9. pH = 1 pH = 2

$[H^+]$ = 0.1 $[H^+]$ = 0.01

V = 50 V = 50

$[H^+]$ of mixture is $[H^+]=\frac{N_1V_1+N_2V_2}{V_1+V_2} \Rightarrow \frac{50(0.1+0.01)}{100}$

$[H^+] \Rightarrow \frac{0.11}{2} \Rightarrow 0.055$

pH = 1.26

11. pH = 7 $[H^+] = 10^{-7}$, $[OH^-] = 10^{-7}$

new pH after addition of base

pH = 12 $[H^+] = 10^{-12}$

$[OH^-] = 10^{-2}$

$[OH^+]$ concentration increase 10^5 times.

13. Relative strength $= \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \sqrt{\frac{3\times10^{-4}}{1.8\times10^{-5}}} \Rightarrow 4 : 1$

16. HCOOH + KOH

40mL,0.5(M) $\xrightarrow{50mL,0.2M}$ HCOOH + H_2O

after reaction is forms Buffer solution

$[HCOOH] = \frac{10}{90}$ $[HCOOK] = \frac{10}{90}$

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

pH = 4 – log (1.8) pH = 3.75

19. Let weak acid is HA its sodium salt is NaA

$K_a = \frac{K_w}{K_H}$ $K_H = CH^2 \Rightarrow 0.1 \quad (0.03)^2$

$K_a = \frac{10^{-14}}{9+10^{-5}}$ $K_a = \approx 1 \quad 10^{-10}$

22. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

100 mL, 0.4 M 100 mL, 0.2M

40 20

After reaction

$[CH_3COOH] = \frac{20}{250}$, $[CH_3COONa] = \frac{20}{200}$

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

$pH = pK_a$ $[H^+] = K_a = 1.8 \quad 10^{-5}$

24. $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

at equivalence the $[CH_3COOH] = \frac{20}{200} \Rightarrow 0.1$

$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$

$pH = \frac{1}{2}[5\log 2 - \log 10^{-1}]$

$pH = \frac{1}{2}[6 - \log 2] \Rightarrow pH = 3 - \log\sqrt{2}$

28. $pH = pK_a + \log\frac{HCO_3^-}{H_2CO_3}$

$7 = 7 - \log + \log\frac{HCO_3^-}{H_2CO_3}\frac{HCO_3^-}{(H_2CO_3)} = 4$

$\%\ HCO_3^- = \frac{4}{5}\times100 \Rightarrow 80\ \%$

30. 2NaOH + $H_3PO_4 \longrightarrow Na_3PO_3$

50mL,0.1M 60mL,0.15

0 7.33

$H_3PO_4 \rightleftharpoons H^+ H_2PO_4^-$

[mass H^+ obtain from first ionization of H_3PO_4]

$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C = \frac{1}{2}pK_a - \frac{1}{2}\log C$

= 1.5 + 1.17 = 2.67

32. $Mg(NO_3)_2 + 2NaF \longrightarrow MgF_2 + 2NaNO_3$

2.5 5

0 0 2.5

$(MgF_2) = \frac{2.5}{35}$

$MgF_2 \longrightarrow Mg^{+2} + 2\ F$

Ionic product

41. AgCNS $\rightleftharpoons$ $Ag^+ + CNS$

$(1-\delta_1)$ $(\delta+\delta_2)$ δ_1

AgCl $\rightleftharpoons$ $Ag^+ + Cl$

$(1-\delta_2)$ $(\delta+\delta_2)$ δ_2

$(K_{sp})_{AgCNS} = (\delta_1)(\delta_1+\delta_2)$ .....(i)

$(K_{sp})_{AgCl} = (\delta_2)(\delta_1+\delta_2)$ .....(ii)

adde equation (i) and (ii)

$(\delta_1+\delta_2)^2 = (K_{sp})_{AgCNS} + (K_{sp})_{AgCl}$

$(\delta_1+\delta_2) = \sqrt{(K_{sp})_{AgCNS} + (K_{sp})_{AgCl}} = \sqrt{1.0\times10^{-12}+1.7\times10^{-10}}$

$(AgT) = (\delta_1+\delta_2) = 1.3 \quad 10^{-5}$ divide eq. ii from i

$\frac{[Cl^-]}{[CNS^-]} = \frac{\delta_2}{\delta_1} = \frac{1.7\times10^{-10}}{1.0\times10^{-12}} \Rightarrow 1.7 \quad 10^2$

47. $IP > K_{sp}$ I.P. $= (Ca^{+2})(F)^2$

I.P. $\Rightarrow (10^{-2})(10^{-3})^2 \Rightarrow 10^{-8}$ $IP > K_{sp}$

53. $pH = p^{HIn} + \log\frac{In^-}{HI_A}$ $6 = 5 + \log\frac{In^-}{HIn}$

$\frac{In^-}{HIn} = 10$

54. At Half way [HIn] = In^-

$pH = 5.5 + \log\frac{[salt]}{[acid]}$ $5.5 = pK_a + \log\frac{[salt]}{[acid]}$

$\log\frac{[salt]}{[acid]} = 0.75 \Rightarrow \frac{[salt]}{[acid]} = 5.62$

4. HCl + NaCl
1 ml, 0.1 99 ml

$[H^+] = \frac{0.1}{100} \Rightarrow 0.001$ pH = 3

6. $HF + H_2O \rightleftharpoons F^- + H_3O^+$
K_a $K_b = K_w$ $pK_a + pK_b = pK_w$
$pK_a = 14 - 10.83$ $pK_a = 3.17$
$K_a = 6.75$ 10^{-4}

9. $h = \sqrt{\frac{K_h}{C}}$ $h = \sqrt{\frac{K_w}{K_a \times C}}$

$h = \sqrt{\frac{10^{-14} \times 8.0}{1.3 \times 10^{-9} \times 1}}$ h = 2.48 %

13. $K_{sp} = s^2$ $s = \sqrt{K_{sp}} = \sqrt{6.4 \times 10^{-5}}$
s = 8 10^{-3} s = 8 mol/m^3

15. $AgNO_3$ + $NH_3 \longrightarrow [Ag(NH_3)_2^+]$
1.6 x
5 10^{-8} (x – 1.6) 0.8

$K_s = \frac{[Ag(NH_3)_2]^+}{(AgNO_3)(NH_3)}$

$10^8 = \frac{0.8}{(5 \times 10^{-8})(x - 1.6)^2}$ $(x - 1.6)^2 = 0.16$

x = 2 M mole of NH_3 = 4

18. $C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$
2 1
1 0 1

$pH = pK_a + \log\frac{[salt]}{[acid]}$ $pH = 4.2 + \log\frac{1}{1}$

pH = 4.2

$C_6H_5COOH + NaOH \longrightarrow C_6H_5COONa + H_2O$
2 2
0 0 2

$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log C$

$pH = 7 + 2.1 + \frac{1}{2}\log\frac{2}{200}$

pH = 9.1 – 1 pH = 8.1

25. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$
0.1 0.1
At 1/3 neutralization
2/3 1/3

$pH = pKa + \log\frac{(salt)}{(acid)}$

$pH_1 = pKa + \log\frac{1/3}{2/3}$ ...(1)

at 2/3 neutralization

$pH_2 = pKa + \log\frac{2/3}{1/3}$ ...(2)

$pH_1 - pH_2 = \log\frac{1}{2} - \log 2$

$= \log\frac{1}{4} = -2\log 2$

27. $HSO_4^- \longrightarrow H^+ + SO_4^{2-}$
1
(1– α) α α

$10^{-2} = \frac{\alpha^2}{1-\alpha}$ $\alpha \Rightarrow 0.09$ pH=1.02

COMPREHENSION BASED QUESTIONS

Comprehension # 1

1. Suppose volume of HCO_3^- = V mL
millimoles of HCO_3^- = 5V
millimoles of H_2CO_3 = 20

$pH = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$

$7.40 = 6.11 + \log\frac{V}{4}$, **V = 78 mL**

3. If CO_2 escapes, $[H^+]$ decreases, hence pH increases. (यदि CO_2 मुक्त होती है, तो $[H^+]$ घटते है अत: pH बढ़ती है)

Comprehension # 2

1. Phosphoric acid with three ionisable hydrogens ions is a tribasic acid. H-atoms are attached to O-atoms, (फॉस्फोरिक अम्ल, तीन आयनीकृत हाइड्रोजन आयनों के साथ त्रिक्षारीय अम्ल है। H-परमाणु ऑक्सीजन परमाणु से जुड़े होते है।)

2. If first step is only taken (यदि केवल प्रथम पद को लिया जाये।)

$pH = \frac{1}{2}[pK_{a_1} - \log c]$ $c = [H_3PO_4] = 0.05$ %

$= \frac{0.05 \times 10}{98} mol L^{-1}(M) = 5.1$ 10^{-3} M

$-\log c = 2.3$, $pK_{a_1} = 2.12$ pH = 2.21

3. $\frac{[H^+]^3[PO_4^{3-}]}{[H_3PO_4]} = K_{a_1}K_{a_2}K_{a_3}$

$3\log[H^+] + \log[PO_4^{3-}]$

$= \log K_{a_1} + \log K_{a_2} + \log K_{a_3} - \log[H_3PO_4]$

$3pH - \log[PO_4^{3-}] = \log[H_3PO_4] = pK_{a_1} + pK_{a_2} + pK_{a_3}$
$21 - \log[PO_4^{3-}] - 3 = 2.12 + 7.21 + 12.32$
$\log[PO_4^{3-}] = -3.65$
$[PO_4^{3-}] = 2.24$ 10^{-4} M

4. $Zn_3(PO_4)_2 \rightleftharpoons 3Zn^{2+} + 2PO_4^{3-}$

$\therefore$ $K_{sp} = [Zn^{2+}]^3 [PO_4^{3-}]^2$
9.1 $10^{-33} = [Zn^{2+}]^3 (2.2$ $10^{-4})^2$
$[Zn^{2+}]^3 = 1.88$ 10^{-25} $[Zn^{2+}] = 5.73$ 10^{-9} M

1.(i) $H_2O \underset{}{\overset{Ka}{\rightleftharpoons}} H^+ + OH^-$

$10^{-7} \quad 10^{-7}$

$K_a = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7}\times10^{-7}}{1000/8} = \frac{10^{-14}}{55.5} = 1.8\ 10^{-16}$

(ii) $K_a \quad K_b = 10^{-14}$

2. $K_a = C\alpha^2 \Rightarrow \frac{\alpha_2}{\alpha_1} = \sqrt{\frac{C_1}{C_2}} = \sqrt{\frac{1}{1/100}} = 10$

3. $K_a = C\alpha^2$

$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{Ka_1}{Ka_2}} = \sqrt{\frac{1.8\times10^{-5}}{6.2\times10^{-10}}}$

4.(a) $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$

$4.50 \quad 2 = pK_a - \log(0.1)$

$9 - 1 = pK_a \qquad pK_a = 8 \qquad K_a = 10^{-8}$

5.(c) $[H^+] = \sqrt{KaC} = \sqrt{1.8\times10^{-6}} = 3 - \log 1.8 = 2.87$

(e) $[H^+] = 10^{-8} + 10^{-7} = 10^{-7}[0.1 + 1]$

$pH = 7 - \log 1.1 = 6.95$

(f) $[OH^-] = 10^{-10} + 10^{-7} = 10^{-7}[1.001]$

$POH = 7 - \log 1.001 = 6.99$

$pH = 7.0004$

(g) $[H^+] = \sqrt{KaC} = \sqrt{1.8\times10^{-5}\times10^{-6}}$

$[H^+] = \sqrt{1.8\times10^{-11}} = \sqrt{18\times10^{-12}} = 4.24 \quad 10^{-6}$

$pH = 6 - \log 4.24 = 5.37$

6. $pK_w = 14 - \log 2.56 = 13.59 \approx 13.6$

$pH = \frac{pK_w}{2} = 6.795$

10. $pH = 11.5 \qquad [H^+] = 10^{-11.5}$

$[OH^-] = 10^{-2.5}$

$NH_4OH \underset{}{\overset{K_b}{\rightleftharpoons}} NH_4^+ + OH^-$

$10^{-2.5} \qquad 10^{-2.5}$

$\frac{10^{-5}}{C} = 1.8 \quad 10^{-5} \qquad C = \frac{1}{1.8} = 0.556\ M$

11. $C = 10^{-2}, [H^+] = 10^{-3}$

$K_a = \frac{10^{-3}\times10^{-3}}{10^{-2} - 10^{-3}} = \frac{10^{-3}}{9} = 1.1 \quad 10^{-4}$

13. $CHCl_2COOH \longrightarrow H^+ + CHCl_2COO^-$

0.01

$0.01 - x \qquad 0.01 + x \qquad x$

$\frac{x(0.01+x)}{0.01-x} = 2.55 \quad 10^{-2}$

$0.01\ x + x^2 = 2.55 \quad 10^{-4} - 2.55 \quad 10^{-2}\ x$

$x^2 + 0.355x - 0.000255 = 0$

$x = \frac{-0.0355 \pm \sqrt{0.04775}}{2} = 1.1 \quad 10^{-2}$

$CHCl_2COO^- = 6.126 \quad 10^{-2}$

14. For weak acid

$[H^+] = \sqrt{K_1C_1 + K_2C_2 \ldots + K_w}$

$= \sqrt{1.8\times10^{-5}\times0.02 + 6.4\times10^{-5}\times.01 + 10^{-14}}$

$= \sqrt{100\times10^{-8}}$

$[H^+] = 10^{-3} \qquad K_a = \frac{[H^+][ACO^-]}{[ACOH]_2}$

$[ACO^\ominus] = 3.6 \quad 10^{-4}$

same $[C_2H_5O_2^\ominus] = 6.4 \quad 10^{-4}$

15. HCN is a weak acid so H^+ due to it can neglect As comparision to HF

$[H^+] = \sqrt{KC} = \sqrt{6.7\times10^{-4}\times0.1} = \sqrt{67\times10^{-6}}$

$= 8.18 \quad 10^{-3}$

$pH = -\log[8.18 \quad 10^{-3}] = 3 - \log[8.18]$

$pH = 2.087$

16. $H_2S \longrightarrow 2H^+ + S^{-2}$

$[H^+] = 2 \quad 10^{-4}, \quad [H_2S] = 0.1\ M$

$K = K_1\ K_2 \qquad K = 10^{-7} \quad 10^{-7}$

$K = 10^{-21}$

$\Rightarrow \quad 10^{-21} = \frac{[2\times10^{-4}]^2[S^{-2}]}{[0.1]} \qquad 10^{-21} = 4 \quad 10^{-8}\ [S^{-2}]$

$\frac{1}{4}\times10^{-14} = [S^{-2}] \qquad 2.5 \quad 10^{-15} = [S^{-2}]$

17.(i) $H_3PO_4 \longrightarrow H^+ + H_2PO_4^- \quad K_1 = 7.225 \quad 10^{-3}$

$0.01\ M\ C \quad (1-\alpha) \quad C\alpha_1 \qquad C\alpha_1$

(ii) $H_2PO_4^- \longrightarrow HPO_4^{-2} + H^+ \qquad K_2 = 6.8 \quad 10^{-8}$

$C\alpha_1(1-\alpha_2) \quad C\alpha_1\alpha_2 \quad [C\alpha_1]$

(iii) $HPO_4^{-2} \longrightarrow PO_4^{-3} + H^+ \quad K_3 = 6.8 \quad 10^{-8}$

$\alpha_1\alpha_2C_1(1-\alpha_3) \quad C(\alpha_1\alpha_2\alpha_3) \quad [C\alpha_1]$

$7.225 \quad 10^{-3} = \frac{C\alpha_1^2}{(1-\alpha_1)} = \frac{0.01\times\alpha_1^2}{1-\alpha}$

RxN. (i)

$(1-\alpha) \quad 0.7225 = \alpha_1^2$

$\alpha_1^2 + 0.7225\ \alpha - 0.7225 = 0$

$\alpha_1 = 0.562$

$\Rightarrow \quad [H^+] = 0.01 \quad 0.562 \qquad [H^+] = 5.6 \quad 10^{-3}$

$[H_2PO_4^\ominus] \approx 5.6 \quad 10^{-3}$ RxN. (ii)

$6.8 \quad 10^{-8} = \frac{[HPO_4^{-2}][H^+]}{[H_2PO_4^-]}$ from [i] reaction.

$\Rightarrow \quad [HPO_4^{-2}] = 6.8 \quad 10^{-8}\ M$ RxN. (iii)

$4.5 \quad 10^{-13} = \frac{[PO_4^{-3}][H^+]}{[HPO_4^{-2}]}$

$\frac{4.5\times10^{-13}\times6.8\times10^{-8}}{5.6\times10^{-3}} = [PO_4^{-3}]$

$5.464 \quad 10^{-18} = [PO_4^{-3}]$

20. $NH_4Cl \longrightarrow NH_4^+ + Cl^-$

$NH_4OH \longrightarrow NH_4^+ + OH^-$

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_4OH]}$

$[NH_4^+]$ = is due to salt because NH_4OH ionise in less amount due to common ions effect

$1.8 \quad 10^{-5} = \dfrac{0.1\times[OH^-]}{0.05} \qquad 9 \quad 10^{-6} = [OH^-]$

21. $HC_2H_3O_2 + NaOH \longrightarrow CH_3COO^{\ominus} + H_2O$

50ml, 0.2M 50ml, 0.1M

10m mol 5m mol

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}H + OH^{\ominus} \rightleftharpoons CH_3COO^{\ominus} + H_2O$$

10 5

5 0 5 5

$pH = pK_a = 5 - \log 1.8 \qquad pH = 4.74$

22. $(NH_4)_2SO_4$

Molarity $(NH_4)_2SO_4 = \left(\dfrac{x}{100}\right)$

Molarity of $NH_4^+ = \left(\dfrac{2x}{100}\right)$

Molarity of $NH_4OH = \left(\dfrac{0.1}{100}\right) = 10^{-3}$

$14 - 9.26 = 4.24 + \log\left(\dfrac{2x/100}{0.1/100}\right)$

$0 = \log(20x) \Rightarrow 1 = 20x$

$x = 1/20$ mole $\qquad x = 0.05$ mole

30. $CH_3COO^{\ominus} + H_2O \rightleftharpoons CH_3COOH + OH^{\ominus}$

0.08 $\qquad K_b = \dfrac{10^{-14}}{1.8\times10^{-5}}$

$\dfrac{x^2}{0.08} = \dfrac{10}{1.8}\times10^{-10} \qquad x^2 = \dfrac{0.8}{1.8}\times10^{-10}$

$x^2 = 0.44 \quad 10^{-10} \qquad x = 0.66 \quad 10^{-5}$

32. $C_5H_6N^+ + H_2O \rightleftharpoons C_5H_5NOH + H^+$

$pH = \dfrac{1}{2}[pK_w - pK_b - \log C]$

$2.699 = \dfrac{1}{2}[14 - pK_b + 0.6]$

$2.398 = 14.6 - pK_b$

$pK_b = 14.6 - 5.398 = 9.802$

$K_b = 10^{-9.802}$

38. $pH = \dfrac{pK_1 + pK_2}{2}$

$pH = \dfrac{11 + 7 - 2\log 4.5}{2} = 9 - \log 4.5 = 8.54$

40. $CH_3COOH + OH^{\ominus} \longrightarrow CH_3COO^- + H_2O$ (WASB)

$pH = \dfrac{1}{2}[pK_w + pK_a + \log C]$

$= \dfrac{1}{2}[14 + 5 - \log 1.9 + \log\dfrac{1}{20}]$

$= \dfrac{1}{2}[19 - \log 1.9 - \log 20]$

$pH = \dfrac{1}{2}[19 - \log 20 \quad 1.9] = 8.78$

$pOH = 5.28 \qquad [OH^{\ominus}] = 10^{-5.28}$

$[OH^{\ominus}] = 10^{-6} \quad 10^{0.72} \qquad [OH^{\ominus}] = 5.24 \quad 10^{-6}$

IONIC EQUILIBRIUM — EXERCISE # 4[B]

1. $Q^+ + H_2O \rightleftharpoons QOH + H^+ \qquad k_w/k_1$

$\dfrac{n_1}{V} = n'_1$

$n'_1 - x \qquad x \qquad x + y$

$R^+ + H_2O \rightleftharpoons ROH + H^+$

$\dfrac{n_2}{V} = n'_2$

$n'_2 - y \qquad y \qquad y+x$

$\dfrac{k_w}{k_1} = \dfrac{x(x+y)}{n'_1 - x} \simeq \dfrac{x(x+y)}{n'_1}$ .....(i)

$\dfrac{k_w}{k_2} = \dfrac{y(x+y)}{n'_2 - y} \simeq \dfrac{y(x+y)}{n'_2}$ .....(ii)

Assuming (माना) $x << n_1'$ & $y << n_2'$

from equation (i) & (ii) (समीकरण (i) व (ii) से)

$x(x + y) = \dfrac{k_w}{k_1} n_1'$ & $y(x + y) = \dfrac{k_w}{k_2} n_2'$

adding both (दोनों को जोड़ने पर)

$(x + y)^2 = k_w\left[\dfrac{n_1'}{k_1} + \dfrac{n_2'}{k_2}\right] = \dfrac{k_w(k_2n_1' + k_1n_2')}{k_1k_2}$

$[H^+] = (x + y) = \sqrt{\dfrac{k_w}{k_1k_2V}(k_2n_1 + k_1n_2)}$

$pH = -\log[H^+]$

$pH = \dfrac{1}{2}\log\left[\left(\dfrac{k_1k_2}{k_w}\right)\dfrac{V}{(k_2n_1 + k_1n_2)}\right]$

2. $Na_4Y + H_2O \rightleftharpoons Na_3HY + NaOH \quad \dfrac{k_w}{k_4} = 1.818\times10^{-4}$

0.1

$0.1 - x \qquad x \qquad x$

$\dfrac{x^2}{0.1 - x} = 1.818 \quad 10^{-4} \Rightarrow 5500.55x^2 + x - 0.1 = 0$

$x = 4.17 \quad 10^{-3}$

$Na_3HY + H_2O \rightleftharpoons Na_2H_2Y + NaOH \quad \frac{k_w}{k_3} = 1.445 \times 10^{-8}$

x

x − y y y + x

since y << x x − y ≃ x, x + y ≃ x

$1.445 \quad 10^{-8} = \frac{y.x}{x} = y$

$Na_2H_2Y + H_2O \rightleftharpoons NaH_3Y + NaOH \quad \frac{k_w}{k_2} = 4.7 \times 10^{-12}$

y

y − z z z + x

y − z ≃ y, z + x ≃ x

$4.7 \quad 10^{-12} = \frac{z.x}{y}$ z = 1.628 10^{-17}

$NaH_3Y + H_2O \rightleftharpoons H_4Y + NaOH \quad \frac{k_w}{k_1} = 9.8 \times 10^{-13}$

z

z − t t t + x

z − t ≃ z, t + x ≃ x

$9.8 \quad 10^{-13} = \frac{t.x}{z}$ t = 3.82 10^{-27}

fraction (भिन्न) $= \frac{t}{0.1}$ = **3.82 10^{-26}**

3. $s = [Zn(OH)_2(aq)] + Zn(OH)^+ + Zn^{+2} + Zn(OH)_3^- + Zn(OH)_4^{-2}$

$s = k_1 + \frac{k_1k_2}{[OH^-]} + \frac{k_1k_2k_3}{[OH^-]^2} + k_1k_4[OH^-] + k_1k_4k_5[OH^-]^2$

$s = 10^{-6} + \frac{10^{-13}}{[OH^-]} + \frac{10^{-17}}{[OH^-]^2} + 10^{-3}[OH^-] + 10^{-2}[OH^-]^2$

(a) pH = 5, pOH = 9, $[OH^-] = 10^{-9}$

$s = 10^{-6} + 10^{-4} + 10 + 10^{-12} + 10^{-20}$ = **10 M**

(b) pH = 9, pOH = 5, $[OH^-] = 10^{-5}$

$s = 10^{-6} + 10^{-8} + 10^{-7} + 10^{-8} + 10^{-12}$ = **1.12 10^{-6} M**

(c) pH = 13, pOH = 1, $[OH^-] = 10^{-1}$

$s = 10^{-6} + 10^{-12} + 10^{-15} + 10^{-4} + 10^{-4}$ = **2 10^{-4} M**

4. Given :

$Ag + \frac{1}{2}Cl_2 \rightleftharpoons AgCl \quad \Delta G_1 = -109.7 kJ/mole^{-1}$

$Ag \longrightarrow Ag^+ + e^- \quad \Delta G_2 = 77.2 kJ/mole^{-1}$

$e^- + \frac{1}{2}Cl_2 \longrightarrow Cl^- \quad \Delta G_3 = -131.2 kJ/mole^{-1}$

so for reaction (अत: अभिक्रिया के लिए)

$AgCl \rightleftharpoons Ag^+ + Cl^- \quad \Delta G = -\Delta G_1 + \Delta G_2 + \Delta G_3$

ΔG = 55.7 kJ/mole

$\Delta G = -RT \ln K_{sp}$

$55.7 \quad 10^{-3} = -8.314 \quad 298 \ln K_{sp}$

K_{sp} = **1.723 10^{-10}**

$1.723 \quad 10^{-10} = [Ag^+][Cl^-] = s^2 \quad 0.05$

s = **3.446 10^{-9} M**

5. $Cu_3(AsO_4)_2 \rightleftharpoons 3Cu^{+2} + 2AsO_4^{-3} \quad K_{sp} = 8 \ 10^{-36}$

3x 2x+2y

$Pb_3(AsO_4)_2 \rightleftharpoons 3Pb^{+2} + 2AsO_4^{-3} \quad K_{sp} = 4.096 \ 10^{-36}$

3y 2y+2x

Let solubility of $Cu_3(AsO_4)_2$ & $Pb_3(AsO_4)_2$ is x & y respectively. (माना $Cu_3(AsO_4)_2$ व $Pb_3(AsO_4)_2$ की विलेयता क्रमश: x व y है।)

$108 \ x^3 (x + y)^2 = 8 \quad 10^{-36}$ .....(i)

$108 \ y^3 (x + y)^2 = 4.096 \quad 10^{-36}$ ....(ii)

$\frac{(i)}{(ii)} \Rightarrow \frac{x^3}{y^3} = \frac{8}{4.096} \Rightarrow x = 1.25 \ y$

putting this in equation (ii) (इसे समीकरण(ii)में रखने पर)

$108 \ y^3 (2.25 \ y)^2 = 4.096 \quad 10^{-36}$

$y = 2.3 \quad 10^{-8} \quad x = 1.25 \ y = 2.875 \quad 10^{-8}$

$[Cu^{+2}] = 3x$ = **8.825 10^{-8}**

$[Pb^{+2}] = 3y$ = **7.1 10^{-8}**

6.(a) $Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^- \quad K_{sp}$

$Al(OH)_4^- \rightleftharpoons Al^{+3} + 4OH^- \quad K$

$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^- \quad \frac{K_{sp}}{K} = 38.46$

$38.46 = \left[\frac{Al(OH^-)_4}{[OH^-]}\right] = \frac{10^{-3}}{[OH^-]}$

$[OH^-] = 2.6 \quad 10^{-5}$

pOH = 4.585

pH = **9.415**

(b) $K_{sp} = [Al^{+3}][OH^-]^3$

$5 \quad 10^{-33} = [1 \quad 10^{-3}][OH^-]^3$

$[OH^-] = 1.7 \quad 10^{-10}$

pOH = 9.767

pH = **4.23**

7. HCl → 0.09 M

CH_3COOH → C_1 = 0.1 M, α_1, $K_{a_1} = 10^{-5}$

$Cl_2CHCOOH$ → C_2 = 0.09 M, α_2, K_{a_2} = ?

pH = 1, $[H^+] = 0.1$

$0.1 = 0.09 + C_1\alpha_1 + C_2\alpha_2$

$C_1\alpha_1 + C_2\alpha_2 = 0.01$ .....(i)

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

C_1

$C_1 - C_1\alpha_1$ $C_1\alpha_1$ 0.1

$Cl_2HCCOOH \rightleftharpoons Cl_2HCCOO^- + H^+$

C_2

$C_2 - C_2\alpha_2$ $C_2\alpha_2$ 0.1

$K_{a_1} = \frac{(C_1\alpha_1)(0.1)}{C_1(1-\alpha_1)} \simeq \alpha_1 \quad 0.1 = 10^{-5}$

$\alpha_1 = 10^{-4}$

putting this in equation (i)(इसे समीकरण (i) में रखने पर)

10^{-4} $0.1 + 0.09\alpha_2 = 0.01$

$\alpha_2 = 0.111$

$$K_{a_2} = \frac{(C_2\alpha_2)(0.1)}{C_2(1-\alpha_2)} = \frac{(0.111)(0.1)}{1-0.111} = \mathbf{1.248 \quad 10^{-2}}$$

8. $C = \frac{10 \times 0.935 \times 1000}{17 \times 100} = 5.5$ M

$K_a = C\alpha^2 \Rightarrow 5.5 \quad 10^{-6} = 5.5\ \alpha^2$

$\alpha = 10^{-3}$

$[OH^-] = C\alpha = 5.5 \quad 10^{-3}$

pOH = 2.26 , **pH = 11.74**

9. $\ln \frac{k_{w_2}}{k_{w_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln \frac{5.474 \times 10^{-14}}{1.08 \times 10^{-14}} = \frac{\Delta H}{8.314}\left(\frac{1}{298} - \frac{1}{323}\right)$

ΔH = **51952.6 J = 51.95 kJ/mole**

10. In begining $[H^+] = \sqrt{K_a C}$

$[H^+] = \sqrt{1.8 \times 10^{-5}} = 0.004242$

pH = 2.372

On doubling pH, new pH(pH दुगुनी करने पर, नयी pH) = 4.744

$[H^+] = 1.8 \quad 10^{-5}$

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

C

C – Cα Cα Cα

$K_a = \frac{(C\alpha)^2}{C(1-\alpha)}$, $C\alpha = [H^+] = 1.8 \quad 10^{-5}$

$1.8 \quad 10^{-5} = \frac{(1.8 \times 10^{-5})^2}{C - C\alpha}$

$C - C\alpha = 1.8 \quad 10^{-5}$

$C = 3.6 \quad 10^{-5}$

$V = \frac{1}{C}$ = **2.77 10^4 L**

11.(a) PV = nRT

1 0.959 = n 0.0821 298

n = 0.03919

volume of H_2O = 1 mL (per volume of H_2O)

(H_2O का आयतन = 1 mL (H_2O का प्रति आयतन))

$C = \frac{n}{V} = \frac{0.03919}{10^{-3}} = 39.19$ M

$pk_b = 3.39 \Rightarrow k_b = 4 \quad 10^{-4}$

$[OH^-] = \sqrt{K_b C} = 0.1252$M

pOH = 0.9023 pH = **13.097**

(b) M = **0.1252** for NaOH (NaOH के लिए 0.1252)

12. $k_1 = 7.5 \quad 10^{-3}$, $k_2 = 6.2 \quad 10^{-8}$, $k_3 = 10^{-12}$

(a) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

6 3

3 – 3

pH = pk_1 = **2.12**

(b) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

6 6

– – 6

$pH = \frac{pk_1 + pk_2}{2}$ = **4.66**

(c) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

4.8 7.2

– 2.4 4.8

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

4.8 2.4

2.4 – 2.4

pH = pk_2 = **7.2**

(d) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

4 10

– 6 4

$NaH_2PO_4 + NaOH \longrightarrow Na_2HPO_4 + H_2O$

4 6

– 2 4

$Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$

4 2

2 – 2

pH = pk_3 = **12**

13. For $H_2CO_3 \rightarrow k_1 = 4.2 \quad 10^{-7}$, $k_2 = 4.8 \quad 10^{-11}$

$H_3PO_4 \rightarrow k_1 = 7.5 \quad 10^{-3}$, $k_2 = 6.2 \quad 10^{-8}$, $k_3 = 10^{-12}$

(a) $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

2 2

– – 2

$pH = \frac{pk_1 + pk_2}{2}$ = **8.347**

(b) $Na_3PO_4 + HCl \longrightarrow Na_2HPO_4 + NaCl$

0.8 1.6

– 0.8 0.8

$Na_2HPO_4 + HCl \longrightarrow NaH_2PO_4 + NaCl$

0.8 0.8

– – 0.8

$pH = \frac{pk_1 + pk_2}{2}$ = **4.66**

(c) $Na_3PO_4 + NaH_2PO_4 \longrightarrow 2Na_2HPO_4$

5 5

– – 10

$pH = \frac{pk_2 + pk_3}{2}$ = **9.6**

(d) $H_3PO_4 + Na_3PO_4 \longrightarrow Na_2HPO_4 + NaH_2PO_4$

4 4

– – 4 4

pH = pk_2 = **7.2**

14. $BOH + HCl \longrightarrow BCl + H_2O$

4 4

– – 4

At end point m moles of BOH = m moles of HCl (अन्त बिन्दु पर BOH के m moles)

$0.16 \quad V = 4 \qquad V = 25$ mL

Total volume (कुल आयतन) = 40 + 25 = 65 mL

$[BCl] = \frac{4}{65}$

since BCl is SAWB

$pH = 7 - \frac{1}{2}pk_b - \frac{1}{2}\log C$

$5.23 = 7 - \frac{1}{2}pk_b - \frac{1}{2}\log\frac{4}{65}$

$pk_b = 4.75$

Now on further adding NaOH (अब पुन: NaOH को मिलाने पर)

$BCl + NaOH \longrightarrow BOH + NaCl$

4 1.8

2.2 – 1.8

$pOH = pk_b + \log\frac{2.2}{1.8} = 4.837 \Rightarrow pH = \mathbf{9.1628}$

15.(a) $pH = pK_a + \log\frac{0.06}{0.05}$

$pH = 3.744 + \log 1.2 = \mathbf{3.823}$

(b) On diluting solution 10 times (विलयन को 10 गुना तनु करने पर)

[HCOOH] = 0.005, [HCOONa] = 0.006

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

0.005

$0.005(1-\alpha) \qquad 0.005\alpha \qquad 0.005\alpha + 0.006$

$K_a = 1.8 \quad 10^{-4} = \frac{(0.005\alpha + 0.006)(0.005\alpha)}{0.005(1-\alpha)}$

$\frac{0.005\alpha^2 + 0.006\alpha}{1-\alpha} = 1.8 \quad 10^{-4}$

$\Rightarrow 27.77\alpha^2 + 34.33\alpha - 1 = 0 \qquad \alpha = 0.0285$

$[H^+] = 0.005\alpha = 1.425 \quad 10^{-4} \qquad pH = \mathbf{3.846}$

(c) On further diluting solution by 10 times (विलयन को पुन: 10 गुना तनु करने पर)

[HCOOH] = 0.0005, [HCOONa] = 0.0006

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

0.0005

$0.0005(1-\alpha) \qquad 0.0005\alpha \qquad 0.0005\alpha + 0.0006$

$K_a = 1.8 \quad 10^{-4} = \frac{(0.0005\alpha + 0.0006)(0.0005\alpha)}{0.0005(1-\alpha)}$

$= \frac{0.0005\alpha^2 + 0.0006\alpha}{1-\alpha} = 1.8 \quad 10^{-4}$

$2.77\alpha^2 + 4.33\alpha - 1 = 0 \Rightarrow \alpha = 0.2047$

$[H^+] = 0.0005\alpha = 1.0235 \quad 10^{-4}$

$pH = \mathbf{3.9899}$

16. Initial (प्रारम्भ में) $pOH = pK_b = 4.744$

Let x mole of NaOH has been added so (माना NaOH के x मोल मिलाये है, अत:)

$[NH_4^+] = 0.1 + x, \quad [NH_3] = 0.1 - x$

$pOH = 5.744$

$5.744 = 4.744 + \log\frac{0.1+x}{0.1-x}$

$1 = \log\frac{0.1+x}{0.1-x}$

$\frac{0.1+x}{0.1-x} = 10 \Rightarrow x = \frac{0.9}{11} = 0.0818$ moles

17. $Na_3PO_4 + H_2O \longrightarrow Na_2HPO_4 + NaOH$

$K = \frac{K_w}{K_3} = 0.0222$

$Na_2HPO_4 + H_2O \longrightarrow NaH_2PO_4 + NaOH$

$K = \frac{K_w}{K_2} = 1.58 \quad 10^{-7}$

$NaH_2PO_4 + H_2O \longrightarrow H_3PO_4 + NaOH$

$K = \frac{K_w}{K_3} = 1.4 \quad 10^{-12}$

since equilibrium constant of 2nd & 3rd reaction is very less, $[OH^-]$ will mainly come from 1st reaction. (चूंकि 2nd व 3rd अभिक्रिया का साम्य नियताकं बहुत कम है, $[OH^-]$ मुख्यत: 1st अभिक्रिया से प्राप्त होगा।)

$Na_3PO_4 + H_2O \longrightarrow Na_2HPO_4 + NaOH$

0.1

$0.1-x \qquad x \qquad x$

$\frac{x^2}{0.1-x} = 0.0222 \Rightarrow 45x^2 + x - 0.1 = 0$

$x = 3.73 \quad 10^{-2}$

$[OH^-] = x = \mathbf{3.73 \quad 10^{-2}\ M}$

$Na_2HPO_4 + NaOH \longrightarrow NaH_2PO_4 + NaOH$

x

$x - y \qquad y \qquad y + x$

$x - y \simeq x, \qquad y + x \simeq x,$ so

$1.58 \quad 10^{-7} = \frac{(y+x)}{(x-y)}y \simeq y$

$NaH_2PO_4 + H_2O \longrightarrow H_3PO_4 + NaOH$

y

$y - z \qquad z \qquad z + x$

$y - z \simeq y, \quad z + x \simeq x$

$1.4 \quad 10^{-12} = \frac{z(x+z)}{(y-z)} = \frac{z \times x}{y} = \frac{z \times 3.73 \times 10^{-2}}{1.58 \times 10^{-7}}$

$z = 5.93 \quad 10^{-18}$

$[H_3PO_4] = z = \mathbf{5.93 \quad 10^{-18}\ M}$

18. pH = 8, $[H^+] = 10^{-8}$, $[OH^-] = 10^{-6}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ K = 5 10^{-13}

0.0005

0.0005–y–z 10^{-8} y

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ $K = \frac{K_w}{K_1} = 2$ 10^{-8}

0.0005

0.0005–y–z z 10^{-6}

since equilibrium constant for first reaction is very less y << z (चूंकि प्रथम कोटि अभिक्रिया के लिए साम्य नियतांक बहुत कम है y << z)

$2 \quad 10^{-8} = \frac{z(10^{-6})}{0.0005 - z}$

51 z = 0.0005, $\Rightarrow$ z = **9.8 10^{-6}**

$[H_2CO_3]$ = 9.8 10^{-6} M

$[HCO_3^-]$ = 0.0005 – 9.8 10^{-6} = **4.9 10^{-4} M**

$5 \quad 10^{-3} = \frac{10^{-8} \times y}{4.9 \times 10^{-4}}$

$[CO_3^{-2}]$ = y = **2.45 10^{-8} M**

19. $Fe^{+3} + H_2O \longrightarrow Fe(OH)^{+2} + H^+$ k = 6.5 10^{-3}

x

0.95x 0.05x 0.05x

$6.5 \quad 10^{-3} = \frac{(0.05)^2 x}{0.95}$ x = 2.47

$[H^+]$ = 0.05x = 0.1235 pH = **0.908**

20. $pH = pK_2 + \log \frac{\text{salt}}{\text{acid}}$

$6.7 = 7.2 + \log \frac{y}{0.005}$

y = 1.58 10^{-3} mole

21. When indicator is half in ionic form pH(जब आधा सूचक आयनिक रूप में है pH) = pK_a = 7.2

pH = 7.2 + log 5 = **7.898**

now with this pH (अब इस pH में)

7.898 = pK_{a_1} + log 4 = pK_{a_1} = 7.2959

again when 50% of new indicator is in ionic form (पुनः जब नया सूचक 50% आयनिक रूप में है।)

pH = pK_{a_1} = **7.2959**

22. 4 m mole of H^+ ion will produce (H^+ आयन के 4m mol बनेगें।)

$[H^+] = \frac{4 \times 10^{-3}}{0.1} = 0.04$

$PO_4^{-3} + H^+ \longrightarrow HPO_4^{-2}$ $\frac{1}{k_3}$

0.02 0.04 0.08

– 0.02 0.1

$HPO_4^{-2} + H^+ \longrightarrow H_2PO_4^-$ $\frac{1}{k_2}$

0.1 0.02

0.08 – 0.02

so now they form a buffer solution of HPO_4^{-2} & $H_2PO_4^-$ (अतः अब यह HPO_4^{-2} व $H_2PO_4^-$ का बफर विलयन बनाते हैं।)

$pH = pk_2 + \log \frac{0.08}{0.02}$ (k_2 = 6.3 10^{-8})

pH = 7.2 + log 4 = **7.8**

23. At equivalence point (तुल्यांक बिन्दु पर)

meq. of HA = meq. of NaOH = 3.612

NaA + HCl $\longrightarrow$ HA + HCl

3.612 1.806

1.356 – 1.806

$pH = pK_a + \log \frac{[S]}{[A]}$

$4.92 = pK_a + \log \frac{1.356}{1.806}$

pK_a = 5.044

Now NaOH + HA $\longrightarrow$ NaA

2 2

– – 2

$[NaA] = \frac{2}{20} = 0.1$

$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 7 + \frac{5.044}{2} + \frac{1}{2}\log 0.1$

pH = **9**

24. In begining let x m mole of BOH are present (प्रारम्भ में माना BOH के x m mole उपस्थित हैं।)

BOH + HCl $\longrightarrow$ BCl + H_2O

x

$\frac{3x}{4}$ $\frac{x}{4}$

$pOH = pk_b + \log \frac{1}{3}$

14 – 9.24 = pk_b – log 3

pk_b = 5.237

k_b = 5.8 10^{-6}

now BCl + NaOH $\longrightarrow$ BOH

$\frac{x}{4}$ 6

– – x

$\frac{x}{4} = 6, \Rightarrow x = 24$

$[BOH] = \frac{24}{50} = 0.48$

$[OH^-] = \sqrt{k_b \times C} = 1.668 \quad 10^{-3}$

pOH = 2.77

pH = **11.22**

25. (a) pH at one fourth neutralization (एक चौथाई उदासीनीकरण पर pH)

$$(pH)_1 = pk_a + \log \frac{x/4}{3x/4} = pk_a + \log \frac{1}{3}$$

pH at three fourth neutralization (तीन चौथाई उदासीनीकरण पर pH)

$$(pH)_2 = pk_a + \log \frac{3x/4}{x/4} = pk_a + \log 3$$

$\Delta pH = (pH)_2 - (pH)_1 = 2 \log 3 =$ **0.9542**

(b) $4.45 = pk_a + \log \frac{x/3}{2x/3} = pk_a - \log 2$

$pk_a =$ **4.751**

(c) $\Delta pH = 2$ i.e.

$(pH)_1 = pk_a + 1, \ (pH)_2 = pk_a - 1$

For $pk_a + 1 \Rightarrow \frac{[S]}{[A]} = 10$

$\frac{x}{a-x} = 10 \Rightarrow x = 10a - 10x$

$$x = \frac{10a}{11}$$

i.e. $\frac{10^{th}}{11}$ **stage**

For $pk_a - 1 \Rightarrow \frac{[S]}{[A]} = \frac{1}{10}$

$$\frac{x}{a-x} = \frac{1}{10}$$

$$x = \frac{a}{11}$$

i.e. $\frac{1}{11}$ **th stage**

26. $Zn(OH)_{2(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2OH^-_{(aq)} \ K_{sp}$

$Zn(OH)_{2(s)} + 2OH^- \rightleftharpoons [Zn(OH)_4]^{-2}_{(aq)} \ K_C$

dissolved $Zn(OH)_2$ is present in form of Zn^{+2} & $[Zn(OH)_4^{-2}]$

so solubility $s = [Zn^{+2}] + [Zn(OH)_4]^{-2}$

(घुलित $Zn(OH)_2$, Zn^{+2} व $[Zn(OH)_4^{-2}]$ के रूप में उपस्थित है।

अत: विलेयता $s = [Zn^{+2}] + [Zn(OH)_4]^{-2}$)

$$s = \frac{K_{sp}}{[OH^-]^2} + K_C[OH^-]^2$$

For min. solubility (न्यूनतम विलेयता के लिए)

$$\frac{ds}{d[OH^-]} = 0 \Rightarrow \frac{-2K_{sp}}{[OH^-]^3} + 2K_C[OH^-] = 0$$

$$[OH^-] = \left(\frac{K_{sp}}{K_C}\right)^{1/4}$$

$[OH^-] = 9.8 \quad 10^{-5}$

pOH = 4.00869

pH = **9.9913**

27. $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^- \ K_{sp}$

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ K_1 \quad K_2$

$AgCl_{(s)} + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-, \ K = K_{sp} K_1 K_2$

0.2

0.2–2x x x

$$K = \frac{x^2}{(0.2-2x)} = K_{sp}K_1K_2 = 0.002828$$

$$\frac{x}{0.2-2x} = 0.05318$$

x = 0.009613

Solubility (विलेयता) = **9.6 10^{-3} M**

28. $[Cl^-] = 0.02$ M

$Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^- \qquad K_{inst} = 4 \quad 10^{-19}$

0.05

$0.05 - x \tilde{-} 0.05 \quad x \quad 2x$

$4 \quad 10^{-19} = \frac{x.(2x)^2}{0.05}$

$\frac{4x^3}{0.05} = 4 \quad 10^{-19} \Rightarrow x = 1.7 \quad 10^{-7}$

$[Ag]\ [Cl] = 1.7 \quad 10^{-7} \quad 0.02 = 3.4 \quad 10^{-9} > K_{sp}$

so **AgCl will precipitate. (अत: AgCl अवक्षेपित होगा।)**

29. After mixing with equal volume (समान आयतन के साथ मिलाने के पश्चात्)

$[Ag^+] = 0.01$ M, HCN = 0.01 M

$HCN \rightleftharpoons H^+ + CN^- \quad K_a$

$Ag^+ + CN^- \rightleftharpoons AgCN_{(s)} \quad \frac{1}{K_{sp}}$

$HCN + Ag^+ \rightleftharpoons H^+ + AgCN_{(s)}$,

$K = \frac{K_a}{K_{sp}} = 2.25 \quad 10^6$

0.01 0.01

x x 0.01

since K value is very high almost all of reactant will convert into product

(चूंकि K मान बहुत उच्च है लगभग सभी क्रियाकारक उत्पाद में परिवर्तित होगें।)

$\frac{0.01}{x^2} = 2.25 \quad 10^6 \qquad X = 6.6 \quad 10^{-5}$

$[Ag^+] =$ **6.66 10^{-5} M**

30. $MA \longrightarrow M^{+2} + A^{-2}$

s s

Let solubility is s. (माना विलेयता s है।)

But some amount of A^{-2} will undergo hydrolysis. Let x is the amount of A^{-2} left in solution.

(लेकिन A^{-2} की कुछ मात्रा जल अपघटित होगी। माना x विलयन में शेष A^{-2} की मात्रा है)

$A^{-2} + H_2O \rightleftharpoons HA^- + OH^- \quad \frac{k_w}{k_2}$

$HA^- + H_2O \rightleftharpoons H_2A + OH^- \quad \frac{k_w}{k_1}$

$\frac{k_w}{k_2} = \frac{[HA^-][OH^-]}{[A^{-2}]} \Rightarrow [HA^-] = \frac{k_w[A^{-2}]}{k_2[OH^-]}$

$\frac{k_w}{k_1} = \frac{[H_2A][OH^-]}{[HA^-]} \Rightarrow [H_2A] = \frac{k_w[HA^-]}{k_1[OH^-]}$

$[H_2A] = \frac{k_w^2}{k_1k_2}\frac{[A^{-2}]}{[OH^-]^2}$

From mass balance (द्रव्यमान सन्तुलन से)

$s = x + \frac{k_w}{k_2}\frac{[A^{-2}]}{[OH^-]} + \frac{k_w^2[A^{-2}]}{k_1k_2[OH^-]^2}$

$s = x + \frac{[H^+]x}{k_2} + \frac{[H^+]^2x}{k_1k_2}$

$x = \frac{s}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}}$

$k_{sp} = [M^{+2}]\,[A^{-2}] = s \cdot x = \frac{s^2}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}}$

$s = \sqrt{k_{sp}\left(1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1k_2}\right)}$

1. $\because$ pH = 1 ; $H^+ = 10^{-1} = 0.1$ M

pH = 2 ; $H^+ = 10^{-2} = 0.01$ M

$\therefore$ $M_1 = 0.1$ $V_1 = 1$

$M_2 = 0.01$ $V_2 = ?$

From

$M_1V_1 = M_2V_2$

$0.1 \quad 1 = 0.01 \quad V_2$

$V_2 = 10$ litre

$\therefore$ volume of water added = 10 – 1 = 9 litre.

2. $H^+ = C\alpha$; $\alpha = \dfrac{[H^+]}{C}$ or $\alpha = \dfrac{10^{-3}}{0.1} = 10^{-2}$

$Ka = C\ \alpha^2 = 0.1 \quad 10^{-2} \quad 10^{-2} = 10^{-5}$

3. $Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq.) + 3OH^-(aq.)$

$27S^4 = K_{sp}$

$$S = \left(\frac{K_{sp}}{27}\right)^{1/4} = \left(\frac{1.6\times10^{-30}}{27}\right)^{1/4}$$

4. pH = 5 means

$[H^+] = 10^{-5}$

$HA \rightleftharpoons H^+ + A^{-1}$

t = 0 c 0 0

teq c(1 – α) cα cα

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{[H^+]^2}{c-[H^+]}$$

But, $[H^+] << C$

$\therefore$ $K_a = (10^{-5})^2 = 10^{-10}$

5. $AgBr \rightleftharpoons Ag^+ + Br^-$

$K_{sp} = [Ag^+]\ [Br^-]$

For precipitation to occur

Ionic product > Solubility product

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5\times10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1ℓ $AgNO_3$ solution

$\therefore$ Number of moles of Br^- needed from KBr = 10^{-11}

$\therefore$ Mass of KBr = $10^{-11} \quad 120 = 1.2 \quad 10^{-9}$ g

6. $H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

0.034–x x x

$$K_1 = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = \frac{x\times x}{0.034-x}$$

$$\Rightarrow 4.2 \quad 10^{-7} \simeq \frac{x^2}{0.034} \Rightarrow x = 1.195 \quad 10^{-4}$$

As H_2CO_3 is a weak acid so the concentration of H_2CO_3 will remain 0.034 as 0.034 >> x.

$x = [H^+] = [HCO_3^-] = 1.195 \quad 10^{-4}$

Now, $HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

x–y y y

As HCO_3^- is again a weak acid (weaker than H_2CO_3) with x >> y.

$$K_2 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = \frac{y\times(x+y)}{(x-y)}$$

Note : $[H_3O^+] = H^+$ from first step(x) and from second step(y) = (x + y)

[As x >> y so x + y $\simeq$ x and x – y $\simeq$ x]

$$\text{So, } K_2 \simeq \frac{y\times x}{x} = y$$

$\Rightarrow K_2 = 4.8 \quad 10^{-11} = y = [CO_3^{2-}]$

So the concentration of $[H^+] \simeq [HCO_3^-]$ = concentrations obtained from the first step. As the first step. As the dissociation will be very low in second step so there will beno change in these concentrations.

$[H^+] = [HCO_3^-] = 1.195 \quad 10^{-4}$ & $[CO_3^{2-}] = 4.8 \quad 10^{-11}$

7. $AgBr \rightleftharpoons Ag^+ = Br^-$

$K_{sp} = [Ag^+]\ [Br]$

For precipitation to occur Ionic product > Solubility product

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5\times10^{-13}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1ℓ $AgNO_3$ solution

$\therefore$ Number of moles of Br^- needed from KBr = 10^{-11}

$\therefore$ Mass of KBr = 10^{-11} 120 = 1.2 10^{-9} g

8. $Na_2CO_3 \longrightarrow 2Na^+ + CO_3^{2-}$

1 10^{-4}M 1 10^{-4}M 1 10^{-4}M

$K_{SP}(BaCO_3) = [Ba^{2+}]\,[CO_3^{2-}]$

$$[Ba^{2+}] = \frac{5.1\ 10^{-9}}{1\times10^{-4}} = 5.1\ 10^{-5}\ M$$

9. In corresponds to choice (c) which is correct answer.

$BA + H_2O \rightleftharpoons BOH + HA$

Base Acid

Now pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pKa - \frac{1}{2}pK_b$$

Substituting given values, we get

$$pH = \frac{1}{2}(14 + 4.80 - 4.78) = 7.01$$

10. Let s = solubility

$AgIO_3 \rightleftharpoons Ag^+ + IO_3^-$

s s

$K_{sp} = [Ag^+]\,[IO_3^-] = s \quad x = s^2$

Given $K_{sp} = 1 \quad 10^{-8}$

$$\therefore \quad s = \sqrt{K_{sp}} = \sqrt{1\times10^{-8}}$$

$= 1.0 \quad 10^{-4}$ mol/lit

$= 1.0 \quad 10^{-4} \quad 283$ g/lit

($\because$ Molecular mass of $AgIO_3$ = 283)

$$= \frac{1.0\times10^{-4}\times283\times100}{1000}\ gm/100ml$$

$= 2.83 \quad 10^{-3}$ gm/100 ml

11. $MX_2 \rightleftharpoons M^{++} + 2X^-$

s 2s

Where s is the solubility of MX_2

then $K_{sp} = 4s^3$; $(2s)^2 = 4 \quad 10^{-12} = 4s^3$; $s = 1 \quad 10^4$

$\therefore [M^{++}] = s = 1\ [M^{++}] = 10 \quad 10^{-4}$

12. $pH = -\log[H^+] = \log\frac{1}{[H^+]}$

$$5.4 = \log\frac{1}{[H^+]}$$

On solving, $[H^+] = 3.98 \quad 10^{-6}$

13. $MX_4 \rightleftharpoons M^{4+} + 4X^-$

S 4S

$K_{SP} = [s]\,[4s]^4 = 256\ s^5$

$$\therefore\ s = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

14. $Mg(OH)_2 \longrightarrow [Mg^{2+}] + 2[OH^-]$

x 2x

$K_{sp} = [Mg]\,[OH]^2 = [x]\,[2x]^2 = x.4x^2 = 4x^3$.

15. $AB_2 \rightleftharpoons A^{+2} + 2B^-$

$[A] = 1.0 \quad 10^{-5}$, $[B] = [2.0 \quad 10^{-5}]$,

$K_{sp} = [B]^2[A] = [2 \quad 10^{-5}]^2\ [1.0 \quad 10^{-5}] = 4 \quad 10^{-15}$