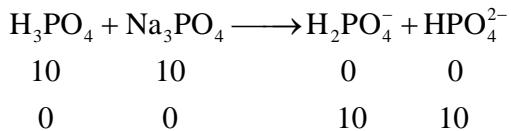


Solutions FOR GET EQUIPPED JEE ADVANCED AND COMPREHENSION

Q.1 [C]

Sol. moles of $\text{H}_3\text{PO}_4 = 0.2 \times 50 = 10$ m moles

moles of $\text{Na}_3\text{PO}_4 = 0.2 \times 50 = 10$ m moles



Buffer of NaH_2PO_4 & Na_2HPO_4

$$\text{pH} = \text{Pka}_2 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 8 + \log 1 = 8$$

Q.2 [A]

Sol. In one litre initial pH=7

Final pH = 4; $[\text{H}^+] = 10^{-4}$

$[\text{H}^+]$ by drop $= 10^{-4} - 10^{-7} = 10^{-4}$

Moles of H^+ in 1L $= 10^{-4}$

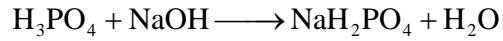
So total moles after 2 drops $= 2 \times 10^{-4}$ in 1L

pH $= 4 - \log 2 = 3.7$

Q.3 [D]

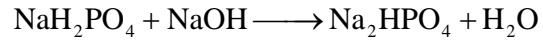
At pH = 7.4 the best buffer is of H_2PO_4^- & HPO_4^{2-}

$$\text{Using } 7.4 = 8 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$



5m mole x = 5

0 0 5m moles



5 x
5 - x x

$$\text{Solving, } 7.4 = 8 + \log\left(\frac{x}{5-x}\right)$$

$$\frac{x}{5-x} = \frac{1}{4}$$

$$x = 1$$

$$\text{total } 5 + 1 = 6 \text{ m moles} = 0.1 \times V \text{ ml}$$

$$V = 60 \text{ ml}$$

Q.4 [A]

Sol. If both MX and M₂Y starts ppting simultaneously then

$$[M^+] = \frac{K_{sp}}{[X^-]} = \frac{10^{-10}}{0.1} = 10^{-9}$$

$$\text{then } K_{sp}(M_2Y) = [M^+]^2 [Y^{-2}]$$

$$= (10^{-9})^2 (0.01) = 10^{-20}$$

In Pure water for M₂Y

$$4s^3 = 10^{-20}$$

$$s = \left(\frac{10^{-20}}{4} \right)^{\frac{1}{3}}$$

Q.5 [B]

Sol. Isoelectronic point implies net charge on the species must be zero so considering it as triprotic acid 2nd ionisation of H⁺ must be complete so it will be amphiprotic & pH = $\frac{pK_{a_2} + pK_{a_3}}{2}$

$$= \frac{8.96 + 10.53}{2}$$

$$= 9.74$$

Comprehensions

Q.13 [A]

Sol. The stronger acid will be more deprotonated than weaker acid at same pH

So it will be less protonated

A & B curves are protonated

Q.14 [C, D]

Sol. for same acid lines must intersect at 0.5 as ordinato, So A & C are pairs & B & D

Q.15 [B]

Sol. $pK_{a_{(\text{stronger})}} = pH = 5$ $K_{a_{\text{stronger}}} = 10^{-5}$

$pK_{a_{(\text{weaker})}} = pH = 7$ $K_{a_{(\text{weaker})}} = 10^{-7}$

$$\frac{10^{-5}}{10^{-7}} = 100$$

Q.16 [C]

Sol. First $[Br^-]$ starts precipitating in the form of AgBr_(s) when $[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{10^{-7}}{10^{-2}} = 10^{-5} M$

after which $[Ag^+]_{\text{solution}} [Br^-]_{\text{solution}} = K_{sp}$ remains constant so a hyperbolic curve.

Q.17 [D]

Sol. When AgCl_(s) starts precipitating

$$[Ag^+]_{\text{solution}} = \frac{K_{sp}}{[Cl^-]} = \frac{10^{-5}}{10^{-2}} = 10^{-3}$$

$$[\text{Ag}^+]_{\text{ppt}} = [\text{Br}^-]_{\text{ppt}} = 10^{-2} - \frac{10^{-7}}{10^{-3}} = 10^{-2} - 10^{-4}$$

$$[\text{Ag}^+]_{\text{total}} = 10^{-3} + 10^{-2} - 10^{-4} = 0.0109$$

Solutions FOR EXPERTISE ATTAINER SUBJECTIVE

Q.1

Sol. $[\text{OH}^-] = 2.5 \times 10^{-3} \times 2 = 5 \times 10^{-3} \text{ M}$

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

(a) For POH to be doubled

$$[\text{OH}^-]_{\text{final}} = [\text{OH}^-]_{\text{initial}}^2$$

$$= 25 \times 10^{-6} > 10^{-6} \text{ so } [\text{OH}^-]_{\text{water}} \text{ negligible conserving moles of } [\text{OH}^-] \text{ from Ba}[\text{OH}]_2$$

$$25 \times 10^{-6} \times V = 5 \times 10^{-3} \times 1$$

$$V = \frac{5 \times 10^{-3}}{25 \times 10^{-6}} = \frac{10^3}{5} = 200 \text{ L}$$

$$\text{Water added} = 200 - 1 = 199 \text{ L}$$

(b) POH to be tripled

$$[\text{OH}^-]_{\text{final}} = [\text{OH}^-]_{\text{initial}}^3$$

$$= 125 \times 10^{-9} = 1.25 \times 10^{-7} < 10^{-6}$$

So $[\text{OH}^-]_{\text{water}}$ in significant

$$[\text{OH}^-]_{\text{water}} = [\text{H}^+]_{\text{water}} = [\text{H}^+]_{\text{net}} = \frac{10^{-14}}{1.25 \times 10^{-7}} = 8 \times 10^{-8} \text{ M}$$

Conserving moles of $[\text{OH}^-]$ from $\text{Ba}[\text{OH}]_2$

$$(12.5 \times 10^{-8} - 8 \times 10^{-8}) \times V = 5 \times 10^{-3} \times 1$$

$$4.5 \times 10^{-8} \times V = 5 \times 10^{-3}$$

$$V = \frac{5 \times 10^{-3}}{4.5 \times 10^{-8}}$$

$$= \left(\frac{10^6}{9} \right) L$$

(c) not possible as POH cannot be more than 7

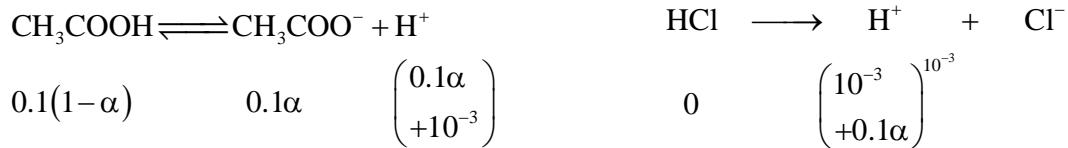
Q.2

Sol. $pH_1 = 3 - \log 2 = 2.7$

$$pH_2 = \frac{1}{2} [pK_a - \log C] = 2.7$$

On mixing the new concentration are

$$[CH_3COOH] = 0.1M \quad [HCl] = 10^{-3}M$$



0.1α cannot be neglected compared to 10^{-3}

$$K_a = \frac{(0.1\alpha + 10^{-3})(0.1\alpha)}{0.1(1-\alpha)} = 2 \times 10^{-5}; \quad 1-\alpha \approx 1$$

$$(0.1\alpha^2) + 10^{-3}\alpha = 2 \times 10^{-5}$$

$$\alpha^2 + 10^{-2}\alpha - 2 \times 10^{-4} = 0$$

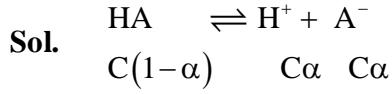
$$\alpha = \frac{-10^{-2} + \sqrt{10^{-4} + 8 \times 10^{-4}}}{2} = \frac{-10^{-2} + 3 \times 10^{-2}}{2} = 10^{-2}$$

$$[H^+]_{\text{net}} = 0.1 \times 10^{-2} + 10^{-3} = 2 \times 10^{-3}$$

$$pH_3 = 2.7$$

$$\text{So} \left(\frac{\text{pH}_1 + \text{pH}_2}{\text{pH}_3} \right) = 2$$

Q.3



$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{(C\alpha)(\alpha)}{(1-\alpha)} = [\text{H}^+] \frac{(\alpha)}{(1-\alpha)}$$

$$\text{pKa} = \text{pH} - \log \left(\frac{\alpha}{1-\alpha} \right)$$

$$\log \left(\frac{\alpha}{1-\alpha} \right) = \text{pH} - \text{pKa}$$

$$\frac{\alpha}{1-\alpha} = 10^{\text{pH}-\text{pKa}}$$

$$\alpha = \frac{10^{\text{pH}-\text{pKa}}}{1+10^{\text{pH}-\text{pKa}}} = \frac{1}{1+10^{(\text{pKa}-\text{pH})}}$$

Q.4

Sol.

(a) For pH to be doubled

$$[\text{H}^+]_{\text{final}} = [\text{H}^+]_{\text{initial}}^2$$

$$C_f \alpha_f = (C_i \alpha_i)^2$$

$$= \left(\sqrt{C_i \text{Ka}} \right)^2 = 0.1 \times 2 \times 10^{-5}$$

$$= 2 \times 10^{-6}$$

$$\text{Also, } \frac{C_f \alpha_f^2}{1-\alpha_f} = \frac{C_i \alpha_i^2}{1-\alpha_i} = 2 \times 10^{-5}$$

$$\frac{(C_f \alpha_f)(\alpha_f)}{1-\alpha_f} = 2 \times 10^{-5}$$

$$2 \times 10^{-6} \times (\alpha_f) = 2 \times 10^{-5}$$

$$\frac{\alpha_t}{1-\alpha_f} = 10; \quad \alpha_f = \frac{10}{11}$$

$$C_f = 2 \times 10^{-6} \times \frac{11}{10} = 2.2 \times 10^{-6}$$

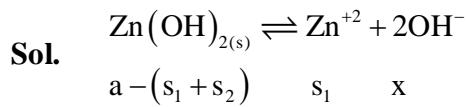
Conserving WA $C_f V_f = C_i V_i$

$$V_f = \frac{10^6}{22}$$

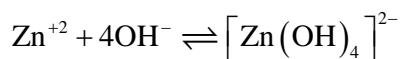
$$V_{\text{water}} = \left(\frac{10^6}{22} - 1 \right) L \approx 45453 L$$

(b) Not possible as pH cannot be > 7

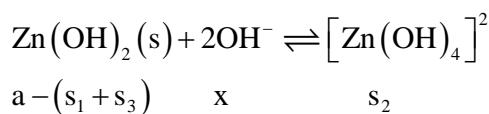
Q.5



$$K_{sp} = [\text{Zn}^{+2}] [\text{OH}^-]^2 \\ = S_1 x^2 \quad \dots \dots \dots (1)$$



$$K_f = \frac{[\text{Zn(OH)}_4]^2}{[\text{Zn}^{+2}] [\text{OH}^-]^4}$$



$$K_{sp} \times K_f = \frac{s_2}{x^2} \quad \dots \dots \dots (2)$$

(1) \times (2)

$$(K_{sp})^2 \times K_f = s_1 - s_2 \approx s^2 \quad (s_1 \approx s_2)$$

$$s^2 = (1.2 \times 10^{-17})^2 \times 10^{16} = 1.44 \times 10^{-18}$$

$$s = 1.2 \times 10^{-9}$$

Solubility of $Zn(OH)_{2(s)}$ is $s_1 + s_2 \approx 2s = 2.4 \times 10^{-9} M$

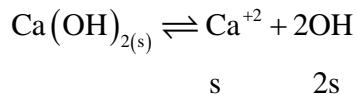
$$[OH^-] = x = \sqrt{\frac{K_{sp}}{s_1}} = \sqrt{\frac{1.2 \times 10^{-17}}{1.2 \times 10^{-9}}} = \sqrt{10^{-8}} = 10^{-4}$$

$$POH = H$$

$$pH = 10$$

Q.6

Sol. Initially saturated solution of $Ca(OH)_2$ so $Ca(OH)_2$ dissolved is given by



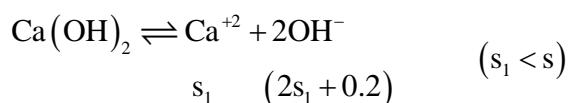
$$K_{sp} = 4s^3 = 4.42 \times 10^{-5}$$

$$S = \sqrt[3]{\frac{4.42 \times 10^{-5}}{4}}$$

$$= 0.022 M$$

$$\text{Moles dissolved} = 0.022 \times \frac{1}{2} = 0.011$$

When NaOH is mixed volume is doubled



$$(s_1)(2s_1 + 0.2)^2 = 4.42 \times 10^{-5}$$

$$(s_1)(s_1 + 0.1)^2 = 1.105 \times 10^{-5}$$

Neglecting s_1

$$s_1 = \frac{1.105 \times 10^{-5}}{0.01} = 1.1 \times 10^{-3}$$

moles of Ca^{+2} dissolved = $1.1 \times 10^{-3} \times 1$ moles

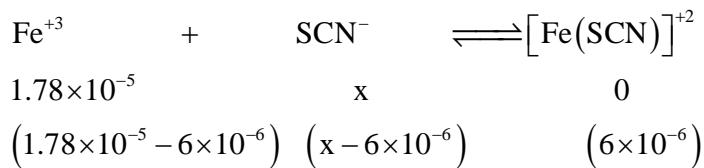
moles of Ca^{+2} deposited = $11 \times 10^{-3} - 1.1 \times 10^{-3} = 9.9 \times 10^{-3}$ moles

moles of $\text{Ca}(\text{OH})_2 = 9.9 \times 10^{-3} \times 74 \text{ gm} = 732.6 \text{ mg}$

Q.7

Sol. Fe^{+3} 1 ppm $\Rightarrow 1 \text{ gm in } 10^6 \text{ gm}$

$$\Rightarrow \frac{1}{56} \text{ moles in } 10^3 \text{ L} \Rightarrow 1.78 \times 10^{-5} \text{ M}$$



$$\frac{6 \times 10^{-6}}{(1.78 \times 10^{-5} - 6 \times 10^{-6})(x - 6 \times 10^{-6})} = \frac{1}{k_{\text{dissociation}}} = \frac{10^3}{7.142}$$

$$\frac{6 \times 10^{-6}}{(11.8 \times 10^{-6})(x - 6 \times 10^{-6})} = \frac{10^3}{7.142}$$

$$x - 6 \times 10^{-6} = \frac{6 \times 7.142}{11.8 \times 10^3} = 3.61 \times 10^{-3} = 0.0036 \text{ M}$$

Q.8

Sol.

$$[\text{NH}_3] = x \text{ M} \quad [\text{NH}_4^+] = (0.6 - x) \text{ M}$$

for Basic Buffer

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{Cl}]}$$

$$14 - \text{pH} = 4.7 + \log \frac{(0.6 - x)}{x}$$

$$0.3 = \log \left(\frac{0.6 - x}{x} \right)$$

$$\frac{0.6 - x}{x} = 2 \quad x = 0.2 \text{ M}$$

$$[\text{NH}_3] = 0.2 \text{ M}$$

$$[\text{NH}_4^+] = 0.4 \text{ M}$$

$$2 \text{ gm of NaOH} = \frac{2}{40} = 0.05 \text{ moles in } 500 \text{ ml}$$

$$\text{or } [\text{NaOH}] = 0.1 \text{ M}$$

$$[\text{NH}_4^+] = 0.4 - 0.1 = 0.3$$

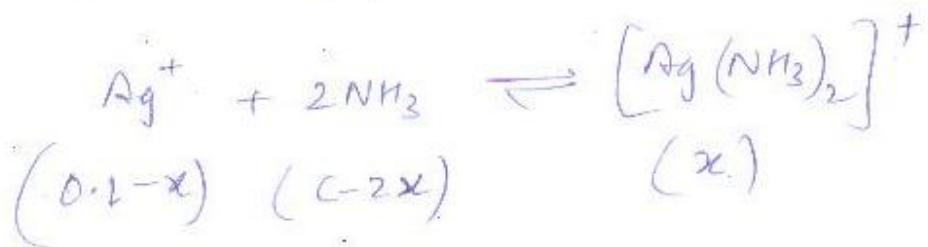
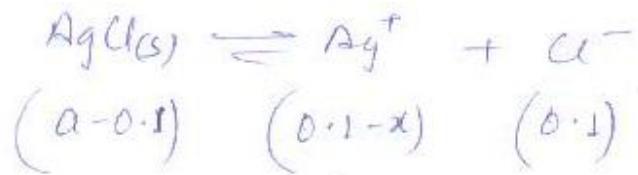
$$[\text{NH}_3] = 0.2 + 0.1 = 0.3$$

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

$$|\Delta \text{pOH}| = 0.3$$

$$|\Delta \text{pH}| = 0.3$$

Q.9
Sol.



two unknowns $c \& x$

$$(0.1 - x)(0.1) = 10^{-10}$$

$$(0.1 - x) = [\text{Ag}^+] = 10^{-9} \text{ M}$$

$$x \approx 0.1 \text{ M}$$

$$K_f = 1.6 \times 10^7 = \frac{x}{(c - 2x)^2 (0.1 - x)}$$

$$1.6 \times 10^7 = \frac{0.1}{(c - 0.2)^2 (10^{-4})}$$

$$(c - 0.2)^2 = \frac{10^8}{1.6 \times 10^7} = \frac{100}{16}$$

$$c - 0.2 = \frac{10}{4} = 2.5 \quad \boxed{c = 2.7 \text{ M}}$$

**Q.10
Sol.**

$$\text{at } [I\text{In}^-] = 4 \times 10^{-5} \text{ M}$$

$$pH = 5 - \log 4 = 4.4$$

$$pH = pK_a + \log (1)$$

$$\boxed{pK_a = 4.4}$$

$$\boxed{K_a = 4 \times 10^{-5}}$$

for acidic color (A)

$$[A] > 8[B]$$

$$\cancel{[H\text{In}]} > 8[I\text{In}^-]$$

$$\frac{[I\text{In}^-]}{[H\text{In}]} < \frac{1}{8}$$

$$pH = 4.4 + \log \left(\frac{1}{8} \right)$$

$$= 4.4 - 0.9 = \boxed{3.5}$$

for Basic color B

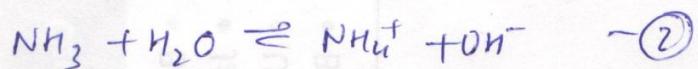
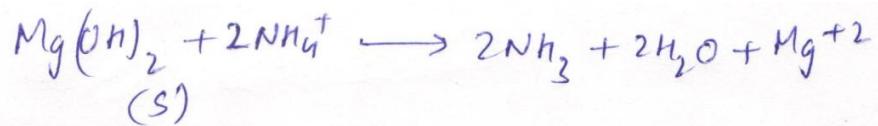
$$[I\text{In}^-] > 20[H\text{In}]$$

$$pH = 4.4 + \log(20)$$

$$\boxed{pH = 5.7}$$

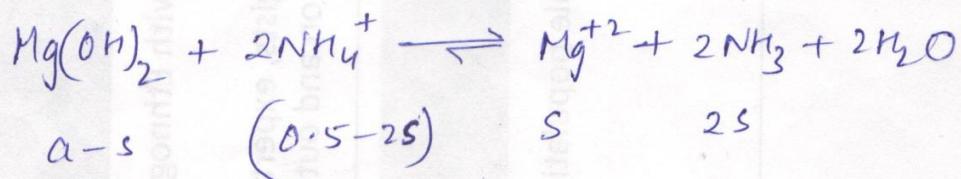
$$pH_{\text{range}} = 3.5 \text{ to } 5.7$$

Q.12
Sol.



Main reaction = (1) - 2 × (2)

$$K_c = \frac{K_{sp}}{K_b^2} = \frac{10^{-11}}{(1.8 \times 10^{-5})^2} = \frac{10^{-11} \times 10^{+10}}{(1.8)^2} \\ = \underline{\underline{3.08 \times 10^{-2}}}$$



$$\frac{(2s)^2(s)}{(0.5 - 2s)^2} = 3.08 \times 10^{-2}$$

INCORRECT
ASSUMPTION
~~(ONO)~~

$$\frac{4 \times 4s^3}{(1 - 4s)^2} = 3.08 \times 10^{-2}$$

$1 - 4s \approx 1$

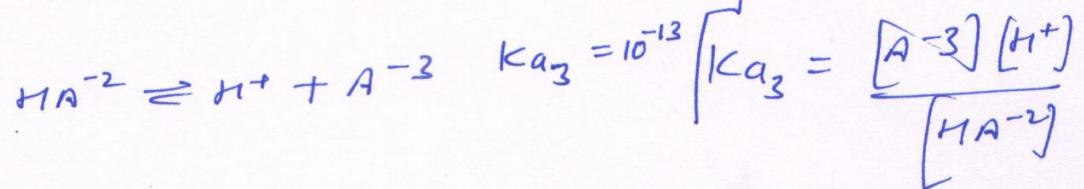
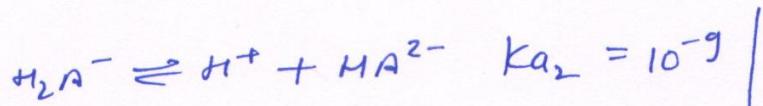
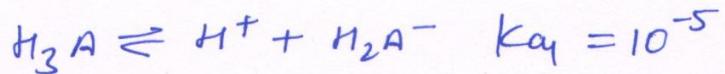
$$s^3 = 0.1925 \times 10^{-2}$$

$$\boxed{s = 0.124}$$

Q.13

Sol.

$$K_{a_1} = 10^{-5} \quad K_{a_2} = 10^{-9} \quad K_{a_3} = 10^{-13}$$



$$x = \frac{[A^{-3}]}{[HA^{2-}]} = \frac{K_{a_3}}{[H^+]}$$

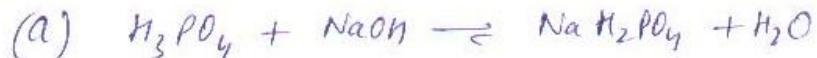
$$[H^+] = \sqrt{C K_{a_1}} = 10^{-3}$$

$$x = \frac{10^{-13}}{10^{-3}} = 10^{-10}$$

$$\boxed{p_x = 10}$$

Answer Verification

**Q.14
Sol.**

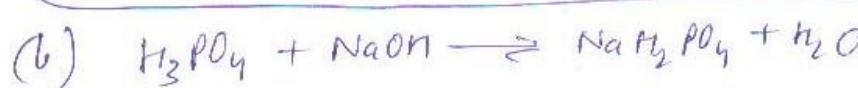


$$\begin{array}{rcl} & \cancel{50 \times 0.12} & 20 \times 0.15 \\ = 6 & & = 3 \\ \hline [3] & [0] & [3] \end{array}$$

$$[\text{H}_3\text{PO}_4] = 3 \text{ M} \quad [\text{NaH}_2\text{PO}_4] = 3 \text{ M}$$

$$\text{pH} = \text{pK}_{\text{a}_1} + \log(1)$$

$$= 3 - \log 7.5 = [2.12]$$



$$\begin{array}{ccc} 6 & 6 & 6 \\ 0 & 0 & \end{array}$$

$$\text{pH} = \frac{\text{pK}_{\text{a}_1} + \text{pK}_{\text{a}_2}}{2} = \frac{2.12 + 7.2}{2} = [4.66]$$



$$40 \times 0.12 \quad 40 \times \cancel{0.18}$$

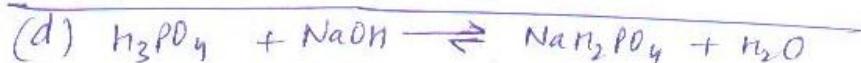
$$= 4.8 \quad = 7.2$$

$$\cancel{40} \quad \cancel{20} \quad \cancel{40}$$



$$\begin{array}{ccc} 4.8 & 2.4 & 0 \\ 2.4 & 0 & 2.4 \end{array}$$

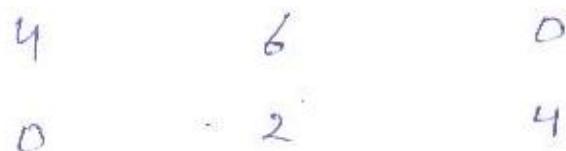
$$\text{pH} = \text{pK}_{\text{a}_2} + \log(1) = [7.2]$$



$$\begin{array}{ccc} 4 & 10 & 0 \\ 0 & 6 & 4 \end{array}$$

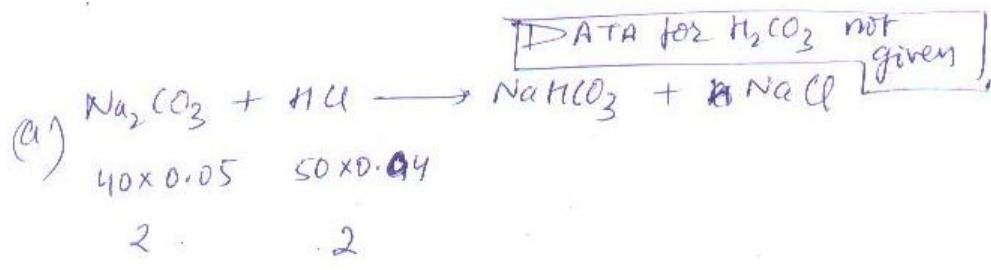
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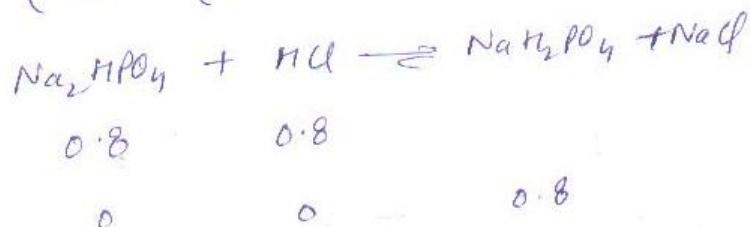
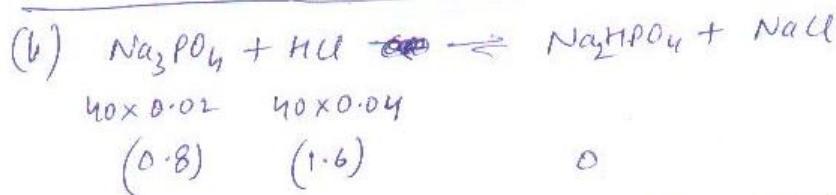


$$\boxed{\text{pH} = \text{p}K_{\text{a}3} = 12}$$

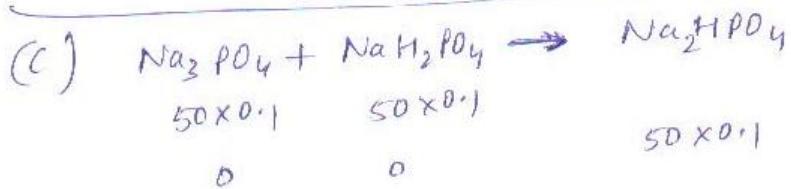
**Q.15
Sol.**



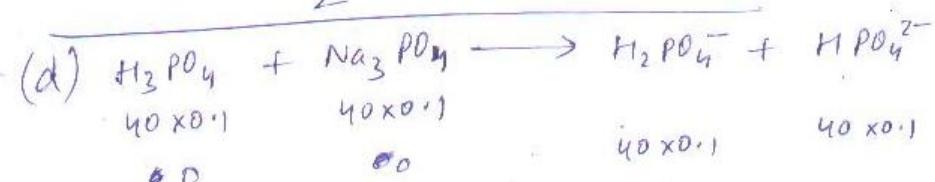
$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \cancel{5.6}$$



$$pH = \frac{pK_{a_2} + pK_{a_3}}{2} = [4.66]$$



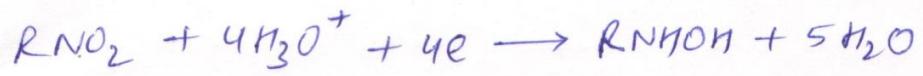
$$pH = \frac{pK_{a_2} + pK_{a_3}}{2} = [9.6]$$



$$pH = pK_{a_2} + \log(1) = [7.2]$$

~~26~~

Q.16
Sol.



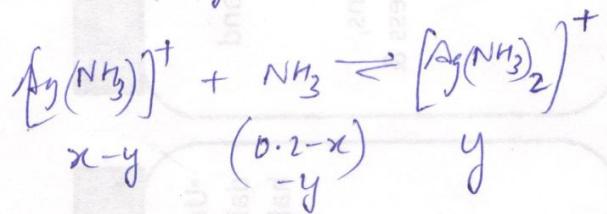
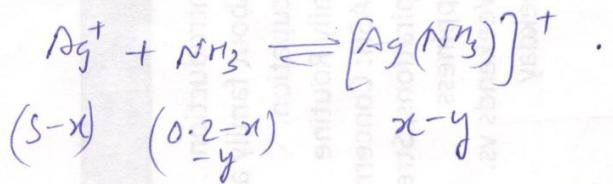
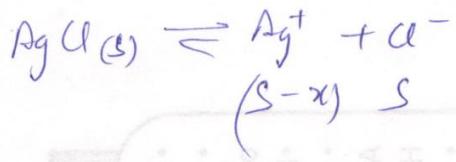
300 ml

0.01 M

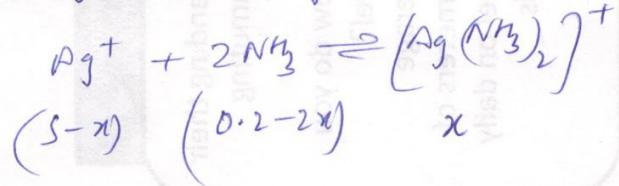
3 mmoles

Ka of acetic acid required

Q.17
Sol.



$x \approx y$. so adding last 2 equations



$$K_{sp} = \boxed{1.7 \times 10^{-10} = (S-x)(S)} \quad K_f = \boxed{16.6 \times 10^6 = \frac{x}{(S-x)(0.2-2x)^2}}$$

$$\frac{(S)(x)}{(0.2-2x)^2} = 1.7 \times 16.6 \times 10^{-4} = 28.28 \times 10^{-4}$$

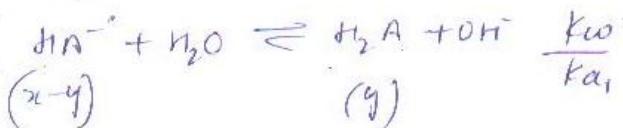
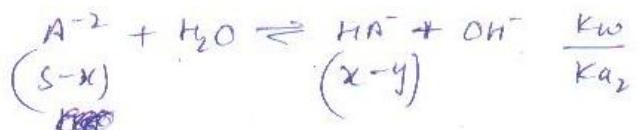
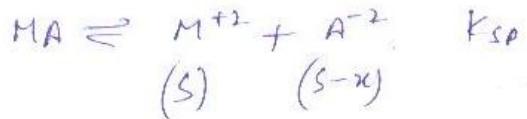
$$\frac{x}{(0.2-2x)^2} = 28.28 \times 10^{-4}$$

$$\frac{S}{(0.2-2S)} = 5.3 \times 10^{-2} \quad \frac{S}{0.1-S} = 1.06 \times 10^{-1} = 0.106$$

$$\frac{S}{0.1} = \frac{0.106}{1.06} = 0.09$$

$$\boxed{S = 9.6 \times 10^{-3}}$$

Q.18
Sol.



$$\frac{(y)[OH^-]}{(x-y)} = \frac{K_w}{K_a} \quad \left(\frac{y}{x-y} \right) = \frac{K_w}{K_a} \times \frac{1}{[OH^-]} = \frac{[H^+]}{K_a} \quad \boxed{\textcircled{1}}$$

$$\frac{(x-y) \text{ [con]} }{(s-x)} = \frac{k_{12}}{k_{22}} \quad \boxed{\left(\frac{x-y}{s-x} \right) = \frac{[H^+]}{k_{22}}} \rightarrow ②$$

$$\text{by } ① \quad \frac{y}{x-y} = \frac{[H^+]}{K_{a_1}} \quad \frac{y}{x} = \frac{[H^+]}{K_{a_1} + [H^+]} \quad \left| \begin{array}{l} y = \frac{[H^+]}{[K_{a_1} + [H^+]]} x \end{array} \right.$$

$$\text{Substituting in (2)} \quad \frac{x}{S-x} = \frac{K_{a_1}[H^+] + [H^+]^2}{K_{a_1} \cdot K_{a_2}}$$

$$\frac{x}{s} = \frac{[H^+] K_{a_1} + [H^+]^2}{K_{a_1} K_{a_2} + K_{a_1}[H^+] + [H^+]^2}$$

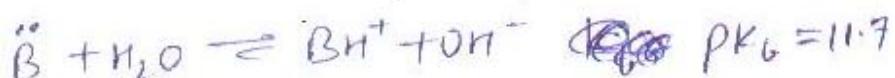
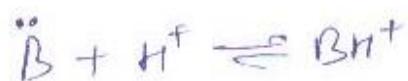
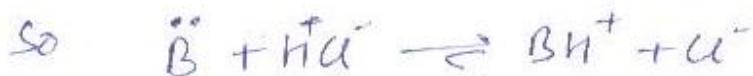
$$(3) (s - x) = (s) \left(s - s \left(\frac{[H^+] K_{a_1} + [H^+]^2}{K_{a_1} K_{a_2} + K_{a_1} [H^+] + [H^+]^2} \right) \right) = K_{SP}$$

$$S^2 \left(\frac{K_{a_1} K_{a_2} + K_{a_1} (H^{+})^2 + (H^{+})^2 - (H^{+})^2 - (H^{+}) K_{a_1}}{K_{a_1} K_{a_2} + K_{a_1} (H^{+})^2 + (H^{+})^2} \right) = K_{sp}$$

$$S = \sqrt{K_{SP} \left(1 + \frac{(I^+)}{k_2} + \frac{(I^+)^2}{k_1 k_2} \right)}$$

Q.19
Sol.

with HCl it behaves as base



Let x mmoles of HCl added



10	x	0
$(10-x)$		(x)

$$\text{pOH} = \text{PK}_b + \log \frac{[\text{BH}^+]}{[\ddot{\text{B}}]}$$

$$14 - 2.6 = 11.7 + \log \left(\frac{x}{10-x} \right)$$

$$-0.3 = \log \left(\frac{x}{10-x} \right)$$

$$\frac{10-x}{x} = 2$$

$$10 = 3x \quad \boxed{x = 3.33 \text{ mmoles}}$$

Q.20
Sol.

as pH ↑ acidic forms ↓
 subsequent basic forms ↑

(A) Curve A = H_3PO_4

$$B = H_2PO_4^-$$

$$C = HPO_4^{2-}$$

$$D = PO_4^{3-}$$

(B) at intersection of A & B

$$[H_3PO_4] = [H_2PO_4^-]$$

$$pH = \frac{pK_{a_1} = 4.7}{[K_{a_1} = 2 \times 10^{-5}]}$$



Similarly $\frac{pH = pK_{a_2} = 7.7}{[K_{a_2} = 2 \times 10^{-8}]}$

$$\text{&} \quad pH = \frac{pK_{a_3} = 10.4}{[K_{a_3} = 4 \times 10^{-11}]}$$

(C) $pH = \frac{1}{2} \left\{ pK_w + pK_{a_3} + \log C \right\}$ $C = \frac{0.1 \times V}{3V}$
 $= \frac{1}{2} \left\{ 14 + 11 - \log 4 + \log \frac{0.1}{3} \right\}$ $[C = 0.1/3]$
 $= \frac{1}{2} \left\{ 22.92 \right\} = 11.46$

