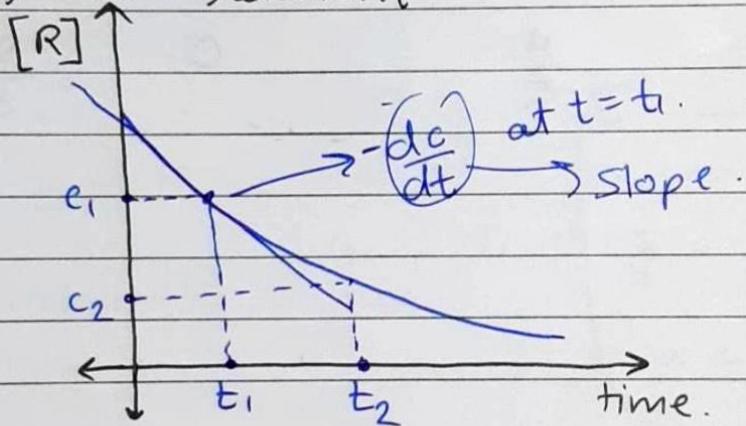
★ Rate of reaction:

it is change in concentration w.r.t time.

It can be defined by two ways.

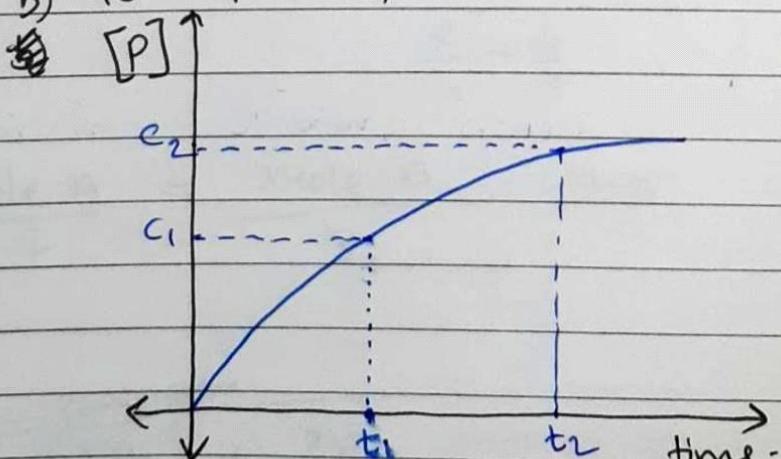
1. average rate:

a) For reactant.



$$\text{rate} = -\frac{(c_2 - c_1)}{(t_2 - t_1)} = -\frac{\Delta c}{\Delta t}$$

b) For product.



$$\text{rate} = \frac{c_2 - c_1}{t_2 - t_1} = \frac{\Delta c}{\Delta t}$$

for solids & liquids

$$d = \frac{\text{mass}}{\text{volume}} = \frac{\text{mass}}{\text{molecular wt.}} \rightarrow \frac{\text{mass}}{\text{molecular wt.}}$$

$$d = M \cdot C$$

$$(d) = (M) \cdot (C)$$

classmate
Date _____
Page _____

2. Instantaneous rate :-

a) rate = $\lim_{\Delta t \rightarrow 0} -\frac{\Delta c}{\Delta t} = -\frac{dc}{dt}$

} For reactant.

b) rate = $\frac{dc}{dt}$

} For product.
represent slope.



$$\frac{\text{mole of A}}{a \times V} = \frac{\text{mole of B}}{b \times V} = \frac{\text{mole of C}}{c \times V} = \frac{\text{mole of D}}{d \times V}$$

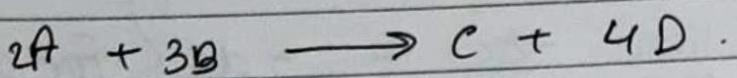
dividing by volume (V).

$$\frac{[A]}{a} = \frac{[B]}{b} = \frac{[C]}{c} = \frac{[D]}{d}$$

∴ rate of reaction :- $-\frac{1}{a} \left(\frac{d[A]}{dt} \right) = -\frac{1}{b} \left(\frac{d[B]}{dt} \right) = \frac{1}{c} \left(\frac{d[C]}{dt} \right) = \frac{1}{d} \left(\frac{d[D]}{dt} \right)$

this is called rate law expression.

Q: Write two rate law expression for this reaction.



$$\text{rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{4} \frac{d[D]}{dt}$$

★ Rate of disappearance of 'A' (r_A)

$$r_A = -\frac{d[A]}{dt} = -\frac{dc_A}{dt}$$

$$r_B = -\frac{d[B]}{dt} = -\frac{dc_B}{dt}$$

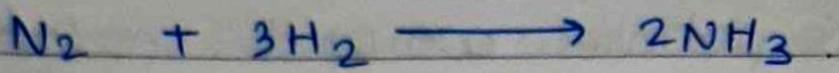
★ Rate of appearance of 'C' (r_C)

$$r_C = \frac{d[C]}{dt} = \frac{dc_C}{dt}$$

Q: For the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$.

rate of disappearance of 'H₂' gas was 4×10^3 mole/litre sec.

calculate rate of appearance of 'NH₃' gas and disappearance of 'N₂' gas.
also calculate rate of reaction.



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

$$-\frac{d[H_2]}{dt} = 4 \times 10^{-3}$$

$$\text{or } \frac{d[NH_3]}{dt} = \frac{8}{3} \times 10^{-3}$$

$$\text{or } -\frac{d[N_2]}{dt} = \frac{4}{3} \times 10^{-3}$$

Method (2) :-

$$\text{rate of reaction.} \left(= \frac{\gamma_{N_2}}{1} = \frac{\gamma_{H_2}}{3} = \frac{\gamma_{NH_3}}{2} \right) \text{ using this find.}$$

$$\text{or rate of reaction} = \frac{4}{3} \times 10^{-3}$$

~~★~~ In this time we will calculate concentration as function of time.

rate of reaction =

$$= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

$$\text{Rate} = \boxed{\frac{\gamma_A}{a} = \frac{\gamma_B}{b} = \frac{\gamma_C}{c} = \frac{\gamma_D}{d}}$$

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT = CRT$$

$$\therefore C = \frac{1}{RT} P$$

$$\therefore \boxed{\# \frac{dc}{dt} = \frac{1}{RT} \frac{dp}{dt}}$$

$$\therefore \boxed{\# \gamma = \frac{1}{RT} \frac{dp}{dt}} \rightarrow \text{for gas}$$

★ Rate of reaction will depend on concentration.

$$\textcircled{a} \quad \text{rate} \propto (\text{concentration})^n$$

where;

$n \rightarrow$ order of reaction.

let rate = $K (\text{concentration})^n$

where,

$K \rightarrow$ rate constant
or

velocity constant
or

specific reaction rate.

Order of reaction can be calculated experimentally

$-\frac{dc}{dt} = K c^n$

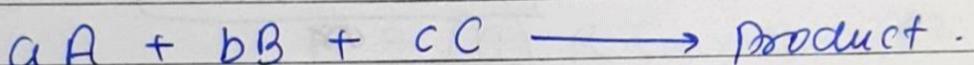
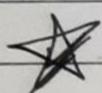
$$\frac{\text{mole/litre}}{\text{sec}} = K (\text{mole/litre})^n$$

unit of $K = \left(\frac{\text{mol}}{\text{litre}} \right)^{1-n} \text{ sec}^{-1}$

| # | order | unit of K. |
|---|-------|---|
| 0 | 0 | $\text{mol lit}^{-1} \text{ sec}^{-1}$ |
| 1 | 1 | lit sec^{-1} |
| 2 | 2 | $\text{mol}^{-1} \text{ lit sec}^{-1}$ |
| 3 | 3 | $\text{mol}^{-2} (\text{lit})^2 \text{ sec}^{-1}$ |
| | : | |

0
↓
oo

Note:- If rate constant with unit is given then we can predict order of the reaction.



~~rate~~

$$\# \text{rate} = K (C_A)^x \cdot (C_B)^y \cdot (C_C)^z$$

"order of reaction w.r.t A = x.

" w.r.t B = y

" w.r.t C = z.

∴ $x + y + z =$ overall order of reaction.

Note:-
oo

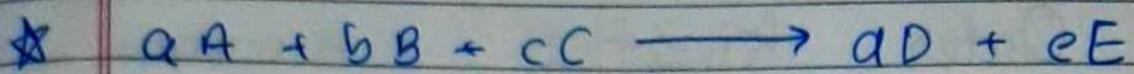
$x, y, z \in$ any Real Number.

but $0 \leq x + y + z \leq 3$

→ overall order must be (+ve)

classmate
Date _____
Page _____

activemass (a_A) \propto C_A
 $a_A = f C_A$ \rightarrow proportionality constant.
 for ideal case $f = 1$



$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = \frac{1}{e} \frac{d[E]}{dt}$$

$$= K (C_A)^x (C_B)^y (C_C)^z$$

$$\boxed{\text{rate.} = \frac{\gamma_A}{a} = \frac{\gamma_B}{b} = \frac{\gamma_C}{c} = \frac{\gamma_D}{d} = \frac{\gamma_E}{e} = K(C_A)^x (C_B)^y (C_C)^z}$$

★ Zero Order Kinetics:

Approach: 1



$$t=0 \quad C_0$$

$$t=t \quad C_t$$

$$\text{rate} = k(C_A)^0$$

$$\therefore -\frac{d[A]}{dt} = k(C_A)^0$$

$$\therefore -\frac{dC_A}{dt} = K$$

$$\therefore \int_{C_0}^{C_t} -dC_A = \int_0^t K dt$$

$$\left(\frac{-C_A}{C_0}\right)_{C_0}^{C_t} = K(t)_0^t$$

$$(C_0 - C_t) = kt$$

$$\therefore C_t = C_0 - kt$$

degree of dissociation : dissociation out of one mole.

classmate

Date _____

Page _____

approach : 2

$\text{A} \longrightarrow \text{product}$.

$$t=0 \quad a - 0$$

$$t=t \quad a-x \quad x.$$

$$\therefore -\frac{d(a-x)}{dt} = k(a-x)^{\circ}$$

$$\frac{dx}{dt} = k.$$

$$\int_0^x dx = \int_0^t k dt.$$

$$x = kt \quad \boxed{\#}$$

$$\therefore C_t = a - x$$

$$\boxed{C_t = a - kt}.$$

$$\# \% \text{ dissociation} = \frac{x}{a} \times 100. = \frac{kt}{a} \times 100$$

$$\# \text{ degree of dissociation} = \frac{x}{a} = \alpha. = \frac{kt}{a}$$

$$1 - \frac{a-x}{a}$$

% reacted = $\frac{x}{a} \times 100 = \frac{kt}{a} \times 100$

% unreacted = $\left(\frac{a-x}{a}\right) \times 100 = \left(\frac{a-kt}{a}\right) \times 100$.

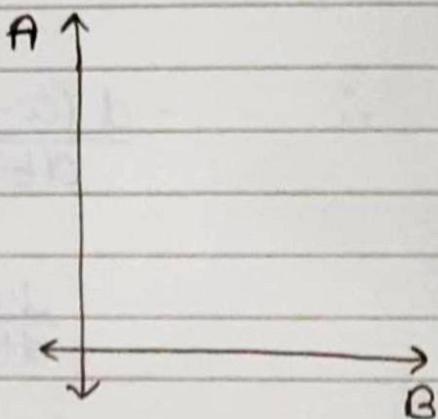
★ Plotting graph:

if linear combination between A and B will be there

then plot st-line.

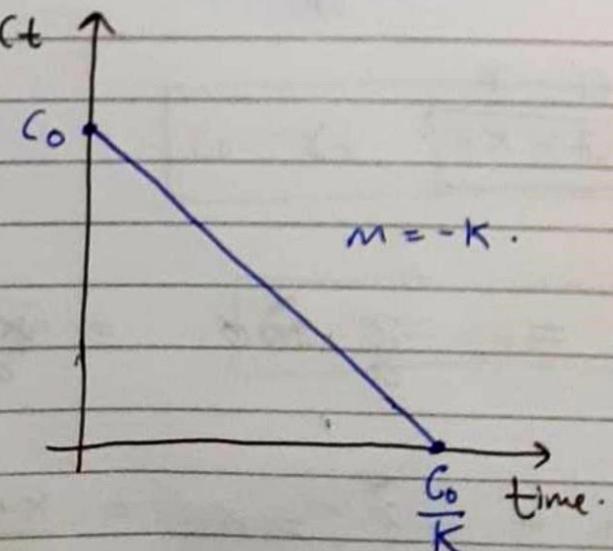
⇒ if $A \propto B$.

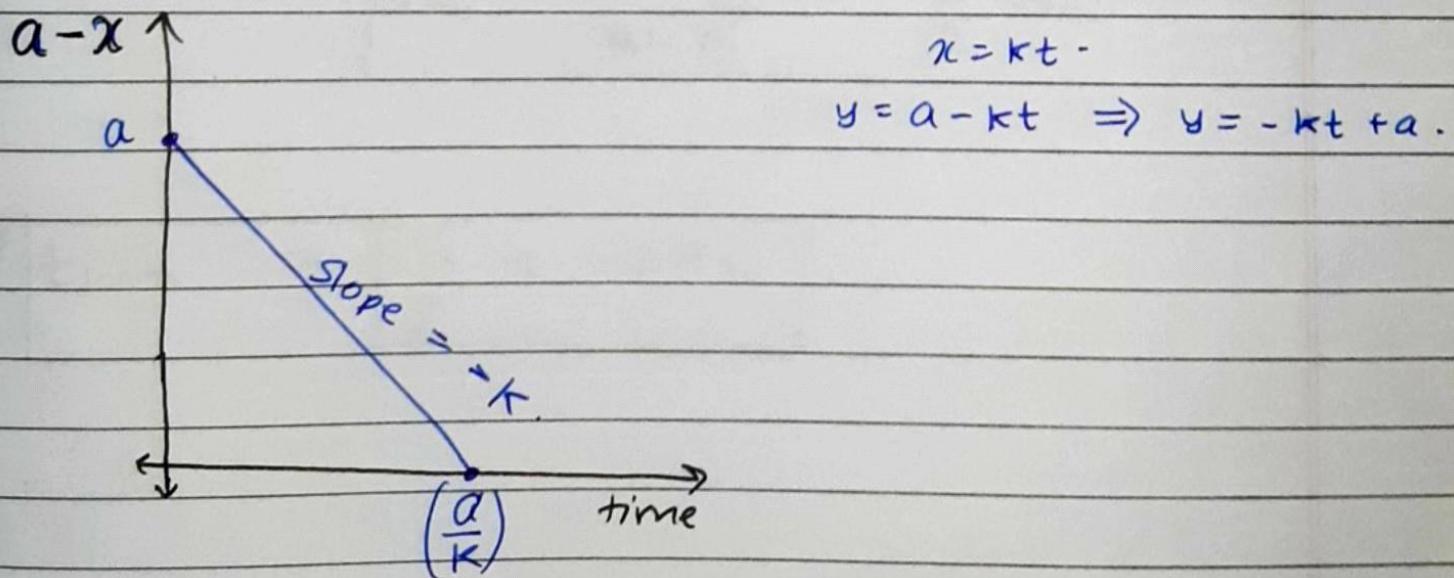
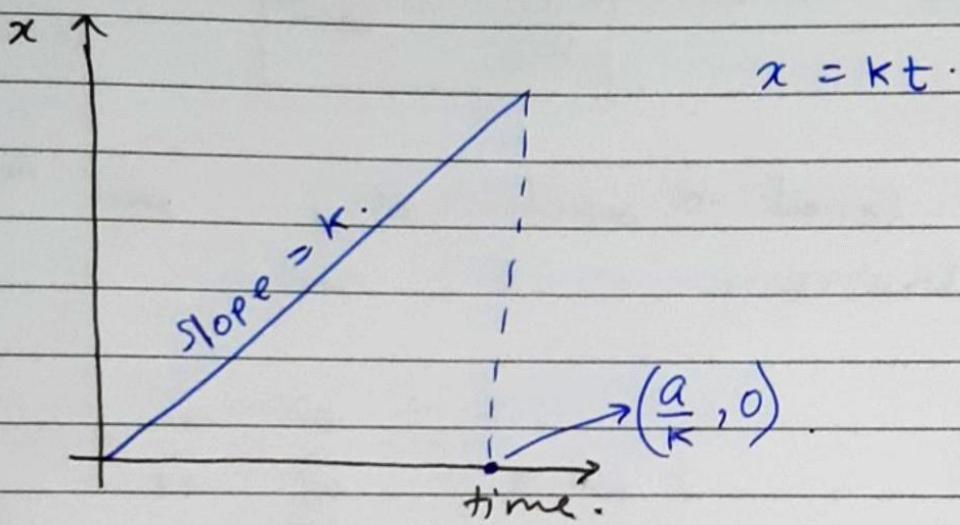
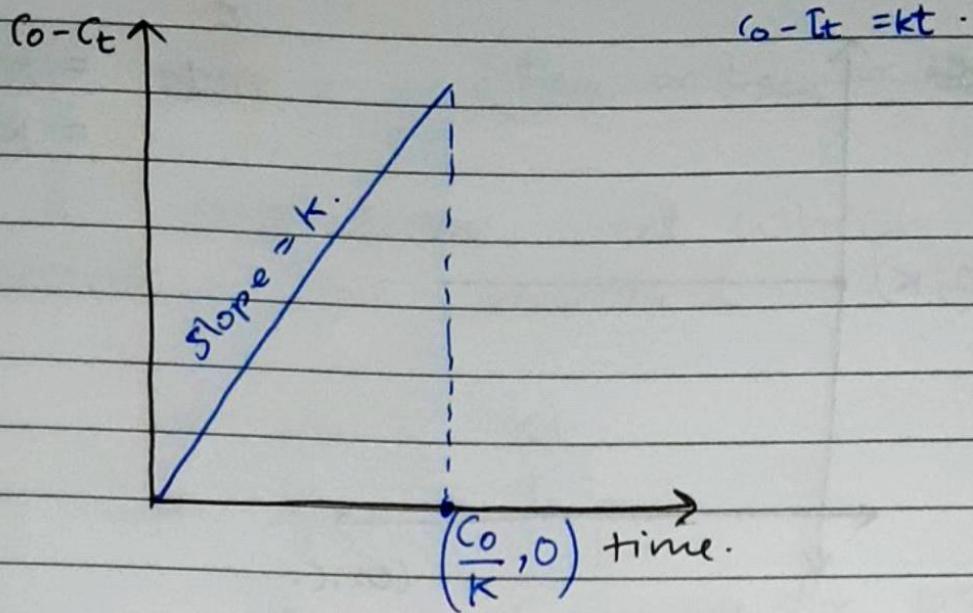
then st-line will pass through origin.



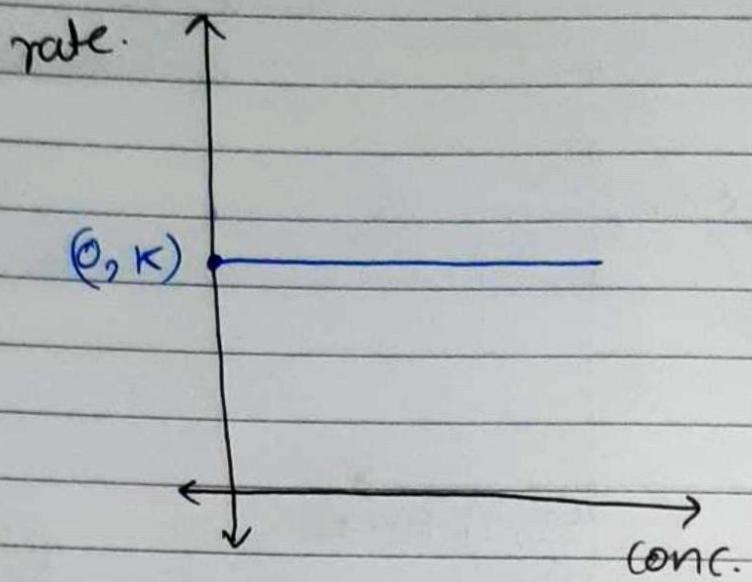
② $C_t = C_0 - kt$

i)





5)

 r

$$\begin{aligned} \text{rate} &= k(c_0)^0 \\ &= k. \end{aligned}$$

★ Half life : $(t_{1/2} \text{ or } t_{50\%} \text{ or } t_{0.5})$

it is the time at which 50% of reactant get reacted

$$C_0 - C_t = kt.$$

$$C_0 - \frac{C_0}{2} = kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{C_0}{2k}} \quad \text{for } 0^{\circ}\text{order kinetics.}$$

$\Rightarrow \frac{3}{4}^{th}$ life : $(t_{3/4} \text{ or } t_{75\%} \text{ or } t_{0.75})$

when 75% reactant get reacted.

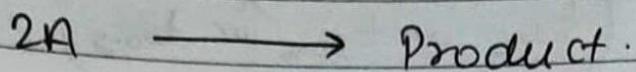
$$C_0 - C_t = kt.$$

$$C_0 - \frac{C_0}{4} = kt_{3/4}$$

$$\boxed{t_{3/4} = \frac{3}{4} \frac{C_0}{k} = \frac{3}{2} t_{1/2}}$$

$$\# \boxed{t_{100\%} = \frac{C_0}{k} = 2 \cdot t_{1/2}}$$

Q1)



$$\text{rate} = k(C_A)^n$$

What is half life of reaction.

$$t=0 \quad C_0$$

$$t_{1/2} \quad C_t$$

$$\begin{aligned} C_0 - C_t &= kt \\ C_0 - \frac{C_0}{2} &= kt_{1/2} \quad \rightarrow \text{WRONG} \\ \Rightarrow t_{1/2} &= \frac{C_0}{2k} \end{aligned}$$

$$-\frac{1}{2} \frac{dC_A}{dt} = k(C_A)^n$$

$$\int_{C_0}^{C_0/2} -dC_A = \int_0^{t_{1/2}} 2k dt$$

$$C_0 - \frac{C_0}{2} = 2kt_{1/2}$$

$$\Rightarrow t_{1/2} =$$

$$\boxed{\text{if } t_{1/2} = \frac{C_0}{4k}}$$

(a:2) $3A \rightarrow \text{product}$.

$$t=0 \cdot C_0$$

$$\gamma_A = K(C_A)^0$$

$$t_{1/2} = ?$$

$$t=t_{1/2} \quad \cancel{\gamma_A}$$

$$\frac{-1}{3} \frac{d[A]}{dt} = K(C_A)^0$$

$$\int_{C_0}^{C_0/2} -dC_A = \int_0^{t_{1/2}} 3K dt$$

wrong
 γ_A is given
 not rate of
 reaction.

$$C_0 - \frac{C_0}{2} = 3K(t_{1/2})$$

$$\frac{C_0}{2} = 3K(t_{1/2})$$

$$t_{1/2} = \frac{C_0}{6K}$$

$$-\frac{dC_A}{dt} = K(C_A)^0$$

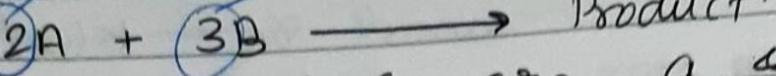
$$\int_{C_0}^{C_0/2} -dC_A = \int_0^{t_{1/2}} K dt$$

$$C_0 - \frac{C_0}{2} = Kt_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{C_0}{2K} \quad \checkmark$$

~~lucky~~
 here is 2 so $\rightarrow K \rightarrow 2K$
 $\therefore K \rightarrow 3K$.

Q: 3)



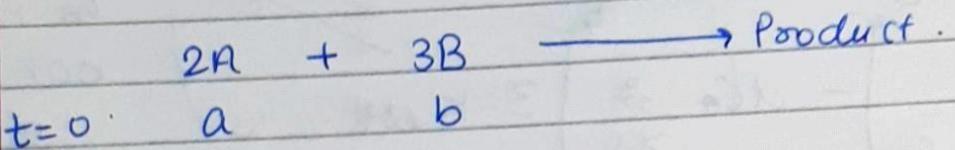
initially C_A & C_B are a & b respectively.

i) calculate concentration of A & B as a function of time.

ii) calculate half life of A & B.

iii) write condition of a & b such that half life of 'A' is equal to half life of 'B'.

given :- rate = $K(C_A)^0 (C_B)^0$



$$-\frac{1}{2} \frac{dC_A}{dt} = -\frac{1}{3} \frac{dC_B}{dt} = K(C_A)^0 (C_B)^0$$

$$\Rightarrow \int_a^{C_{At}} -dC_A = \int_0^t 2K dt$$

$$\Rightarrow a - C_{At} = 2Kt$$

$$\Rightarrow C_{At} = a - 2Kt$$

$$\int_b^{C_{Bt}} -dC_B = \int_0^t 3K dt$$

$$b - C_{Bt} = 3Kt$$

$$C_{Bt} = b - 3Kt$$

ii) at half time

$$C_{\text{part}} = \frac{a}{2}$$

$$\therefore (t_{1/2})_A = \frac{1}{2K} \left(a - \frac{a}{2} \right)$$

$$(t_{1/2})_A = \frac{a}{4K}$$

$$\therefore (t_{1/2})_B = \frac{1}{3K} \left(b - \frac{b}{2} \right)$$

$$(t_{1/2})_B = \frac{b}{6K}$$

$$\frac{a}{24K} = \frac{b}{36K}$$

$$3a = 2b$$

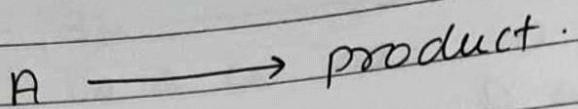
$$\Rightarrow 3a - 2b = 0$$

#brick $\Rightarrow \frac{a}{b} = \frac{2}{3} \Rightarrow$ in ratio of coefficient of A & B.



First order kinetics:

Page



$$t=0$$

$$C_0$$

$$t=t$$

$$C_t$$

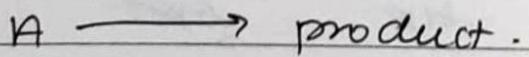
$$\text{rate} = k(C_A)$$

$$-\frac{dC_A}{dt} = k C_A$$

$$\int_{C_0}^{C_t} -\frac{dC_A}{C_A} = \int_0^t k dt$$

$$\left[-\ln(C_A) \right]_{C_0}^{C_t} = \int_0^t k dt = kt$$

$\boxed{\ln\left(\frac{C_0}{C_t}\right) = kt} \quad \dots (1)$



$$t=0$$

$$a$$

$$t=t$$

$$a-x$$

$$-\frac{d(a-x)}{dt} = k(a-x)$$

$$-\frac{dx}{dt} = ka - xk - k(a-x)$$

$$\int_0^x -\frac{dx}{(a-x)} = -\int_0^t k dt$$

~~ln~~ $\ln x = 2.303 \log x$.
 $\log 2 = 0.3010 \approx 0.3$
 $\log 3 = 0.4771 \approx \cancel{0.48} 0.48$.

classmate

Date _____

Page _____

$$[\ln(a-x)]^x_0 = -kt.$$

∴ # $\boxed{\ln \left(\frac{a-x}{a} \right) = -kt} \quad \dots (2)$

From (1) .

$$\ln \left(\frac{C_0}{C_t} \right) = kt.$$

$$\frac{C_0}{C_t} = e^{kt}.$$

∴ # $\boxed{C_t = C_0 e^{-kt}}$

→ remaining concentration

From (2) .

$$\cancel{\ln} \cdot \frac{a-x}{a} = e^{-kt}.$$

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

→ dissociated concentration

$\boxed{x = C_0 - C_t}$