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

When concentration of CH_3COOH is 1.0 M, 'α' is negligible.

$$[H^+] = \sqrt{K_aC} = 4.24 \times 10^{-3} \text{ M}$$

$$pH = -\log\left(424 \times 10^{-3}\right) = 2.37$$

Now, let us assume that solution is diluted to a volume where concentration of CH_3COOH (without considering ionisation) is x.

$$\underset{x(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{x\alpha}{CH_3COO^-} + \underset{x\alpha}{H^+}$$

$$K_a = \frac{x\alpha^2}{1-\alpha}$$

Also, desired $pH = 2 \times 2.37 = 4.74$

$$[H^+] = 1.8 \times 10^{-5} = x\alpha$$

$$K_a = 1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5}\alpha}{1-\alpha}$$

$\alpha = 0.5$ and $x = 3.6 \times 10^{-5}$ M

Volume (final) $= 1/3.6 \times 10^{-5} = 27.78 \times 10^3 L$.

32. Initial concentration of $K_2C_2O_4 = \frac{0.152}{0.50} = 0.304$ M,

Also for the following equilibrium:

$$Ag_2CO_3(s) + \underset{0.340-x}{K_2C_2O_4(aq)} \rightleftharpoons Ag_2C_2O_4(s) + \underset{x}{K_2CO_3}$$

$$K = \frac{[CO_3^{2-}]}{[C_2O_4^{2-}]} \times \frac{[Ag^+]^2}{[Ag^+]^2} = \frac{K_{sp}(Ag_2CO_3)}{K_{sp}(Ag_2C_2O_4)}$$

Given, $0.304 - x = 0.0358$

$$\Rightarrow \quad x = 0.2682 \quad \Rightarrow \quad K = \frac{0.2682}{0.358} = 7.5$$

$$K_{sp}(Ag_2CO_3) = K \times K_{sp}(Ag_2C_2O_4) = 7.5 \times 1.29 \times 10^{-11} = 9.675 \times 10^{-11}$$

33. Let 40 mL of base contain x mmol of BOH.

$$\begin{array}{lll} BOH + HCl \longrightarrow BCl + H_2O & & \\ x-0.5 & 0.5 & \text{when 5 mL acid is added} \\ x-2 & 2.0 & \text{when 20 ml of acid is added} \end{array}$$

When pH is 10.04, pOH = 3.96 and when pH is 9.14, pOH is 4.86. Therefore,

$$3.96 = pK_b + \log\frac{0.50}{x-0.5} \qquad \text{......(i)}$$

$$3.96 = pK_b + \log\frac{2.0}{x-2} \qquad \text{......(ii)}$$

Subtracting Eq. (i) from Eq. (ii) gives

$0.90 = \log\left(\frac{2}{x-2} \times \frac{x-0.5}{0.5}\right) \quad \Rightarrow \quad 28 = \frac{4\left(x-0.5\right)}{x-2}$

$\Rightarrow$ $x = 3.5$, substitution in equation (i) gives

$3.96 = pK_b + \log\frac{0.5}{3} \quad \Rightarrow \quad K_b = 1.8 \times 10^{-5}$

34. $K_{sp} = 4S^3 = 4.42 \times 10^{-5}$

$S = 0.022M$

mmol of $Ca(OH)_2$ in 500 mL saturated solution = 11

mmol of NaOH in 500 mL 0.40 M solution = 200

Total mmol of $OH^- = 200 + 2 \times 11 = 222$

$[OH^-] = 0.222$ M

Solubility in presence of NaOH $= \frac{K_{sp}}{[OH^-]^2}$

mmol of Ca^{2+} remaining in solution = 0.9

mmol of $Ca(OH)_2$ precipitated = 10.1

mg of $Ca(OH)_2$ precipitated $= 10.1 \times 7.4 = 747.4$ mg

35.(D) $75mL\frac{m}{5}HCl = 15mmol\,HCl$

$25mL\frac{M}{5}NaOH = 5mmol\,NaOH$

After neutralization, $10mmol\ HCl$ will be remaining in $100\,mL$ of solution.

Molarity of HCl in the final solution $= \frac{10}{100} = 0.10$

$pH = -\log[H^+] = -\log(0.10) = 1$

36. For H_2S, $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$K = K_1 \times K_2 = 1.3 \times 10^{-20}$

Minimum $[S^{2-}]$ required to begin precipitation of

$[S^{-2}] = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}$

$K = 1.3 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = [H^+]^2\ \frac{(1.2 \times 10^{-19})}{0.10}$

$[H^+] = 0.10$ M $\quad \Rightarrow \quad pH = 1$

37. Mixing H_2CO_3 with $NaHCO_3$ results in buffer solution.

$pH = pK_a + \log\frac{[NaHCO_3]}{[H_2CO_3]} = pK_a + \log\frac{n(NaHCO_3)}{n(H_2CO_3)}$

$\Rightarrow$ $7.4 = -\log(7.8 \times 10^{-7}) + \log\frac{x}{20} \quad \Rightarrow \quad x = 400$ mmol

$\Rightarrow$ $NaHCO_3 = 5 \times V \quad \Rightarrow \quad V = 80$ mL

38. For salts of weak acid and weak base.

$pH = 7 + \frac{1}{2}(pK_a - pK_b) = 7 + \frac{1}{2}(3.8 - 4.8) = 6.50$

39. $CN^- \rightleftharpoons H_2O \rightleftharpoons HCN + OH^-$

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

$[OH^-] = \sqrt{k_h C} = \sqrt{2 \times 10^{-5} \times 0.5} = \sqrt{10^{-5}}$

$pOH = 2.5$ and $pH = 11.5$

40. $K_a(NH_4^+) = 5.6 \times 10^{-10}$

$$K_b(NH_3) = K_w / K_a = \frac{10^{-14}}{5.6 \times 10^{-16}} = 1.8 \times 10^{-5}$$

i.e. $NH_3 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4^+ + OH^-$

$$K = \frac{k_1}{k_2} = 1.8 \times 10^{-5} \quad \Rightarrow \quad k_1 = Kk_2 = 1.8 \times 10^{-5} \times 3.4 \times 10^{10} = 6.12 \times 10^5$$

41. I_2

P_2O_5 : Acidic

Na_2O_2 and MgO : Basic

42. More: CH_3NH_2 is stronger base than CH_3OH.

***43.(BC)** pH of 10^{-8} M solution will be between 6 and 7 never 8. The conjugate base of an acid is formed by removing a proton (H^+) from acid. Therefore, HPO_4^{2-} is conjugate base of $H_2PO_4^-$.

$H_2O \rightleftharpoons H^+ + OH^- \qquad \Delta H > 0$

Increasing temperature will increase equilibrium constant of the above endothermic reaction. At the mid-point of titration $pH = pK_a$

44.(B) NaCN is basic salt, has highest pH while HCl has lowest pH. NaCl is neutral salt has $pH = 7$ while NH_4Cl is acidic salt, has pH less than 7.

***45.(ABC)** $CH_3COOH + CH_3COONa$ = Buffer solution

$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

If HCl is taken in limited quantity, final solution will have both CH_3COOH and CH_3COONa needed for buffer solution.

Ammonia and ammonium chloride forms basic buffer.