Solutions FOR GET EQUIPPED JEE ADVANCED AND COMPREHENSION

Q.1 **[C]**

Sol. moles of $H_3PO_4 = 0.2 \times 50 = 10$ m moles

moles of $Na_3PO_4 = 0.2 \times 50 = 10$ m moles

$$\begin{array}{cccc} H_3PO_4 + & Na_3PO_4 \longrightarrow & H_2PO_4^- + & HPO_4^{2-} \\ 10 & 10 & 0 & 0 \\ 0 & 0 & 10 & 10 \end{array}$$

Buffer of NaH_2PO_4 & Na_2HPO_4

$$pH = Pka_2 + \log \frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 8 + \log 1 = 8$$

Q.2 **[A]**

Sol. In one litre initial pH=7

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

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

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

So total moles after 2 drops = 2×10^{-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-}

Using $7.4 = 8 + \log \frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4\right]}$

$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

5m mole $\quad x = 5$

$0 \quad 0 \quad$ 5m moles

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

$5 \quad x$

$5 - x \quad x$

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

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

x = 1

total 5 + 1 = 6 m moles $= 0.1 \times V\,ml$

V = 60 ml

Q.4 [A]

Sol. If both MX and M_2Y starts ppting simultaneously then

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

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

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

In Pure water for M_2Y

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

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

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 & $pH = \frac{Pka_2 + Pka_3}{2}$

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

= 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. $pKa_{(stronger)} = pH = 5$ $\qquad Ka_{stronger} = 10^{-5}$

$pKa_{(weaker)} = pH = 7$ $\qquad Ka_{(weaker)} = 10^{-7}$

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

Q.16 [C]

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

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

Q.17 [D]

Sol. When $AgCl_{(s)}$ starts precipitating

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

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

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

Solutions FOR EXPERTISE ATTAINER SUBJECTIVE

Q.1

Sol. $\left[OH^-\right] = 2.5\times10^{-3}\times 2 = 5\times10^{-3}M$

POH = 3 – log 5 = 2.3

(a) For POH to be doubled

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

$= 25\times10^{-6} > 10^{-6}$ so $\left[OH^-\right]_{water}$ negligible conserving moles of $\left[OH^-\right]$ from $Ba\left[OH\right]_2$

$25\times10^{-6}\times V = 5\times10^{-3}\times1$

$V = \frac{5\times10^{-3}}{25\times10^{-6}} = \frac{10^3}{5} = 200L$

Water added = 200 – 1 = 199L

(b) POH to be tripled

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

$= 125\times10^{-9} = 1.25\times10^{-7} < 10^{-6}$

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

$\left[OH^-\right]_{water} = \left[H^+\right]_{water} = \left[H^+\right]_{net} = \frac{10^{-14}}{1.25\times10^{-7}} = 8\times10^{-8}M$

Conserving moles of $\left[OH^-\right]$ from $Ba\left[OH\right]_2$

$\left(12.5\times10^{-8} - 8\times10^{-8}\right)\times V = 5\times10^{-3}\times1$

$4.5\times10^{-8}\times V=5\times10^{-3}$

$$V=\frac{5\times10^{-3}}{4.5\times10^{-8}}$$

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

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

Q.2

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

$$pH_2=\frac{1}{2}\left[pKa-\log C\right]=2.7$$

On mixing the new concentration are

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

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$0.1(1-\alpha) \quad\quad 0.1\alpha \quad\quad \begin{pmatrix}0.1\alpha\\+10^{-3}\end{pmatrix}$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$0 \quad\quad \begin{pmatrix}10^{-3}\\+0.1\alpha\end{pmatrix} \quad\quad 10^{-3}$$

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

$$Ka=\frac{\left(0.1\alpha+10^{-3}\right)\left(0.1\alpha\right)}{0.1\left(1-\alpha\right)}=2\times10^{-5};\quad 1-\alpha\approx1$$

$$\left(0.1\alpha^2\right)+10^{-3}\alpha=2\times10^{-5}$$

$$\alpha^2+10^{-2}\alpha-2\times10^{-4}=0$$

$$\alpha=\frac{-10^{-2}+\sqrt{10^{-4}+8\times10^{-4}}}{2}=\frac{-10^{-2}+3\times10^{-2}}{2}=10^{-2}$$

$$\left[H^+\right]_{net}=0.1\times10^{-2}+10^{-3}=2\times10^{-3}$$

$$pH_3=2.7$$

$$\text{So}\left(\frac{pH_1 + pH_2}{pH_3}\right) = 2$$

Q.3

Sol.

$$\begin{array}{lll} HA & \rightleftharpoons H^+ + & A^- \\ C(1-\alpha) & C\alpha & C\alpha \end{array}$$

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

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

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

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

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

Q.4

Sol.

(a) For pH to be doubled

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

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

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

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

Also, $\dfrac{C_f\alpha_1^2}{1-\alpha_f} = \dfrac{C_i\alpha_i^2}{1-\alpha_i} = 2\times 10^{-5}$

$$\frac{(C_f\alpha_f)(\alpha_f)}{1-\alpha_f} = 2\times10^{-5}$$

$$2\times10^{-6}\times(\alpha_f) = 2\times10^{-5}$$

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

$$C_f = 2\times10^{-6}\times\frac{11}{10} = 2.2\times10^{-6}$$

Conserving WA $C_f V_f = C_i V_i$

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

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

(b) Not possible as pH cannot be > 7

Q.5

Sol.

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{+2} + 2OH^-$$
$$a-(s_1+s_2) \qquad s_1 \qquad x$$

$$K_{sp} = [Zn^{+2}][OH^-]^2$$

$$= S_1x^2 \qquad \ldots\ldots\ldots\ldots(1)$$

$$Zn^{+2} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$$

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

$$Zn(OH)_2(s) + 2OH^- \rightleftharpoons [Zn(OH)_4]^2$$
$$a-(s_1+s_3) \qquad x \qquad s_2$$

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

$(1)\times(2)$

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

$s^2 = (1.2\times10^{-17})^2 \times 10^{16} = 1.44\times10^{-18}$

$s = 1.2\times10^{-9}$

Solubility of $Zn(OH)_{2(s)}$ is $s_1 + s_2 \approx 2s = 2.4\times10^{-9}$ M

$[OH^-] = x = \sqrt{\frac{K_{sp}}{s_1}} = \sqrt{\frac{1.2\times10^{-17}}{1.2\times10^{-9}}} = \sqrt{10^{-8}} = 10^{-4}$

POH = H

pH = 10

Q.6

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

$$Ca(OH)_{2(s)} \rightleftharpoons \underset{s}{Ca^{+2}} + \underset{2s}{2OH}$$

$K_{sp} = 4s^3 = 4.42\times10^{-5}$

$S = \sqrt[3]{\frac{4.42\times10^{-5}}{4}}$

= 0.022 M

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

When NaOH is mixed volume is doubled

$$Ca(OH)_2 \rightleftharpoons \underset{s_1}{Ca^{+2}} + \underset{(2s_1+0.2)}{2OH^-} \qquad (s_1 < s)$$

$$(s_1)(2s_1+0.2)^2 = 4.42\times10^{-5}$$

$$(s_1)(s_1+0.1)^2 = 1.105\times10^{-5}$$

Neglecting s_1

$$s_1 = \frac{1.105\times10^{-5}}{0.01} = 1.1\times10^{-3}$$

moles of Ca^{+2} dissolved $= 1.1\times10^{-3}\times1$ moles

moles of Ca^{+2} deposited $= 11\times10^{-3} - 1.1\times10^{-3} = 9.9\times10^{-3}$ moles

moles of $Ca(OH)_2 = 9.9\times10^{-3}\times74\text{ gm} = 732.6\text{ mg}$

Q.7

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

$$\Rightarrow \frac{1}{56}\text{ moles in } 10^3\text{L} \Rightarrow 1.78\times10^{-5}\text{M}$$

Fe^{+3}	+	SCN^-	$\rightleftharpoons$	$[Fe(SCN)]^{+2}$
1.78×10^{-5}		x		0
$(1.78\times10^{-5}-6\times10^{-6})$		$(x-6\times10^{-6})$		(6×10^{-6})

$$\frac{6\times10^{-6}}{(1.78\times10^{-5}-6\times10^{-6})(x-6\times10^{-6})} = \frac{1}{k_{dissociation}} = \frac{10^3}{7.142}$$

$$\frac{6\times10^{-6}}{(11.8\times10^{-6})(x-6\times10^{-6})} = \frac{10^3}{7.142}$$

$$x-6\times10^{-6} = \frac{6\times7.142}{11.8\times10^3} = 3.61\times10^{-3} = 0.0036\text{ M}$$

Q.8

Sol.

$[NH_3] = x\,M \qquad [NH_4Cl] = (0.6 - x)\,M$

for Basic Buffer

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_4Cl]}$$

$$14 - 9 = 4.7 + \log\left(\frac{0.6 - x}{x}\right)$$

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

$$\frac{0.6 - x}{x} = 2 \qquad x = 0.2\,M$$

$$\boxed{NH_3 = 0.2M}$$

$$\boxed{[NH_4Cl] = 0.4M}$$

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

or $[NaOH] = 0.1\,M$

$[NH_4^+] = 0.4 - 0.1 = 0.3$

$[NH_3] = 0.2 + 0.1 = 0.3$

$pOH = pK_b = 4.7$

$|\Delta pOH| = 0.3$

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

Q.9
Sol.

$$AgCl_{(s)} \rightleftharpoons Ag^{+} + Cl^{-}$$
$$(a-0.1) \quad (0.1-x) \quad (0.1)$$

$$Ag^{+} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^{+}$$
$$(0.1-x) \quad (c-2x) \quad (x)$$

two unknowns c & x

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

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

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

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

$$1.6 \times 10^{7} = \frac{0.1}{(c-0.2)^2(10^{-9})}$$

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

$$c - 0.2 = \frac{10}{4} = 2.5 \qquad \boxed{c = 2.7\,M}$$

Q.10
Sol.

at $[HCl] = 4 \times 10^{-5}$ M

$pH = 5 - \log 4 = 4.4$

$pH = pKa + \log(1)$

$\boxed{pKa = 4.4}$ $\boxed{Ka = 4 \times 10^{-5}}$

for acidic color (A)

$[A] > 8[B]$

$[HIn] > 8[In^-]$ $\frac{[In^-]}{[HIn]} < \frac{1}{8}$

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

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

for Basic color B

$[In^-] > 20[HIn]$

$pH = 4.4 + \log(20)$

$\boxed{pH = 5.7}$

$pH_{range} = 3.5$ to 5.7

Q.12
Sol.

$$Mg(OH)_2 (s) + 2NH_4^+ \longrightarrow 2NH_3 + 2H_2O + Mg^{+2}$$

$$Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2OH^- \quad -(1)$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad -(2)$$

Main reaction = (1) − 2×(2)

$$K_c = \frac{K_{sp}}{K_b^2} = \frac{10^{-11}}{(1.8\times10^{-5})^2} = \frac{10^{-11}\times10^{+10}}{(1.8)^2}$$

$$= 3.08\times10^{-2}$$

$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons Mg^{+2} + 2NH_3 + 2H_2O$$

$$a-s \quad (0.5-2s) \quad s \quad 2s$$

$$\frac{(2s)^2(s)}{(0.5-2s)^2} = 3.08\times10^{-2}$$

INCORRECT ASSUMPTION ~~CONC.~~

$$\frac{4\times4s^3}{(1-4s)^2} = 3.08\times10^{-2}$$

$1-4s \simeq 1$

$$s^3 = 0.1925\times10^{-2}$$

$$\boxed{s = 0.124}$$

Q.13
Sol.

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

$H_3A \rightleftharpoons H^+ + H_2A^- \quad K_{a_1} = 10^{-5}$

$H_2A^- \rightleftharpoons H^+ + HA^{2-} \quad K_{a_2} = 10^{-9}$

$HA^{-2} \rightleftharpoons H^+ + A^{-3} \quad K_{a_3} = 10^{-13}$

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

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

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

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

$pX = 10$

Answer Verification

Q.14
Sol.

(a) $H_3PO_4 + NaOH \rightleftharpoons NaH_2PO_4 + H_2O$

~~50×0.12~~

$50 \times 0.12 \quad 20 \times 0.15$

$= 6 \quad = 3$

$3 \quad 0 \quad 3$

$[H_3PO_4] = 3/V \quad [NaH_2PO_4] = 3/V$

$pH = pKa_1 + \log(1)$

$= 3 - \log 7.5 = \boxed{2.12}$

(b) $H_3PO_4 + NaOH \rightleftharpoons NaH_2PO_4 + H_2O$

$6 \quad 6$

$0 \quad 0 \quad 6$

$pH = \frac{pKa_1 + pKa_2}{2} = \frac{2.12 + 7.2}{2} = \boxed{4.66}$

(c) $H_3PO_4 + NaOH \rightleftharpoons NaH_2PO_4 + H_2O$

$40 \times 0.12 \quad 40 \times 0.18$

$= 4.8 \quad = 7.2$

$NaH_2PO_4 + NaOH \rightleftharpoons Na_2HPO_4 + H_2O$

$4.8 \quad 2.4 \quad 0$

$2.4 \quad 0 \quad 2.4$

$pH = pKa_2 + \log(1) = \boxed{7.2}$

(d) $H_3PO_4 + NaOH \rightleftharpoons NaH_2PO_4 + H_2O$

$4 \quad 10 \quad 0$

$0 \quad 6 \quad 4$

continued

Continued

$$H_2PO_4^- + NaOH \rightleftharpoons HPO_4^{2-} + H_2O$$

4	6	0
0	2	4

$$HPO_4^{2-} + OH^- \rightleftharpoons PO_4^{3-} + H_2O$$

4	2	0
2	0	2

$$pH = pKa_3 = 12$$

Q.15
Sol.

DATA for H_2CO_3 not given

(a) $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$40 \times 0.05 \quad 50 \times 0.04$

$2 \quad 2$

$0 \quad 0 \quad 2$

$$pH = \frac{pKa_1 + pKa_2}{2} =$$

(b) $Na_3PO_4 + HCl \rightleftharpoons Na_2HPO_4 + NaCl$

$40 \times 0.02 \quad 40 \times 0.04$

$(0.8) \quad (1.6) \quad 0$

$Na_2HPO_4 + HCl \rightleftharpoons NaH_2PO_4 + NaCl$

$0.8 \quad 0.8$

$0 \quad 0 \quad 0.8$

$$pH = \frac{pKa_1 + pKa_2}{2} = \boxed{4.66}$$

(c) $Na_3PO_4 + NaH_2PO_4 \longrightarrow Na_2HPO_4$

$50 \times 0.1 \quad 50 \times 0.1$

$\quad \quad 50 \times 0.1$

$0 \quad 0$

$$pH = \frac{pKa_2 + pKa_3}{2} = \boxed{9.6}$$

(d) $H_3PO_4 + Na_3PO_4 \longrightarrow H_2PO_4^- + HPO_4^{2-}$

$40 \times 0.1 \quad 40 \times 0.1$

$\quad \quad 40 \times 0.1 \quad 40 \times 0.1$

$0 \quad 0$

$$pH = pKa_2 + \log(1) = \boxed{7.2}$$

Q.16
Sol.

$$RNO_2 + 4H_3O^+ + 4e \longrightarrow RNHOH + 5H_2O$$

300 ml
0.01 M
3 mmoles

Ka of acetic acid required

Q.17
Sol.

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$
$$(S-x) \quad S$$

$$Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$$
$$(S-x) \quad (0.2-x-y) \quad x-y$$

$$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$
$$x-y \quad (0.2-x-y) \quad y$$

$x \approx y$ so adding last 2 equations

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$
$$(S-x) \quad (0.2-2x) \quad x$$

$$K_{sp} = 1.7\times10^{-10} = (S-x)(S) \qquad K_f = 16.6\times10^{+6} = \frac{x}{(S-x)(0.2-2x)^2}$$

$$\frac{(S)(x)}{(0.2-2x)^2} = 1.7\times16.6\times10^{-4} = 28.28\times10^{-4}$$

$x \approx S$
$$\frac{S^2}{(0.2-2S)^2} = 28.28\times10^{-4}$$

$$\frac{S}{(0.2-2S)} = 5.3\times10^{-2} \qquad \frac{S}{0.1-S} = 1.06\times10^{-1} = 0.106$$

$$\frac{S}{0.1} = \frac{0.106}{1.106} = 0.09$$

$$\boxed{S = 9.6\times10^{-3}}$$

Q.18
Sol.

$$MA \rightleftharpoons M^{+2} + A^{-2} \quad K_{sp}$$
$$(S) \quad (S-x)$$

$$A^{-2} + H_2O \rightleftharpoons HA^- + OH^- \quad \frac{K_w}{K_{a_2}}$$
$$(S-x) \qquad (x-y)$$

$$HA^- + H_2O \rightleftharpoons H_2A + OH^- \quad \frac{K_w}{K_{a_1}}$$
$$(x-y) \qquad (y)$$

$$\frac{(y)[OH^-]}{(x-y)} = \frac{K_w}{K_{a_1}} \qquad \boxed{\left(\frac{y}{x-y}\right) = \frac{K_w}{K_{a_1}} \times \frac{1}{[OH^-]} = \frac{[H^+]}{K_{a_1}}} \quad \text{—(1)}$$

$$\frac{(x-y)[OH^-]}{(S-x)} = \frac{K_w}{K_{a_2}} \qquad \boxed{\left(\frac{x-y}{S-x}\right) = \frac{[H^+]}{K_{a_2}}} \quad \text{—(2)}$$

by (1) $\frac{y}{x-y} = \frac{[H^+]}{K_{a_1}}$ $\quad \frac{y}{x} = \frac{[H^+]}{K_{a_1}+[H^+]}$ $\quad \boxed{y = \frac{[H^+]}{(K_{a_1}+[H^+])} x}$

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

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

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

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

$$\boxed{S = \sqrt{K_{sp}\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)}}$$

Q.19
Sol.

with HCl it behaves as base

so $\ddot{B} + \overset{+}{H}Cl^{-} \rightleftharpoons BH^{+} + Cl^{-}$

$\ddot{B} + H^{+} \rightleftharpoons BH^{+}$

$\ddot{B} + H_2O \rightleftharpoons BH^{+} + OH^{-}$ $pK_b = 11.7$

Let x m moles of HCl added

$\ddot{B} + H^{+} \Rightarrow BH^{+}$

$10 \quad x \quad 0$

$(10-x) \quad (x)$

$pOH = pK_b + \log\frac{[BH^{+}]}{[\ddot{B}]}$

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

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

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

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

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

$[H_3PO_4] = [H_2PO_4^-]$

$pH = pKa_1 = 4.7$

$\boxed{Ka_1 = 2 \times 10^{-5}}$

(C) similarly $pH = pKa_2 = 7.7$

$\boxed{Ka_2 = 2 \times 10^{-8}}$

& $pH = pKa_3 = 10.4$

$\boxed{Ka_3 = 4 \times 10^{-11}}$

(C) $pH = \frac{1}{2}\{pK_w + pKa_3 + \log c\}$ $\quad c = \frac{0.1 \times V}{3V}$

$= \frac{1}{2}\{14 + 11 - \log 4 + \log \frac{0.1}{3}\}$ $\quad \boxed{C = 0.1/3}$

$= \frac{1}{2}\{22.92\} = 11.46$