46. $Ag^+ \quad + \quad 2CN^- \quad \rightleftharpoons \quad Ag(CN)_2^-$

Initial: 0.03 0.10 0

Equilibrium: x 0.10 – 0.06 0.03

$$K = \frac{1}{4 \times 10^{-19}} = 2.5 \times 10^{-18} \quad \Rightarrow \quad K = 2.5 \times 10^{18} = \frac{0.03}{(0.04)^2 x}$$

$$x = 7.50 \times 10^{-18} \text{ M}$$

47. Partial pressure of SO_2 in air $= 10^{-5}$atm

$$[SO_2]_{aq} = 1.3653 \times 10^{-5} \text{ mol L}^{-1}$$

$\because$ $pK_a = 1.92$ and concentration of H_2SO_3 is very low, it is almost completely iodised as:

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

$$[H^+] = 1.3653 \times 10^{-5} M$$

$$pH = -\log(1.365 \times 10^{-5}) = 4.86$$

48.(A) $A_pB_q \rightleftharpoons pA + qB$

pS qS

$$K_{sp} = (qS)^p (qS)^q = S^{(p+q)}.p^p.q^q$$

49.(D) Alkali metal salts are usually more soluble than the salts of transition metals. Also, CuS is less soluble than ZnS because of $3d^9$ configuration of Cu^{2+}. Therefore, solubility order is $Na_2S > ZnS > CuS$

50.(C) Minimum S^{2-} concentration would be required for precipitation of least soluble HgS

For HgS, S^{2-} required for precipitation is $[S^{2-}] = \frac{K_{sp}}{[Hg^{2+}]} = \frac{10^{-54}}{10^{-3}} M$

51. At the end-point, $[A^-] - 0.05$

$$K_b = (A^-) = K_w / K_a = 2 \times 10^{-9}$$

$$[OH^-] = \sqrt{K_b C} = \sqrt{2 \times 10^{-9} \times 0.05} = 10^{-5}$$

pOH = 5 and pH = 9

52.(A) $K_h(X^-) = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$

$$\alpha = \sqrt{\frac{K_h}{C}} = \frac{10^{-9}}{0.10} = 10^{-4}$$

% hydrolysis $= 0.01$

53.(B) $CH_3NH_2 + HCl \rightarrow CH_3NH_3^+ + Cl^-$

Initial : 0.10 0.08 0 0

Final : 0.02 0 0.08 0.08

$$pOH = pK_b + \log\frac{[CH_3NH_3^+]}{[CH_3NH_2]} = -\log(5 \times 10^{-4}) + \log\frac{0.08}{0.02} = 3.9$$

$$pH = 14.pOH = 10.1 \quad \Rightarrow \quad [H^+] = 8 \times 10^{-11}$$

54.(D) MX : $K_{sp} = S^2 = 4 \times 10^{-8}$

$\Rightarrow \quad S = 2 \times 10^{-4}$

MX_2 : $K_{sp} = 4S^3 = 3.2 \times 10^{-14} \Rightarrow S = 2 \times 10^{-5}$

M_3X : $K_{sp} = 27S^4 = 2.7 \times 10^{-15} \Rightarrow S = 10^{-4}$

Order of solubility is $MX > M_3X > MX_2$

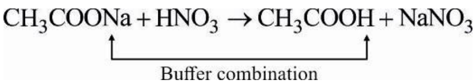
55. The hydrolysis reaction is $A^- + H_2O \rightleftharpoons AH + OH^-$

$$K_h = \frac{K_w}{K_a} = 10^{-10}$$

$$[OH^-] = \sqrt{K_h C} = 10^{-6}$$

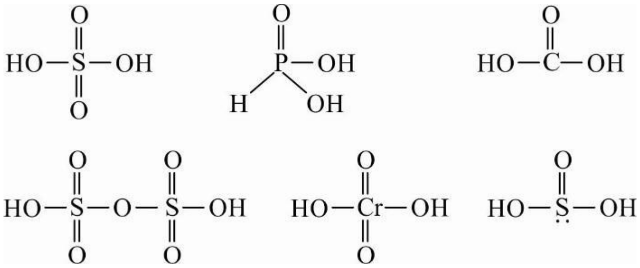
56.(3) Basic salts solution will have $pH > 7$, will change colour of litmus paper red to blue KCN, K_2CO_3 and $LiCN$ are the only basic salt among these

***57.(CD)** In HNO_3 and CH_3COOHa combination, if HNO_3 is present in limiting amount, it will be neutralized completely, leaving behind some excess of CH_3COONa

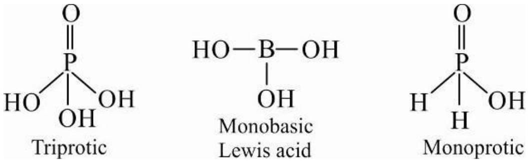


$$CH_3COONa + HNO_3 \rightarrow CH_3COOH + NaNO_3$$

58.(6) Diprotic acids = 6



Others are



59.(7) If is a case of simultaneous solubility of salts with a common ion. Here, solubility product of $CuCl$ is much greater than of $AgCl$, it can be assumed that Cl - in solution comes mainly from $CuCl$.

$$[Cl^-] = \sqrt{K_{sp}(CuCl)} = 10^{-3} M$$

Now, for $AgCl$, $K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-] = [Ag^+] \times 10^{-3}$

$\Rightarrow \quad [Ag^+] = 1.6 \times 10^{-7}$

60. **(a)** $E = 0.164 = -0.059 \log \dfrac{[Ag^+]_{anode}}{0.10}$

$[Ag^+]_{anode} = 1.66 \times 10^{-4}$ M1

$[CrO_4^{2-}] = \dfrac{[Ag^+]}{2} = 8.3 \times 10^{-5}$ M

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.66 \times 10^{-4})^2(8.3 \times 10^{-5}) = 2.3 \times 10^{-12}$

(b) pH of HCl = 2

$\therefore \quad [H^+] = 10^{-2} M$

Moles of H^+ ions in 200 mL of 10^{-2} M HCl solution $= \dfrac{10^{-2}}{1000} \times 200 = 2 \times 10^{-3}$

Similarly, pH of NaOH = 12

$\therefore \quad [H^+] = 10^{-12}$ M or $[OH^-] = 10^{-2}$ M $\quad \left[\because\ [H^+][OH^-] = 10^{-14}\ M\right]$

Moles of OH^- ion in 300 mL of 10^{-2}M NaOH solution $= \dfrac{10^{-2}}{1000} \times 300 = 3 \times 10^{-3}$

Total volume of solution after mixing = 500 mL

Moles of OH^- ion left in 500 mL of solution $= (3 \times 10^{-3}) - (2 \times 10^{-3}) = 10^{-3}$

Solution $= \dfrac{10^{-3}}{500} \times 1000 = 2 \times 10^{-3}$ M

$pOH = -\log(2 \times 10^{3}) = -\log 2 + 3\log 10 = -0.3 \simeq 103 = 2.699$

$\therefore \quad pH = 14 - 2.699 = 11.301$

61.(B) Plan in presence of common ion (in this case Ag^+ion) solubility of sparingly soluble salt is decreased.

Let solubility of Ag_2CrO_4 in presence of 0.1M

$AgNO_3 = x$

$$\underset{}{Ag_2CrO_4} \rightleftharpoons \underset{2x}{2Ag^+} + \underset{x}{CrO_4^{2-}}$$

$$AgNO_3 \rightleftharpoons \underset{0.1}{Ag^+} + \underset{0.1}{NO_3^-}$$

Total $[Ag^+] = (2x + 0.1)M \approx 0.1$ M

As $x <<< 0.1M$

$[CrO_4^{2-}] = xM$

Thus, $[Ag^+]^2[CrO_4^{2-}] = K_{sp}$

$(0.1)^2(x) = 1.1 \times 10^{-12}$

$\because \quad x = 1.1 \times 10^{-10} M$

62.(A) Heat capacity of calorimeter $= \dfrac{57 \times 10^3 \times 0.1 - (4.2 \times 200 \times 5.7)}{5.7} = 1000 - 840 = 160\ J/K$

Energy required to dissociate 0.1 moles of CH_3COOH (100 ml, 2M)

$= (57 \times 10^3 \times 0.1) - (4.2 \times 200 \times 5.6) - (160 \times 5.6)$

$= (57 \times 10^3 \times 0.1) - (1000 \times 5.6) = 1000 \times 0.1 = 100\,J$

$\Rightarrow$ Enthalpy of dissociation $= \dfrac{100\,J}{0.1\,moles} = 1000\,J/moles = 1\,kJ/mol$

63.(B) $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

$t = 0$ (m. moles) $\quad 200 \quad 100$

$t = t_{eq} \quad \begin{matrix} 100 + x \\ \approx 100 \end{matrix} \quad \begin{matrix} 100 - x \\ \approx 100 \end{matrix}$

$\Rightarrow \quad CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \Rightarrow \quad K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \dfrac{100 \times y}{100}$

$t = t_{eq} \quad \approx 100 \quad \approx 100 \quad y$

(m. moles)

$\Rightarrow \quad [H^+] = y = K_a = 2 \times 10^{-5} = 10^{0.3} \times 10^{-5} = 10^{-4.7} \quad \Rightarrow \quad pH = 4.7$

64.(4.47) $AB(S) \rightleftharpoons A^+(aq) + B^-(aq)$ ....(A)

$B^-(aq) + H^+(aq) \rightleftharpoons HB(aq)$ .... (B)

On adding equation (A) and (B)

$AB(s) + H^+(aq) \rightleftharpoons A^+(aq) + HB(aq)$

$a \quad 10^{-3} \quad 0 \quad 0$

$a - s \quad 10^{-3} \quad s \quad s$

$$K_{sp} \times \frac{1}{K_a} = \frac{[A^+][HB]}{[H^+]}$$

$$\frac{2 \times 10^{-10}}{1 \times 10^{-8}} = \frac{S^2}{10^{-3}} \quad \Rightarrow \quad S^2 = 2 \times 10^{-2} \times 10^{-3}$$

$\Rightarrow \quad S^2 = 2 \times 10^{-5} \quad \Rightarrow \quad S = 4.47 \times 10^{-3} = y \times 10^{-3} \quad \Rightarrow \quad y = 4.47$

65.(D) **P** $\Rightarrow \quad CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$20 \times 0.1 \quad 20 \times 0.1$

$10 \times 0.1 \quad 0 \quad 10 \times 0.1$ (Acidic Buffer)

No effect of dilution on $[H^+]$

Q $\Rightarrow \quad CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$ (salt of W/A and S/B)

$20 \times 0.1 \quad 20 \times 0.1 \quad 20 \times 0.1$

$$[H^+] = \sqrt{\frac{K_w \times K_a}{C}} \; ; \; [H^+]_{old} = \sqrt{\frac{K_w \times K_a}{C}} \; ; \; [H^+]_{new} = \sqrt{\frac{K_w \times K_a}{\left(\frac{C}{2}\right)}} = [H^+]_{old} \times \sqrt{2}$$

R $\Rightarrow \quad NH_3 + HCl \longrightarrow NH_4Cl$ (salt of W/B and S/A)

$20 \times 0.1 \quad 20 \times 0.1 \quad 20 \times 0.1$

$$[H^+] = \sqrt{\frac{K_w \times C}{K_b}} \; ; \; [H^+]_{old} = \sqrt{\frac{K_w \times C}{K_b}} \; ; \; [H^+]_{new} = \sqrt{\frac{K_w \times C}{K_b \times 2}} = [H^+]_{old} \times \frac{1}{\sqrt{2}}$$

S $\Rightarrow \quad Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$

No effect of dilution on $[H^+]$ as solution remain saturated.