① $K_{sp} = (1)^1 (3)^3 s^4 = 27 s^4$

$s = \left(K_{sp}/27 \right)^{1/4}$

② $K_a = \frac{x^2}{C-x} = \frac{(10^{-5})^2}{1-10^{-5}} = 10^{-10}$ $(x = [H^+])$

③

for ppt. $\boxed{Q_{sp} > K_{sp}}$

$Q_{sp} = [Ca^{+2}] [F^-]^2$

④ $K_a = \frac{x^2}{C-x} = \frac{(10^{-3})^2}{0.1-10^{-3}} = \frac{10^{-6}}{0.1} = 10^{-5}$

⑤

for dilution, $M_1 V_1 = M_2 V_2$

$10^{-1} \times 1 = 10^{-2} \times V_2$

$V_2 = 10 L$

Volume of H_2O added $= V_2 - V_1 = 10 - 1 = 9 L$

⑥ $K_{sp} = [Ba^{+2}] [CO_3^{2-}]$

$[Ba^{+2}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{10^{-4}} = 5.1 \times 10^{-5} M$

⑦ $[OH^-] = M = 5 \times 10^{-2}$

$pOH = 2 - \log 5$; $pH = 14 - pOH$

$= 12 + \log 5 = 12.70$

⑧ $Hg_2Cl_2 \Rightarrow K_{sp} = (1)^1 (2)^2 s^3 = 4s^3$

$Cr_2(SO_4)_3 \Rightarrow K_{sp} = (2)^2 (3)^3 s^5 = 108 s^5$

$BaSO_4 \Rightarrow K_{sp} = (1)^1 (1)^1 s^2 = s^2$

$CrCl_3 \Rightarrow K_{sp} = (1)^1 (3)^3 s^4 = 27 s^4$

⑨

$$pH = pKa + \log(S/a) \quad \text{(Buffer solution)}$$

$$= 4.76 + \log \frac{(7.5/82)}{(5/60)} = 4.80$$

⑩ Buffer solution resist pH change, so when small amount of acid or base is added pH remain almost same.

⑪

$$Ksp = (3)^3 (4)^4 s^7 = 6912\, s^7$$

⑫

$$pH = 7 + \tfrac{1}{2} pKa - \tfrac{1}{2} pKb = 6.9$$

⑬

$$pH = pKa + \log(S/a)$$

$$6 = 5 + \log(S/a) \Rightarrow \log(S/a) = 1$$

$$\Rightarrow \left(\frac{S}{a}\right) = 10$$

⑭

$$\begin{array}{ccccc} NH_3 & + & HCl & \longrightarrow & NH_4Cl \\ 10 & & 5 & & - \\ 5 & & \times & & 5 \end{array}$$

↑ Basic Buffer ↑

$$pOH = pKb + \log(S/b) = 4.75 + \log(5/5) = 4.75$$

$$pH = 14 - 4.75 = 9.25$$

⑮ CH_3COOK is most basic because it is salt of strong base with weak acid.

⑯ Methyl orange is yellow in basic medium while pinkish red in acidic medium.

⑰ $H_2S\,(aq.) \rightleftharpoons 2H^+\,(aq.) + S^{2-}\,(aq.) : K_{eq} = K_1 \times K_2$

$$K_1 \times K_2 = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

$$1\times10^{-7} \times 1.2\times10^{-13} = \frac{(0.2)^2\,[S^{2-}]}{0.1}$$

$$[S^{2-}] = 3\times10^{-20}\ M$$

⑱ Let initial concn. of Ba^{+2} is C_1 & Volume $= 500-50$
$= 450$ ml

When ppt. just begin to form

$$K_{sp} = 1\times10^{-10} = [Ba^{+2}]\,[SO_4^{2-}]$$

$$1\times10^{-10} = \left[\frac{C_1\times450}{500}\right]\left[\frac{1\times50}{500}\right]$$

$$C_1 = 1.1\times10^{-9}\ M$$

⑲ (i) $[H^+] = \frac{\frac{1}{5}\times 75 - \frac{1}{5}\times 25}{100} = 10^{-1} \Rightarrow pH = 1$

(ii) $[H^+] = [OH^-] \Rightarrow pH = 7$

(iii) $[H^+] = \frac{\frac{1}{10}\times 55 - \frac{1}{10}\times 45}{100} = 10^{-2} \Rightarrow pH = 2$

(iv) $[H^+] = \frac{\frac{1}{10}\times 60 - \frac{1}{10}\times 40}{100} = \frac{2}{100}$ ~~⇒ pH~~ $= 2\times 10^{-2}$

$pH = 2 - \log 2 = 1.7$

⑳ $K_{sp} = 4s^3 \Rightarrow s = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2\times 10^{-8}}{4}\right)^{1/3}$

$S = 2\times 10^{-3}$ mol/L

$2\times 10^{-3} = \frac{\text{moles of } PbCl_2}{V_{(L)}} = \frac{(0.1/278)}{V}$

$V = 0.18L$

㉑ $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq.) + CO_3^{2-}(aq.)$; K_{sp}

'x' $\quad (2x + 0.1) \quad x$

$\simeq 0.1$

$K_{sp} = 8\times 10^{-12} = (0.1)^2 (x)$

$x = 8\times 10^{-10}$ M

(22) gm equivalent of HCl ≡ Na_2CO_3

$$M \times 25 \times 1 = 30 \times 0.1 \times 2$$

$$M = \frac{6}{25}$$

gm equi. of HCl ≡ NaOH

$$\frac{6}{25} \times V = 30 \times 0.2$$

$$V = 25 \text{ ml}$$

(23)

$$Ca(OH)_2 + Na_2SO_4 \longrightarrow \underset{(ppt.)}{CaSO_4} + 2NaOH$$

t=0 moles	$\frac{100}{1000} = 0.1$ (ppt.) as Ksp given	$\frac{2}{143} = 1.4 \times 10^{-2}$ (L.R.)	— (Ksp given)	—
finally		×	1.4×10^{-2} moles	2.8×10^{-2} moles

mass of $CaSO_4 = 1.4 \times 10^{-2} \times 136 = 1.9$ gm

$$(OH^-) = \frac{2.8 \times 10^{-2}}{(100/1000)} = 0.28 \text{ mol/L}$$

OH^- are only due to NaOH, as $Ca(OH)_2$ is ppt.

(24) Theory based

㉕ $H_2SO_4 + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + 2H_2O$

$20 \times 0.1 = 2$ $\quad 30 \times 0.2 = 6$ $\quad -$

(L.R.)

$\times \qquad \underbrace{2 \qquad\qquad 2}_{\text{Buffer}}$ $\qquad NH_4^+ = 2 \times (NH_4)_2SO_4$

$$pOH = pK_b + \log\left(\frac{S}{b}\right) = 4.7 + \log\left(\frac{2 \times 2}{2}\right) = 5$$

$$pH = 14 - pOH = 14 - 5 = 9$$

㉖ $K_{sp} = (3)^3 (4)^4 s^7 = 6912 s^7$

㉗ When HCl is added to NaOH, first pH decrease slowly but near the equivalence point sudden change (decrease) is observed.

㉘ $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log c$

$= 7 - \frac{1}{2} \times 5 - \frac{1}{2} \log(2 \times 10^{-2}) = 5.35$

㉙ $K_{sp} = 4s^3 = 4 \times (1.84 \times 10^{-5})^3$

$Cd(OH)_2\,(s) \rightleftharpoons Cd^{+2}\,(aq.) + 2OH^-\,(aq.)\,;\; K_{sp}$

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

$= 10^{-2}$ (buffer)

$K_{sp} = 4 \times (1.84 \times 10^{-3})^3 = x\,(10^{-2})^2$

$x = 2.49 \times 10^{-10}$ M