Daily Tutorial Sheet - 15 | Level-3

159. Millimoles of monobasic weak acid taken = Millimoles of NaOH required for end point

$= 30 \times 0.1 = 3$

Upon addition of 20 ml alkali:

Number of millimoles of salt formed = 2

Number of millimoles of acid left = 3 – 2 = 1

pH = 6.3

From Henderson's equation,

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\text{salt}]}{[\text{Acid}]}$$

$$6.3 = \mathrm{pK_a} + \log\frac{2}{1}$$

$\therefore \quad \mathrm{pK_a} = 6.3 - 0.3 = 6 \text{ or } K_a = 10^{-6}$

160. The anion of the salt being conjugate base of a weak acid will hydrolyse in the following three steps.

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad K_{h_1} = \frac{K_w}{K_3} = \frac{10^{-14}}{1.0 \times 10^{-12}} = 10^{-2}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons HPO_4^{-} + OH^- \qquad K_{h_2} = \frac{K_w}{K_2} = \frac{10^{-14}}{2.5 \times 10^{-8}} = 4 \times 10^{-7}$$

$$H_2PO_4^{-} + H_2O \rightleftharpoons H_3PO_4 + OH^- H \qquad K_{h_3} = \frac{K_w}{K_1} = \frac{10^{-16}}{5.0 \times 10^{-3}} = 2 \times 10^{-12}$$

K_{h_3} and K_{h_3} being quite smaller as compared to K_{h_1} , so consider only the 1st step hydrolysis so as to simplify the calculation.

The pOH of the solution may be given by the formula.

$$\mathrm{pOH} = \frac{1}{2}[\mathrm{pK_w} - \mathrm{pK_3} - \log C] = \frac{1}{2}\left[14 - 12 - \log 0.1\right] = \frac{1}{2} \times 3 = 1.5$$

So, $\quad \mathrm{pH} = 12.5$

161. Let the number of millimole of weak base contained in 25 mL solution be x.

Upon addition of 10 mL 0.5 M HCl i.e. 5 millimole HCl, the salt formed will be 5 millimole and base remaining unreacted will be (x – 5) millimole.

For a base buffer mixture

$$[OH^-] = K_b \frac{[\text{base}]}{[\text{salt}]}$$

i.e. $\quad \mathrm{pOH} = \mathrm{pK_b} + \log\frac{[\text{salt}]}{[\text{base}]}$

$\because \quad \mathrm{pH} = 8.6$

$\therefore \quad \mathrm{pOH} = 5.4 \text{ and } [OH^-] = 10^{-5.4}$

So, $\quad 10^{-5.4} = K_b \frac{[x-5]}{5} \qquad \text{.......(1)}$

Upon addition of 25 mL 0.5 M HCl i.e. 12.5 millimole HCl, the salt formed will be 12.5 millimole and base remaining unreacted will be (x – 12.5) millimole.

$\because$ pH = 8

$\therefore$ pOH = 6 and $[OH^-] = 10^{-6}$

The mixture is again a basic buffer mixture for which

$$10^{-6} = \frac{K_b(x-12.5)}{12.5} \qquad \text{....... (2)}$$

Dividing equation (1) by (2)

$$10^{0.6} = \frac{2.5\left(x-5\right)}{x-12.5} \quad \Rightarrow \quad 4 = \frac{2.5\left(x-5\right)}{x-12.5} \quad \Rightarrow \quad 4x-50 = 2.5x-12.5$$

$\therefore$ x = 25

Molarity of base solution $= \dfrac{\text{No. of millimole}}{\text{Volume in mL}} = \dfrac{25}{25} = 1M$

Putting the value of x in equation (2) :

$K_b = 10^{-6}$

Upon addition of 0 mL acid

$$\begin{array}{ccccc} BOH & \rightleftharpoons & B^+ & + & OH^- \\ C & & 0 & & 0 \\ C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$[OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}} = \sqrt{K_b \cdot C}$$

(neglecting α in comparison to unity which is true for concentrated solution).

$= \sqrt{10^{-6} \times 1} = 10^{-3}M \quad \therefore \quad$ pOH = 3 and pH = 11

At the end point :

The end point will reach when 50 mL 0.5 M HCl is added. 25 mL 1.0 M BOH i.e. 25 millimole of BOH will react with 50 × 0.5 HCl i.e. 25 millimole of HCl to form 25 millimole of salt. The total volume of solution will be 75 mL.

$\therefore \quad [\text{salt}] = \dfrac{25}{75} = \dfrac{1}{3}M$

The solution will be acidic due to salt hydrolysis. The pH of such a solution will be given by the expression.

$$pH = \frac{1}{2}[pK_a - pK_b - \log C] = \frac{1}{2}[14 - 6 - \log\frac{1}{3}] = 4.239$$

162. pH = 9.0

$\therefore \quad [H^+] = 10^{-9}M$ and $[OH^-] = 10^{-5}M$

$[Mg^{2+}][OH^-] = 10^{-5}M$

$$[Mg^{2+}] = \frac{8.9 \times 10^{-12}}{(10^{-5})^2} = 8.9 \times 10^{-2} = 0.089M$$

Thus in saturated solution of $Mg\left(OH\right)_2$, only 0.089 mol L^{-1} of Mg^{2+} will remain dissolved.

Hence the amount of Mg^{2+} to be precipitated out $= 0.1 - 0.089 = 0.011$ mol L^{-1}

163. Molarity of ammonia may be calculated as,

$$M = \frac{x \times d \times 10}{M_B}$$

x = % solute by weight

d = density of solution

M_B = molecular weight of solute

$$M = \frac{10 \times 0.99 \times 10}{17} = 5.823$$

$$K_w = K_a \times K_b$$

$$10^{-14} = 5 \times 10^{-10} \times K_b$$

$$K_b = 2 \times 10^{-5}$$

We known, $[OH^-] = \sqrt{C \cdot K_b}$ for monoacidic base.

$$= \sqrt{5.823 \times 2 \times 10^{-5}} = 0.01079\,M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.01079} = 9.268 \times 10^{-12}\,M$$

164. The solubility equation is

$$Cd(OH)_2(s) \rightleftharpoons Cd^{2+} + 2OH^-$$

$$K_{sp} = [Cd^{2+}][OH^-]^2 = 2 \times 10^{-14}$$

Now $[Cd^{2+}] = 0.010$ M (coming from $CdCl_2$)

$\therefore$ Maximum $[OH^-]$ so that precipitation does not occur is

$$[OH^-]^2 = \frac{2.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 2 \times 10^{-12} \text{ or } [OH^-] = 1.4 \times 10^{-6}\,M$$

Now $[OH^-]$ is derived from

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{[NH_4^+][1.4 \times 10^{-6}]}{[0.010]} \text{ or } [NH_4^+] = 1.3 \times 10^{-1}\,M$$

$\therefore$ NH_4^+ ion that must be supplied is 0.13 M

[Assuming very small dissociation of NH_3 / NH_4OH in presence of NH_4Cl]