eg: Some enzyme catalyzed reactions and reactions which occur on metal surface are few examples zero order reaction.

- $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$
- $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$
- reaction b/w acetone and bromine.
- dissociation of HI on gold surface.
- absorption of gases on metal surface.

→* Integrated Rate expression (rate eqn) for. ZOR:

⟹ for a general zero order rxn;

$$R \longrightarrow P$$

$$-\frac{d[R]}{dt} = K \cdot [R]^0$$

$$\text{Or } -\frac{d[R]}{dt} = K \quad \therefore \boxed{d[R] = -K \cdot dt}$$

⟹ integrating above equation;

$$\boxed{[R] = -Kt + C} \text{ — eq(1)} \quad [\because C \text{ is integrated constant}]$$

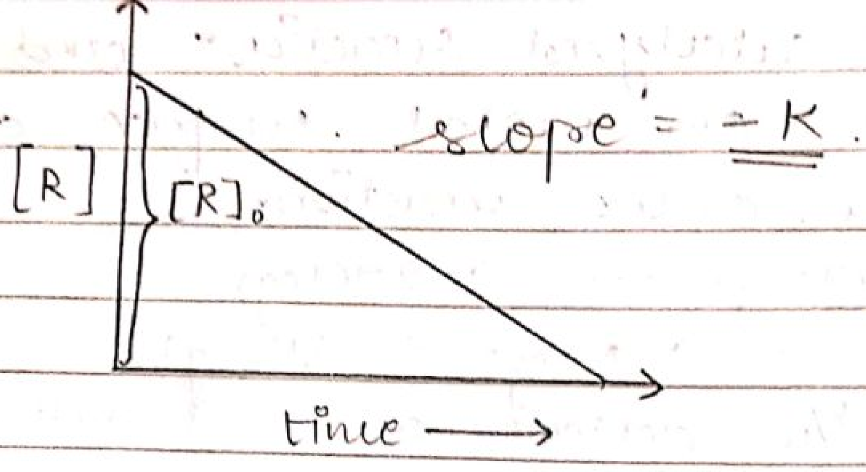
at time = 0 ⟹ $[R] = [R]_0$ ∴, $C = [R]_0$

⟹ put the following value in eqn(1).

$$\boxed{[R] = -Kt + [R]_0} \text{ — eq(11)}$$

here;

$[R]$ = concn of reactant at time 't'.
$[R]_0$ = initial concn of reactant.
K = rate constant.



Half life for zero order reaction:

in this case:

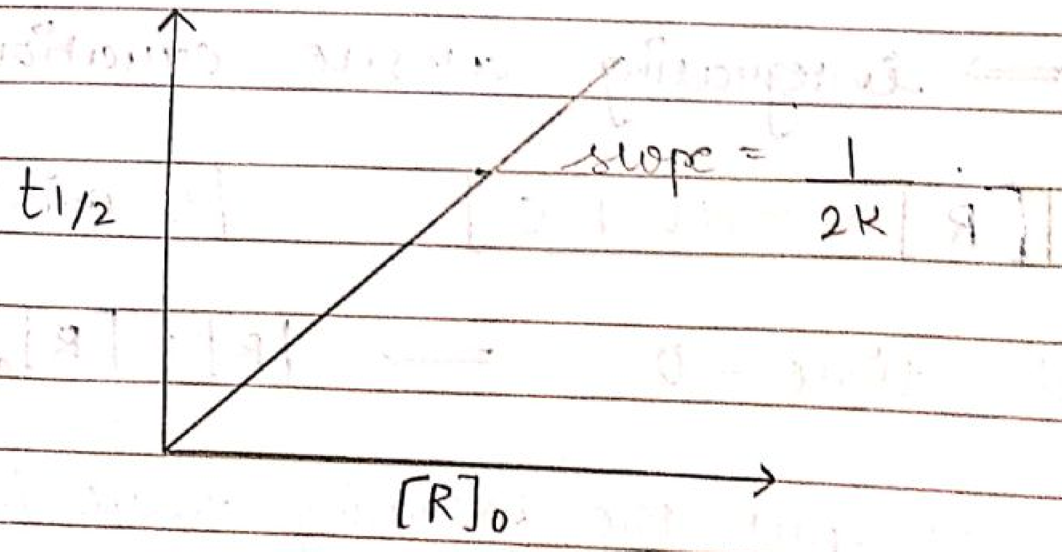
$$t = t_{1/2} \quad \therefore, \quad [R] = [R]_0/2$$

from eq(11):

$$\boxed{Kt = [R]_0 - [R]}$$

$$t_{1/2} = \frac{1}{K}\left[[R]_0 - \frac{[R]_0}{2}\right]$$

$$\boxed{t_{1/2} = \frac{[R]_0}{2 \cdot K}}$$



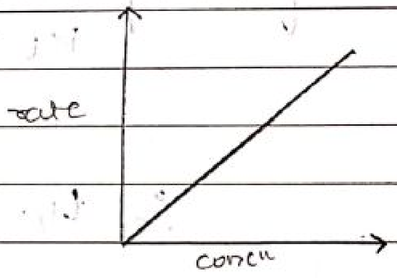
* First Order Reaction: (Imp. (Board) [illegible]

- reaction in which, rate of reaction is directly proportional to first power of the concentration of reactants.
- eg:
  - all naturals and artificial radioactive decay of unstable nuclei take place by 1st ord. kine
  - $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
  - $2N_2O_5 \longrightarrow NO_2 + O_2$
  - $2N_2O \longrightarrow 2N_2 + O_2$
  - $2H_2O_2 \longrightarrow 2H_2O + O_2$

*→ Integrated rate expression for FOR:

$$R \longrightarrow P$$

- $$\frac{-d[R]}{dt} = k[R]^1$$
- $$\frac{d[R]}{[R]} = -kt$$



⟹ integrating above eqn;

$$\boxed{\ln[R] = -kt + C} \text{ — eq(1)}$$

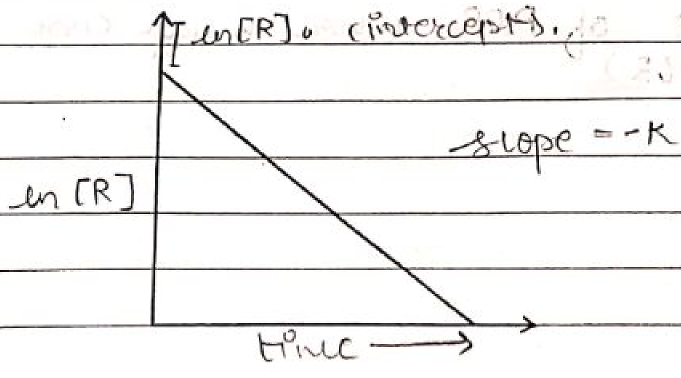
at

$$t = 0 \qquad [R] = [R]_0$$

$$\therefore C = \ln[R]_0$$

⟹ putting the value in eqn(1)

$$\boxed{\ln[R] = -kt + \ln[R]_0} \text{ — eq(II)}$$



$$Kt = \ln[R]_0 - \ln[R]$$

$\therefore$, $\boxed{Kt = \ln\frac{[R]_0}{[R]}}$ or. $\boxed{Kt = 2.303 \cdot \log\frac{[R]_0}{[R]}}$ eq (III)

$$\therefore, \boxed{t = \frac{2.303}{K}\log\frac{[R]_0}{[R]}}$$

→** Half life for first order reaction:

in this case;

$t = t/2$ $\therefore, [R] = [R]_0/2$

from eq (III);

$$Kt = 2.303 \log\frac{[R]_0}{[R]}$$

$$\therefore, t_{1/2} = \frac{2.303}{K}\log\frac{\cancel{[R]_0}}{\cancel{[R]_0}/2}$$

$$t_{1/2} = \frac{2.303}{K}\log 2$$

$$\therefore, \boxed{t_{1/2} = \frac{0.693}{K}}$$

Q: 7 $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ $K = 6.2 \times 10^{-4}$ sec^{-1}.

Find value of ROR when molar concn of N_2O_5 is 1.25 mole/ltr. (FOR)

→ rate $= \frac{d[R]}{dt} \longrightarrow K \cdot [R]$

$\Rightarrow (6.2 \times 10^{-4})(125 \times 10^{-2})$

$\Rightarrow 62 \times 10^{-5} \times 125 \times 10^{-2}$

$\Rightarrow 775 \times 10^{-7} \longrightarrow 7.75 \times 10^{-6}$ mol/lt.sec

Q:8 in the case of 'ZOR' ratio of required time for 75% completion to 50% completion is?

→

ROR ⇒ $Kt = [R]_0 - [R]$

C:1

$Kt = 100 - 25$

$t = \frac{75}{K}$ — eq(1)

C:2

$Kt = 100 - 50$

$t = \frac{50}{K}$ — eq(11)

(equating both).

$\frac{\overset{3}{\cancel{75}}}{\cancel{K}} : \frac{\overset{2}{\cancel{50}}}{\cancel{K}}$ → ratio = 1.5

3:2

Q:9 K for ZOR is 2×10^{-2} mol/ltr.sec. If conc^n^ of reactant after 25 sec is 0.5M initial conc^n^.

→ $Kt = [R]_0 - [R]$.

$(2 \times 10^{-2})(25) = x - 0.5$

$x = 0.5 + 0.5$ → 1M.

Q:10. A FOR is found to have $K = 5.5 \times 10^{-14}\ s^{-1}$. Find half-life for FOR:

→ $t_{1/2} \rightarrow \frac{0.693}{5.5 \times 10^{-14}}$

→ 1.26×10^{13} secs

Q:11 Show that in FOR time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of rxn.

$[R]_n = [R]_0 - 0.999[R]_0$

→ $K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

$$K = \frac{2.303}{t} \cdot \log \frac{[R]_0}{[R]_0 - 0.999[P]_0}$$

$$= \frac{2.303}{10} \log 10^3$$

$$\boxed{t = \frac{6.909}{K}}$$

- for half-life rxn

$$t_{1/2} = \frac{0.693}{K} \implies \frac{t}{t_{1/2}} = \frac{6.909}{\cancel{K}} \times \frac{\cancel{K}}{0.693} \rightarrow \underline{10}$$

*** NOTE:**

- remaining molar concⁿ after 'nth' half-life for First Order Reaction. is : $\frac{\text{initial conc}^n}{2^n}$

Q:12 in FOR reacting substance has half-life of 10mins. what fraction of substance will be left after an hour reaction occurred?

→ 1 half-life rxn takes 10mins.

∴ no. of ½ life rxn in 1hour (60mins) = 6 rxns

$$= \frac{1}{2^6} \longrightarrow \frac{1}{64} \text{ of } [R]_0$$

*** NOTE:**

$$100 \text{ mol/ltr} \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5$$

$$\downarrow t_{1/2}$$

$$1.5 \xleftarrow{t_{1/2}} 3.125 \xleftarrow{t_{1/2}} 6.25$$

Q:13 in 'FOR' amount of reactant decayed in 3 half lives (let a be initial amount) would be:

→ remaining molar concn $= \frac{1}{2^3} \longrightarrow \frac{a}{8}$ (R)

initial molar concn $= 1 \longrightarrow a$ $(R)_0$.

∴, amt of Reactant $= (R)_0 - (R)$.
$= a - a/8$
$\longrightarrow$ $\underline{7a/8}$.

Q:14 if $[R]_0$ of reactant is 50 mol/ltr for 'FOR' how many half lifes are required to consume it.

→ $50 \xrightarrow{} 25 \longrightarrow 12.5 \longrightarrow 6.25 \longrightarrow 3.125 \longrightarrow 1.5 \longrightarrow 0.78$

$\downarrow$

$0.0875 \xleftarrow{⑦} 0.175 \longleftarrow 0.35$

⑨ half lifes req

Q:15 'FOR' $[R]_0$ is 20 mol/ltr " find no. of 1/2 life req. → after [R] being 2.5 mol/ltr.

→ $20 \longrightarrow 10 \longrightarrow 5 \longrightarrow 2.5$.

③ half-lifes.

Q:16 Rate constant for rxn is $\ln 2/10$ min^{-1}. what will be the order of rxn and time taken to change concn from 1M to 0.25M.

→ $t = \frac{\ln 2}{K}$

∴, $t = \frac{\cancel{\ln 2}}{\cancel{\ln 2}/10}$

$t_{1/2} = 10$mins.

∴, $t_{1/2} = 2 \times 10$
$= \underline{20\text{mins}}$
(2 half-lifes).

$1 \xrightarrow{1} 0.5 \xrightarrow{2} 0.25$

$t = \frac{2.303}{K} \log \frac{1}{0.25}$ 4

$= \frac{2.303 \times 10}{2.303 \times 0.3010} \times \overset{2}{0.602}$

$t = \underline{20\text{mins}}$

→ unit of K for ZOR.

Q:17 K of $A \rightarrow 2B$ is 1×10^{-3} (mol/Ltr. min). If $[R]_0$ of A is 1 mole/Ltr then conc^n of B after 100 min.

→ $A \longrightarrow 2B$

Ini: a $\quad 0$

$a-x$ $\quad 2x$.

∴, $[R] = [R]_0 - Kt$.

$\cancel{a}-x = \cancel{a} - Kt$

$\underline{x = Kt}$. $\quad$ ∴, $x = 10^{-1}$ or 0.1 mol/Ltr.

$10^{-3}\times10^{2}$

∴, $2x = 1\times10^{-1}\times 2$

$= 0.2$ mol/Ltr.

* Methods to determine 'Order of Reaction':

(A.) On the basis of effect of conc^n on rate:

$A \longrightarrow$ Product (for a general reaction).

$$\text{Rate}_i = K[A]^n \longleftarrow eq(I)$$

after increase in conc^n of reactant 'x times':

$$\text{Rate}_f = K[xA]^n$$

$$\text{Rate}_f = x^n K[A]^n \longleftarrow eq(II)$$

comparing eq^n (I) and (II)

$$\boxed{\text{Rate}_f = x^n\cdot\text{Rate}_i}$$

CASE:01. if conc^n of reactant increases 'x times' but the rate doesn't get any impact then it's an "zero order reaction".

CASE:02. if conc^n of reactant increases 'x times' after than rate increases by 'x times' then its a "First order reaction".

CASE:03 if conc^n of reactant increases 'x times' resulting 'x^n times' increase in rate then its a "n^{th} order reaction".

eg: conc^n of reactant ↑ 2 times
rate ↑ 4 times.
⇒ which is '2^n' ∴ "2^2 times"
∴ second order reaction.

CASE:04 if conc^n of reactant increases 'x times' but there is a decrease in rate then its a "Negative order reaction".

$$\boxed{\text{Rate}_f = \frac{1}{x^n} \cdot \text{Rate}_i}$$

Q:18 board Data for the reaction $A + B \longrightarrow C$ is

Exp.	$[A]_0$	$[B]_0$	ini. rate
1.	0.012	0.035	0.10
2.	0.024	0.035	0.80
3.	0.012	0.070	0.10
4.	0.024	0.070	0.80

(a) $r = K[B]^3$ (b) $r = K[A]^3$ (c) $r = K[A][B]^4$
(d) $r = K[A]^2[B]^2$

on the basis of following find:
(a) rate law or rate eqn.
(b) order of rxn w.r.t A
(c) order of rxn w.r.t B
(d) overall net order of rxn.

⟹

exp.	$[A]_0$		$[B]_0$	Rate	
1	0.012	↑2x	0.035	0.10	↑ 8x (2^3x)
2	0.024		0.035	0.80	

∴ OOR wrt to A ⟶ 3^{rd} order rxn

exp.	$[A]_0$	$[B]_0$		Rate	
1	0.012	0.035	↑2x	0.10	no change
3	0.012	0.070		0.10	

∴ OOR wrt to B ⟶ 0 order rxn.

∴ Net order of rxn ⟹ 3+0 ⟶ 3^{rd} order rxn.

(a) ∴ Rate eqn ⟹ $K[A]^3[B]^0$

Q:19. $2A + B \longrightarrow C + D$.

exp.	[A]/mole/ltr	[B]/mole/ltr.	Rate.
1.	0.1	0.1	6×10^{-3}
2.	0.3	0.2	7.2×10^{-2}
3.	0.3	0.4	2.88×10^{-1}
4.	0.4	0.1	2.40×10^{-2}

Determine rate law and rate constant for rxn.

(B) Comparing data and reaction rate & conc^n :

- $\text{Rate}_1 = K[A]^n$ —— eq(I)
- $\text{Rate}_2 = K[A_2]^n$ —— eq(II)

comparing eq^n (I) and eq^n (II).

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[A_1]^n}{[A_2]^n}$$

$$\text{i.e., } \frac{\text{Rate}_1}{\text{Rate}_2} = \left[\frac{A_1}{A_2}\right]^n$$

$$\text{i.e., } \boxed{\log\left(\frac{r_1}{r_2}\right) = n \cdot \log\left(\frac{A_1}{A_2}\right)}$$

$$\text{i.e., } \boxed{n = \frac{\log(r_1/r_2)}{\log(A_1/A_2)}}$$

(C.) Half life method:

- this method is based upon the fact that the "half changed time is inversely proportional to initial conc^n of reactant which rises to power 1 less than the order of reactant".

$$\text{i.e., } \boxed{t_{1/2} = \frac{1}{a^{n-1}}}$$

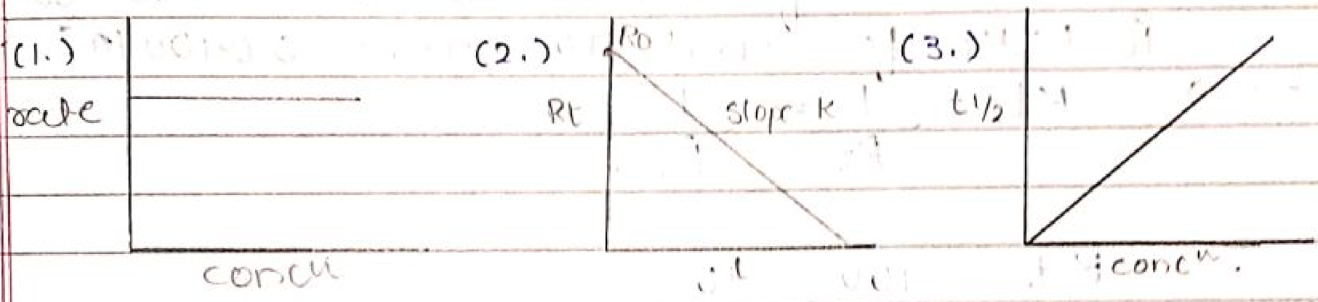
- For zero order reaction: $t_{1/2} = 0$

- For first order reaction: half life is independent of initial concentration

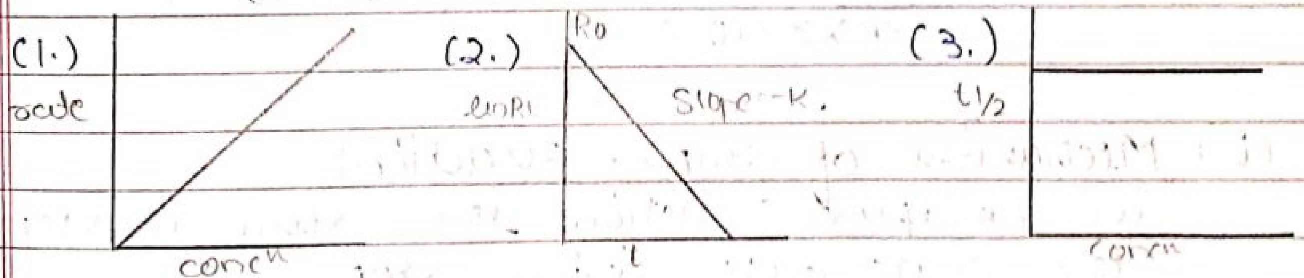
(D.) Graphical representation:

- Applicable only when one reactant is available in a reaction.

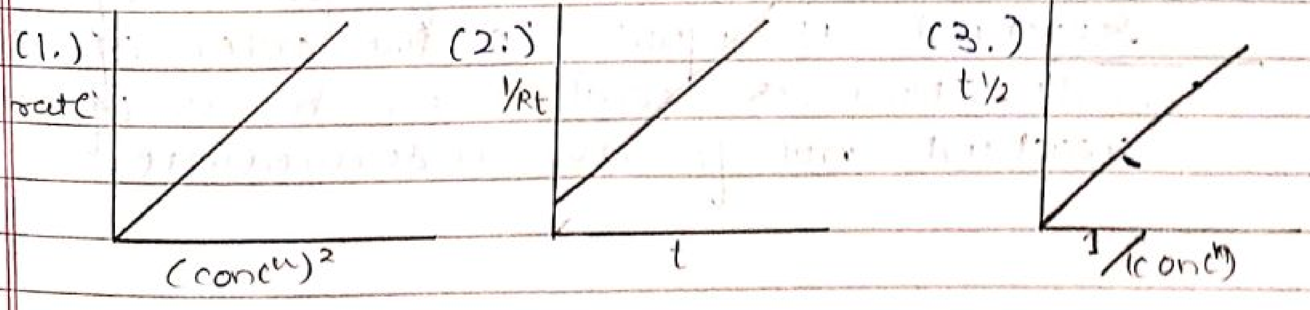
→ Graph for 'ZOR': $(Kt = R_0 - R_t)$



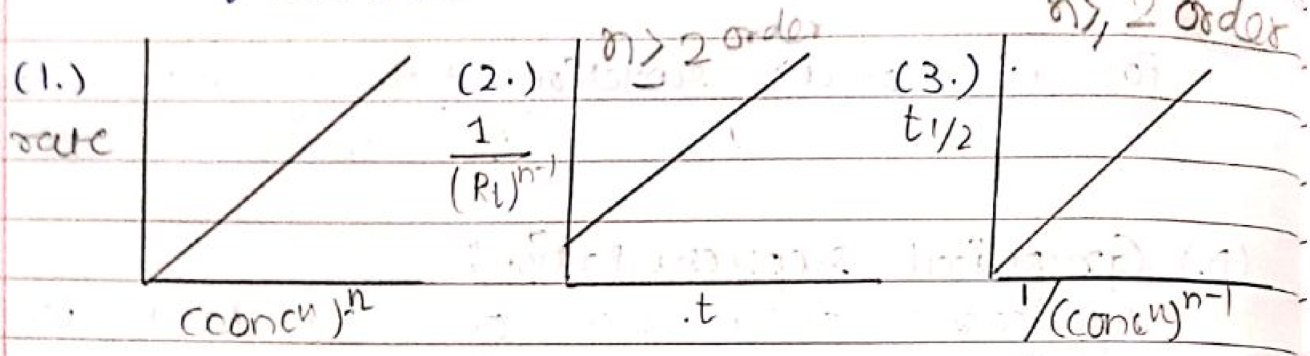
→ Graph for 'FOR': $(Kt = \ln R_0 - \ln R_t)$



→ Graph for 'SOR': $(Kt = 1/R_t - 1/R_0)$ $\therefore t_{1/2} \propto 1/a^{n-1}$



→ Graph for 'n^th' order reaction:



Q:20 A 'SOR' has rate constant of 2×10^{-3} L/mol·sec. If initial conc^n of reactant is 0.2 M. How long will it take for conc^n to become 0.0400 M?

→ $$Kt = \frac{1}{R_t} - \frac{1}{R_0}.$$

$$K\cdot t = \frac{100}{4} - \frac{10}{2}.$$

$$t = \frac{\cancel{80}\ \cancel{20}\ 10}{\cancel{4}\times\cancel{2}\times10^{-3}} \longrightarrow t = 10^4 \text{ secs}$$

By

(E.) Mechanism of complex reaction:

- in complex reaction the slowest step is the rate determining step.
- therefore, firstly one should show the rate law of slow step reaction.
- now, the summation of power of conc^n of reactant is equal to the order of reaction
- rate law is written in terms of conc^n of reactant not for an intermediate.