

Ques. How many mole of $(\text{NH}_4)_2\text{SO}_4$ should be added to 500ml of NH_4OH 0.01M NH_4OH solution to prepared a buffer of pH 8.28 If pka value of ammonium ion is 9.26.

→ Mole of $(\text{NH}_4)_2\text{SO}_4 = \eta \text{ mol}$

$$\text{Eq. of } (\text{NH}_4)_2\text{SO}_4 = \eta \times 2 \text{ eq.}$$

v.f. = 2

$$\text{Eq. of } \text{NH}_4\text{OH} = N \times \text{Vol (L)}$$

v.p. = 0.01 \times \frac{500}{1000}

$$= 5 \times 10^{-3}$$

$$\text{pH} = 8.26 \Rightarrow \text{pOH} = 5.74$$

$$\text{pKa} (\text{NH}_4^+) = 9.26 \Rightarrow \text{pKb} (\text{NH}_4\text{OH}) = 4.74$$

$$\text{pOH} = \text{pKb} + \log \frac{(\text{Salt})}{(\text{Base})}$$

$$5.74 = 4.74 + \log \frac{(2\eta)}{(5 \times 10^{-3})}$$

$$1 = \log \left(\frac{2\eta}{5 \times 10^{-3}} \right)$$

$$\frac{2\eta}{5 \times 10^{-3}} = \text{Antilog}(1) = 10^1$$

$$2\eta = 5 \times 10^{-3}$$

$$\eta = 2.5 \times 10^{-2} \text{ mol}$$

Ques 0.02M of HCl is added in a mixture of 0.1M CH_3COONa and 0.1M acetic acid then calculate the pH of resulting solution (Given pka of CH_3COOH is 4.74).
↑
Acetic acid

$$pH = pK_a + \log \frac{(\text{Salt})}{(\text{Acid})} = \frac{(\text{C. Base})}{(\text{Acid})} = \left(\frac{\text{CH}_3\text{COO}^-}{\text{CH}_3\text{COOH}} \right) + H^+$$

$$pH = 4.74 + \log \left(\frac{0.1 - 0.02}{0.1 + 0.02} \right)$$

$$= 4.74 + \log \left(\frac{0.08}{0.12} \right)$$

$$= 4.74 + 0.18$$

$$= 4.56$$

Ques. Calculate the pH of 10 L solution that contains 60 mg of acetic acid (CH_3COOH) and 20 g Sodium hydroxide (NaOH) (Given K_a of $\text{CH}_3\text{COOH} = 2 \times 10^{-5}$)

~~$pH = pK_a + \log \frac{(\text{Salt})}{(\text{Acid})}$~~



No. of eq. = moles \times v.f.

$$\frac{60 \times 10^{-3}}{60} \times 1$$

$$\frac{20 \times 10^{-3}}{40} \times 1$$

Initial = 1×10^{-3}

0.5×10^{-3}

LR

Final = 0.5×10^{-3}
WA

0.5×10^{-3}
WASA

0.5×10^{-3}

$$pH = pK_a + \log \frac{(\text{Salt})}{(\text{Acid})}$$

$$= 4.7 + \log \left(\frac{0.5 \times 10^{-3}}{0.5 \times 10^{-3}} \right)$$

$$pH = 4.7$$

Ques. In previous question ~~40g~~ 40g of NaOH.

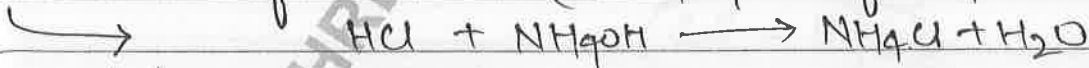


No. of eq. = mol x v.f

$\frac{60 \times 10^3}{60} \times 1$	$\frac{40 \times 10^3}{40}$		
1×10^{-3}	1×10^{-3}		
0	0	1×10^{-3}	1×10^{-3}
		was salt	

$$\begin{aligned} \text{pH} &= 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c \\ &= 7 + \frac{1}{2} (4.7) + \frac{1}{2} \log \left(\frac{1 \times 10^{-3}}{10} \right) \\ &= 7 + 2.35 + \frac{1}{2} (-4) \\ &= 7 + 2.35 - 2 \\ \text{pH} &= 7.35 \end{aligned}$$

Ques. Calculate the pH of a solution prepared by mixing 50ml of 0.02M ~~NaOH~~ NH_4OH with 50ml of 0.02M of HCl (Given $\text{p}K_b$ of $\text{NH}_4\text{OH} = 4.7$).



No. of eq. = N x vol (L)

$\frac{0.02 \times 1 \times 50}{1000}$	$\frac{0.02 \times 1 \times 50}{1000}$		
Initially 1×10^{-3}	$= 1 \times 10^{-3}$		
finally —	—	1×10^{-3}	1×10^{-3}
		SAWES	

$$\begin{aligned} \text{pH} &= 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log c \\ &= 7 - \frac{1}{2} (4.7) - \frac{1}{2} \log \left(\frac{1 \times 10^{-3}}{0.1} \right) \end{aligned}$$

$$= 7 - 2.35 - \frac{1}{2}(-2)$$

$$= 7 - 2.35 + 1$$

$$= 5.65$$

Q In previous question 0.01M of HCl. Calculate pH



$$\text{No. of eq} = N \times \text{Vol}(l)$$

$$= \frac{0.01 \times 1 \times 50}{1000} \quad \frac{0.02 \times 1 \times 50}{1000}$$

Initially $\frac{0.5 \times 10^{-3}}{\text{LR}}$

1×10^{-3}

finally \ominus

$\frac{0.5 \times 10^{-3}}{\text{WB}}$

$\frac{0.5 \times 10^{-3}}{\text{SAWB}}$

0.5×10^{-3}

$$\text{pOH} = \text{pK}_b + \log \frac{(\text{Salt})}{(\text{Base})}$$

$$\text{pOH} = \text{pK}_b = 4.7$$

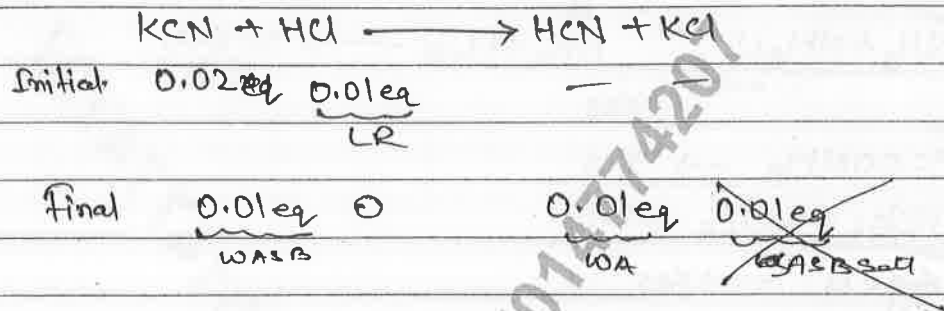
$$\text{pH} = 9.3$$



[Weak electrolytes] > [Strong electrolytes] \Rightarrow Buffer

[Weak electrolytes] = [Strong electrolytes] \Rightarrow Salt

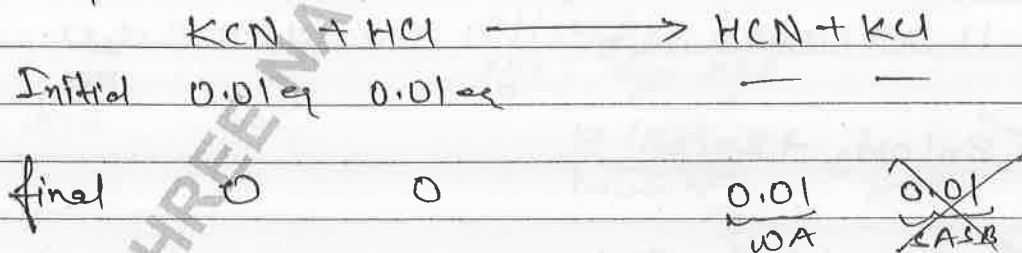
Ques: 0.02mole of KCN and 0.01mole of HCl are mixed in the aqueous solution then find out the ^{pH of} resulting solution (Given K_a of HCN = 10^{-6})



$$pH = pK_a + \log \left(\frac{\text{Salt}}{\text{Acid}} \right)$$

$$pH = pK_a = 6$$

Ques: In previous question 0.01mole of KCN then calculate pH.



$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log c$$

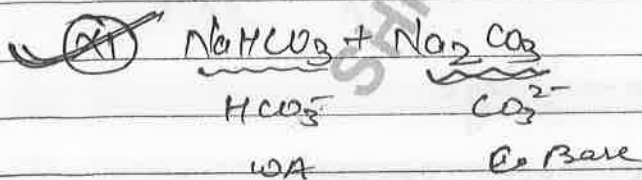
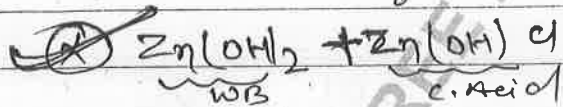
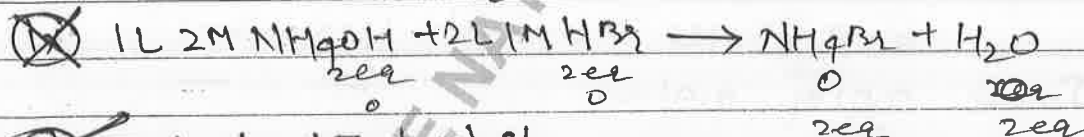
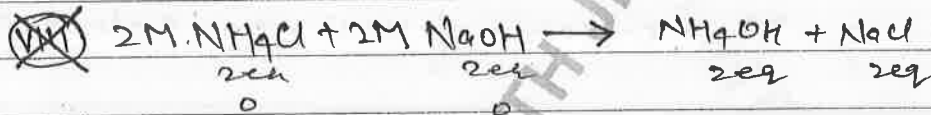
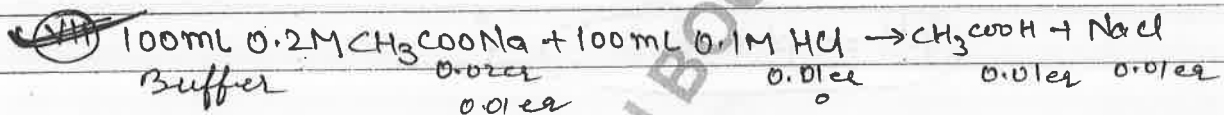
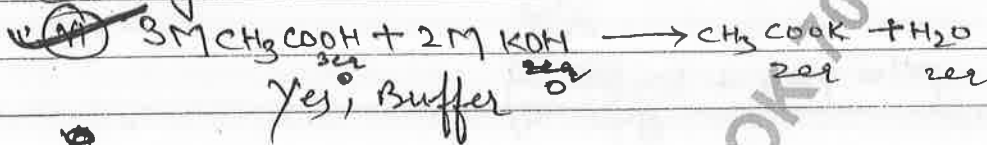
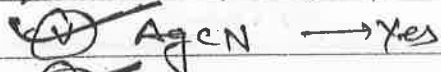
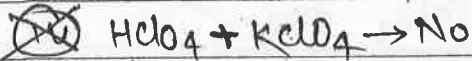
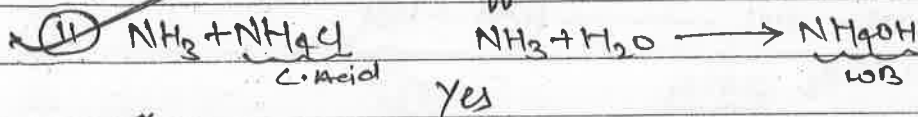
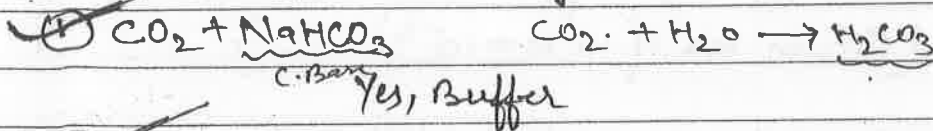
$$= \frac{1}{2} (6) - \frac{1}{2} \log \left(\frac{0.001}{1} \right)$$

$$= 3 - \frac{1}{2} \log (10^{-3})$$

$$= 3 - \frac{1}{2} (-3)$$

$$= 3 + 1.5 = 4.5$$

Ques: Which of the following will act as a buffer solution.



Ques. Calculate the buffer capacity of 1L acidic buffer solution whose pH changed from 3.9 to 3.4 on adding 4mol of HCl into it.

$$B.C. = \frac{\text{No. of moles added}}{\text{pH change}}$$

$$= \frac{4}{0.5} = 8$$

INDICATOR :-

Ques. Which indicator is suitable for the titration of HClO_4 with

CaOH :-

HClO_4
SA

CaOH
SB

(I) MeOH

(II) HPh

(III) Both

(IV) N.O.T.

Q. which indicator is suitable for the titration of HCOOH &

KOH
SB

(I) MeOH

(II) HPh

(III) Both

Q. which indicator is suitable for the titration of NH_4Cl &

NaOH
SB

SAWA Salt

weakly acid

(I) MeOH

(II) HPh

(III) Both

Ques. Methyl Orange can be used as indicator for the titration of w.o.f. ?

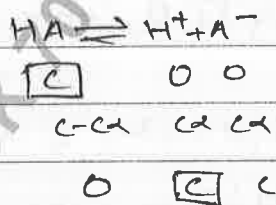
- (I) HI & RbOH
 (II) HF & CsOH
 (III) H_2S_2 & NH_4OH
 (IV) ~~Both (I) & (II)~~

pH Calculation: —

(I) for SA and SB: —

for SA $\Rightarrow [\text{H}^+] = c$

for SB $\Rightarrow [\text{OH}^-] = c$



Ques. Calculate the pH $6 \times 10^{-5} \text{ M}$ HCl solution

$$[\text{HCl}] = 6 \times 10^{-5} \text{ M, N}$$

v.f. = 1

$$[\text{H}^+] = c = 6 \times 10^{-5} \text{ N}$$

$$\text{pH} = -\log(6 \times 10^{-5})$$

$$= 5 - \log 6 = 4.22$$

Ques. Calculate the pH of 4.9 mg of H_2SO_4 present in 200 mL solution?



$$4.9 \times 10^{-3}$$

$$[\text{H}_2\text{SO}_4] = 4.9 \times 10^{-3}$$

~~pH = -\log(4.9 \times 10^{-3})~~

$$(\text{H}_2\text{SO}_4) = c = M \times v.f.$$

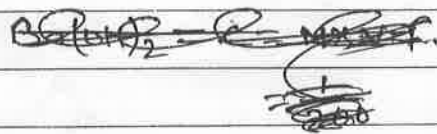
$$= \frac{4.9 \times 10^{-3}}{98 \times \frac{200}{1000}} \times 2$$

$$\Rightarrow 5 \times 10^{-4} \text{ N}$$

$$\text{pH} = 4 - \log 5$$

$$= 3.3$$

Ques Calculate the pH of $\frac{1}{200}$ $\text{Ba}(\text{OH})_2$ solution at 90°C temp.



$$\text{Ba}(\text{OH})_2 = \frac{1}{200} \text{ N}$$

$$[\text{OH}^-] = C = \frac{1}{200} \text{ N} = 5 \times 10^{-3} \text{ N}$$

$$\text{pOH} = 3 - \log 5 = 2.3$$

$$\text{pH} = 12 - 2.3$$

$$= \underline{9.7}$$

Q Calculate the mass of $\text{Ba}(\text{OH})_2$ that is required to prepared 1L of a solution having pH equal to 12. (Given $\text{Ba} = 137$)

$$\text{Ba}(\text{OH})_2 = 171$$

~~$\text{Ba}(\text{OH})_2 = \frac{1}{10^2}$~~

$$= \frac{1}{10^2} \times 2$$

$$= \frac{2}{10^2}$$

$$\text{pH} = 12$$

$$\text{pOH} = 10^{-2} \text{ N} = [\text{Ba}(\text{OH})_2]$$

~~$\text{Ba}(\text{OH})_2 = 10^{-2} \text{ N} = \frac{1}{10^2}$~~

$10^{-2} \Rightarrow \text{mass}$

$$\text{Ba}(\text{OH})_2 = 10^{-2} = \text{M} \times \text{V} \cdot \text{f}$$

$$10^{-2} = \frac{\text{mass}}{171 \times 1} \times 2$$

$$\text{mass} = 0.855 \text{ g}$$

Ques. Calculate the pH of $10^{-7} M$ HCl solution

$$\begin{aligned}
 [HCl] &= 10^{-7} & [H^+] &= 10^{-7} N \\
 [H^+]_{HCl} &= 10^{-7} & [H^+]_{H_2O} &= 10^{-7} N \\
 &= 7 - \log 10 & \text{Total } [H^+] &= 10^{-7} + 10^{-7} \\
 & & &= 2 \times 10^{-7} N \\
 & & \text{pH} &= 7 - \log 2 \\
 & & &= 6.7
 \end{aligned}$$

pH of very dilute solⁿ of SA & SB :-

⇒ Very dilute ⇒ Conc. $\leq 10^{-7}$ ($10^{-7}, 10^{-8}, 10^{-9}$) solⁿ.

⇒ Consider (H^+) & (OH^-) of H_2O

Ques. Calculate the pH of $10^{-8} M$ NaOH solⁿ.

$$[OH^-] = 10^{-8} N$$

$$[OH^-]_{NaOH} = 10^{-8} N$$

$$[OH^-]_{H_2O} = 10^{-7} M$$

$$\text{Total } [OH^-] = 10^{-8} + (10 \times 10^{-8})$$

$$= 11 \times 10^{-8}$$

$$\text{pOH} = \log 11 \approx 8 - \log 11$$

$$= 8 - 1.04$$

$$= 6.94$$

$$\text{pH} = 14 - 6.94 = 7.04$$

Note:— For very dilute solⁿ, the pH value range from

for SA \Rightarrow 6.7 to 7
for SB \Rightarrow 7 to 7.3

Ques. The pH of 10^{-10} M KOH solⁿ will be

- (i) 10
- (ii) 4
- (iii) 6.98
- (iv) 7.02

Ques. The pH of 10^{-5} M HCl solⁿ solⁿ dilute 1000 times will be

- (i) 5
- (ii) 9
- (iii) 6.96
- (iv) 7.04

Law of Dilution:—

Eq. Before dilution = Eq. of after dilution

$$N_i V_i = N_f V_f$$

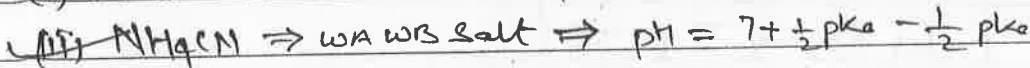
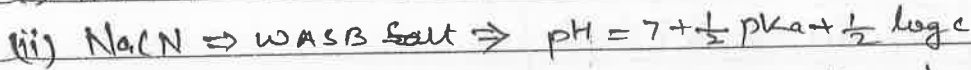
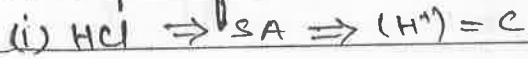
$$10^{-5} \times 1 = N_f \times 1000$$

$$N_f = 10^{-8} N$$

Ques. The pH of a solution having the (H^+) concentration equal to 10^{-9} N will be.

- (i) 9
- (ii) 5
- (iii) 6.98
- (iv) 7.02

ues. The pH of w.o.f. solution does not depends up dilution



ues. The pH of 1L solution is found to be 2 then determine the required volume of water to change its pH to 4.

1L \rightarrow pH=2 $\quad V_i = 1\text{L}$ $\text{pH}=2 \Rightarrow (\text{H}^+) = 10^{-2}\text{N} = N_i$
 pH=4 $\quad V_f = ?$ $\text{pH}=4 \Rightarrow (\text{H}^+) = 10^{-4}\text{N} = N_f$

Law of dilution

$$N_i V_i = N_f V_f$$

$$10^{-2} \times 1 = 10^{-4} \times V_f$$

$$V_f = 100\text{L}$$

$$\therefore \text{Req. Vol.} = 100 - 1$$

$$\text{of H}_2\text{O} = 99\text{L}$$

ues. The pH of 10L solution is found to be 11 then calculate the required vol. of H_2O to change its pH to 8.

$V_i = 10\text{L}$ $\text{pH}=11 \Rightarrow (\text{OH}^-) = 10^{-3}\text{N} = N_i$
 $V_f = ?$ $\text{pH}=8 \Rightarrow (\text{OH}^-) = 10^{-6}\text{N} = N_f$

$$N_i V_i = N_f V_f$$

$$10^{-3} \times 10 = V_f \times 10^{-6}$$

$$10^{-10} = V_f \times 10^{-8}$$

$$V_f = 10$$

$$pH = 11 \Rightarrow pOH = 3 \Rightarrow [OH^-] = 10^{-3} N = N_i$$

$$pH = 8 \quad pOH = 6 \Rightarrow [OH^-] = 10^{-6} N = N_f$$

$$N_i V_i = N_f V_f$$

$$10^{-3} \times 10 = 10^{-6} \times V_f$$

$$V_f = 10^4 L$$

$$\therefore \text{Req. Vol.} = 10^4 - 10$$

$$\text{of } H_2O = \underline{\underline{9990 L}}$$

$$\sqrt{C} \propto \frac{1}{\sqrt{V}}$$

Ques. Calculate the no. of mole of HCl that must be removed from 1L of aqueous solution of HCl so, that its pH changes from 2 \rightarrow 3.

$$pH = 2 \Rightarrow [H^+] = 10^{-2} N \Rightarrow \text{Eq. of } (H^+)_i = 10^{-2} \times 1 = 10^{-2} \text{ eq.}$$

$$pH = 3 \Rightarrow [H^+] = 10^{-3} N \Rightarrow \text{Eq. of } (H^+)_f = 10^{-3} \times 1 = 10^{-3} \text{ eq.}$$

$$\begin{aligned} \text{Eq. of } (H^+) \text{ to be removed} &= 10^{-2} - 10^{-3} \\ &= (10 \times 10^{-3}) - 10^{-3} \\ &= 9 \times 10^{-3} \text{ eq.} \end{aligned}$$

$$\begin{aligned} \text{Eq. of HCl to be removed} &= \text{Moles of HCl to be removed} \times v.f \\ 9 \times 10^{-3} &= \text{moles} \times 1 \end{aligned}$$

\therefore Moles of HCl

$$\text{to be removed} = \underline{\underline{9 \times 10^{-3} \text{ moles}}}$$

PH of mixture of SA & SB :—

(A) Homogenous mixture :—

$$N_f V_f \Rightarrow N_1 V_1 + N_2 V_2$$

Vol. of final solⁿ = $V_f = (V_1 + V_2)$

Normality of final solⁿ = $N_f = (H^+)_{\text{final}}$ or $(OH^-)_{\text{final}}$

(B) Heterogenous mixture :—

(i) $(NV)_{\text{acid}} > (NV)_{\text{base}}$

$$N_f V_f = (NV)_{\text{acid}} - (NV)_{\text{base}}$$

$N_f = (H^+)_{\text{final}}$
 Solⁿ of acidic

(ii) $(NV)_{\text{acid}} < (NV)_{\text{base}}$

$$N_f V_f = (NV)_{\text{base}} - (NV)_{\text{acid}}$$

$N_f = (OH^-)_{\text{final}}$
 Solⁿ of basic

(iii) $(NV)_{\text{acid}} = (NV)_{\text{base}}$

Solⁿ will be neutral

Ques Calculate of pH of solution prepared by mixing 300ML $N/10$ HNO_3 900ML $N/20$ H_2SO_4 & 300ML $N/30$ HCl .

~~$N_f V_f = N \times 300$~~

$$N_1V_1 + N_2V_2 + N_3V_3$$

$$\left(\frac{1}{10} \times 300\right) + \left(\frac{1}{20} \times 400\right) + \left(\frac{1}{30} \times 300\right) \Rightarrow N_f (1000)$$

$$N_f = \frac{60}{1000} N \Rightarrow 6 \times 10^{-2} N = [H^+]$$

$$\begin{aligned} \therefore \text{pH} &= 2 - \log 6 \\ &= \underline{1.22} \end{aligned}$$

Ques. Calculate the pH of solⁿ prepared by mixing
KOH \Rightarrow 200 mL $\frac{M}{10}$, 400 mL $\frac{M}{20}$ $\text{Ba}(\text{OH})_2$ & 300 mL $\frac{M}{30}$ NaOH

If 1100 mL extra water added.

$$N_1V_1 + N_2V_2 + N_3V_3$$

$$200\left(\frac{1}{10} \times 200\right) + \left(\frac{1}{20} \times 400\right) + \left(\frac{1}{30} \times 300\right) \Rightarrow N_f (2000)$$

$$N_f = \frac{40}{2000} N = \cancel{4 \times 10^{-2} N} = \cancel{[OH^-]}$$

$$\Rightarrow 3.5 \times 10^{-2} N = [OH^-]$$

$$\begin{aligned} \therefore \text{pOH} &= 2 - \log 3.5 = 2 - 0.54 \\ &= 1.46 \end{aligned}$$

$$\begin{aligned} \text{pH} &= 14 - 1.46 \\ &= \underline{12.54} \end{aligned}$$

Ques. Calculate the pH of a solution prepared by mixing 200 mL of solⁿ having pH equal to 2 when 300 mL of solⁿ having pH = 4

$$\begin{aligned} 200 \text{ mL pH} = 2 &\Rightarrow [H^+] = 10^{-2} N \Rightarrow N_1 \\ 300 \text{ mL pH} = 3 &\Rightarrow [H^+] = 10^{-3} N \Rightarrow N_2 \end{aligned}$$

$$N_f V_f = N_1 V_1 + N_2 V_2$$

$$N_f (500) = (10^{-2} \times 200) + (10^{-3} \times 300)$$

$$N_f = \frac{2.03}{500} = 4 \times 10^{-3} N = [H^+]$$

$$\begin{aligned} \text{pH} &= 3 - \log 4 \\ &= 2.4 \end{aligned}$$

Ques. pH = ? 300 mL $\frac{N}{10}$ HNO₃ with 700 mL $\frac{N}{20}$ KOH

$$N_1 V_1 + N_2 V_2 = N_f (1000)$$

$$\left(\frac{1}{10} \times 300 \right) + \left(\frac{1}{20} \times 700 \right) = N_f (1000)$$

$$30 + 35 = N_f (1000)$$

$$N_f = \frac{65}{1000}$$

$$\text{No. of meq} = N \times V_1 (\text{mL})$$

$$= \frac{1}{10} \times 300 = 30 \text{ meq.}$$

$$\text{meq of KOH} = \frac{1}{20} \times 700 = 35 \text{ meq.}$$

$$(N \cdot V)_{\text{base}} > (N \cdot V)_{\text{acid}}$$

$$N_f V_f = (NV)_{\text{base}} - (NV)_{\text{acid}}$$

$$N_f / 1000 = 35 - 30 = 5$$

$$N_f = 5 \times 10^{-3} N = (OH^-)$$

$$\therefore pOH = 3 - \log 5 = 2.3 \Rightarrow pH \approx 11.7$$

Ques. 9.8 mg H_2SO_4 with 4 mg $NaOH$ in 10L solⁿ?

$$\begin{aligned} \text{Eq. of } H_2SO_4 &= (\text{moles} \times v.f) \\ &= \frac{9.8 \times 10^{-3}}{98} = 2 \times 10^{-4} \end{aligned}$$

$$\begin{aligned} N_f V_f &= (2 \times 10^{-4}) - (1 \times 10^{-4}) \\ N_f / 10 &= (2 \times 10^{-4}) - (1 \times 10^{-4}) \end{aligned}$$

$$\begin{aligned} \text{Eq. of } NaOH &= \text{mole} \times v.f \\ &= \frac{4 \times 10^{-3}}{40} = 1 \times 10^{-4} \text{ eq} \end{aligned}$$

$$N_f = 1 \times 10^{-5} N = (H^+)$$

$$\begin{aligned} \text{pH} &= 5 \end{aligned}$$

$$(NV)_{\text{acid}} > (NV)_{\text{base}}$$

Ques. 200 mL $pH = 2 = (H^+) = 10^{-2} N$

300 mL $pH = 12 = pOH = 2 \Rightarrow (OH^-) = 10^{-2} N$

$$(NV)_{\text{acid}} = 10^{-2} \times 200 = 2 \text{ meq.}$$

$$(NV)_{\text{base}} = 10^{-2} \times 300 = 3 \text{ meq.}$$

$$(NV)_{\text{base}} > (NV)_{\text{acid}}$$

$$N_f V_f = (NV)_{\text{base}} - (NV)_{\text{acid}}$$

$$N_f / 500 = 3 - 2 \Rightarrow 1$$

$$N_f = \frac{1}{500} = 2 \times 10^{-3} N$$

$$pOH = 3 - \log 2$$

$$= 2.7$$

$$pH = 11.3$$

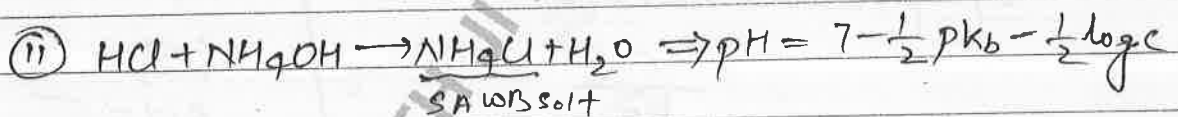
Ques. The pH of 100mL 0.01M HCl solution will remain unchanged in

- (i) 100mL 0.01M NaCl
- (ii) 100mL 0.01M NH₄OH
- (iii) 100mL 0.01M HCl
- (iv) 100mL 0.01M NaOH

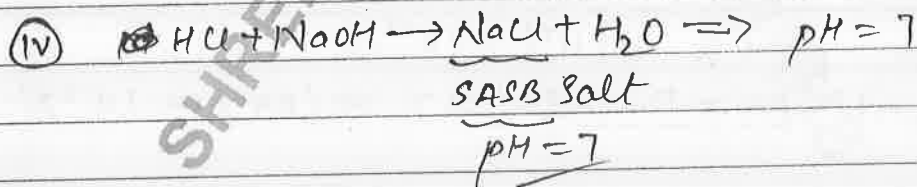
$$0.01M HCl = [H^+] \Rightarrow 10^{-2} N$$

$$pH = 2$$

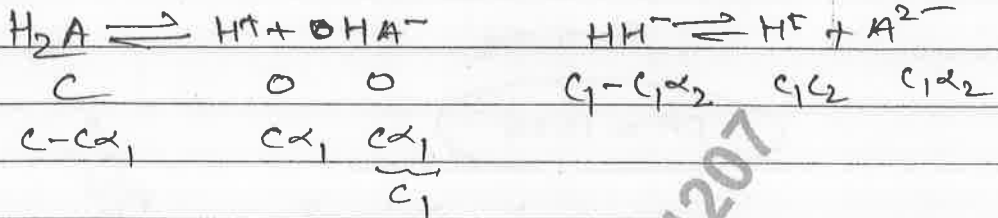
$$(i) [H^+] = \frac{100 \times 0.01}{200} = 5 \times 10^{-3} \Rightarrow pH = 2.3$$



$$(iii) [H^+] = \frac{100 \times 0.01 + (100 \times 0.01)}{200} \Rightarrow 10^{-2} N \Rightarrow pH = 2$$



Polyacidic base and polybasic acids: —



$$\text{Total } (\text{H}^+) = \text{C}\alpha_1 + \text{C}_1\alpha_2$$

$$= \text{C}\alpha_1 + \text{C}_1\alpha_2$$

$$\boxed{\text{Total } (\text{H}^+) = \text{C}\alpha_1 (1 + \alpha_2)}^*$$

Ques. Calculate the pH of $2 \times 10^{-4} \text{M}$ H_3PO_4 solution if α_1 is 100%, α_2 is 50%, and α_3 is negligible.

$$(\text{H}^+) = \text{C}\alpha_1 (1 + \alpha_2)$$

$$= 2 \times 10^{-4} \times 1 (1 + 0.5)$$

$$= 3 \times 10^{-4} \text{N}$$

$$\text{pH} = 4 - \log 3$$

$$= 3.52$$

↳ 3rd step ka Valency factor एक ही है। Because 3rd step में एक ही H^+ बाहर आ रहा है।

Ques. Calculate the pH of 10^{-3}M $\text{Mg}(\text{OH})_2$ solution if α_1 is 80% & α_2 is 50%.

$$(\text{OH}^-) = \text{C}\alpha_1 (1 + \alpha_2)$$

$$= 10^{-3} \times \frac{80}{100} \left(1 + \frac{50}{100} \right)$$

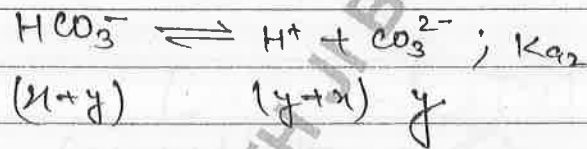
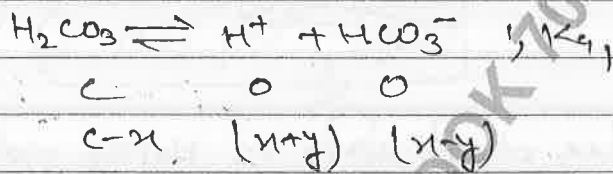
$$= 10^{-3} \times 0.8 (1 + 0.5)$$

$$= 1.2 \times 10^{-3} \text{N}$$

$$\begin{aligned} \text{pOH} &= 3 - \log 2.2 \\ &= 3 - 0.34 \\ &= 2.66 \end{aligned}$$

$$\text{pH} = 11.06$$

Ques. Calculate pH ^{bicarbonate} $[\text{HCO}_3^-]$ & ^{carbonate} $[\text{CO}_3^{2-}]$ concentration present in 0.025M H_2CO_3 if $K_{a1} = 4 \times 10^{-7}$ and $K_{a2} = 7 \times 10^{-11}$



$$[\text{H}^+] = x+y \approx x$$

$$[\text{HCO}_3^-] = x-y \approx x$$

$$[\text{CO}_3^{2-}] = y$$

$$K_{a1} = \frac{(x+y)(x-y)}{(c-x)}$$

$$\text{As } K_{a1} \gg \gg \gg K_{a2}$$

$$\therefore x \gg y$$

$$\therefore K_{a1} \approx \frac{x^2}{c}$$

$$x = \sqrt{K_{a1} \times c}$$

$$x = \sqrt{4 \times 10^{-7} \times 0.025}$$

$$x = 10^{-4}$$

$$\therefore [\text{HCO}_3^-] \approx [\text{H}^+] \approx x \approx 10^{-4} \text{ M}$$

$$\therefore \text{pH} = 4$$

$$K_{a2} = \frac{[x][y]}{[x-y]} = \frac{x \cdot y}{x} = y$$

$$\therefore [\text{CO}_3^{2-}] = y = K_{a2} = 7 \times 10^{-11} \text{ M}$$

OR

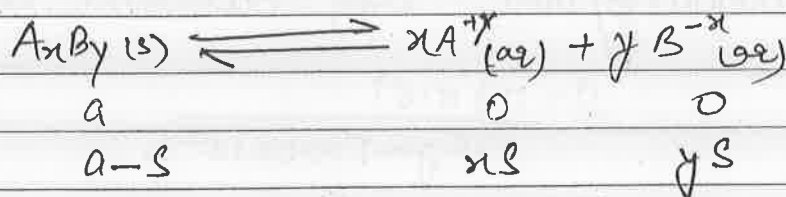
As $K_{a1} \gg \gg K_{a2}$

$$[\text{H}^+] = \sqrt{K_{a1} \times c}$$

$$[\text{1st anion}] = [\text{H}^+] = \sqrt{K_{a1} \times c}$$

$$[\text{2nd anion}] = K_{a2}$$

Solubility Product (K_{sp}): —



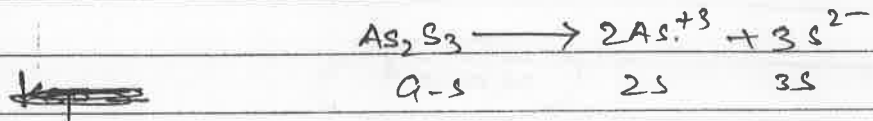
$$K_{sp} = (A^{+y})^x \cdot (B^{-x})^y$$

$$K_{sp} = (xs)^x \cdot (ys)^y$$

$$K_{sp} = x^x \cdot y^y \cdot s^{(x+y)}$$

Ques. Calculate the K_{sp} value of (As_2S_3) if its solubility is found to be $1 \times 10^{-5} \text{ mol L}^{-1}$

Ans:-



$$\begin{aligned} K_{sp} &= (As^{+3})^2 \cdot (S^{2-})^3 \\ &= (2s)^2 \cdot (3s)^3 \\ &= 2^2 \cdot 3^3 \cdot s^{2+3} \\ &= 4 \times 27 \times (10^{-5})^5 \\ &= 108 \times 10^{-25} \\ &= 108 \times 10^{-25} \\ &\approx 1.08 \times 10^{-23} \text{ mol}^5 \text{ L}^{-5} \end{aligned}$$

Ques. The K_{sp} value of $CaCl_2$ is 3.2×10^{-11} then determine its solubility.

$$\begin{aligned} K_{sp} &= [Ca^{+2}] \cdot [Cl^{-}]^2 \\ 3.2 \times 10^{-11} &= (s) \cdot (2s)^2 \\ 3.2 \times 10^{-11} &= 1 \cdot 2^2 \cdot s^{(1+2)} \\ s &= (8 \times 10^{-12})^{1/3} \\ s &= 2 \times 10^{-4} \text{ M} \end{aligned}$$

Ques. The solubility of Ag_2CrO_4 is found to be 0.000118 g/10 mL then determine the K_{sp} value.

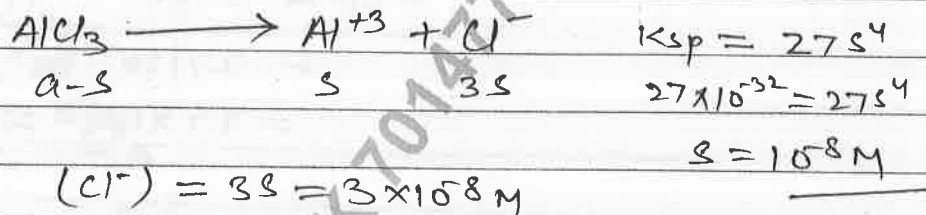
$$\begin{aligned} s &= \frac{118 \times 10^{-7}}{236 \text{ g mol}^{-1} \times 10 \times 10^{-3} \text{ L}} \\ s &= 5 \times 10^{-6} \end{aligned}$$

$$K_{sp} = S^2 = (5 \times 10^{-6})^2$$

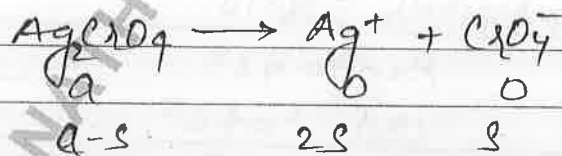
$$= 25 \times 10^{-12}$$

$$= 2.5 \times 10^{-11} \text{ mol}^2 \text{ L}^{-2}$$

Ques. The K_{sp} value for AlCl_3 is found to be 2.7×10^{-31} then determine the chloride ions concentration in its saturated solution.



Ques. Calculate the K_{sp} value of Ag_2CrO_4 if the concentration of Ag^+ in its saturated solution is found to be $2 \times 10^{-4} \text{ M}$



~~$$K_{sp} = (2s)^2 \cdot s$$~~
~~$$= 4s^3$$~~
~~$$= (2 \times 10^{-4})^2 \cdot s$$~~

$$\text{Ag}^+(2s) = 2 \times 10^{-4} \text{ M}$$

$$s = 10^{-4}$$

$$K_{sp} = 4s^3$$

$$= 4(10^{-4})^3$$

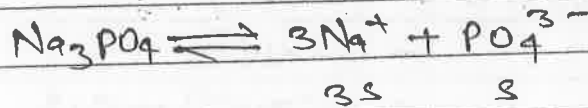
$$= 4 \times 10^{-12}$$

Ques. Calculate the K_{sp} value of Na_3PO_4 if 100 mL of its saturated solution contain 0.069 mg of Na^+ .

~~$$K_{sp} = (3s)^3 (s)$$~~

$$[\text{Na}^+] = \frac{0.069 \times 10^{-3}}{23 \times \frac{100}{1000}}$$

$$[\text{Na}^+] = 3 \times 10^{-5} \text{ M}$$



$$K_{sp} = 3s = 3 \times 10^{-5} \text{ M}$$

$$s = 10^{-5}$$

$$K_{sp} = 27s^3$$

$$= 27(10^{-5})^3$$

$$= 27 \times 10^{-15} = 2.7 \times 10^{-14}$$

Ques. The K_{sp} value of $\text{Mg}(\text{OH})_2$ is found to be 4×10^{-12} . Then determine pH of its saturated solution.

~~$K_{sp}(\text{Mg})$~~

$$K_{sp} \text{Mg}(\text{OH})_2 = 4 \times 10^{-12}$$

$$K_{sp} = 4s^3$$

$$4 \times 10^{-12} = 4s^3$$

$$s = 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 2s = 2 \times 10^{-4}$$



$$\text{pOH} = 4 - \log 2 = 3.7$$

$$\text{pH} = 14 - 3.7 = 10.3$$

Ques. Calculate the required volume of water to dissolve 1g CaCO_3 if its K_{sp} value is found to be 1×10^{-10} .

$$K_{sp}(\text{CaCO}_3) = 1 \times 10^{-10}$$

A B.

श्री नाथ जी बुक डिपो

Zerox, Spiral Baining, NCERT Book,
Old Book Purchase & Sell,
Study Material Purchase & Sell,
Hand Writing Notes, Online Form

मातृ छाया होस्टल शॉप नं. 2 ऐलन सत्यार्थ गेट नं. 2 के
सामने, जवाहर नगर, कोटा (राज.) मो. 7014774207

$$K_{sp} = s^2$$

$$1 \times 10^{-10} = s^2$$

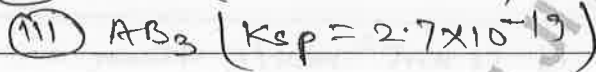
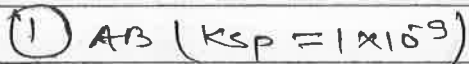
$$s = 10^{-5} \text{ mol L}^{-1}$$

$$10^{-5} \text{ mol of CaCO}_3 \rightarrow 1 \text{ L}$$

$$= (10^{-5} \times 100) \text{ g of CaCO}_3 \rightarrow 1 \text{ L}$$

$$1 \text{ g of CaCO}_3 \rightarrow \frac{1}{10^{-3}} = 10^3 \text{ L}$$

Ques. Arrange the following decreasing order of their solubility -



$$S_1 > S_2 > S_3$$



$$K_{sp} = s^2 = 1 \times 10^{-9}$$

$$s_1 = \sqrt{K_{sp}}$$

$$= \sqrt{10^{-9}} = 10^{-4.5} \text{ M}$$

(ii) $K_{sp} = 4s^3 \Rightarrow s_2 = \left(\frac{K_{sp}}{4}\right)^{1/3}$

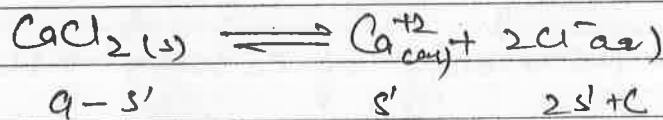
$$= \left(\frac{4 \times 10^{-18}}{4}\right)^{1/3} = 10^{-6} \text{ M}$$

(iii) $K_{sp} = 27s^4 \Rightarrow s_3 = \left(\frac{K_{sp}}{27}\right)^{1/4} =$

$$= \left(\frac{27 \times 10^{-20}}{27}\right)^{1/4} = 10^{-5} \text{ M}$$

② Effect of common on ~~solubility~~ Solubility:—

Let the new solubility be s'

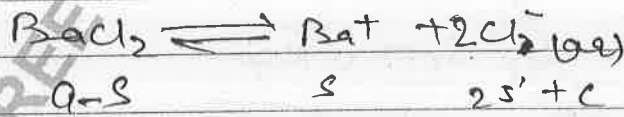


$$K_{sp} = \frac{(\text{Ca}^{+2}) \cdot (\text{Cl}^{-})^2}{(s') \cdot (2s'+c)^2} = s'c^2$$

$$K_{sp} = s'c^2$$

$$s' = \frac{K_{sp}}{c^2}$$

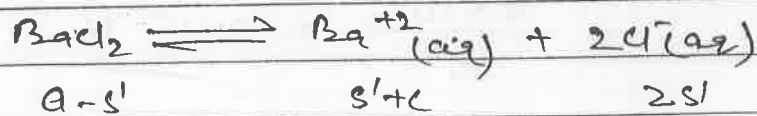
Ques. The solubility of BaCl_2 is 4×10^{-6} mol/L then determine its solubility in the presence of 0.04M BaSO_4 solution.



$$K_{sp} = 4s^3$$

$$K_{sp} = \frac{(\text{Ba}^{+2}) \cdot (\text{Cl}^{-})^2}{(s) \cdot (2s'+c)^2} = s'c^2$$

$$s' = \frac{4 \times 10^{-6}}{(0.04)^2} = \frac{4 \times 10^{-4}}{4}$$



$$K_{sp} = (\text{Ba}^{+2}) \cdot (\text{Cl}^{-})^2$$

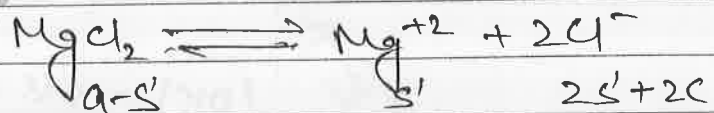
$$K_{sp} = (s'+c) \cdot (2s')^2$$

$$K_{sp} = 4s'^2c$$

$$s' = \frac{K_{sp}}{4c} = \left(\frac{4 \times 64 \times 10^{-18}}{4 \times 4 \times 10^{-2}} \right)^{\frac{1}{2}}$$

$$= 4 \times 10^{-8} \text{ M}$$

Ques. In a 10L saturated solution 19mg MgCl_2 is dissolved then determine its solubility in the presence of 10^{-2} M CaCl_2 solution.



$$s(\text{MgCl}_2) = \frac{19 \times 10^{-3}}{95 \times 10} = 2 \times 10^{-5}$$

~~$$K_{sp} = 4s^3$$~~

$$K_{sp} = (\text{Mg}^{+2}) \cdot (\text{Cl}^{-})^2$$

$$K_{sp} = (s') (2s'+2c)^2$$

$$K_{sp} = 4c^2 s'$$

$$s' = \frac{K_{sp}}{4c^2} = \frac{4s^3}{4c^2}$$

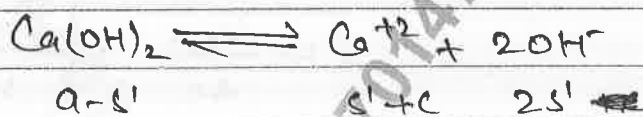
$$= \frac{(2 \times 10^{-5})^3}{(10^{-2})^2}$$

$$= \frac{8 \times 10^{-15}}{10^{-4}} = 8 \times 10^{-11} \text{ M}$$

Ques. The K_{sp} value of Co(OH)_2 is 4×10^{-15} then determine its pH in the presence of 10^{-3} M CaSO_4 solution.

~~K_{sp}~~

$$K_{sp}(\text{Co(OH)}_2) = 4 \times 10^{-15}$$



$$K_{sp} = (\text{Co}^{+2}) \cdot (\text{OH})^2$$

$$= (s'+c) \cdot (2s')^2$$

$$K_{sp} = 4s'^2 c$$

$$s' = \frac{K_{sp}}{4s'c} = \left(\frac{4 \times 10^{-15}}{4 \times 10^{-3}} \right)^{1/2}$$

$$= 10^{-6} \text{ M}$$

$$(\text{OH}) = 2s' = 2 \times 10^{-6}$$

$$\text{pOH} = 6 - \log 2$$

$$= 6 - 0.3 = 5.7$$

$$\text{pH} = 14 - 5.7$$

$$= 8.3$$

Ques. The solubility of AgCl will be max. in.

(I) $0.1 \text{ M NaCl} = s' = \frac{K_{sp}}{c}$

(II) $0.1 \text{ M CaCl}_2 = s' = \frac{K_{sp}}{2c}$ ↓ common ion conc. ↑ solubility

(III) $0.1 \text{ M AlCl}_3 = s' = \frac{K_{sp}}{3c}$

(IV) Same

3) Condition for precipitation: —

Ques. Which of the following concentration to lead the precipitation of CaF_2 if its K_{sp} value is

(I) 10^{-4}M , 10^{-5}M $(\text{Ca}^{2+}) (\text{F}^-)^2 \cdot 2 \times 10^{-12}$

(II) 10^{-5}M ; 10^{-4}M

(III) 10^{-5}M ; 10^{-3}M

(IV) All of these



(I) I.P. = $10^{-14} < K_{sp}$

(II) I.P. = $10^{-13} < K_{sp}$

(III) I.P. = $10^{-11} > K_{sp}$

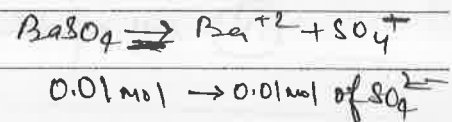
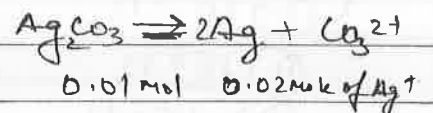
Ques. 100ml 0.1M Ag_2CO_3 is mixed with 100ml 0.1M BaSO_4 then determine that the precipitation of (Ag_2SO_4) will take place or not. If its K_{sp} value is 1×10^{-5} .

Solⁿ:-

~~I.P. = $(\text{Ag}^+)^2 \cdot (\text{SO}_4^{2-})$~~
I.P. = $(\text{Ag}^+)^2 \cdot (\text{SO}_4^{2-})$
= $\left(\frac{0.02}{0.2}\right)^2 \cdot \left(\frac{0.01}{0.2}\right)$

I.P. = $5 \times 10^{-4} > K_{sp}$

ppt. will occur



Ques. The K_{sp} value of $\text{Mg}(\text{OH})_2$ is 1.2×10^{-12} then determine the pH at which a solution containing $\text{Mg}^{2+} = 1.2 \text{M}$ will ~~begin~~ ^{begin} to ppt.

$$I.P = K_{sp}$$

~~$$1.2 \times 10^{-12}$$~~

$$(Mg^{+2})(OH^-)^2 = 1.2 \times 10^{-12}$$

~~$$(1.2)(OH^-)^2 = 1.2 \times 10^{-12}$$~~

$$(OH^-) = 10^{-6} M$$

$$pOH = 6$$

$$pH = 14 - 6$$

$$\underline{\underline{8}}$$

Ques. The K_{sp} value of $BaCl_2$ is 1×10^{-14} then determine the chloride ion concentration at which a solution containing $(Ba^{+2}) = 10^{-4} M$ will ppt out

(A) $10^{-4} M$

(B) $10^5 M$

(C) $10^6 M$

(D) All of these

$$K_{sp}(BaCl_2) = 1 \times 10^{-14}$$

$$I.P. > K_{sp}$$

$$(Ba^{+2}) \cdot (Cl^-)^2 > 1 \times 10^{-14}$$

$$(10^{-4}) \cdot (Cl^-)^2 > 10^{-14}$$

$$(Cl^-)^2 > 10^{-10}$$

$$Cl^- > 10^{-5} M$$

Ques If in a solution containing $(Cl^-) = (I^-) = (Br^-) = (CO_3^{2-}) = 0.1M$ $AgNO_3$ is added then determine which of the following ppt out first.

Given:-

① $K_{sp}(AgCl) = 1 \times 10^{-10}$

② $K_{sp}(AgBr) = 1 \times 10^{-12}$

③ $K_{sp}(AgI) = 1 \times 10^{-14}$

④ $K_{sp}(Ag_2CO_3) = 1 \times 10^{-16}$

① AgCl ② AgBr

~~③ AgI~~

④ ~~Ag₂CO₃~~

① $(Ag^+) \cdot (Cl^-) = 10^{-10} \Rightarrow (Ag^+) = 10^{-9}M$

② $(Ag^+) \cdot (Br^-) = 10^{-12} \Rightarrow (Ag^+) = 10^{-11}M$

~~③ $(Ag^+) \cdot (I^-) = 10^{-14} \Rightarrow (Ag^+) = 10^{-13}M$~~

④ $(Ag^+)^2 (CO_3^{2-}) = 10^{-16} \Rightarrow (Ag^+)^2 = 10^{-14}M$

$Ag^+ = 10^{-7.5}$

Group precipitation of salt:—

Analysis of basic radicals depends upon K_{sp} value, common ion & odd ion effect.

$K_{sp}(I) < K_{sp}(II) < K_{sp}(III) \dots < K_{sp}(VII)$

Low K_{sp} value \Rightarrow Easy (earlier) ppt

Few Important point:—
→ Solution having name pH.

Ques. 0.01M CH_3COOH (acetic acid) ($K_a = 2 \times 10^{-5}$) is inohydric with 0.2M formic acid solution the determine the ionisation constant of formic acid (HCOOH)

$$K_{a1}C_1 = K_{a2}C_2$$

$$(2 \times 10^{-5})(0.01) = K_{a2}(0.2)$$

$$K_{a2} = 10^{-6}$$

Ques. The ionisation constant of two weak acid AHA & HB is 3.6×10^{-9} and 4×10^{-6} respectively then determine which acid is stronger and by how many times.

HA	HB
$K_a = 3.6 \times 10^{-9}$	$K_a = 4 \times 10^{-6}$

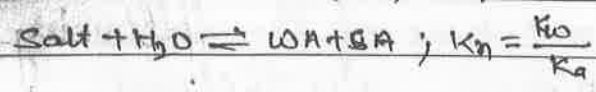
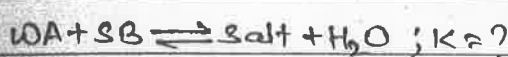
$$R.S = \frac{HB}{AHA} = \sqrt{\frac{K_a(HB)}{K_a(AHA)}} = \sqrt{\frac{4 \times 10^{-6}}{36 \times 10^{-10}}}$$

$$= \sqrt{\frac{10^4}{9}}$$

$$= \frac{100}{3} = \underline{33.3}$$

HB is stronger by 33.3 times

Ex+1
Ques (50)



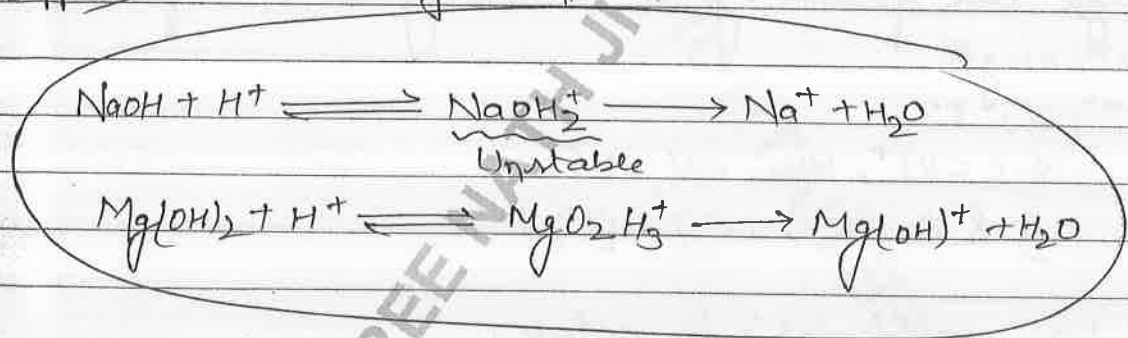
(43) $h = \sqrt{\frac{K_w}{K_b \cdot c}}$

$K = \frac{1}{K_n}$
 $K_n = \frac{10^{-14}}{10^{-4}} = 10^{-10}$
 $K = \frac{1}{10^{-10}} = 10^{10}$

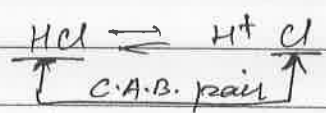
(53) WASB salt

$h = \sqrt{\frac{K_w}{K_n \cdot c}} = \sqrt{\frac{10^{-14}}{3.5 \times 10^{-3} \times 5 \times 10^{-2}}}$
 $= \sqrt{\frac{10^{-8}}{17.5}} = \frac{10^{-4}}{13} = \frac{100 \times 10^{-6}}{13}$
 $= 7.7 \times 10^{-6}$

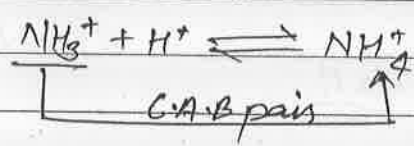
Bronsted - Lowery Concept:



Acid $\rightleftharpoons H^+ + C \cdot$ Base



~~Base~~ Base + $H^+ \rightleftharpoons C \cdot$ Acid



Ques. Write down the c. acid & c. base of the following species.

	Base $+H^+$	C. Acid	Acid $-H^+$	C. Base
(i) H_2O				
(ii) CH_3COOH		H_3O^+		OH^-
(iii) HCO_3^-		CH_3COOH^+		CH_3COO^-
(iv) HPO_4^{2-}		H_2CO_3		CO_3^{2-}
		$H_2PO_4^-$		PO_4^{3-}

Ques. Which of the following will act as strongest base.

- (i) $NO_2^- \Rightarrow HNO_2$
- (ii) $Br^- \Rightarrow HBr$
- (iii) $CN^- \Rightarrow HCN$
- (iv) $ClO_4^- \Rightarrow HClO_4$

Ques. Arrange the following in decreasing order of basic strength.

- (i) Br^-, F^-, Cl^-, I^-

A.S = HI^+, HBr, HCl, HF

B.S $\Rightarrow F^- > Cl^- > Br^- > I^-$

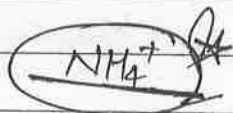
Ques. W.O.F. has amphoteric in nature.

- (i) HS^-
- (ii) NH_4^+ only does not accept
- (iii) H_2O
- (iv) All

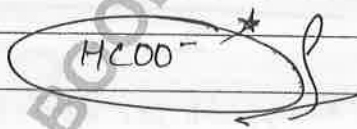
Ques. W.O.F. is a base of hydrazoic acid ~~N_3H~~

- (i) NH_4^+
 - (ii) NH_2^-
 - (iii) N_3^-
 - (iv) N_2H^-
- N_3H

Ques. In the rxn $\text{HBr} + \text{NH}_3 \rightleftharpoons \text{Br}^- + \text{NH}_4^+$ which one will act as weak acid.

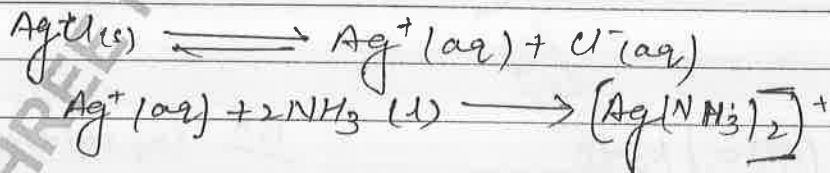


Ques. $\text{HCOO}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HCOOH} + \text{H}_2\text{O}$ which one will act as strong base.



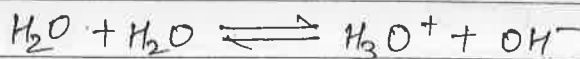
* Some imp. point :-

① Ag^+ , Pb^{+2} , Cu^{+2} etc. increase in the presence of NH_3 because they form a stable complex with NH_3

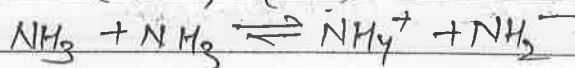


② Fe^{+2} is not ppt in third group because of its light K_{sp} value.

③ Autoprotolysis:-



$$K_{AP} = (\text{H}_3\text{O}^+) \cdot (\text{OH}^-)$$



$$K_{AP} = (\text{NH}_4^+) \cdot (\text{NH}_2^-)$$

④ pH of mixtures of weak acids or weak bases.

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

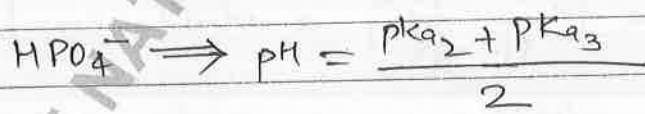
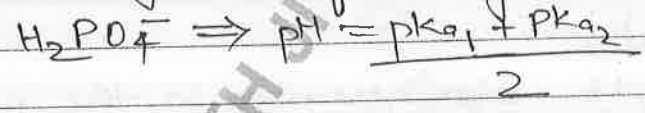
$$[OH^-] = \sqrt{K_{b1}C_1 + K_{b2}C_2}$$

⑤ pH of Ampholytic species

$$[H^+] = \sqrt{K_n \times K_{(n+1)}}$$

$$pH = \frac{pK_n + pK_{(n+1)}}{2}$$

n = Magnitude of change on ampholytic species.

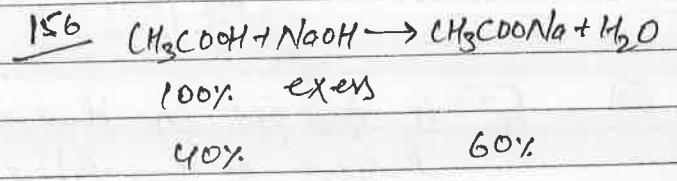


Ex #1
 Que. 148

$$[H^+] = \sqrt{K_a \times C}$$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

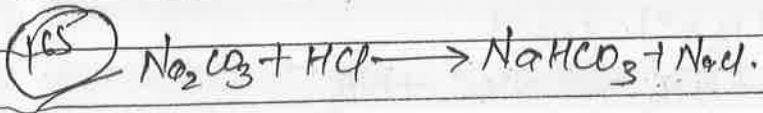
$$[H^+] = K_a \times \frac{[Acid]}{[Salt]} = (10^{-3})$$



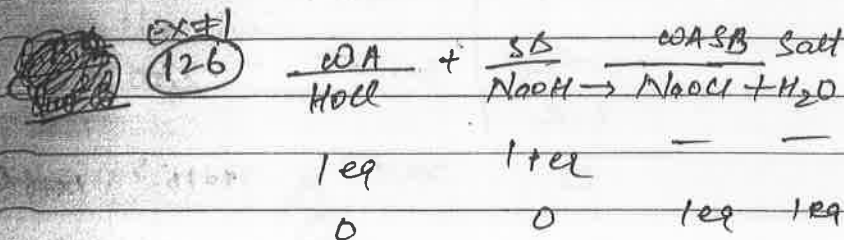
$$pH = pK_a + \log \frac{60}{40}$$

$$= 4.7 + 0.18$$

$$= \underline{4.88}$$



BB-2
Q.2 cation
(2.) (ii), (iii) (iv)



$$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$= 7 + \frac{1}{2} (8) = 11$$

EX#1
(92)

I.P. = K_{sp}

$$[Ag^+][I^-] = 10^{-10} M$$

$$[Ag^+](0.06) = 10^{-10} M$$

$$[Ag^+] = \frac{1}{6} \times 10^{-8} M$$

$$\frac{AgCl = 10^{-10}}{AgI = 4 \times 10^{-16}}$$

I.P. = K_{sp}

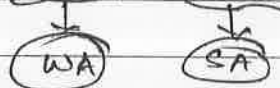
$$[Ag^+][I^-] = 4 \times 10^{-16}$$

$$\left(\frac{1}{6} \times 10^{-8}\right) [I^-] = 4 \times 10^{-16}$$

$$[I^-] = 2.4 \times 10^{-7} M$$

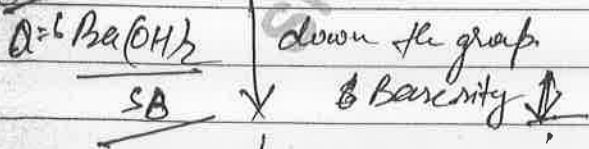
(171) $pK_{b1} < pK_{b2}$

$$K_{b1} > K_{b2}$$



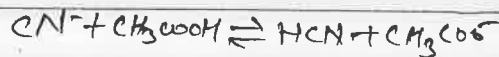
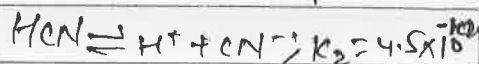
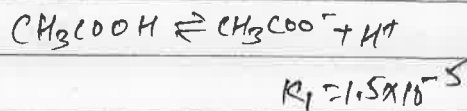
min pH

EX#11



EX#II

Ques 10



$$K = \frac{K_1}{K_2}$$

EX#1

(17) find the volume of H_2O needed required to dissolve 1g of

EX#11 $CaSO_4$

(42) 10^{-3}

Collection

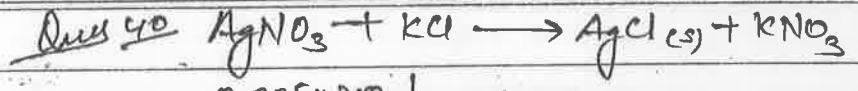
Ques 48 $\alpha = \sqrt{\frac{K_b}{C}}$

$$= \sqrt{\frac{1.7 \times 10^{-9}}{0.1}}$$

$$= \sqrt{1.7 \times 10^{-8}}$$

$$= 1.3 \times 10^{-4} \times 100$$

$$= 0.013\%$$



$$0.005 \times \frac{200}{1000} \quad | \quad 0.01 \times \frac{300}{1000}$$

$$\frac{1 \times 10^{-3} \text{ mol}}{1.0 \text{ L}}$$

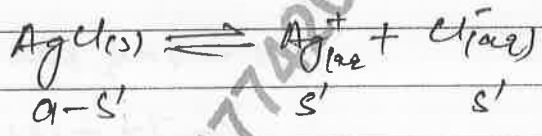
$$3 \times 10^{-3}$$

0

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

$$9 \times 10^{-3}$$

$$1 \times 10^{-3}$$



$$K_{sp} = (s')(s'+c)$$

Ques 49 6.5×10^{-6}
Ans \rightarrow

Ques 49: $\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$

$$s' = \frac{K_{sp}}{c} = \frac{1.8 \times 10^{-10}}{\frac{2 \times 10^{-3}}{\frac{500}{1000}}}$$

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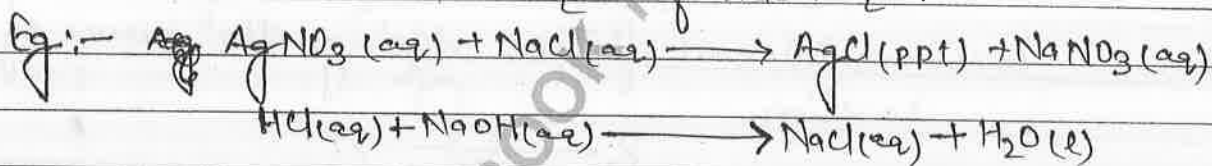
CHEMICAL KINETICS

Chemical kinetics is a branch of chemistry that deals with the rate of rxn, the factors affecting rate of rxn and the mechanism with which a rxn proceeds.

Classification of rxn on the basis of speed:—

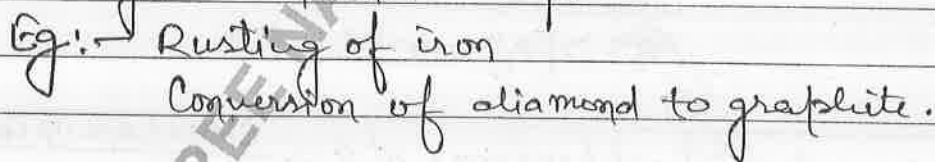
(i) Very fast rxn:—

Generally these rxn involved ionic species and are known as ionic rxn. these rxn takes 10^{-14} to 10^{-16} sec for completion. so it is impossible to determine the rate of such rxn.



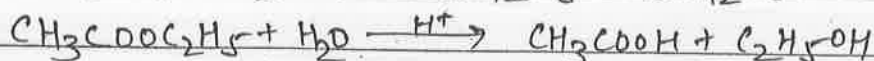
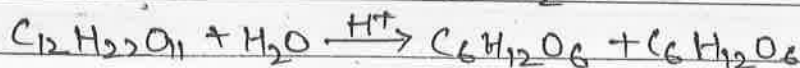
(ii) Very slow rxn:—

These rxn occurs very slowly and they may takes day or months to show any measurable change at normal temp.



(iii) Moderate or slow rxns:—

These rxn show measurable changes at normal temp. and hence the rate of such rxn can be easily determine. generally these rxn are molecules in nature.



Rate of Reaction (R.O.R.):—

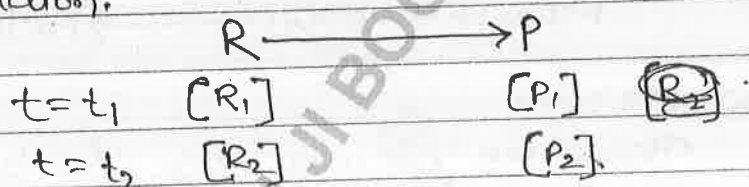
R.O.R. is define as the change in concentration of a reactant or a product per unit time.

$$\text{R.O.R.} = \frac{\text{Change in conc. of a reactant or product}}{\text{Time taken for that change}}$$

R.O.R. ke Types:—

① Average Rate (rav. or r_2):—

It is define as the rate of rxn measured over an interval of time during the course of the reaction.



$$[R_2] < [R_1] \Rightarrow t \uparrow \quad R \downarrow$$

$$[R_2] > [R_1] \Rightarrow t \uparrow \quad P \uparrow$$

$$\begin{aligned} \text{Avg. rate of disappearance of R} &= \frac{\text{Decrease in conc. of R}}{\text{Time taken}} \\ &= \frac{-(R_2) - (R_1)}{t_2 - t_1} = \frac{-\Delta(R)}{\Delta t} \end{aligned}$$

$$\text{Avg. rate of appearance of P} = \frac{\text{Increase in conc. of P}}{\text{Time taken}}$$

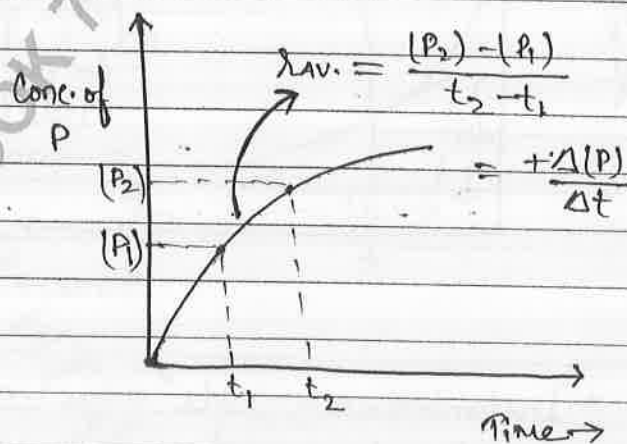
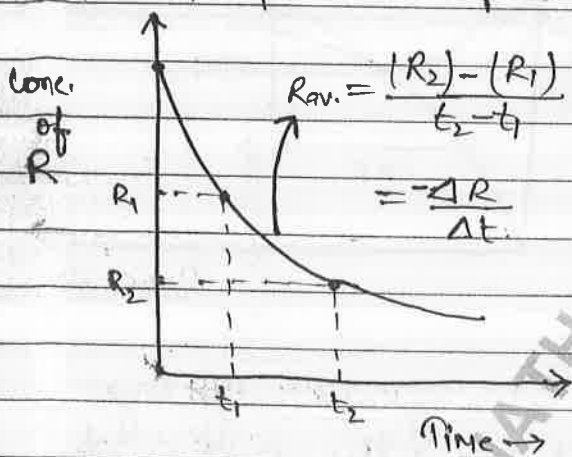
$$= \frac{(P_2) - (P_1)}{t_2 - t_1} = + \frac{\Delta(P)}{\Delta t}$$

(3) \therefore Avg. rate of rxn $= -\frac{\Delta(R)}{\Delta t} = +\frac{\Delta(P)}{\Delta t}$

Note:—

- As ΔR is negative quantity (because the conc. of reactant is decreasing) so it is multiple by -1 to make R.O.R a positive quantity.
- R.O.R is always positive but change in conc. can be (+)ive or (-)ive.

Graphical representation:—



(2) Instantaneous Rate (limit):—

It is define as the rate of rxn measured at a particular instant of time during the course of the reaction.

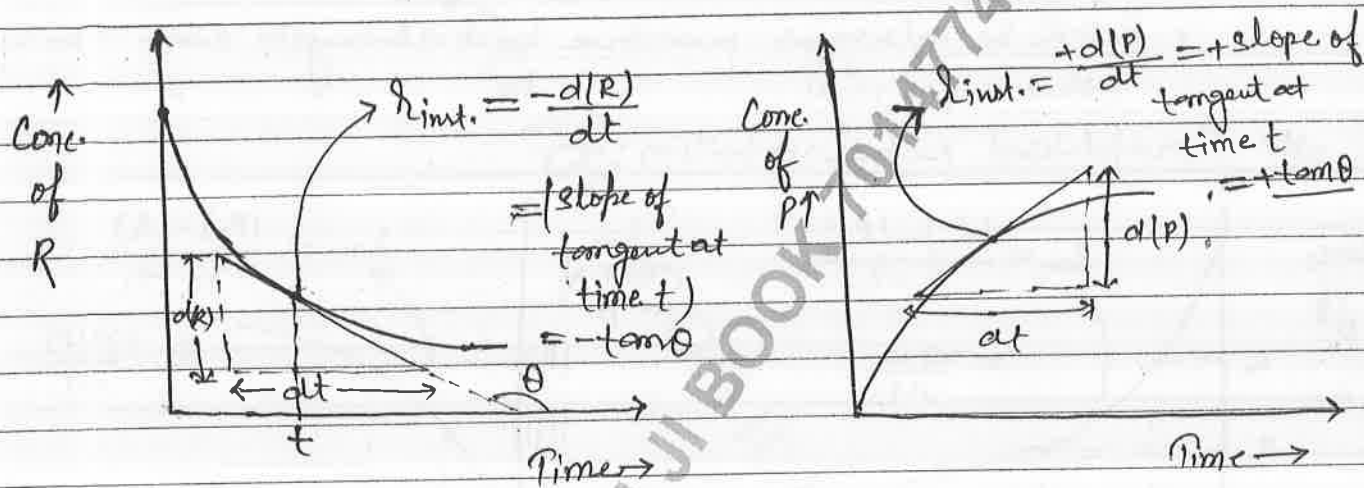
- It is obtained when we considered the avg. rate at the smallest time interval ' Δt ' i.e. when $\Delta t \rightarrow 0$.

$$R_{limit} = \lim_{\Delta t \rightarrow 0} (R_{avg})$$

• Inst. Rate of disappearance of R = $\lim_{\Delta t \rightarrow 0} \left(\frac{-\Delta[R]}{\Delta t} \right) = -\frac{d[R]}{dt}$

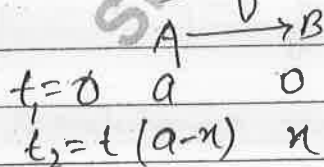
• Inst. rate of appearance of P = $\lim_{\Delta t \rightarrow 0} \left(\frac{+\Delta[P]}{\Delta t} \right) = +\frac{d[P]}{dt}$

• Inst. rate of rxn = $-\frac{d[R]}{dt} = +\frac{d[P]}{dt}$



• Instantaneous rate can be determined graphically by drawing a tangent at time 't' on the curve of Conc. vs time and calculating its slope.

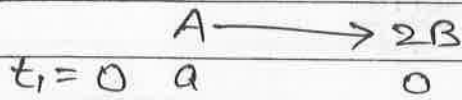
R.O.R. in terms of stoichiometry of rxn: —



$$\text{R.O.D. of A} = \frac{-(A_2 - A_1)}{t_2 - t_1} = \frac{-[(a-x) - (a)]}{t-0} = \frac{x}{t}$$

$$\text{R.O.A. of B} = \frac{+(B_2) - (B_1)}{t_2 - t_1} = \frac{+(x - 0)}{t-0} = \frac{x}{t}$$

$$R.O.R. = (R.O.D)_A = (R.O.A)_B$$



$$t_1 = 0 \quad a \quad 0$$

$$t_2 = t \quad (a-x) \quad 2x$$

$$(R.O.D)_A = \frac{x}{t}$$

$$(R.O.A)_B = \frac{2x}{t}$$

$$(R.O.A)_B = 2(R.O.D)_A$$

$$R.O.R. = (R.O.D)_A = \frac{(R.O.A)_B}{2}$$

In general,

$$R.O.R. = \frac{R.O.D. \text{ or } R.O.A.}{\text{Stoichiometry coefficient}}$$

Note: —

In individual rate are divided by there respective ^{stoichiometric} coefficient in balance chemical rxn then they becomes equal to each other as well as equal to rate of rxn

for a rxn,



$$R.O.D. \text{ of } A = -\frac{\Delta(A)}{\Delta t} \text{ or } -\frac{d(A)}{dt}$$

$$R.O.D. \text{ of } B = -\frac{\Delta(B)}{\Delta t} \text{ or } -\frac{d(B)}{dt}$$

श्री नाथ जी बुक डिपो
Zerox, Spiral Baining, NCERT Book,
Old Book Purchase & Sell,
Study Material Purchase & Sell,
Hand Writing Notes, Online Form
मातृ छाया होस्टल शॉप नं. 2 फ़ैलन सत्यार्थ गेट नं. 2 के
सामने, जवाहर नगर, कोटा (राज.) मो. 7014774207

$$\text{R.O.A. of C} = \frac{+\Delta(C)}{\Delta t} \text{ or } +\frac{d(C)}{dt}$$

$$\text{R.O.A. of D} = \frac{+\Delta(D)}{\Delta t} \text{ or } +\frac{d(D)}{dt}$$

$$\begin{aligned} \text{Avg. R.O.R.} &= \frac{1}{a} \left(-\frac{\Delta(A)}{\Delta t} \right) = \frac{1}{b} \left(-\frac{\Delta(B)}{\Delta t} \right) \\ &= \frac{1}{c} \left(\frac{+\Delta(C)}{\Delta t} \right) = \frac{1}{d} \left(\frac{+\Delta(D)}{\Delta t} \right) \end{aligned}$$

$$\begin{aligned} \text{Inst. R.O.R.} &= \frac{1}{a} \left(-\frac{d(A)}{dt} \right) = \frac{1}{b} \left(-\frac{d(B)}{dt} \right) \\ &= \frac{1}{c} \left(\frac{+d(C)}{dt} \right) = \frac{1}{d} \left(\frac{+d(D)}{dt} \right) \end{aligned}$$

Unit of R.O.R. :-

$$\text{R.O.R.} = \frac{\text{Change in conc.}}{\text{time taken}} = \frac{+\Delta(C)}{\Delta t} \text{ or } \pm \frac{d(C)}{dt}$$

$$\begin{aligned} \text{Unit of Rate} &= (\text{Conc.}) \text{ time}^{-1} \\ &\left(\begin{array}{l} \text{mol l}^{-1} \text{ s}^{-1} \\ \text{mol l}^{-1} \text{ min}^{-1} \end{array} \right) \end{aligned}$$

Note :-

for an ideal gas,

$$PV = nRT$$

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

$$P = (c) RT$$

At const. T

$$P \propto (c)$$

↳ For gaseous rxn at constant temp. concentration is directly proportional to partial pressure of species and hence rate can also be expressed as the rate of change of in partial pressure of the reactant or the product.

$$\text{R.O.R.} = \frac{\text{Change in Pressure}}{\text{Time taken}} = \pm \frac{\Delta P}{\Delta t} \text{ or } \pm \frac{dP}{dt}$$

$$\text{Unit of rate} = (\text{Pressure}) \text{ time}^{-1}$$

(atm s⁻¹
atm min⁻¹)

Relation b/w various forms of R.O.R. for gaseous rxn:-

As we know, $PV = nRT$

$$(c) = \frac{n}{V} = \frac{P}{RT}$$

$$\left[\left(\pm \frac{d(c)}{dt} \right) = \frac{1}{V} \left(\pm \frac{dn}{dt} \right) = \frac{1}{RT} \left(\pm \frac{dP}{dt} \right) \right]$$

Rate in terms
of molar ~~conc.~~
Conc.

Rate in terms
of moles

Rate in terms of
Partial pressure

$$PV = nRT$$

\downarrow \downarrow \downarrow \downarrow
 L mol \rightarrow $0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$
 atm

Ques for a rxn $2A \rightarrow 3B$ write down the expression of the following.

(i) Avg. (R.O.D.)_A

(ii) Inst. R.O.R. in terms of A $\Rightarrow \frac{1}{2} \left(-\frac{d(A)}{dt} \right)$

(iii) Inst. R.O.A._B

(iv) Avg. R.O.R. in terms of B $\Rightarrow \frac{1}{3} \left(+\frac{\Delta(B)}{\Delta t} \right)$



(i) Avg (R.O.D.)_A = $-\frac{\Delta(A)}{\Delta t}$

(iii) $+\frac{d(B)}{dt}$

Ques. for a rxn $N_2 + 3H_2 \rightarrow 2NH_3$ the R.O.A. of NH_3 is $2 \times 10^4 \text{ mol L}^{-1} \text{ sec}^{-1}$ then determine the R.O.D. of N_2 & H_2 and also determine the rate of rxn.

$$\text{R.O.A.}(NH_3) = 2 \times 10^4 \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{R.O.R} = \frac{-d(N_2)}{dt} = \frac{1}{3} \left(-\frac{d(H_2)}{dt} \right) = \frac{1}{2} \left(+\frac{d(NH_3)}{dt} \right)$$

$$\text{R.O.A.}(NH_3) = +\frac{d(NH_3)}{dt} = 2 \times 10^4 \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{R.O.D.}(N_2) = -\frac{d(N_2)}{dt} = \frac{1}{2} \left(+\frac{d(NH_3)}{dt} \right)$$

$$= \frac{1}{2} (2 \times 10^4) \Rightarrow 10^4 \text{ mol}^{-1} \text{ s}^{-1}$$

$$\text{R.O.D)}_{\text{H}_2} = -\frac{d(\text{N}_2)}{dt}$$

$$= \frac{3}{2} \left(\frac{+d(\text{NH}_3)}{dt} \right) \Rightarrow \frac{3}{2} \times 2 \times 10^4$$

$$= 3 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{R.O.R.} = \frac{1}{2} \left(\frac{+d(\text{NH}_3)}{dt} \right) = \frac{1}{2} (2 \times 10^4)$$

$$= 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

Ques

$2\text{A} \rightarrow 3\text{B} + 4\text{C}$ If the no. of mole of B increased by $6 \times 10^{-3} \text{ mol}$ in 10 sec in a 10L container then determine R.O.A.)_B & (R.O.D.)_A and the R.O.R.

$$\text{R.O.R.} = \frac{1}{2} \left(-\frac{\Delta(\text{A})}{dt} \right) = \frac{1}{3} \left(\frac{+\Delta(\text{B})}{dt} \right) = \frac{1}{4} \left(\frac{+\Delta(\text{C})}{dt} \right)$$

$$\text{R.O.A.)}_B = \frac{+\Delta(\text{B})}{dt} = \frac{6 \times 10^{-3}}{10 \text{L} \times 10 \text{s}} = 6 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{R.O.A.)}_C = \frac{+\Delta(\text{C})}{dt} = \frac{4}{3} (6 \times 10^{-5}) = 8 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{R.O.D.)}_A = \left(-\frac{\Delta(\text{A})}{dt} \right) = \frac{2}{3} (6 \times 10^{-5}) = 4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{R.O.R.} = \frac{1}{3} (6 \times 10^{-5}) = 2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

Ques: For a rxn $3X \rightarrow P$ if the conc. of X change from $0.9M$ to $0.6M$ in 5min . then calculate the R.O.R.

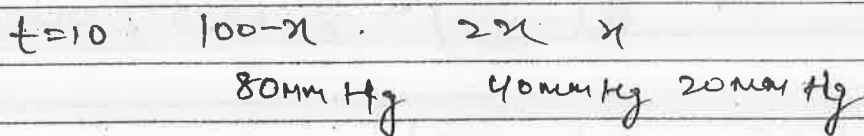
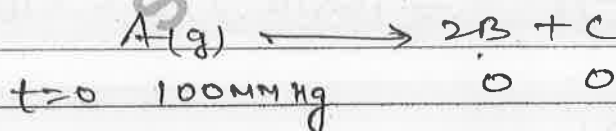


$$\begin{aligned} \text{R.O.R.} &= \frac{1}{3} \left(\frac{\Delta(X)}{\Delta t} \right) \\ &= \frac{1}{3} \left(\frac{-(0.9 - 0.6)}{5} \right) \\ &= \frac{0.1}{5} = \cancel{0.02}^{-1} \\ &= 0.02 \text{ Mol l}^{-1} \text{ min}^{-1} \end{aligned}$$

Ques For a rxn $A(g) \rightarrow 2B(g) + C(g)$ the pressure increases from 100mm Hg to 140mm Hg in 10sec then determine the R.O.R. and the R.O.A) of B & C .

~~$$\text{R.O.R.} = \left(\frac{-\Delta(A)}{\Delta t} \right) = \frac{1}{2} \left(\frac{+\Delta(B)}{\Delta t} \right) = \left(\frac{+\Delta(C)}{\Delta t} \right)$$~~

~~$$\text{R.O.A)}_B = \frac{+\Delta(B)}{\Delta t} =$$~~



$$\text{Total pressure} = 140\text{mm Hg}$$

$$100 - x + 2x + x = 140$$

$$x = 20\text{mm Hg}$$

$$R.O.R. = -\frac{\Delta P_A}{\Delta t} = \frac{1}{2} \left(+\frac{\Delta P_B}{\Delta t} \right) = +\frac{\Delta P_C}{\Delta t}$$

$$R.O.R. = -\frac{\Delta P_A}{\Delta t} = -\frac{(80-100)}{10-0} = 2 \text{ MM Hg s}^{-1}$$

$$R.O.A)_B = +\frac{\Delta P_B}{\Delta t} = 2 \times R.O.R. = 2 \times 2 = 4 \text{ MM of Hg s}^{-1}$$

$$R.O.A)_C = +\frac{\Delta P_C}{\Delta t} = R.O.R. = 2 \text{ MM Hg s}^{-1}$$

Ques. For the decomposition of N_2O_5 at $127^\circ C$ ^{temp.} then of initial pressure of N_2O_5 is 114 MM Hg and after 20 sec. the pressure of N_2O_5 mixture becomes 133 MM Hg then calculate the R.O.R. in $\text{mol L}^{-1} \text{ s}^{-1}$.

Initial-	N_2O_5	\longrightarrow	N_2O_4	$+$	$\frac{1}{2} O_2$
$t=0$	114		0		0
$t=20$	$(114-x)$		x		$\frac{1}{2}x$
	$114-38$		38		19 MMHg
	76 MMHg				

Total pressure = 133 MM of Hg

$$114 - x + x + \frac{1}{2}x = 133$$

$$114 + \frac{1}{2}x = 133$$

$$x = 38 \text{ MM Hg}$$

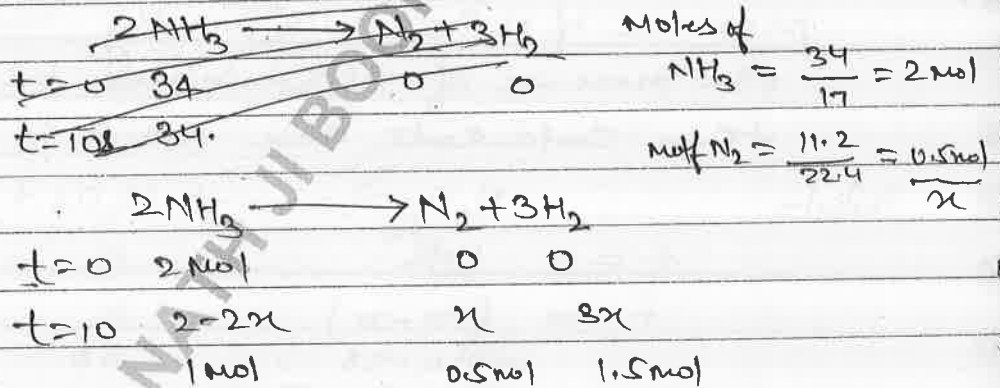
$$R.O.R. = +\frac{\Delta P_{N_2O_4}}{\Delta t} = \frac{38-0}{20-0}$$

$$= \frac{38}{20} = 1.9 \text{ MM Hg s}^{-1}$$

$$R.O.R = 1.9 \times \frac{1}{760} = 2.5 \times 10^{-3} \text{ atm s}^{-1}$$

$$\begin{aligned} \pm \frac{dc}{dt} &= \frac{1}{RT} \left(\pm \frac{dP}{dt} \right) \\ &= \frac{1}{0.0821 \times 400} \times 2.5 \times 10^{-3} \\ &= \frac{2.5 \times 10^{-3}}{32.84} = 7.6 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Ques. In the rxn $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ 34g of NH_3 is taken in 500ml container after 10 sec the volume occupied by N_2 at STP condition found to be 11.2L then determine the R.O.D. of NH_3 .



$$\begin{aligned} \text{R.O.D.}_{\text{NH}_3} &= \frac{\Delta(\text{NH}_3)}{dt} \\ &= \frac{-(1-2)}{\frac{500}{1000} \times 10} = 0.2 \text{ mol L}^{-1} \text{ sec}^{-1} \end{aligned}$$

Ques In the rxn $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$, the rate of formation of NO is 6g/min; then calculate the R.O.D. of NO_2



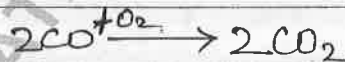
$$\text{R.O.R.} = \frac{1}{2} \left(-\frac{d(\text{NO}_2)}{dt} \right) = \frac{1}{2} \left(+\frac{d(\text{NO})}{dt} \right) = +\frac{d(\text{O}_2)}{dt}$$

$$\text{R.O.A.}_{\text{NO}} = \frac{+d(\text{NO})}{dt} = \frac{6\text{g/min}}{30\text{g/mol}} = 0.2\text{ mol/min}^{-1}$$

$$\text{R.O.D.}_{\text{NO}_2} = \frac{-d(\text{NO}_2)}{dt} = \frac{+d(\text{NO})}{dt} = 0.2\text{ mol/min}^{-1}$$

$$0.2\text{ mol/min}^{-1} \times 46\text{g/mol}^{-1} = \underline{9.2\text{g/min}^{-1}}$$

Ques. In the rxn $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$ 1.6g/L^{-1} O_2 disappears in 10 sec. then determine the R.O.A. CO_2 in $\text{g/L}^{-1}\text{sec}^{-1}$



$$\text{R.O.R.} = \frac{1}{2} \left(-\frac{d(\text{CO})}{dt} \right) = -\frac{d(\text{O}_2)}{dt} = \frac{1}{2} \left(+\frac{d(\text{CO}_2)}{dt} \right)$$

$$\text{R.O.D.}_{\text{O}_2} = \frac{-d(\text{O}_2)}{dt} = \frac{1.6\text{g/L}^{-1}}{10\text{s}} = \frac{0.16\text{g/L}^{-1}\text{s}^{-1}}{32\text{g/mol}^{-1}}$$

$$= 5 \times 10^{-3}\text{ mol/L}^{-1}\text{s}^{-1}$$

$$\text{R.O.A.}_{\text{CO}_2} = \frac{+d(\text{CO}_2)}{dt} = 2 \left(\frac{-d(\text{O}_2)}{dt} \right) = 2 \times (5 \times 10^{-3})$$

$$= 10^{-2}\text{ mol/L}^{-1}\text{s}^{-1}$$

$$\approx 10^{-2}\text{ mol/L}^{-1}\text{s}^{-1} \times 44\text{g/mol}^{-1} = 0.44\text{g/L}^{-1}\text{s}^{-1}$$

eg. $aA + bB \rightarrow cC$ If $-\frac{d(A)}{dt} = 2x \left(-\frac{d(B)}{dt} \right) = 1.5x \left(\frac{d(C)}{dt} \right)$

then find out the ratio of ~~A:B:C~~ a:b:c

$$R.O.R. = \frac{1}{a} \left(-\frac{d(A)}{dt} \right) = \frac{1}{b} \left(-\frac{d(B)}{dt} \right) = \frac{1}{c} \left(+\frac{d(C)}{dt} \right)$$

on comparing,

$$\frac{1}{a} = 1 \quad a = 1$$

$$\frac{1}{b} = 2 \quad b = \frac{1}{2}$$

$$\frac{1}{c} = 1.5 \quad c = \frac{1}{1.5} = \frac{2}{3}$$

$$a : b : c$$

$$1 : \frac{1}{2} : \frac{2}{3}$$

$$6 : 3 : 4$$

Ques for a rxn $xA \rightarrow yB$ If $0.48 + \log \left(-\frac{d(A)}{dt} \right) = 0.7 + \log \left(\frac{d(B)}{dt} \right)$ then find out the ratio of x:y

$$R.O.R. = \frac{1}{x} \left(-\frac{d(A)}{dt} \right) = \frac{1}{y} \left(+\frac{d(B)}{dt} \right)$$

$$\log 3 + \log \left(-\frac{d(A)}{dt} \right) = \log 5 + \log \left(+\frac{d(B)}{dt} \right)$$

$$3 \left(-\frac{d(A)}{dt} \right) = 5 \left(+\frac{d(B)}{dt} \right) \quad \text{--- (1)}$$

$$\frac{1}{x} \left(-\frac{d(A)}{dt} \right) = \frac{1}{y} \left(+\frac{d(B)}{dt} \right) \quad \text{--- (2)}$$

On comparing,

$$\frac{1}{x} = 3 \Rightarrow x = \frac{1}{3}$$

$$\frac{1}{y} = 5 \Rightarrow y = \frac{1}{5}$$

$$x : y$$

$$\frac{1}{3} : \frac{1}{5}$$

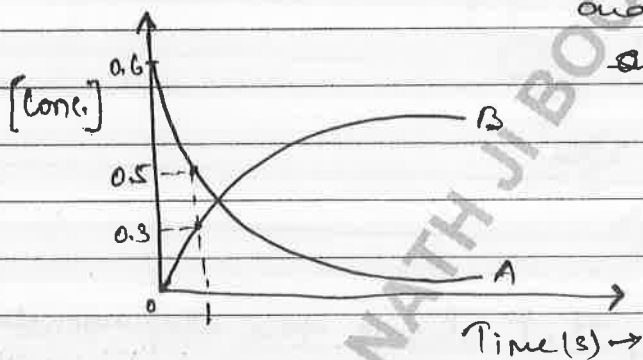
$$\frac{5}{3} : 1$$

श्री नाथ जी बुक डिपो

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सामने, जवाहर नगर, कोटा (राज.) मो. 7014774207

Ques. for a rxn $A \rightarrow nB$ calculate the ~~rate~~ R.O.A.)_A and R.O.A.)_B in b/w 0 → 0.1 and also calculate value of n



$$R.O.A.)_A = \frac{\Delta(A)}{\Delta t} = \frac{-(0.5 - 0.6)}{1 - 0} = 0.1 \text{ mol l}^{-1} \text{ s}^{-1}$$

$$R.O.A.)_B = \frac{\Delta(B)}{\Delta t} = \frac{+(0.3 - 0)}{1 - 0} = 0.3 \text{ mol l}^{-1} \text{ s}^{-1}$$

$$= 0.1 = \frac{1}{n} \left(+ \frac{\Delta(B)}{\Delta t} \right)$$

$$= 0.1 = \frac{1}{n} (0.3)$$

$$n = \frac{0.3}{0.1} = \underline{\underline{3}}$$

Ques. for a rxn $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ if $-\frac{d(\text{NH}_3)}{dt} = k_1(\text{NH}_3)$;

$+\frac{d(\text{N}_2)}{dt} = k_2(\text{NH}_3)$; $+\frac{d(\text{H}_2)}{dt} = k_3(\text{NH}_3)$ then find

out the relation b/w k_1, k_2 & k_3 .

$$\text{R.O.R} = \frac{1}{2} \left(-\frac{d(\text{NH}_3)}{dt} \right) = \left(\frac{d(\text{N}_2)}{dt} \right) = \frac{1}{3} \left(\frac{d(\text{H}_2)}{dt} \right)$$

$$\Rightarrow \frac{k_1(\text{NH}_3)}{2} = k_2(\text{NH}_3) = \frac{k_3(\text{NH}_3)}{3}$$

$$= \frac{k_1}{2} = k_2 = \frac{k_3}{3}$$

$$\Rightarrow 3k_1 = 6k_2 = 2k_3$$

Rate law : —

An expression that shows the dependency of the rate of rxn on the conc. of reactant is known as rate law.

Acc. to rate law the rate of rxn at any time is \propto to the product of conc. of reactant at that time with each term raised to ~~some~~ some power which may or may not be same as stoichiometric coefficient of the reactant species in a balanced chemical rxn. ~~ie.~~ that is it has to be found experimentally.

* Rate law is an experimental concept.
for a rxn,



Acc. to rate law,

$$\text{Rate} \propto [A]^x \cdot [B]^y$$

$$\boxed{\text{Rate} = k[A]^x \cdot [B]^y}$$

Rate law / Equation / Expression

$$k = \text{Rate const.} / \text{velocity} / \text{specific} / \text{rxn rate}$$

$$x = \text{Order of rxn w.r.t. A} \quad [x \neq a \text{ or } x = 0]$$

$$y = \text{Order of rxn w.r.t. B} \quad [y \neq b \text{ or } y = b]$$

$$x + y = n \Rightarrow \text{Overall order of rxn}$$

$$\boxed{\frac{1}{a} \left[\frac{-d(A)}{dt} \right] = \frac{1}{b} \left[\frac{-d(B)}{dt} \right] = \frac{1}{c} \left[\frac{+d(C)}{dt} \right] = \frac{1}{d} \left[\frac{+d(D)}{dt} \right] = k[A]^x \cdot [B]^y}$$

Differential rate law

Rate Constant (k): ———

the R.O.R. at unit conc. of reactant is known as rate constant.

$$\text{If } (A) = (B) = 1 \text{ mol l}^{-1}$$

$$\text{Rate} = k[A]^x \cdot [B]^y$$

$$\text{Rate} = k(1)^x \cdot (1)^y$$

$$\therefore \boxed{\text{Rate} = k}$$

↳ For a x^n rate constant does not depends on conc. of reactant ~~by~~ but it depends only on temp. and catalyst.

↳ Larger the value of k faster is the x^n .

~~Order~~ Order of R^{x^n} : —

The sum of power ~~raised~~ ^{raised} to each conc. terms in rate law expression is known as order of x^n

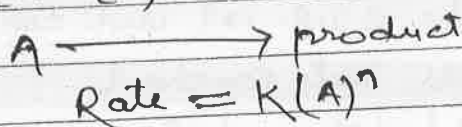
Order of x^n can be zero, (Hive and fractional

Notes - Order w.r.t. a particular species can be (-)ive but overall x^n can never be (-)ive.

Order of x^n is an experimental quantity.
Significance of order is that it indicates how sensitive the rate is to the change in conc. of reactant.

Unit of rate constant: —

For a x^n ,



$$k = \frac{\text{Rate}}{(A)^n} = \frac{(\text{conc.}) \text{time}^{-1}}{(\text{conc.})^n}$$

$$\text{Unit of } k = (\text{conc.})^{1-n} \text{ time}^{-1}$$

$n = \text{order of rxn}$

$$K = (\text{conc.})^{1-n} \text{ time}^{-1}$$

$$= (\text{mol l}^{-1})^{1-n} \text{ s}^{-1}$$

$$K = \text{mol}^{(1-n)} \text{ l}^{(n-1)} \text{ s}^{-1}$$

Q Unit of K depends on order of rxn

0th order rxn $\Rightarrow K = \text{mol l}^{-1} \text{ s}^{-1}$

1st order rxn $\Rightarrow K = \text{s}^{-1}$

2nd order rxn $\Rightarrow K = \text{mol}^{-1} \text{ l s}^{-1}$

for gaseous rxn

$$\text{Unit of } K = (\text{Pressure})^{1-n} \cdot \text{time}^{-1}$$

Ques for a rxn the rate law equation is given as $R = K(C)^{3/2}$
Then the unit of rate const will be.

$$K = \text{mol}^{(1-n)} \text{ l}^{(n-1)} \text{ s}^{-1}$$

$$K = \text{mol}^{-1/2} \text{ l}^{1/2} \text{ s}^{-1}$$

Ques for a gaseous rxn. $A(g) + 2B(g) \rightarrow C(g)$ the rate law is given as $\text{Rate} = K(A)(B)^2$ then find out the effect on rate of rxn if

(i) Conc. of both A & B are tripled

(ii) pressure of only B is half

(iii) Volume of container is reduced to $\frac{1}{4}$ th of initial volume.

$$\textcircled{i} \quad \text{Rate}_i = k(A)(B)^2 \quad \text{--- (1)}$$

$$\begin{aligned} \text{Rate}_f &= k(3A)(3B)^2 \\ &= 27 \cdot k(A)(B)^2 \\ &= 27 \times \text{Rate}_i \end{aligned}$$

$$\textcircled{iii} \quad \text{Rate}_i = k\left(\frac{n_A}{V}\right)\left(\frac{n_B}{V}\right)^2 \quad \text{--- (1)}$$

$$\textcircled{ii} \quad \text{Rate}_i = kP_A \cdot P_B^2 \quad \text{--- (1)}$$

$$\begin{aligned} \text{Rate}_f &= k(P_A) \cdot \left(\frac{P_B}{2}\right)^2 \\ &= \frac{1}{4} \cdot k(P_A)(P_B)^2 \end{aligned}$$

$$\text{Rate}_f = \frac{1}{4} \text{Rate}_i$$

$$\begin{aligned} \text{Rate}_f &= k\left(\frac{n_A}{V/4}\right)\left(\frac{n_B}{V/4}\right)^2 \\ &= 64 \cdot k\left(\frac{n_A}{V}\right)\left(\frac{n_B}{V}\right)^2 \end{aligned}$$

$$\text{Rate}_f = 64 \times \text{Rate}_i$$

Ques. In a rxn $2A + B \rightarrow$ products when the conc. of A is tripled then the rate is also tripled and when the conc. of B is increased ~~to~~ ^{by} 9 times then rate is also tripled then find out rate law of the rxn.

$$\Delta \text{Rate} \propto (\Delta C)^{\text{order}} \quad \star$$

$$\text{Rate} = k(A)^x \cdot (B)^y$$

$$\Delta \text{rate} \propto (\Delta C_A)^x$$

$$(3)^1 \propto (3)^x$$

$$\underline{x=1}$$

$$\Delta \text{rate} \propto (\Delta C_B)^y$$

$$(3) \propto (1)^y$$

$$(3)^1 \propto (3)^{2y}$$

$$1 = 2y$$

$$y = \frac{1}{2}$$

$$\text{Rate} = k(A)^1(B)^{1/2}$$

$$\text{Overall order of rxn} = 1 + \frac{1}{2}$$

$$= \frac{3}{2}$$

Q. In the rxn $3P + 2Q \rightarrow$ product when the conc. of P is doubled the rate becomes 8 times and when conc. of Q is doubled the rate becomes $\frac{1}{4}$ th of the original rate then find out rate law & overall order of rxn.

$$\Delta \text{rate} \propto (\Delta C_P)^{\text{order}}$$

$$(P) \propto (2)^x$$

$$(8) \propto (2)^x$$

$$(2)^3 \propto (2)^x$$

$$x = 3$$

$$\Delta \text{rate} \propto (\Delta C_Q)^y$$

$$\left(\frac{1}{4}\right) \propto (2)^y$$

$$(2)^{-2} \propto (2)^y$$

$$y = -2$$

$$\text{Overall order of rxn} = k(P)^3(Q)^{-2}$$

$$= 3 - 2 = 1$$

Note:—

(-)ve order means if the conc. of that species is from R.O.R. is.

Ques. In the rxn $A+B \rightarrow C+D$ when a conc. of B is tripled the rate becomes 27 times when the conc. of both A & B is doubled then rate becomes 4 times then determine the rate law of the rxn.

$$R = k(A)^x(B)^y$$

$$\begin{aligned} \Delta \text{rate} &\propto (\Delta C_A)^x \\ 27 &\propto (3)^x \\ (3)^3 &\propto (3)^x \\ x &= 3 \end{aligned}$$

$$\begin{aligned} \Delta \text{rate} &\propto (\Delta C_B)^y \\ \Delta \text{rate} &\propto (\Delta C_A)^x \cdot (\Delta C_B)^y \\ (4) &\propto (2)^3 \cdot (2)^y \end{aligned}$$

$$\begin{aligned} \frac{1}{2} &\propto (2)^y \\ 2^{-1} &\propto (2)^y \end{aligned}$$

$$\begin{aligned} \text{Rate} &= k(A)^3(B)^{-1} \\ \text{Overall order} &= 3 - 1 \\ &= 2 \end{aligned}$$

$$y = -1$$

Ques. In the rxn $P+3Q+R \rightarrow \text{products}$ when the conc. of P is doubled the rate is also doubled when the conc. of P & Q are tripled the rate becomes 9 times and when the conc. of both Q & R are doubled then rate also doubled then determine overall order of rxn.

$$R = k(P)^x(Q)^y(R)^z$$

$$\begin{array}{l|l} \Delta \text{rate} \propto (\Delta C_P)^x & \Delta \text{rate} \propto (\Delta C_P)^x (\Delta C_Q)^y \\ (2)^1 \propto (2)^x & (9) \propto (3)^1 (3)^y \\ \underline{x=2} & (9)^1 \propto (3)^y \\ & \underline{y=1} \end{array}$$

$$\begin{array}{l} \Delta \text{rate} \propto (\Delta C_A)^y (\Delta C_B)^z \\ (2) \propto (2)^1 \cdot (2)^z \\ \text{①} \\ 1 = 1 + z \\ \underline{z=0} \end{array}$$

$$\begin{array}{l} \text{Rate} = k(P)^1(Q)^1(R)^0 \\ \text{O.O.R} = 1 + 1 + 0 = 2 \end{array}$$

Ques. In the rxn $A+B \rightarrow C+D$ when the conc. of A doubled then the rate becomes 2.82 times and when the conc. of B is tripled the rate is also tripled. find out overall order of rxn.

$$R = k[A]^x[B]^y$$

$$\begin{array}{l} \Delta \text{rate} \propto (\Delta C_A)^x \\ (2.82)^1 \propto (2)^x \\ (2 \times 1.41) \propto (2)^x \\ (2\sqrt{2}) \propto (2)^x \\ (2)^{3/2} \propto (2)^x \\ \underline{x = 3/2} \end{array}$$

$$\begin{array}{l} \Delta \text{rate} \propto (\Delta C_B)^y \\ (3)^1 \propto (3)^y \\ \underline{y=1} \end{array}$$

$$\begin{array}{l} \text{Rate} = k[A]^x[B]^y \\ = \frac{3}{2} + 1 \\ = \underline{\underline{\frac{5}{2}}} \end{array}$$

OP

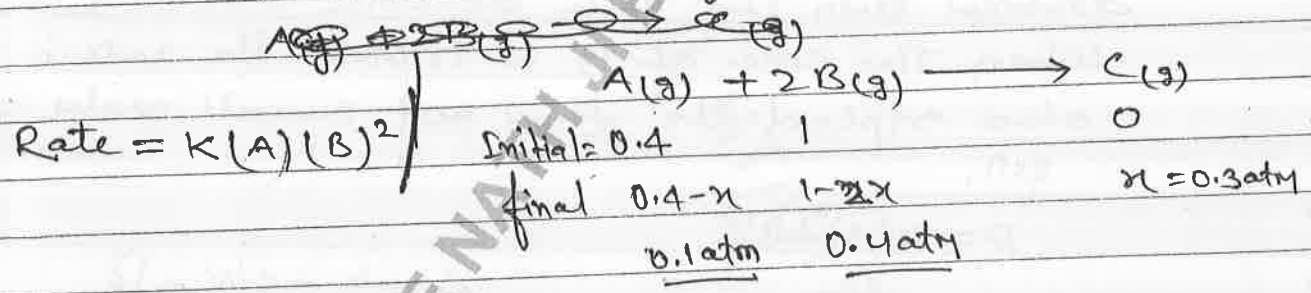
$$(2.82) \propto (2)^x$$

$$\log 2.82 = x \log 2$$

$$0.45 = x(0.3)$$

$$x = \frac{0.45}{0.3} = \underline{\underline{\frac{3}{2}}}$$

Ques. for a rxn $A(g) + 2B(g) \rightarrow C(g)$ the rate law is given as $\text{Rate} = k[A](B)^2$. If the initial pressure of A & B are 0.4 atm and 1 atm respectively and after a certain time the pressure of C is found to be 0.3 atm then find out the ratio new rate of rxn and initial rate of rxn.



$$\frac{\text{Rate}_f}{\text{Rate}_i} = \frac{k(0.1)(0.4)^2}{k(0.4)(1)^2}$$

$$= \frac{1}{25} = \underline{\underline{0.04}}$$

Ques. Determine the rate law for the following rxn with the help of given experimental data.



(P)	(Q)	R.O.R. (M s ⁻¹)
0.05M	0.05M	1.2 × 10 ⁻³
0.10M	0.05M	2.4 × 10 ⁻³
0.05M	0.10M	1.2 × 10 ⁻³

$$\Delta \text{rate} \propto (\Delta C_P)^x$$

$$(2)^1 \propto (2)^x$$

$$x = 1$$

$$\Delta \text{rate} \propto (\Delta C_Q)^y$$

$$2 \propto (2)^y$$

$$(2)^0 \propto (2)^y$$

$$y = 0$$

$$\text{Rate} = k(P)^1(Q)^0$$

$$0.0.R = 1 + 0 = 1$$

Ques Find out the rate constant of the following rxn with the help of experimental data.



(A ₂)	(B ₂)	(R.O.R.) _{AB}	R.O.R. = $\frac{R.O.A}{2}$
0.1M	0.1M	2.5 × 10 ⁻³ M s ⁻¹	1.25 × 10 ⁻³
0.2M	0.1M	5 × 10 ⁻³ M s ⁻¹	2.5 × 10 ⁻³
0.2M	0.2M	20 × 10 ⁻³ M s ⁻¹	10 × 10 ⁻³

$$\Delta \text{rate} \propto (\Delta C_{A_2})^x$$

~~$$(2)^1 \propto (2)^x$$~~

$$(2)^1 \propto (2)^x$$

$$x = 1$$

$$\Delta \text{rate} \propto (\Delta C_{B_2})^y$$

$$(4) \propto (2)^y$$

$$(2)^2 \propto (2)^y$$

$$y = 2$$

$$\text{Rate} = k(A_2)^1(B_2)^2$$

$$1.25 \times 10^{-3} = k(0.1)(0.1)^2$$

$$= \underline{1.25}$$

7.2

Ques.	(A)	(B)	R.O.R (ms ⁻¹)
	0.1M	0.1M	6×10^{-3}
	0.3M	0.2M	$7.2 \times 10^{-2} = 72 \times 10^{-3}$
	0.3M	0.4M	$2.88 \times 10^{-1} = 288 \times 10^{-3}$
	0.5M	0.5M	?

$$\Delta \text{rate} \propto (\Delta C_B)^y$$

$$12 \propto (2)^y$$

$$12^2 \propto (2)^y$$

$$y = 2$$

$$\Delta \text{rate} \propto (\Delta C_A)^x (\Delta C_B)^y$$

$$12 \propto (3)^x (2)^2$$

$$(3)^1 \propto (3)^x$$

$$x = 1$$

$$\text{Rate} = k(A)^1(B)^2$$

$$\frac{6 \times 10^{-3}}{\text{Rate}} = \frac{k(0.1)(0.1)^2}{k(0.5)(0.5)^2}$$

$$\text{Rate} = 6 \times 10^{-3} \times 125$$

$$= 0.75 \text{ ms}^{-1}$$

Ques.	(P)	(Q)	R.O.R (ms ⁻¹)
	0.03M	0.03M	3×10^{-5}
	0.06M	0.06M	$1.2 \times 10^{-4} = 12 \times 10^{-5}$
	0.09M	0.06M	$2.7 \times 10^{-4} = 27 \times 10^{-5}$

$$\Delta \text{rate} \propto (\Delta C_P)^x$$

$$\left(\frac{9}{4}\right) \propto \left(\frac{3}{2}\right)^x$$

$$\left(\frac{3}{2}\right)^2 \propto \left(\frac{3}{2}\right)^x$$

$$x = \frac{3}{2}$$

$$\Delta \text{rate} \propto (\Delta C_P)^x (\Delta C_Q)^y$$

$$(4) \propto (2)^2 (2)^y$$

$$(1) \propto (2)^y$$

$$(2)^0 \propto (2)^y$$

$$y = 0$$

$$\text{Rate} = k(P)^2(Q)^0$$

$$\text{O.O.R.} = 2 + 0 = 2$$

Ques In a rxn $2A(g) + B \longrightarrow$ product if the volume of vessel is reduced to $\frac{1}{2}$ rd of its original volume then how many times the rate of rxn will be.

(i) 9 times

(ii) 18 times

(iii) 27 times

(iv) Can't be predicted

— when (i) option is not given

then 27 times is considered.

— Rate law is practical concept.

Mechanism of rxn (Determination of Rate law):—

(i) Single step rxns:—

A rxn that complete in one step that is reactant^{are} directly converted into product are known as elementary rxn.

• Intermediate are not formed during the rxn.

Note → • Zero order rxn can never be elementary rxn.

For elementary rxn,

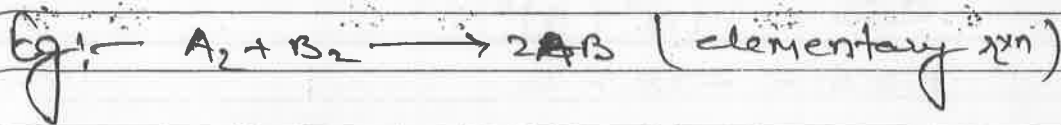
order w.r.t. each reactant = Stoichiometric coefficient of that reactant in the balanced chemical equation.

For a elementary rxn,



$$\text{Rate} = k(A)^a \cdot (B)^b$$

Note →



$$\text{Rate} = k (A_2)^1 (B_2)^1$$

$$\text{Order w.r.t. } A_2 = 1$$

$$\text{--- " --- } B_2 = 1$$

$$\text{O.O.R.} = 1 + 1 = 2$$

② Multi step rxn :-

The rxn that involves two or more steps for the conversion of reactant into product are known as multi-step or complex rxn.

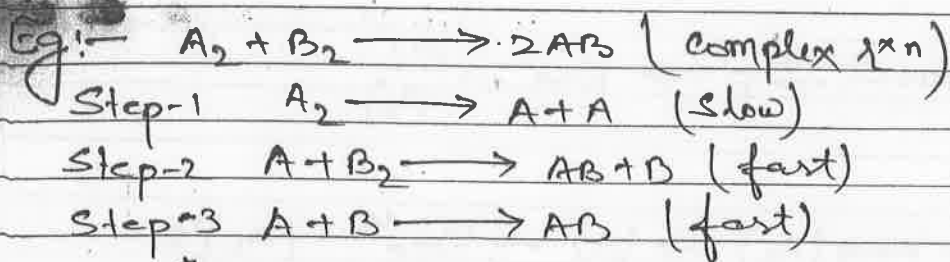
- Intermediate are formed during the rxn.
- Every step in a complex rxn is an elementary rxn.

for complex rxn,

$$\text{Order w.r.t each reactant} = \text{Stoichiometric coefficient of the reactant in the slowest step of the mechanism.}$$

(Only when the slowest step does not contain intermediate)

Slowest step / RDS / Rate controlling step \Rightarrow It controls the overall R.O.R.



* $\boxed{\text{Rate} = k[A_2]^1}$ Acc. to the slowest step.

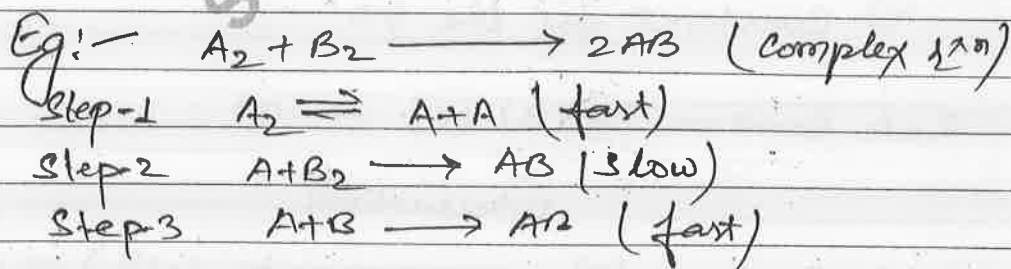
Order w.r.t. $A_2 = 1$

— " — $B_2 = 0$ } As it is not present in Rate law

O.O.R. = $1 + 0 = 1$

* Rate law can only contain the conc. terms of reactant and early product no intermediate term can be present

- If any intermediate is present in the rate equation which is provided by the slowest step then it should be removed with the help of reversible step given in the mechanism.



Using slowest step $\Rightarrow \text{Rate} = k(A)(B_2)$ — (1)

~~Rate~~
Intermediate

Using slowest step $\Rightarrow K_{eq} = \frac{(A)^2}{(A_2)}$

$$(A^2) = K_{eq} (A_2) \Rightarrow (A) = \underbrace{K_{eq}^{1/2}}_{\text{Put in (1)}} (A_2)^{1/2}$$

$$\text{Rate} = (k \cdot K_{eq})^{1/2} (A_2)^{1/2} (B)^1$$

$$\text{Rate} = k' (A_2) (B_2)$$

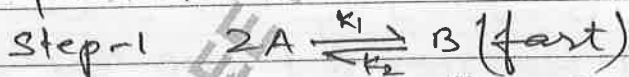
Order w.r.t. $A_2 = \frac{1}{2}$

Order w.r.t. $B_2 = 1$

O.O.R. = $\frac{1}{2} + 1 = \frac{3}{2}$

$$k' = k \cdot K_{eq}^{1/2}$$

Ques For a rxn $2A + C \rightarrow P$ the following ~~steps~~ mechanism has been proposed



then determine rate law and rate constant for the rxn.

$$\text{Rate law} = k_3 \underbrace{(B)}_{\text{Intermediate}} (C) \quad \text{--- (1)}$$

$$K_{eq} = \frac{k_1}{k_2} = \frac{(B)}{(A)^2} \Rightarrow (B) = \frac{k_1}{k_2} (A)^2 \quad \text{Put in (1)}$$

$$\text{Rate} = \left(k_3 \cdot \frac{k_1}{k_2} \right) (A)^2 (C)$$

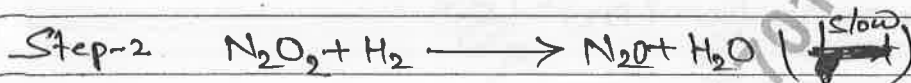
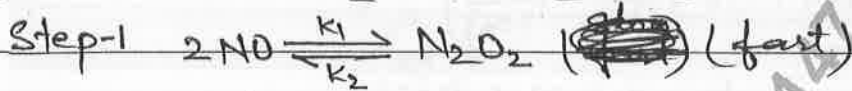
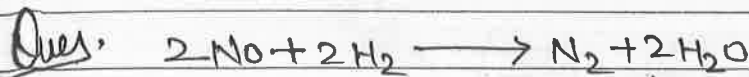
$$\text{Rate} = K (A)^2 (C)$$

$$K = \frac{k_3 \cdot k_1}{k_2}$$

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Study Material Purchase & Sell,
Hand Writing Notes, Online Form

मातृ छाया होस्टल शॉप नं. 2 ऐलन सत्यार्थ गेट नं. 2 के
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$$\text{Rate} = k_3 (\text{N}_2\text{O}_2) (\text{H}_2) \quad \text{--- (1)}$$

$$\frac{k_1}{k_2} = \frac{(\text{N}_2\text{O}_2)}{(\text{NO})^2} \implies \text{N}_2\text{O}_2 = \frac{k_1}{k_2} (\text{NO})^2$$

put in (1)

$$\text{Rate} = \left(k_3 \cdot \frac{k_1}{k_2} \right) (\text{NO})^2 (\text{H}_2)$$

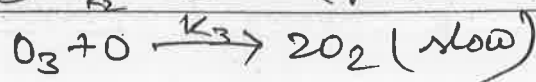
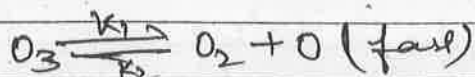
$$\text{Rate} = K (\text{NO})^2 (\text{H}_2)$$

$$K = \frac{k_3 \cdot k_1}{k_2}$$

Ques: Determine the order of the following rxn.
with the help of following rxn.



Mechanism



EX#1 1-10, 11-30.

EX#2 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20
PAGE NO. 17, 33
DATE 6/11/14/15, 20
22, 31, 39

$$\text{Rate} = k_3 (O_3) \cdot (O) \quad \text{--- (D)}$$

$$\frac{k_1}{k_2} = \frac{(O_2)(O)}{(O_3)} \Rightarrow (O) \Rightarrow \frac{k_1}{k_2} \frac{(O_2)}{(O_3)}$$

put in (D)

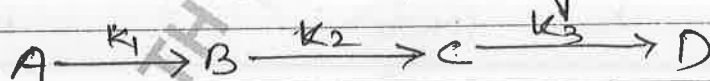
$$\text{Rate} = k_3 (O)_3 \left(\frac{k_1}{k_2} \cdot \frac{(O_2)}{(O_3)} \right)$$

$$\text{Rate} = k_3 \cdot \frac{k_1}{k_2} \cdot (O_3)^2 (O_2)^{-1}$$

$$\text{Rate} = k (O_3)^2 (O_2)^{-1}$$

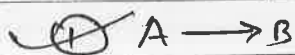
$$\text{Order of rxn} = 2 - 1 = 1$$

Ques. A rxn $A \rightarrow D$ occurs in following consecutive step.



If $k_1 < k_2 < k_3$

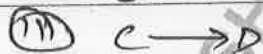
then determine w.o.f is R.D.S.



$k_1 \Rightarrow \text{min.}$



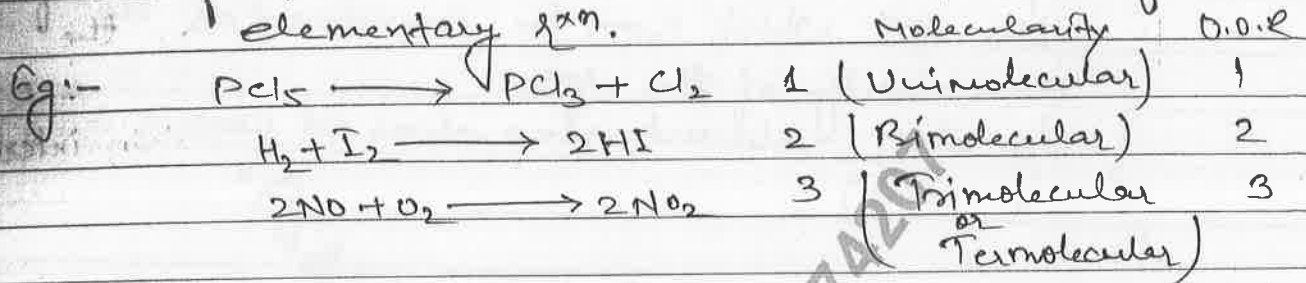
slowest step R.D.S



Molecularity of rxn: —

→ The no. of reacting species (atom, molecules, ions) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical rxn is known as molecularity.

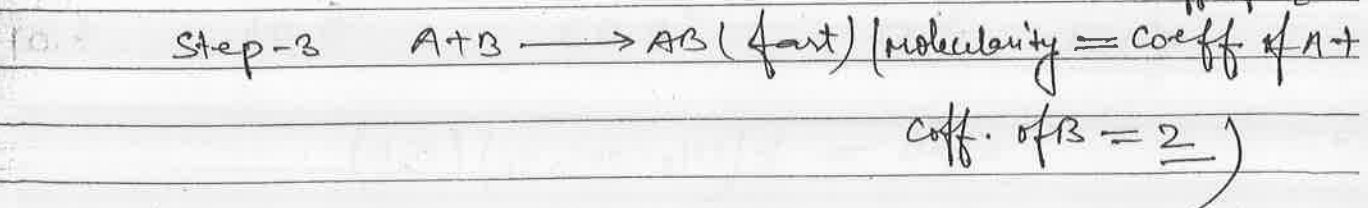
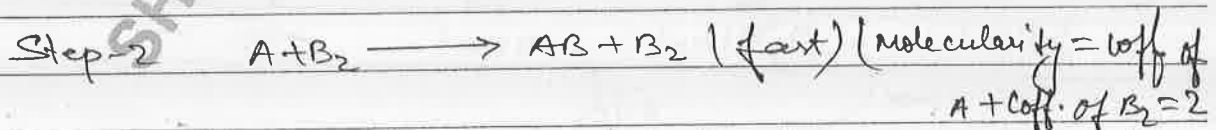
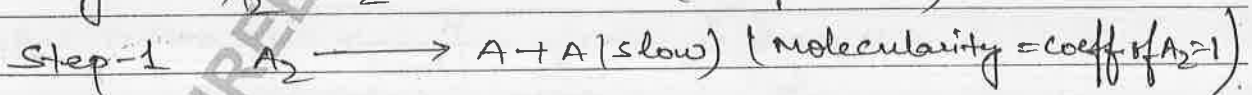
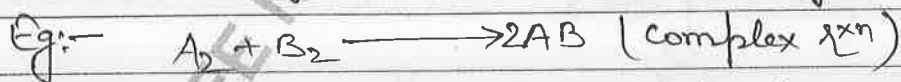
→ It is theoretical quantity i.e. It can be determined from a balanced chemical equation of an elementary rxn.



→ In elementary rxn molecularity is equal to its order.

→ molecularity can be a positive integer (1, 2, 3) but it can not be negative, 0 or fraction.

→ Total molecularity of a complex rxn is meaningless because the concept of molecularity is applied only for elementary rxn. In complex rxn the molecularity of each step of mechanism is defined separately as they are all elementary.



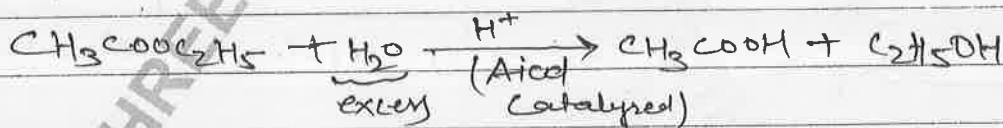
↳ Generally in complex rxn the molecularity of slowest step is same as the overall order of the rxn which can be considered as the molecularity of the rxn.
(Only when slowest step does not contain intermediate)

↳ Generally the max value of molecularity or order is 3 because the chances of effective collision of more than 3 molecules are very rare.

Pseudo first Order rxn:
OR Pseudo Unimolecular rxn:-

↳ The rxn in which the value of order of rxn is 1 but molecularity is more than 1 are known as pseudo first order rxn.

Eg:- Hydrolysis of ester in acidic medium.



Initial	0.01 mol	10 mol	—	—
final	0	0.99	0.01	0.01
	100%	0.1%		

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5](\text{H}_2\text{O})$$

$$(\text{H}_2\text{O}) = \text{Constant} \left. \begin{array}{l} \text{As it is present in excess} \\ (k \cdot \text{H}_2\text{O}) = k' \end{array} \right\}$$

↳ Hydrolysis of ester in alkaline medium is a second order rxn because in it NaOH is used as a reactant.

<u>Molecularity</u>	<u>Order</u>
(i) Theoretical	↳ Experimental
(ii) Always a +ve integer	↳ Can be 0, +ve or fractional.
(iii) Applicable for elementary rxn but meaningless for complex rxn	↳ Applicable for both elementary or complex.
(iv) Intermediate are considered	↳ Intermediate are not considered.
(v) Does not changes with experimental condition such as Concentration Conc. pressure, temp. etc.	↳ May changes with experimental condition.
	$2HI \xrightarrow{Au} H_2 + I_2$ (Order)
	$2HI \xrightarrow{A} H_2 + I_2$ (2 nd order)

Ques for a rxn $A + 2B \rightarrow c$ the rate law is given as $\text{rate} = k(A)(B)^2$ from find out the order of rxn if A is taken as in excess.

$$\text{Rate} = k \underbrace{(A)}_{\text{excess}} (B)^2$$

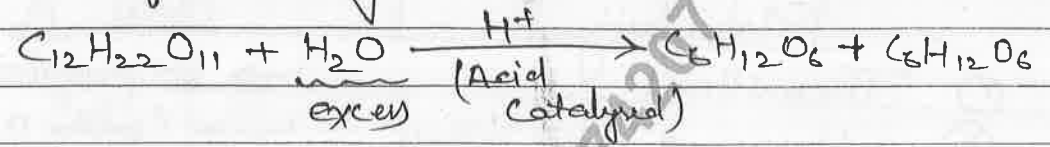
$$\text{Rate} = k' (B)^2$$

$$\text{Order} = 2$$

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5]$$

Order = 1 ; Molecularity = 2

Eg:- Inversion of cane sugar



$$\text{Rate} = k' (\text{C}_{12}\text{H}_{22}\text{O}_{11}) (\text{H}_2\text{O})$$

$$k \cdot \text{H}_2\text{O} = k' \quad \left\{ \text{As } (\text{H}_2\text{O}) = \text{constant} \right\}$$

$$\text{Rate} = k' (\text{C}_{12}\text{H}_{22}\text{O}_{11})$$

Order = 1
 molecularity = 2

Conclusion:-

If a reactant is taken in excess then its conc. doesn't get altered much during the course of the rxn hence it is taken as constant i.e. rate does not depend on such substances & hence they are not considered to determine the order of rxn.

Note:- If a substance is taken in excess the molecularity remain unchanged but order changes.

Note:- Hydrolysis of ester in acidic medium is a first order rxn because in it H⁺ act as catalyst.

Ques for the acidic hydrolysis of sugar the rate const. is $2 \times 10^3 \text{ Mol}^{-1} \text{ min}^{-1}$ determine the pseudo rate constant if the conc. of H_2O taken in excess is 55.5 mol l^{-1}

$$\text{Rate} = k (\text{C}_{12}\text{H}_{22}\text{O}_{11}) (\text{H}_2\text{O})$$

$$\text{Rate} = k' (\text{C}_{12}\text{H}_{22}\text{O}_{11})$$

$$k' = k (\text{H}_2\text{O})$$

$$= 2 \times 10^3 \times 55.5$$

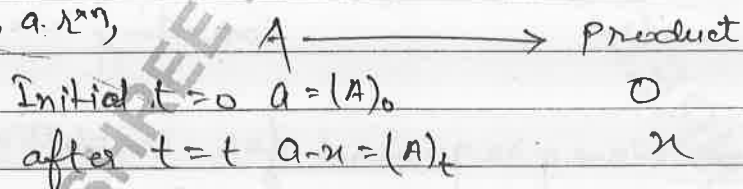
$$= 0.111 \text{ min}^{-1}$$

Study of Different Order rxn: —

(i) Zero order rxn: —

The rxn in which the rate of rxn does not depend on the conc. of reactant are known as zero order rxn.

For, a rxn,



$$\text{Rate} = k (A)^0$$

$$\boxed{\text{Rate} = k}$$

for zero order rxn

R.O.R. = Rate constant

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

Unit of $k = \text{Mol l}^{-1} \text{ s}^{-1} =$

$$d(A) = -k dt$$

unit of R.O.R

On integrating,

$$\int_{(A)_0}^{(A)_t} d(A) = -k \int_0^t dt$$

$$(A)_t - (A)_0 = -kt$$

$$(A)_0 - (A)_t = kt$$

Integrated Rate law,

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

$$x = kt$$

$a = (A)_0 \Rightarrow$ Initial conc. of reactant at time $t=0$

$(a-x) \Rightarrow (A)_t =$ Remaining conc. of reactant after time t .

$x = (A)_0 - (A)_t \Rightarrow$ Amount of reactant converting into product

General

Note:—

$t_x \Rightarrow$ time required for completion of a part of $x\%$.

At $t = t_x$

$$(A)_t = a - x = a - ax = a(1-x)$$

$$(A)_t = (A)_0 (1-x)$$

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

The time period in which the conc. of reactant is reduced to half of its initial value is known as half life period.

$$[A]_t = [A]_0 (1 - \alpha) = [A]_0 (1 - 0.5)$$

$$= 0.5 [A]_0 = \frac{[A]_0}{2}$$

$$[A]_0 - \frac{[A]_0}{2} = kt_{50\%}$$

$$t_{50\%} = \frac{[A]_0}{2k}$$

↳ for a zero order rxn the half life period is \propto to the initial conc. of the reactant.

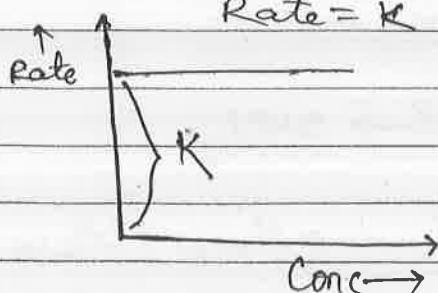
$t_{100\%}$ (time required for completion of rxn)

$$[A]_t = 0$$

$$[A]_0 = kt_{100\%}$$

$$t_{100\%} = \frac{[A]_0}{k} = 2 \times t_{50\%}$$

Graph:— (i) Rate vs Conc.

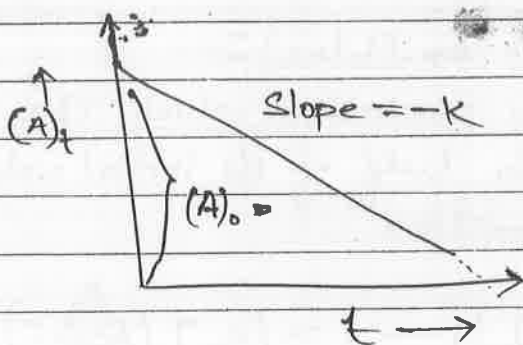


(ii) $(A)_t$ vs t

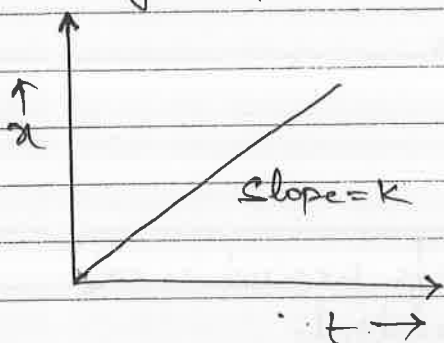
$$[A]_0 - (A)_t = kt$$

$$(A)_t = -kt + [A]_0$$

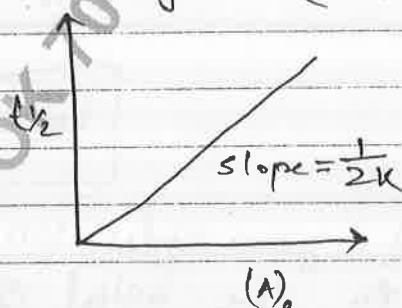
$$y = mx + c$$



(iii) $x \propto t$
 $x = kt$
 $y = mx$



(iv) $t_{1/2} \propto (A)_0$
 $t_{1/2} = \left(\frac{1}{2k}\right) (A)_0$
 $y = mx$

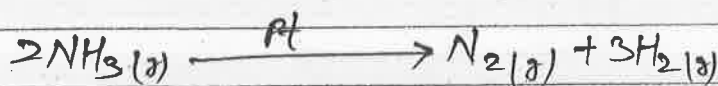
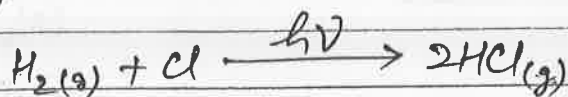


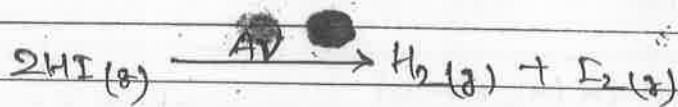
↳ Zero order rxn are always complex rxn.

↳ for zero order rxn the R.O.R is constant throughout the rxn.

↳ Zero order rxn are relatively uncommon but they occur under special conditions. Some enzyme catalyzed rxn and the rxn which occurs on metal surface are few examples of zero order rxn.

Examples of '0' order rxns: —



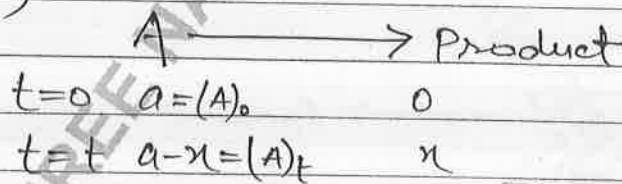


* Adsorption of gases on metal surface

→ At low pressure rate of adsorption is proportional to the ~~pressure~~ surface area covered which is proportional to the pressure or conc. of gas. Hence order is first. But at high pressure the complete surface area gets covered by the gas & rate becomes independent of pressure and conc. of gas. Hence the order is zero.

first order rxn: —

The rxn in which R.O.R \propto to the conc. of reactant are known as first order rxn for a rxn,



$$\text{Rate} = k(A)^1$$

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

$$\frac{d(A)}{dt} = -kt$$

On integrating,

$$\int_{(A)_0}^{(A)_t} \frac{d(A)}{(A)} = -k \int_0^t dt$$

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$$\ln(A)_t - \ln(A)_0 = -kt$$

$$kt = \ln(A)_0 - \ln(A)_t$$

$$kt = \ln \left(\frac{(A)_0}{(A)_t} \right) \quad \text{--- (1)}$$

$$\therefore kt = 2.303 \log_{10} \left(\frac{(A)_0}{(A)_t} \right) = \left(\frac{a}{a-x} \right) \quad \text{--- (2)}$$

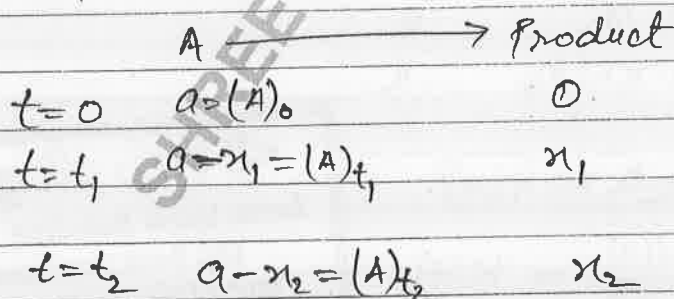
Integrated rate law

from equation (1)

$$\frac{(A)_0}{(A)_t} = e^{kt}$$

$$(A)_t = (A)_0 \cdot e^{-kt} \quad \text{Whithey Equan.}$$

for a rxn:—



from eqn. — (1)

$$\ln(A)_t = -kt + \ln(A)_0$$

At time t_1

$$\ln(A)_{t_1} = -kt_1 + \ln(A)_0 \quad \text{--- (a)}$$

At time t_2 ,

$$\ln(A)_{t_2} = -kt_2 + \ln(A)_0 \quad \text{--- (b)}$$

$$\text{(a)} - \text{(b)} \Rightarrow \ln(A)_{t_1} - \ln(A)_{t_2} = -kt_1 + kt_2$$

$$\therefore k(t_2 - t_1) = \ln \left(\frac{(A)_{t_1}}{(A)_{t_2}} \right)$$

$$k(t_2 - t_1) = 2.303 \log_{10} \left(\frac{(A)_{t_1}}{(A)_{t_2}} \right) = \frac{a - x_1}{a - x_2}$$

Integral formula.

$(A)_{t_1}$ = Remaining conc. of reactant after time t_1

$(A)_{t_2}$ = " " " " time t_2

x_1 = Decomposed of reactant in t_1

x_2 = " " " " in t_2

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

$$kt_{1/2} = 2.303 \log_{10} \left(\frac{(A)_0}{(A)_{1/2}} \right)$$

$$kt_{1/2} = 2.303 \log_{10} (2)$$

$$\therefore t_{1/2} = \frac{0.693}{k}$$

Eg: — $A \cdot t_{1/2} = 10 \text{ min}$
 $100 \text{ M} \xrightarrow{10 \text{ min}} 50 \text{ M}$
 $10 \text{ M} \xrightarrow{10 \text{ min}} 5 \text{ M}$

→ for a first order rxn the half life period is independent of the initial conc. of reactant.

⇒ $t_{3/4}$ or $t_{75\%}$ (time required for completion of 75% of rxn.)

$$(A)_t = (A)_0 (1 - \alpha) = (A)_0 \left(1 - \frac{3}{4}\right)$$

$$\therefore (A)_t = \frac{(A)_0}{4}$$

$$K t_{75\%} = 2.303 \log_{10} \left(\frac{(A)_0}{(A)_0/4} \right)$$

$$K t_{75\%} = 2.303 \log_{10} (4)$$

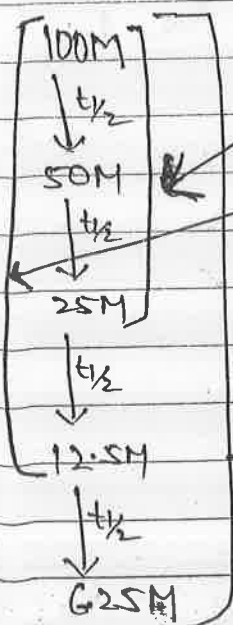
$$t_{75\%} = \frac{2 \times 2.303 \log_{10} (2)}{K}$$

$$\therefore t_{75\%} = 2 \times t_{50\%}$$

$$t_{87.5\%} = 3 \times t_{50\%}$$

$$t_{93.75\%} = 4 \times t_{50\%}$$

$$t_{99.99\%} = 10 \times t_{50\%}$$



① A_t vs t

② $\log \frac{A}{A_t}$ vs t

③ Rate vs Conc.

④ $\log A_t$ vs t

⑤ $t_{1/2}$ vs A_0

⑥ t_{100}

PAGE NO.

DATE: / /

⇒ Successive half lives are equal in 1st order rxn

⇒ Remaining conc. of reactant

after 'n' half lives ⇒ $(A)_t = \frac{(A)_0}{2^n}$

⇒ No. of half lives (n) = $\frac{\text{Total time}}{t_{1/2}}$

100M = $(A)_0$

↓ $t_{1/2}$

50M = $\frac{(A)_0}{2} = \frac{(A)_0}{2^1}$

↓ $t_{1/2}$

25M = $\frac{(A)_0}{4} = \frac{(A)_0}{2^2}$

↓ $t_{1/2}$

12.5M = $\frac{(A)_0}{8} = \frac{(A)_0}{2^3}$

↓ $t_{1/2}$

6.25M = $\frac{(A)_0}{16} = \frac{(A)_0}{2^4}$

⇒ $t_{100\%}$ (time required for completion of rxn)

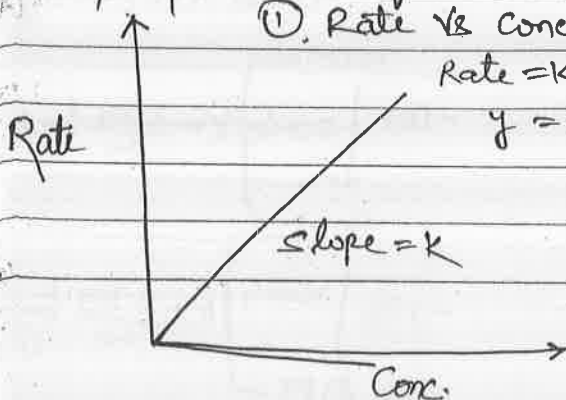
$t_{100\%} = \infty$

Graphical representation:

① Rate vs Conc.

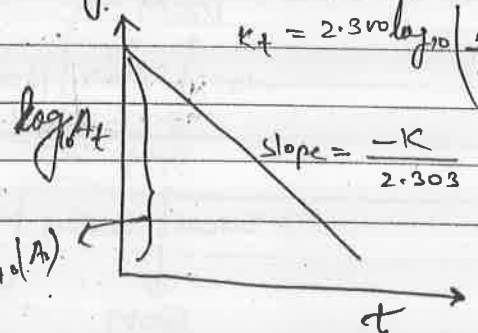
Rate = $k(A)$

$y = mx$

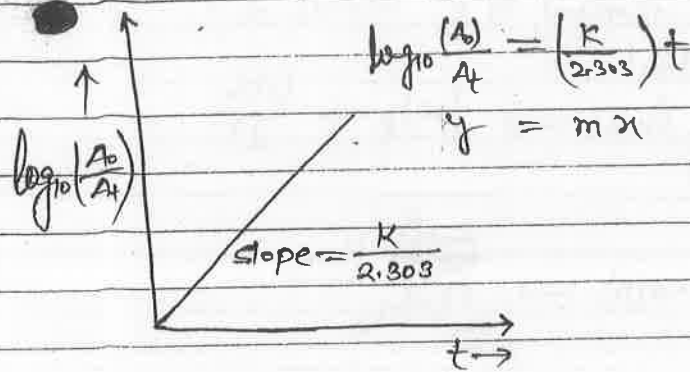


② $\log \frac{A_0}{A_t}$ vs t

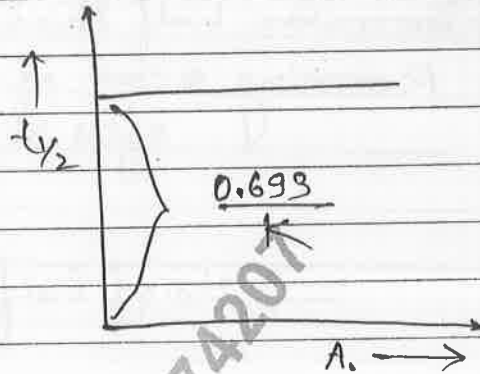
$k_t = 2.303 \log_{10} \left(\frac{A_0}{A_t} \right)$



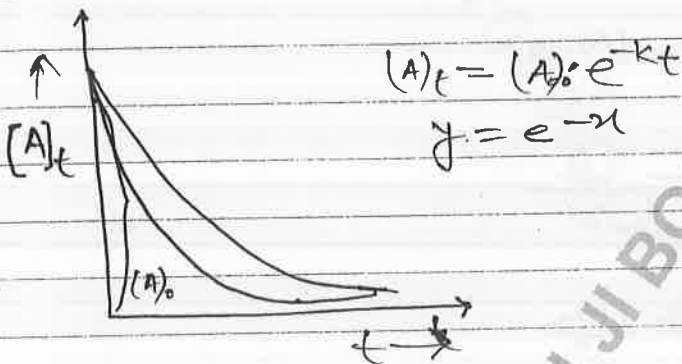
(iii) $\log_{10} \frac{A_0}{A_t} \propto t$



(iv) $t_{1/2} \propto A_0$



(v) $A_t \propto e^{-kt}$



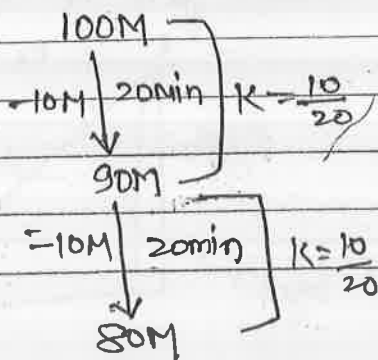
⇒ Examples of 1st order rxns :-



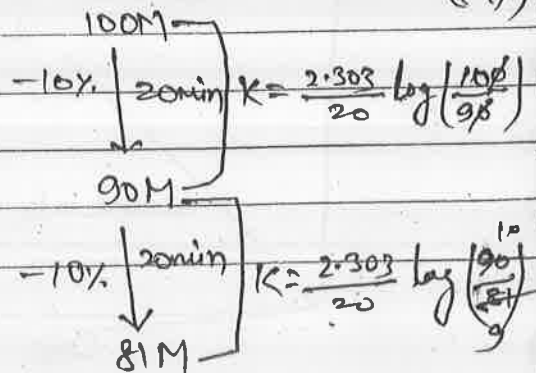
All radioactive decay.

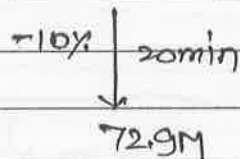
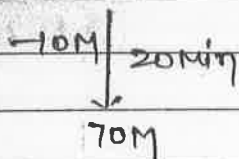
⇒ Unit of $k = \text{time}^{-1}$

Note: — 0 order $(A_0) - (A_t) = kt$



1st Order $kt = 2.303 \log \frac{(A_0)}{(A_t)}$





↳ For a zero order rxn in equal time intervals equal amount of reactant is consumed.

↳ For a first order rxn in equal time intervals equal %age of reactant amount is consumed.

n^{th} Order rxn's : —

$$kt = \frac{1}{(n-1)} \left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] \Rightarrow n \neq 1$$

Integrated rate law

$$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1}}{[A]_0^{n-1}} \right] \Rightarrow n \neq 1$$

$n = \text{Order of rxn}$

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left[\frac{[A]_{0,2}}{[A]_{0,1}} \right]^{n-1}$$

↳ for all order rxn's

Half life method used for determining order of rxn.

2nd Order rxn's: —

$$kt = \frac{1}{(A)_t} - \frac{1}{(A)_0}$$

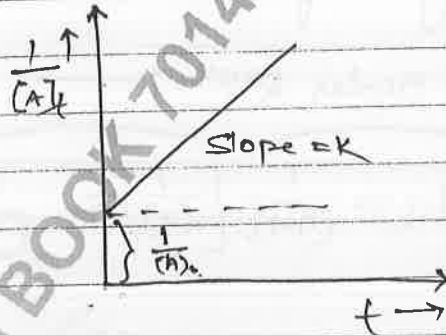
$$t_{1/2} = \frac{1}{k \cdot (A)_0}$$

Graph:-

① $\frac{1}{(A)_t}$ vs t

$$\left(\frac{1}{(A)_t}\right) = k(t) + \frac{1}{(A)_0}$$

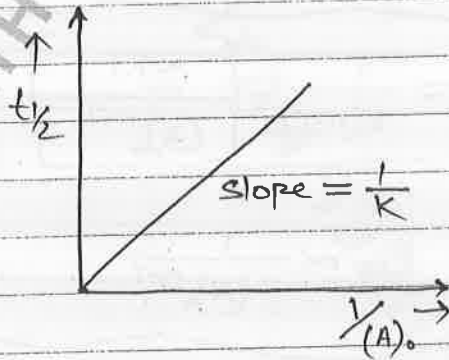
$$y = mx$$



② $t_{1/2}$ vs $\frac{1}{(A)_0}$

$$t_{1/2} = \left(\frac{1}{k}\right) \left(\frac{1}{(A)_0}\right)$$

$$y = mx$$



3rd Order rxn's: —

$$kt = \frac{1}{2} \left[\frac{1}{(A)_t^2} - \frac{1}{(A)_0^2} \right]$$

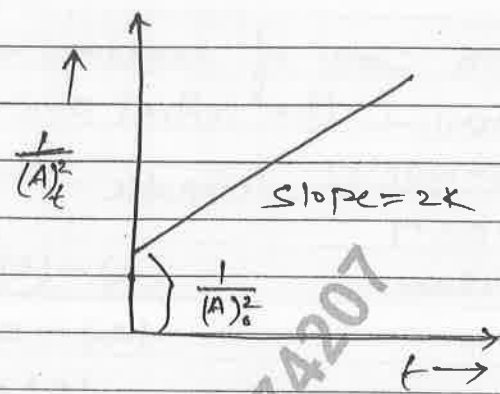
$$t_{1/2} = \frac{1}{2k \cdot (A)_0^2}$$

Graphs:

① $\frac{1}{(A)_t} \text{ vs } t$

$$\left(\frac{1}{(A)_t} \right) = 2k(t) + \frac{1}{(A)_0}$$

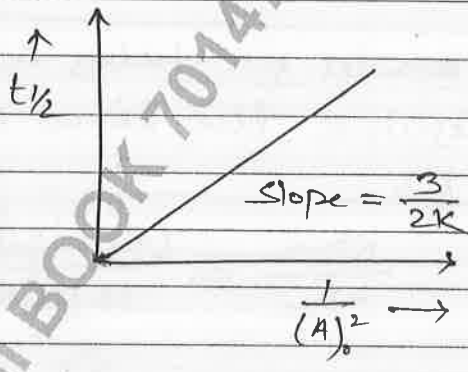
$y = mx$



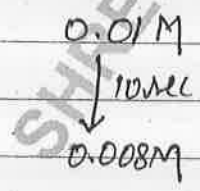
② $t_{1/2} \text{ vs } \frac{1}{(A)_0}$

$$t_{1/2} = \left(\frac{3}{2k} \right) \cdot \left(\frac{1}{(A)_0} \right)$$

$y = mx$



Ques ① for a zero order rxn $A \rightarrow B$ the initial conc. of A is 0.01M and after 10sec its conc. is found to be 0.008M then determine $t_{50\%}$ and $t_{100\%}$ for the rxn.



$$(A)_0 - (A)_t = kt$$

$$0.01 - 0.008 = k(10)$$

$$k = \frac{0.002}{10}$$

$$= 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$t_{50\%} = \frac{(A)_0}{2k}$ $= \frac{0.01}{2(2 \times 10^{-4})} = 25 \text{ sec.}$	$t_{100\%} = \frac{(A)_0}{k}$ $= 2 \times t_{50\%}$ $= 2 \times 25 \text{ sec}$ $= 50 \text{ sec.}$
--	---

Ques 2) For a rxn conc. of reactant is 0.5M after 25 sec. then determine the initial conc. of if rate constant is $2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ \rightarrow 0 order

$$(A)_t = 0.5 \text{ M}$$

After $t = 25 \text{ sec.}$

$$(A)_0 - (A)_t = kt$$

$$(A)_0 - 0.5 = 2 \times 10^{-2} (25)$$

$$(A)_0 = 1 \text{ M}$$

Ques 3) A 0 order rxn takes 40 sec for ^{20%} completion then determine the time required for 80% completion of rxn.

$$\frac{kt_{80\%}}{kt_{20\%}} = \frac{(A)_0 - (A)_t}{(A)_0 - (A)_t}$$

$$= \frac{(A)_0 - 0.8(A)_0}{(A)_0 - 0.2(A)_0}$$

$$\frac{k(40)}{kt_{80\%}} = \frac{0.2(A)_0}{0.8(A)_0}$$

$$t_{80\%} = 40 \times 40 = 160 \text{ sec.}$$

Ques 4) 3.4g of NH_3 is taken in 5L container then determine the time required for 60% decomposition of NH_3 if $k = 2 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

$$(A)_0 = \frac{3.4}{17 \times 5} = 4 \times 10^{-2} \text{ M}$$

$$(A)_t = (A)_0(1-\alpha) = (A)_0(1-0.6)$$

$$= 0.4(A)_0 = (4 \times 10^2)$$

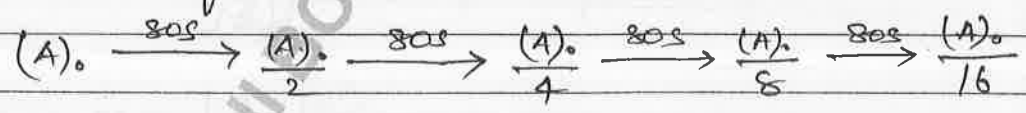
$$= \underline{1.6 \times 10^2 M}$$

$$(A)_0 - (A)_t = kt$$

$$(4 \times 10^2) - (1.6 \times 10^2) = (2 \times 10^{-5}) t_{60\%}$$

$$t_{60\%} = \frac{2.4 \times 10^2}{2 \times 10^{-5}} = 1.2 \times 10^3 \text{ sec}$$

Ques 5) the half period of a first order rxn is 80 sec. then calculate the time in which $1/16^{\text{th}}$ part of reactant is left.



$$t = 80 \times 4$$

$$= 320 \text{ sec.}$$

OR

$$kt = 2.303 \log_{10} \left(\frac{(A)_0}{(A)_t} \right)$$

$$\frac{0.693}{80} = 2.303 \log_{10} \left(\frac{(A)_0}{(A)_0/16} \right)$$

~~$$\frac{0.693}{80} \times t = 4 \times 2.303 \log_{10} 2$$~~

$$t = 80 \times 4 = 320 \text{ sec.}$$

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{80}$$

Q6) The rate constant of a first order rxn is 2.303 sec^{-1} and the initial conc. of reactant is 1 M then determine the %age of initial conc. of reactant that converted into product after ~~sec~~ 1 sec and also determine R.O.R at that time.

$$k t = 2.303 \log \left(\frac{(A)_0}{(A)_t} \right)$$

$$(2.303)(1) = 2.303 \log_{10} \left(\frac{1}{(A)_t} \right)$$

$$\frac{1}{(A)_t} = 10^1 \Rightarrow (A)_t = \underline{0.1 \text{ M}}$$

$$\% \text{ decomposition} = \frac{(A)_0 - (A)_t}{(A)_0} \times 100$$

$$= \frac{1 - 0.1}{1} \times 100 = 90\%$$

$$\text{Rate} = k(A)$$

$$= 2.303 (0.1)$$

$$= 0.2303 \text{ Mol L}^{-1} \text{ s}^{-1}$$

Q7) A first order rxn takes 5 min for 80% completion when the initial conc. of reactant is 1.5 M then determine the time required for 80% completion of the same rxn when the initial conc. of reactant 20 min .

→ Independent of the initial conc. of reactant.

$$\frac{2.303}{5} \log_{10} \left(\frac{1.5}{0.3} \right) = \frac{2.303}{t_{80\%}} \log_{10} \left(\frac{20}{4} \right)$$

$$t_{80\%} \Rightarrow \underline{5 \text{ min}}$$

Note: In first order rxn the time required for the completion a definite fraction of reaction is always same and it is independent from the initial conc. used in the rxn.

Ques. ② The half life of a radioactive isotope is 12.3 yrs. If the amount of isotope left undecayed after 49.2 yrs is 3g, determine the initial mass of isotope.

$$\text{No. of half life } (n) = \frac{\text{total time}}{t_{1/2}} = \frac{49.2}{12.3} = 4$$

$$(A)_t = \frac{(A)_0}{2^n}$$

$$3 = \frac{(A)_0}{2^4}$$

$$(A)_0 = 48g$$

Ques. ③ In a first order rxn the R.O.R is $0.04 \text{ mol l}^{-1} \text{ s}^{-1}$ at 10 sec and $0.03 \text{ mol l}^{-1} \text{ s}^{-1}$ at 20 sec. then determine the ~~the~~ $t_{1/2}$ of a rxn.

$$k(t_2 - t_1) = 2.303 \log_{10} \left(\frac{(A)_{t_1}}{(A)_{t_2}} \right) \quad \left| \quad \frac{\text{Rate}_{t_1}}{\text{Rate}_{t_2}} = \frac{k(A)_{t_1}}{k(A)_{t_2}} \right.$$

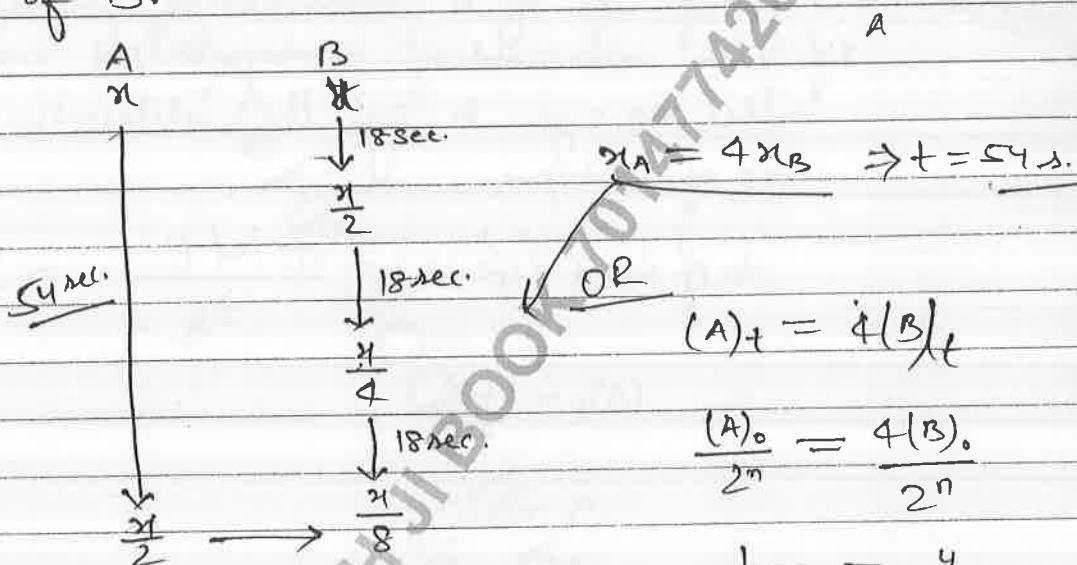
$$\frac{0.693}{t_{1/2}} (20 - 10) = 2.303 \log_{10} \left(\frac{0.04}{0.03} \right) \quad \left| \quad \frac{0.04}{0.03} = \frac{(A)_{t_1}}{(A)_{t_2}} \right.$$

$$\frac{0.3}{t_{1/2}} (10) = 0.12$$

$$t_{1/2} = \frac{0.3 \times 10}{0.12}$$

$$= \underline{\underline{25 \text{ sec}}}$$

Ques 10) Two compd A and B dissociate acc. to first order rxn and their respective half life period are 54 sec. and 18 sec. If the initial conc. of A and B is equal then determine the time in which the conc. of A becomes equal 4 times of B.



$$x_A = 4x_B \Rightarrow t = 54 \text{ s.}$$

OR

$$(A)_t = 4(B)_t$$

$$\frac{(A)_0}{2^m} = \frac{(B)_0}{2^n}$$

$$\frac{1}{2^{t/54}} = \frac{4}{2^{t/18}}$$

$$\frac{2^{t/18}}{2^{t/54}} = 4$$

$$2^{t/18 - t/54} = 2^2$$

$$\frac{t}{18} - \frac{t}{54} = 2$$

$$\frac{2t}{54} = 2$$

$$t = 54 \text{ s.}$$

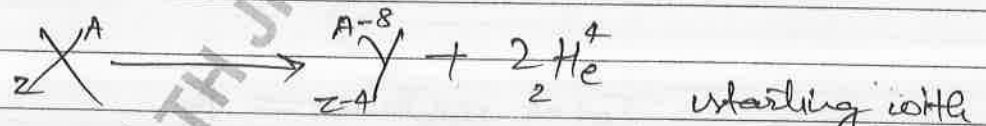
Ques 1) for a first order rxn $A \rightarrow P$ if $t_{99\%} = 10 \text{ min}$ then determine $t_{99.9\%} = ?$

$$\frac{k t_{99\%}}{k t_{99.9\%}} = \frac{2.303 \log_{10} \left(\frac{(A)_0}{\frac{A_0}{100}} \right)}{2.303 \log_{10} \left(\frac{(A)_0}{\frac{0.1}{100} \times (A)_0} \right)}$$

$$\frac{10}{t_{99.9\%}} = \frac{\log_{10}(100)}{\log_{10}(1000)} = \frac{2}{3}$$

$$t_{99.9\%} = \frac{10 \times 3}{2} = 15 \text{ min.}$$

Ques 2) the following radioactive disintegration follow first order kinetics



1 mole of X determine the volume of He collected at STP after 20 days if the half period is λ is 10 days



$$t=0 \quad 1 \text{ mol}$$

$$t=20 \text{ day} \quad (1-x) = 0.25$$

$$x = 0.75$$

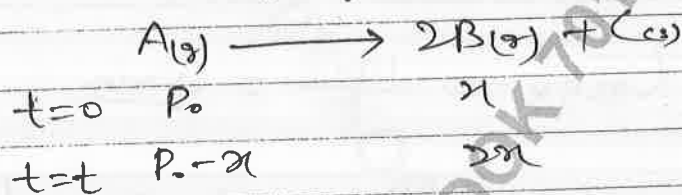
$$2x = 2 \times 0.75 = 1.5 \text{ mol}$$

$$\text{No. of half lives (n)} = \frac{\text{total time}}{t_{1/2}} = \frac{20}{10} = 2$$

$$(A)_t = \frac{(A)_0}{2^n} = \frac{1}{2^2} = 0.25 \text{ mol}$$

$$\therefore \text{Vol. of He. at STP} = 1.5 \times 22.4 = \underline{\underline{33.6 \text{ L}}}$$

Ques ③ for a first order rxn $A(g) \rightarrow 2B(g) + C(g)$ the initial pressure of A is P_0 and after time t the total pressure is P_T then determine the rate constant of the rxn.



$$\text{Total pressure} = P_T$$

$$P_0 - x + 2x = P_T$$

$$P_0 + x = P_T$$

$$x = (P_T - P_0)$$

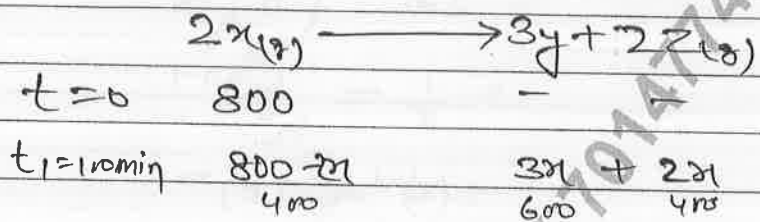
$$k = \frac{2.303}{t} \log_{10} \left(\frac{[A]_0}{[A]_t} \right)$$

$$k = \frac{2.303}{t} \log_{10} \left(\frac{P_0}{P_0 - x} \right)$$

$$k = \frac{2.303}{t} \log_{10} \left(\frac{P_0}{P_0 - (P_T - P_0)} \right)$$

$$k = \frac{2.303}{t} \log_{10} \left(\frac{P_0}{2P_0 - P_T} \right)$$

Ques 19) In a first order rxn $2X(g) \rightarrow 3Y(g) + 2Z(g)$ the initial pressure of X is 800 mmHg and after 100 min. the total pressure of the rxn mixture is found to be 1400 mmHg then determine the value of rate constant and the half life period for the rxn.



$$800 - 2x + 3x + 2x = 1400$$

$$800 - 2x = 1400$$

$$2x = 1400 - 800$$

$$x = \frac{600}{2} = 300$$

$$k = \frac{2.303}{100} \log \left(\frac{800}{400} \right)$$

$$= \frac{2.303}{100} \log(2)$$

$$= \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.93 \times 10^{-3}}$$

$$= 100 \text{ min}$$

Ques. 15 Determine the order of rxn with the help of given data.

(A) ₀	t _{1/2}
0.1M	40s
0.5M	200s

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

$$= \frac{40}{200} = \left(\frac{0.5}{0.1} \right)^{n-1}$$

$$= \frac{1}{5} = (5)^{n-1}$$

$$= (5)^{-1} = (5)^{n-1}$$

$$-1 = n-1$$

$$\boxed{n=0}$$

Ques. 16

(P) ₀	t _{1/2}
50 mmHg	3.64 min.
100 mmHg	1.82 min
200 mmHg	0.91 min

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

$$\frac{3.64}{1.82} = \left(\frac{100}{50} \right)^{n-1}$$

$$2 = (2)^{n-1}$$

$$1 = n-1$$

$$\boxed{n=2}$$

Note:— Special care for 1st order rxn's:—
If information is given in terms of volume, then—

$$kt = 2.303 \log_{10} \left(\frac{V_0 - V_t}{V_0 - V_\infty} \right)$$

V_0 = Initial vol. of reagent (reactant or product)

V_t = Vol. of reagent after time t

V_{∞} = Vol. of reagent at the end of reaction or after very long time

Ques (17) The dissociation of Diazonium chloride is a 1st order rxn the volume of Nitrogen obtained after 10 sec & after a very long time interval is found to be 50 ml & 100 ml respectively, then find out the rate constant of rxn.



$$k_t = 2.303 \log_{10} \left(\frac{V_0 - V_0}{V_0 - V_t} \right)$$

$$= 2.303 \log_{10} \left(\frac{100 - 0}{100 - 50} \right)$$

$$k = \frac{2.303}{10} \log_{10} (2)$$

\approx

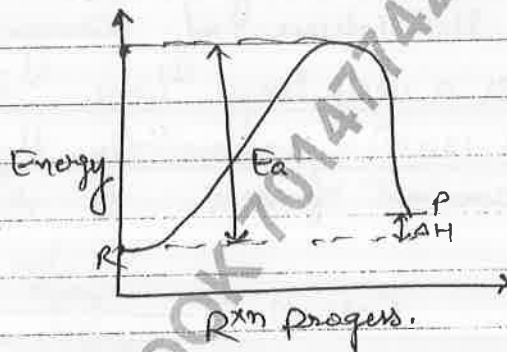
$$= \frac{0.693}{10} = 6.93 \times 10^{-2} \text{ s}^{-1}$$

→ In case of reactant if V_0 is not given then consider it as zero because at the end of rxn reactant completely convert into product.

Collision Theory: - from module

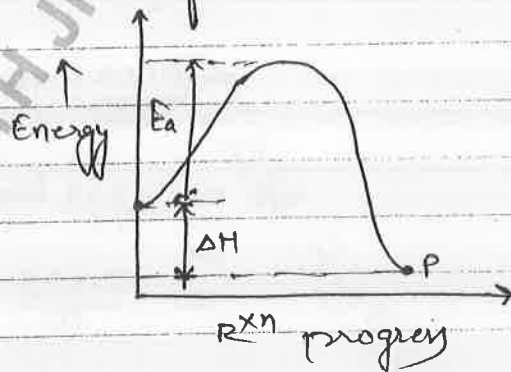
Q. Which of the following is a correct relation for endothermic relation.

- (I) $E_a = \Delta H$
- (II) $E_a > \Delta H$
- (III) $E_a < \Delta H$
- (IV) Any of these

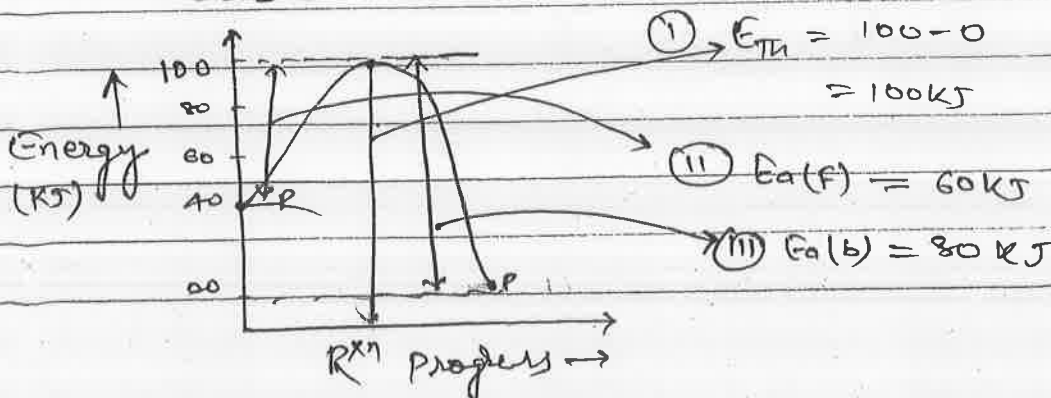


Ques. W.O.F is correct relation for endothermic relation,

- (I) $E_a = |\Delta H|$
- (II) $E_a \geq |\Delta H|$
- (III) $E_a < |\Delta H|$
- (IV) Any of these.

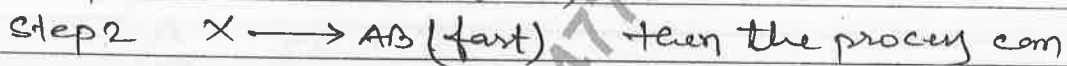
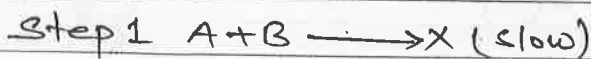


Ques. for a rxn $R \rightleftharpoons P$ Determine E_{TH} , E_a and heat of rxn $E_a(f)$ and $E_a(b)$ with the help of following curve.

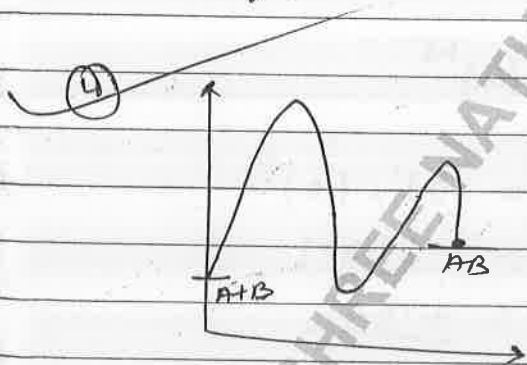
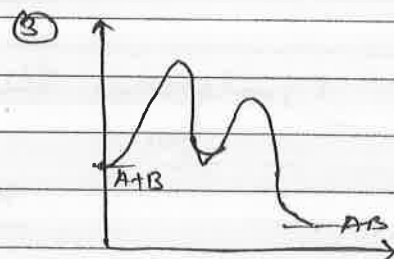
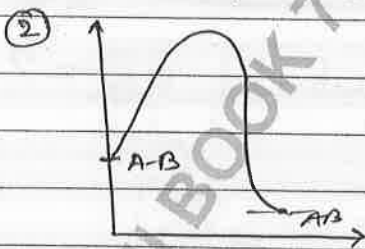
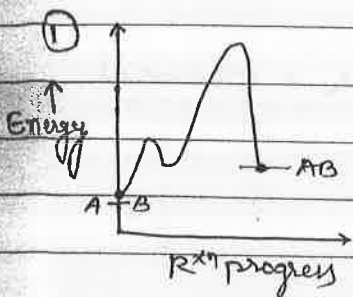


$$\Delta H = E_a(f) - E_a(b) \\ = 60 - 80 \\ = -20 \text{ kJ}$$

Ques. An endothermic rxn occurs in ~~two~~ 2 steps as follows.



then the process can be best described by w.o.f. graphs.



$$E_a \propto \frac{1}{R.O.R}$$

Factor Affecting R.O.R :-

श्री नाथ जी बुक डिपो
Zerox, Spiral Baining, NCERT Book,
Old Book Purchase & Sell,
Study Material Purchase & Sell,
Hand Writing Notes, Online Form
मातृ छाया होस्टल शॉप नं. 2 ऐलन सत्यार्थ गेट नं. 2 के
सामने, जवाहर नगर, कोटा (राज.) मो. 7014774207

Ques. The temp of rxn is 10°C if the temp is increased by 50°C then R.O.R ^{becomes} how many times.

$$\frac{R_2}{R_1} = (4)^{\frac{50}{10}}$$

$$\frac{R_f}{R_i} = (2)^{\frac{50}{10}}$$

$$= 2^5 = 32$$

$$R_f = 32 R_i$$

Ques. Determine the value of $\frac{k_{40}}{k_{25}} = ?$ for a chemical rxn

$$\frac{k_{40}}{k_{25}} = (2)^{\frac{\Delta T}{10}}$$

$$\frac{k_{40}}{k_{25}} = (2)^{\frac{15}{10}} = (2)^{1.5}$$

$$= (2)^{3/2} = (2)^1 \cdot (2)^{1/2}$$

$$= 2 (1.41)$$

$$= \underline{2.82}$$

Ques. The rate of a rxn is 5.23 times when the temp is raised from 40°C to 7°C if the temp coefficient of the rxn is 3 then determine temp T°C.

~~$$\frac{R_2}{R_1} = (3)^{\frac{\Delta T}{10}}$$~~

$$\frac{R_2}{R_1} = 3^{\frac{\Delta T}{10}}$$

$$\frac{5.23 \text{ Rate}_2}{\text{Rate}_1} = (3)^{\frac{\Delta T}{10}}$$

$$5.23 = 3^{\frac{\Delta T}{10}}$$

$$3 \times 1.73 = (3)^{\frac{\Delta T}{10}}$$

$$3\sqrt{3} = (3)^{\frac{\Delta T}{10}}$$

$$(3)^{3/2} = (3)^{\frac{\Delta T}{10}}$$

$$\frac{3}{2} = \frac{t-40}{10}$$

$$t-40 = 15$$

$$t = 55^\circ\text{C}$$

OR

$$5.23 = (3)^{\frac{\Delta T}{10}}$$

$$\log 5.23 = \frac{\Delta T}{10} \log 3$$

$$0.72 = \frac{\Delta T}{10} (0.48)$$

$$\frac{3 \times 0.72}{0.48} = \frac{\Delta T}{10}$$

$$\frac{3}{2} = \frac{\Delta T}{10}$$

$$t = 55^\circ\text{C}$$

Ques The temp coefficient of two rxn are 2 & 3 respectively if the initial rate of these rxn at 30°C are in the ratio 1:2 then find out the ratio of their rate at 70°C temp.

~~...~~

$$R^{xn 1} = (r_i)_1 \cdot (r_f)_1 \Rightarrow M = 2$$

$$R^{xn 2} = (r_i)_2 \cdot (r_f)_2 \Rightarrow M = 3$$

$$\frac{(r_f)_1}{(r_i)_2} = \frac{(r_i)_1 \cdot M \left(\frac{\Delta T}{10}\right)}{(r_i)_2 \cdot M \left(\frac{\Delta T}{10}\right)}$$

$$= \frac{1}{2} \times \frac{(2)^{\frac{40}{10}}}{(3)^{\frac{40}{10}}}$$

$$= \frac{1}{2} \times \frac{2^4}{3^4} = \frac{8}{81}$$

Arrhenius Equation: \rightarrow

$$k = Ae^{-E_a/RT}$$

A = Arrhenius Equation

(It is a constant specific to a particular rxn)

(It does not depends on temp.)

\rightarrow Unit of k = Unit of A

$$e^{-E_a/RT} = \text{Unitless}$$

$$\frac{k}{A} = e^{-E_a/RT}$$

\Rightarrow Boltzmann factor

\Rightarrow fraction of molecules having energy $\geq E_a$

OR

Fraction of active molecules.

E_a = Activation energy

(Unit = J mol^{-1}
OR Cal mol^{-1})

R = Universal Gas constant.

($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ OR $2 \text{ Cal mol}^{-1} \text{ K}^{-1}$)

T = Temp. (Unit = Kelvin)

* On \uparrow ing T = K \uparrow ses

If $T \rightarrow \infty \Rightarrow k = A$

$$\rightarrow T \downarrow \Rightarrow e^{-E_a/RT} \downarrow \Rightarrow e^{-E_a/RT} \uparrow$$

$$K \uparrow \Rightarrow ROR \uparrow$$

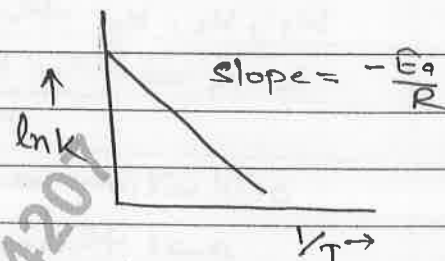
Ques - The slope of the graph b/w $\ln k$ vs $1/T$ is -2000 then calculate the E_a in Kcal/mol .

$$\text{Slope} = -\frac{E_a}{R} = -2000$$

$$E_a = 2000 \times R$$

$$= 2000 \times 2$$

$$= \frac{4000}{1000} = 4 \text{ Kcal mol}^{-1}$$



Ques for elementary rxn $A \rightarrow B$; $k_1 = 10^{16} e^{-2000/T}$

$C \rightarrow D$; $k_2 = 10^{14} e^{-1000/T}$

then calculate the temp at which the rate constant of both the rxn are equal.

$$k_1 = k_2$$

$$10^{16} e^{-\frac{2000}{T}} = 10^{14} e^{-\frac{1000}{T}}$$

$$\frac{10^{16}}{10^{14}} = \frac{e^{-\frac{1000}{T}}}{e^{-\frac{2000}{T}}}$$

$$10^2 = e^{\frac{1000}{T}}$$

$$\log_{10} 10^2 = \ln e^{\frac{1000}{T}}$$

$$\ln 10^2 = \frac{1000}{T} \ln e$$

$$2.303 \log_{10} (10)^2 = \frac{1000}{T}$$

$$2.303 \times 2 \log_{10} 10 = \frac{1000}{T}$$

$$4.606 = \frac{1000}{T}$$

$$T = \frac{1000}{4.606} = 217 \text{ K}$$

Q1. A chemical rxn occurs in 3 steps having rate constant k_1, k_2, k_3 the overall rate constant of rxn is $k = \frac{k_1 \cdot k_3}{k_2}$ then determine the overall

activation energy of rxn if E_a is first, second and third step are 30, 40 and 60 KJ mol^{-1} respectively

$$k = \frac{k_1 \cdot k_3}{k_2}$$

$$A \cdot e^{-E_a/RT} = \frac{A_1 \cdot e^{-E_{a1}/RT} \times A_3 \cdot e^{-E_{a3}/RT}}{A_2 \cdot e^{-E_{a2}/RT}}$$

$$A e^{-E_a/RT} = \left(\frac{A_1 \times A_3}{A_2} \right) \cdot e^{\left(\frac{-E_{a1} - E_{a3} + E_{a2}}{RT} \right)}$$

On comparing:

$$-E_a = -E_{a1} = E_{a3} + E_{a2}$$

$$E_a = 30 + 60 - 40 = 50 \text{ KJ mol}^{-1}$$

Multiplication \Rightarrow Addition

Division \Rightarrow Subtraction

Q2. Calculate the value of preexponential factor & E_a with help of following eqn.

$$\log_{10} K = 6 - \frac{2000}{T}$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT} \quad \text{--- (2)}$$

on comparing: —

$$\log_{10} A = 6$$

$$A = 10^6$$

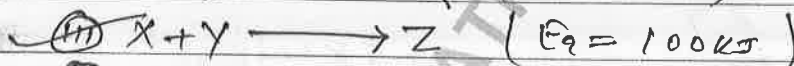
$$\frac{E_a}{2.303RT} = \frac{2000}{T}$$

$$E_a = 2000 \times 2.303R$$

$$= \frac{2000 \times 2.303 \times 2}{1000}$$

$$= 9.2 \text{ Kcal mol}^{-1}$$

Ques. The value of $\frac{k_{310}}{k_{290}}$ is max. for w.o.f. rxn
changing K.



$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Same

→ On rising the temp the k is rate constant or R.O.R is max. for the rxn having the max. value of E_a .

Q. At 500K temp in a rxn 0.001% of the total molecules are active molecules then determine the E_a in Kcal mol^{-1} .

$$\text{fraction of active molecules} = e^{-\frac{E_a}{RT}} = 0.001\%$$

$$= e^{-\frac{E_a}{RT}} = \frac{0.001}{100} = 10^{-5}$$

$$\ln e^{-\frac{E_a}{RT}} = \ln 10^{-5}$$

$$-\frac{E_a}{RT} = 2.303 \log_{10}(10^{-5})$$

$$-\frac{E_a}{2 \times 500} = (2.303)(-5)$$

$$E_a = \frac{2.303 \times 5 \times 2 \times 500}{1}$$

$$= 11.5 \text{ Kcal mol}^{-1}$$

Q. The E_a of a rxn is $46.06 \text{ Kcal mol}^{-1}$ at 500K temp. then determine the fraction of molecules having energy greater than equal to E_a .

$$\text{fraction of molecules having energy} \geq E_a \Rightarrow \frac{K}{A} = e^{-\frac{E_a}{RT}}$$

$$\ln\left(\frac{K}{A}\right) = \ln e^{-\frac{E_a}{RT}}$$

$$2.303 \log_{10}\left(\frac{K}{A}\right) = -\frac{E_a}{RT} = \frac{-46.06 \times 7000}{2 \times 500}$$

$$\log_{10}\left(\frac{K}{A}\right) = \frac{-46.06}{2.303} = -20$$

$$\therefore \frac{K}{A} = \text{Antilog}(-20) = (10^{-20})$$

Ques The value of rate constant is doubled when the temp is raised from 27°C to 37°C then calculate the E_a in KJ mol^{-1}

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log_{10} \left(\frac{2k_1}{k_1} \right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{310} \right)$$

$$0.3 = \frac{E_a}{19.15} \left(\frac{10}{300 \times 310} \right)$$

$$E_a = \frac{0.3 \times 19.15 \times 300 \times 310}{1000}$$

$$E_a = 53.4 \text{ KJ mol}^{-1}$$

Ques A hydrogenation rxn is carried out at 500°C if the same rxn is carried out at the same rate at 400°C in the presence of catalyst then activation energy decreased by 20 KJ mol^{-1} then determine the E_a of the rxn.

$$k_1 = k_2$$

$$Ae^{-\frac{E_a}{RT_1}} = Ae^{-\frac{E_a - 20}{RT_2}}$$

$$\frac{E_a}{RT_1} = \frac{E_a - 20}{RT_2}$$

$$\frac{E_a}{500} = \frac{E_a - 20}{400}$$

$$4E_a = 5E_a - 100$$

$$E_a = 100 \text{ KJ mol}^{-1}$$

Ques At 27°C ~~temp~~ E_a of a rxn is 60 kJ mol⁻¹ if the same rxn is carried out in the presence of catalyst then E_a decreases to 30 kJ mol⁻¹ then determine how many times rate of rxn ~~red~~ in the presence of catalyst.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k_2}{k_1} = ?$$

absence of catalyst

$$\log_{10} k_1 = \log_{10} A - \frac{E_{a1}}{2.303RT} \quad \text{--- (I)}$$

In the presence of catalyst

$$\log_{10} k_2 = \log_{10} A - \frac{E_{a2}}{2.303RT} \quad \text{--- (II)}$$

$$\text{(II)} - \text{(I)}$$

$$\begin{aligned} \log_{10} \left(\frac{k_2}{k_1} \right) &= \frac{E_{a1} - E_{a2}}{2.303RT} \\ &= \frac{(60 - 30) \times 1000}{2.303 \times 8.314 \times 300} \end{aligned}$$

$$\log_{10} \left(\frac{k_2}{k_1} \right) = \frac{30 \times 1000}{19.15 \times 300} = 5.22$$

$$\frac{k_2}{k_1} = 10^{5.22} = 10^5 \times 10^{0.22}$$

$$= 1.7 \times 10^5 \text{ times}$$

Q.11. The half life period of a first order rxn is 20 min & 5 min at 27°C and 47°C respectively then calculate the value of E_a in KJ mol⁻¹.

Ans = 55.3 KJ

Effect of catalyst:—

Rate of a photochemical rxn \propto Intensity of light

Rate $\propto I$

$$\text{Rate} = \phi I$$

ϕ = No. of molecules reacted or product formed

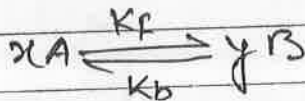
Quantum efficiency or yield.

S Solution

Some extra point:—

① Reversible rxn's:—

For a rev. rxn,



Both forward & backward rxn are elementary

$$\text{Rate}_f = k_f (A)^x$$

$$\text{Rate}_b = k_b (B)^y$$

$$\text{Rate}_{\text{net}} = \text{Rate}_f - \text{Rate}_b$$

$$\text{Rate}_{\text{net}} = k_f (A)^x - k_b (B)^y$$

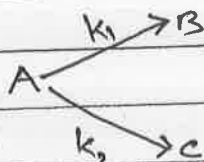
$$\text{Rate}_{\text{net}} = \frac{1}{x} \left(\frac{-d(A)}{dt} \right) = \frac{1}{y} \left(\frac{+d(B)}{dt} \right) = k_f (A)^x - k_b (B)^y$$

Ques. For a rxn $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ determine the net rate of disappearance of NO_2

~~$$\text{Rate}_{\text{net}} = 2 \left(\frac{d(\text{NO}_2)}{dt} \right) = \left(\frac{d(\text{N}_2\text{O}_4)}{dt} \right)$$~~

$$\frac{-d(\text{NO}_2)}{dt} = 2 \left((k_1 (\text{NO}_2))^2 - k_2 (\text{N}_2\text{O}_4) \right)$$

② Parallel first order rxn:—
OR Side rxn



$$A \xrightarrow{k_1} B$$

$$\text{Rate}_1 = k_1 (A)$$



$$\text{Rate}_2 = k_2(A)$$

$$\text{Rate}_{\text{overall}} = \text{Rate}_1 + \text{Rate}_2$$

$$= k_1(A) + k_2(A)$$

$$= (k_1 + k_2)(A)$$

$$\boxed{\text{Rate}_{\text{overall}} = k_{\text{overall}} \cdot (A)}$$

$$k_{\text{overall}} = (k_1 + k_2)$$

$$\% \text{ yield of B} = \left(\frac{k_1}{k_1 + k_2} \right) \times 100$$

$$\% \text{ yield of C} = \left(\frac{k_2}{k_1 + k_2} \right)$$

Ques for a rxn $A \xrightleftharpoons[k_2]{k_1} B$ If k_1 & k_2 are $1.26 \times 10^{-4} \text{ s}^{-1}$ and

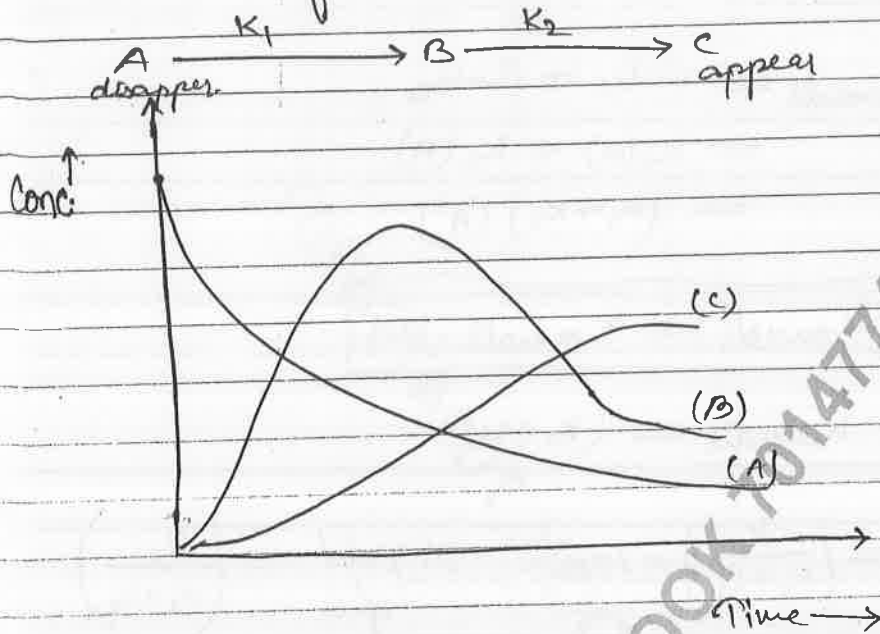
$3.4 \times 10^{-5} \text{ s}^{-1}$ then determine overall rate constant and % yield of B & C.

$$k_{\text{overall}} = (k_1 + k_2) \quad \left| \quad \% \text{ yield of B} = \left(\frac{k_1}{k_1 + k_2} \right) \times 100$$

$$B = 78.7\%$$

$$C = 21.3\%$$

(iii) Consecutive first order rxn:—



$$(t_{\max})_{(B)} = \frac{1}{(k_1 - k_2)} \ln \left(\frac{k_1}{k_2} \right)$$

Time at which
 conc. of B is max^m

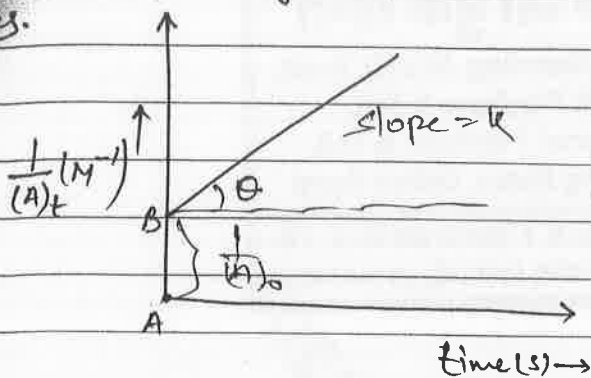
~~(R.O.D.)_A = k₁(A)~~

(R.O.A)_C = k₂(B)

(R.O.A)_B = k₁(A) - k₂(B)

Question on higher Order:—

Ques.



If $\theta = \tan^{-1}(0.5)$ & $[A]_0 = 2 \text{ L mol}^{-1}$
then find initial rate of rxn?

2nd order

$$\text{Slope} = \tan \theta = 0.5 = k$$

$$\text{Intercept} = \frac{1}{(A)_0} = 2 \text{ L mol}^{-1}$$

$$(A)_0 = 0.5 \text{ mol l}^{-1}$$

$$\begin{aligned} \text{Rate} &= k(A)^2 \\ &= 0.5(0.5)^2 \\ &= 0.125 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

Ques In 2nd order rxn the time taken for reactant concⁿ to decreased from 0.28M to 0.4M is 10sec. then determine what will be the time taken for reactant ~~concentration~~ concⁿ to decreased from 0.8M \rightarrow 0.1M

$$k t_1 = \frac{1}{(A)_t} - \frac{1}{(A)_0}$$

$$k t_2 = \frac{1}{(A)_t} - \frac{1}{(A)_0}$$

$$\frac{10}{t_2} = \frac{1}{0.4} - \frac{1}{0.8}$$

$$\frac{1}{0.1} - \frac{1}{0.8}$$

$$\frac{10}{t} = \frac{2.5 - 1.25}{10 - 1.25}$$

$$t = 70 \text{ sec}$$

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