S-II

(1.)

$H_2SO_4(aq.) \longrightarrow H^+(aq.) + HSO_4^-(aq.)$

0.2 — $(0.2+x)$ — $(0.2-x)$

0 — — —

$HSO_4^-(aq.) \rightleftharpoons H^+(aq.) + SO_4^{2-}(aq.)$; K_2

$(0.2-x)$ — $(0.2+x)$ — x

0.2 — 0.2 — —

$$K_2 = 10^{-2} = \frac{(0.2+x)\ x}{(0.2-x)}$$

$$0.2\times10^{-2} - 10^{-2}x = 0.2x + x^2$$

$$x^2 + 0.21x - 2\times10^{-3} = 0$$

$$x = 9.13\times10^{-3}\ M$$

$\Rightarrow [SO_4^{2-}] = x = 9.13\times10^{-3} M$

$[H_2SO_4] = 0$

$[H^+] = 0.2 + x = 0.209\ M$

$[HSO_4^-] = 0.2 - x = 0.191\ M$

(2)

as $K_{b_1} >> K_{b_2} \Rightarrow OH^-$ is given by I step only

$$NiCl(aq.) + H_2O \rightleftharpoons NiOH^+(aq.) + OH^-(aq);\ K_{b_1}$$

0.2		—	—
$(0.2-x) \simeq 0.2$		x	x

$$\left[\because \frac{K_{b_1}}{0.2} < 10^{-3} \Rightarrow (0.2-x) \simeq 0.2\right]$$

$$K_{b_1} = \frac{x^2}{0.2}$$

$$[OH^-] = x = \sqrt{K_{b_1} \times 0.2} = \sqrt{16 \times 10^{-8}}$$

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

$$pOH = 4 - \log 4$$

$$pH = 14 - pOH = 10 + \log 4 = 10.6$$

(3)

$NaOH(aq.) \longrightarrow Na^+(aq.) + OH^-(aq.)$

$0 \qquad 10^{-4} \qquad 10^{-4}$

$RNH_2(aq.) \overset{+H_2O}{\rightleftharpoons} RNH_3^+(aq.) + OH^-(aq.) : K_b$

$10^{-2} \qquad - \qquad 10^{-4}$ (from NaOH)

$(10^{-2}-x) \simeq 10^{-2} \qquad x \qquad (10^{-4}+x)$

$\left[\because \frac{K_b}{10^{-2}} < 10^{-3} \Rightarrow (10^{-2}-x) \simeq 10^{-2}\right]$

$$K_b = 2\times10^{-6} = \frac{x(10^{-4}+x)}{10^{-2}}$$

$$2\times10^{-8} = 10^{-4}x + x^2$$

$$x^2 + 10^{-4}x - 2\times10^{-8} = 0$$

$$x = 10^{-4}\,M$$

$$[OH^-] = 10^{-4} + x = 2\times10^{-4}\,M$$

(4) Salt of strong base & weak acid

$C_6H_5O^-(aq.) + H_2O \rightleftharpoons C_6H_5OH(aq.) + OH^-(aq.)$

$(c-x) \simeq c = 10^{-3}M \qquad x \qquad x$

$$K_h = \frac{10^{-14}}{K_a} = \frac{10^{-14}}{0.6\times10^{-10}} = \frac{10^{-4}}{0.6}$$

$$\frac{10^{-4}}{0.6} = \frac{x^2}{10^{-3}}$$

$$[OH^-] = x = \sqrt{\frac{10^{-4}\times10^{-3}}{0.6}} = \frac{10^{-3}}{\sqrt{6}}$$

$$pOH = 3 + \tfrac{1}{2}\log 6$$

$$pH = 14 - pOH = 11 - \tfrac{1}{2}\log 6 = 10.52$$

(5) all salts having amphiprotic anion so.

(i) $NaHCO_3 \Rightarrow pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

$= \frac{7 - \log 4.2 + 11 - \log 4.8}{2}$

$= 8.35$

(ii) Na_2HPO_4 :- $pH = \frac{pK_{a_2} + pK_{a_3}}{2}$

$= \frac{8 - \log 6.2 + 12}{2}$

$= 9.6$

(iii) NaH_2PO_4 :- $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

$= \frac{3 - \log 7.5 + 8 - \log 6.2}{2}$

$= 4.66$

⑥ $pOH = pK_b + \log \frac{[NH_4Cl]}{[NH_3]}$

$(14-9) = 5 - \log 2 + \log\left(\frac{[NH_4Cl]}{0.25}\right)$

$\Rightarrow \frac{[NH_4Cl]}{0.25} = 2 \Rightarrow [NH_4Cl] = 0.5\,M$

When KOH is added to buffer

$KOH + NH_4Cl \longrightarrow NH_4OH + KCl$
(or NH_3)

initially (500×0.1) (200×0.5) (200×0.25)
$= 50$ $= 100$ $= 50$

finally x 50 100

Buffer soln.

New $pOH = pK_b + \log\left(\frac{S}{b}\right)$

$= 5 - \log 2 + \log\left(\frac{50}{100}\right)$

$= 5 - 2\log 2$

New $pH = 14 - pOH = 9 + 2\log 2$

$= \underline{9.6}$

• (7.) I S.A. & S.B. react so

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

milli	2	1	—
-moles	1	x	1

After rxn $[HCl] = \frac{1}{10+10+10} = \frac{1}{30}$ M

finally $[HA] = \frac{0.1 \times 10}{10+10+10} = \frac{1}{30}$ M

$$HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.) \quad : K_a$$

$\frac{1}{30}$	$\frac{1}{30}$ (from HCl)	—
$(\frac{1}{30} - x) \simeq \frac{1}{30}$	$(\frac{1}{30} + x) \simeq \frac{1}{30}$	x

[x is negligible as $\frac{K_a}{C} < 10^{-3}$]

$$K_a = 10^{-5} = \frac{1/30 \cdot [A^-]}{1/30}$$

$$[A^-] = \underline{\underline{10^{-5}}} \text{ M}$$

(8.)

$$HCN + KOH \longrightarrow KCN + H_2O$$

1.50×0.5	$V_2 \times 1.5$	—
$= 75$	$= 75$	
X	X	75 millimoles

$$\text{Concn. (C)} = \frac{75}{150 + V_2} = \frac{75}{200}$$

$$= 3.75 \times 10^{-1} \text{ M}$$

Salt formed (KCN) undergo hydrolysis

$$CN^-(aq.) + H_2O \rightleftharpoons HCN(aq.) + OH^-(aq.)$$

$(C - x) \simeq C$	x	x

$$K_h = \frac{10^{-14}}{K_a} = \frac{x^2}{C - x} = \frac{x^2}{C}$$

$$x = [HCN] = \sqrt{\frac{10^{-14}}{3.75 \times 10^{-9}} \times 3.75 \times 10^{-1}}$$

$$= \underline{\underline{10^{-3} \text{ M}}}$$

⑨ Let solubility of AgBr is 'x' mol/L

$$AgBr(s) \rightleftharpoons Ag^+(aq.) + Br^-(aq) \quad ; \quad K_{sp}$$

$$x \qquad\qquad x$$

$$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq) \quad ; \quad K_f$$

$$x \qquad 0.4 \qquad\qquad -$$

$$\sim \qquad (0.4-2x) \qquad\qquad x$$

$$AgBr(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + Br^-(aq.)$$

$$(0.4-2x) \qquad\qquad x \qquad\qquad x$$

$$K_{sp} \times K_f = \frac{x^2}{(0.4-2x)^2}$$

$$\sqrt{K_{sp} \times K_f} = \frac{x}{0.4-2x}$$

$$x = 2.8 \times 10^{-3} \ M$$

(10.) Let solubility of PbI_2 is 's' mol/L

$$PbI_2(s) \rightleftharpoons Pb^{+2}(aq.) + 2I^-(aq.) \quad ; \quad K_{sp}$$

's' 0.9S 1.8S

$$K_{sp} = [Pb^{+2}]\ [I^-]^2$$

$$1.4 \times 10^{-8} = (0.9S)\ (1.8S)^2$$

$$S = \left(\frac{1.4 \times 10^{-8}}{0.9 \times (1.8)^2}\right)^{1/3}$$

$$= 1.6 \times 10^{-3}\ M$$