Daily Tutorial Sheet - 14	Level-3

153. $HCOOH \rightleftharpoons H^+ + HCOO^-$

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

Since both are present in mixture and therefore,

$[H^+]$ by $HCOOH = [H^+]$ by CH_3COOH

$C_1\alpha_1 = C_2\alpha_2$

$\sqrt{K_{a_1} \times C_1} = \sqrt{K_{a_2} \times C_2}$

$\sqrt{2.4 \times 10^{-4} \times 0.5} = \sqrt{1.8 \times 10^{-5} \times C_2}$

$\therefore \quad C_{CH_3COOH} = 6.666\,M$

154. Let, 'a' Meq. of BOH is initially present

	BOH	+ HCl	$\longrightarrow$ BCl	+ H_2O
Initial Meq.	a	–	0	0
At 1/4th equivalence	$\left(a - \frac{a}{4}\right) = \frac{3a}{4}$	–	$\frac{a}{4}$	–

At this point, pH = 9.24

$\therefore \quad pOH = 14 - 9.25 = 4.76$

$\therefore \quad pOH = pK_b + \log \frac{[BCl]}{[BOH]}$

$4.76 = pK_b + \log \frac{a/4}{3a/4} = pK_b - \log 3$

$\therefore \quad K_b = 5.79 \times 10^{-6}$

When further 6 Meq. of base was added

	BCl	+ NaOH	$\longrightarrow$ BOH	+ NaCl
Initial Meq.	a/4	6	0	0
After Meq.	0	0	6	6

$\therefore \quad \frac{a}{4} = 6 \quad \Rightarrow \quad a = 24$

Now, total Meq. of BOH in 50 ml solution $= \left(a - \frac{a}{4}\right) + 6 = 18 + 6 = 24$

$\therefore \quad$ Molarity of BOH $= \frac{24}{50}M = 0.48\,M$

$\left[OH^-\right] = \sqrt{5.77 \times 10^{-6} \times 0.48} = 1.664 \times 10^{-3}$

$\therefore \quad pOH = -\log\left(1.664 \times 10^{-3}\right) = 2.778$

$\therefore \quad pH = 14 - 2.778 = 11.222$

155. $pH = pK_a + \log\frac{[salt]}{[acid]}$

Let x mole of HCl (x < 0.01) be added

$$NaCN + HCl \longrightarrow NaCl + HCN$$

or $\quad CN^- \quad + \quad H^+ \quad \longrightarrow \quad HCN$

0.01	x	0	. . . initially
0.01 – x	0	x	. . . upon completion

Thus, $8.5 = -\log(4.0\times10^{-10}) + \log\frac{(0.01-x)}{x}$

Upon solving $x = 8.85\times10^{-3}M$

156. $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Zn^{2+}][OH^-]^2 = 1.8\times10^{-17}$

And for the complex formation

$Zn^{2+}(aq) + 4NH_3 \rightleftharpoons [Zn(NH_3)]^{2+}$

$$K_{stability} = \frac{\left[Zn(NH_3)_4\right]^{2+}}{\left[Zn^{2+}\right]\left[NH_3\right]^4}$$

Since the value of $K_{stability}$ is too high it may be assumed that all of Zn^{2+} is complexed.

$\therefore$ If x be the molar solubility of $Zn(OH)_2$ in 1 M solution, then at equilibrium

$[NH_3] = 1-4x\,[OH^-] = 2x,$ and $[Zn(NH_3)_4]^{2+} = x$

$\therefore$ $K_{sp}\{Zn(OH)_2\} = [Zn^{2+}](2x)^2 = 4x^2[Zn^{2+}]$ ...(a)

and $K_{stability} = \frac{x}{(1-4x)^4[Zn^{2+}]}$ ...(b)

Multiplying (a) & (b) we get

$$K = K_{sp}\cdot K_{stability} = \frac{4x^3}{(1-4x)^4} = 4x^3 \text{ (approximately)}$$

$\therefore$ $4x^3 = 1.8\times10^{-17}\times1.64\times10^{10}$ or $x = 4.19\times10^{-3}$ moles / lit

157. Here actually two situations arise

$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$ .... (i)

(s) $\quad$ (s – x)

$\therefore$ $K_{sp}(AgCN) = s(s-x)$

$CN^-(aq) + H^+(aq) \rightleftharpoons HCN$ .... (ii)

(s – x) $\quad 10^{-3} \quad$ x

and $\frac{1}{K_a} = \frac{x}{(s-x)\times10^{-3}}$

$\therefore \qquad \dfrac{K_{sp}}{K_a} = \dfrac{s \cdot x}{10^{-3}} = \dfrac{1.2 \times 10^{-16}}{4.8 \times 10^{-10}} = \dfrac{1}{4} \times 10^{-6} = 2.5 \times 10^{-7}$

or $\qquad s \cdot x = 2.5 \times 10^{-10}$ or $x = \dfrac{2.5 \times 10^{-10}}{S}$

$\therefore \qquad s\left(s - \dfrac{2.5 \times 10^{-10}}{s}\right) = 1.2 \times 10^{-16}$

or $\qquad s^2 - 2.5 \times 10^{-10} = 1.2 \times 10^{-16}$

or $\qquad s^2 = 2.5 \times 10^{-10} + 1.2 \times 10^{-16} \approx 2.5 \times 10^{-10}$

$\therefore \qquad s = 1.6 \times 10^{-3}$ mol / lit

158. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$

$\qquad\qquad\qquad\qquad S \qquad 2S$

$K_{sp} = S(2S)^2 = 4S^3 = 4(2 \times 10^{-4})^3 = 3.2 \times 10^{-11} M^3$

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^- \qquad\qquad K_c = K_{sp}$

$2NH_4^+ + 2OH^- \rightleftharpoons 2NH_4OH \qquad\qquad K_c = \dfrac{1}{K_b^2}$

$Mg(OH)_2(s) + 2NH_4^+ \rightleftharpoons Mg^{2+} + 2NH_4OH \qquad K_c = \dfrac{3.2 \times 10^{-11}}{\left(1.8 \times 10^{-5}\right)^2}$

$\qquad 0.50 - 2x \qquad\qquad x \qquad\qquad 2x \qquad\qquad = 9.87 \times 10^{-2}$

$\dfrac{x(2x)^2}{(0.50)^2} = 9.87 \times 10^{-2} \qquad \therefore \qquad x = 0.1833\,M$