

UNIT # 07 (PART - II)

IONIC EQUILIBRIUM

EXERCISE # 1

9. $\text{pH} = 1$ $\text{pH} = 2$
 $[\text{H}^+] = 0.1$ $[\text{H}^+] = 0.01$
 $V = 50$ $V = 50$

$$[\text{H}^+] \text{ of mixture is } [\text{H}^+] = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \Rightarrow \frac{50(0.1 + 0.01)}{100}$$

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

$$\text{pH} = 1.26$$

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

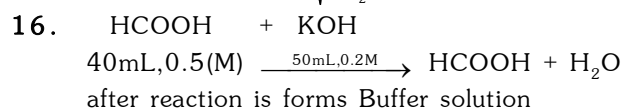
new pH after addition of base

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

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

$[\text{OH}^+]$ concentration increase 10^5 times.

13. Relative strength $= \sqrt{\frac{K_{a1}}{K_{a2}}} = \sqrt{\frac{3 \times 10^{-4}}{1.8 \times 10^{-5}}} \Rightarrow 4 : 1$



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

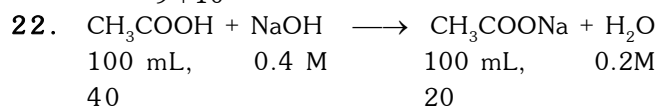
$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \quad \text{pH} = \text{pK}_a$$

$$\text{pH} = 4 - \log (1.8) \quad \text{pH} = 3.75$$

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

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

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

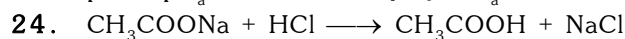


After reaction

$$[\text{CH}_3\text{COOH}] = \frac{20}{250}, \quad [\text{CH}_3\text{COONa}] = \frac{20}{200}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

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



$$\text{at equivalence the } [\text{CH}_3\text{COOH}] = \frac{20}{200} \Rightarrow 0.1$$

$$\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log C$$

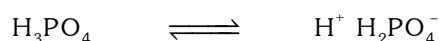
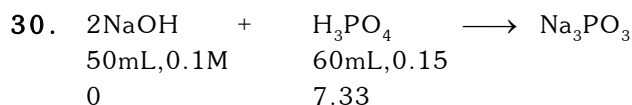
$$\text{pH} = \frac{1}{2} [5 \log 2 - \log 10^{-1}]$$

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

28. $\text{pH} = \text{pK}_a + \log \frac{\text{HCO}_3^-}{\text{H}_2\text{CO}_3}$

$$7 = 7 - \log + \log \frac{\text{HCO}_3^-}{\text{H}_2\text{CO}_3} \frac{\text{HCO}_3^-}{(\text{H}_2\text{CO}_3)} = 4$$

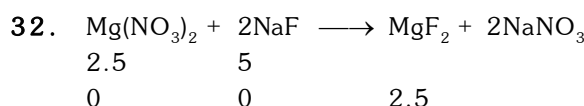
$$\% \text{HCO}_3^- = \frac{4}{5} \times 100 \Rightarrow 80 \%$$



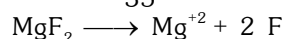
[mass H^+ obtain from first ionization of H_3PO_4]

$$\text{pH} = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log C = \frac{1}{2} \text{pK}_a - \frac{1}{2} \log C$$

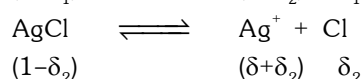
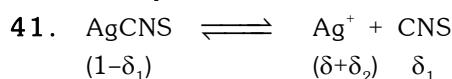
$$= 1.5 + 1.17 = 2.67$$



$$(\text{MgF}_2) = \frac{2.5}{35}$$



Ionic product



$$(K_{sp})_{\text{AgCNS}} = (\delta_1)(\delta_1 + \delta_2) \quad \dots\dots\dots(i)$$

$$(K_{sp})_{\text{AgCl}} = (\delta_2)(\delta_1 + \delta_2) \quad \dots\dots\dots(ii)$$

adde equation (i) and (ii)

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

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

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

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

47. $\text{IP} > K_{sp} \quad \text{I.P.} = (\text{Ca}^{+2}) (\text{F})^2$
 $\text{I.P.} \Rightarrow (10^{-2}) (10^{-3})^2 \Rightarrow 10^{-8} \quad \text{IP} > K_{sp}$

53. $\text{pH} = \text{pHln} + \log \frac{\text{In}^-}{\text{HIn}} \quad 6 = 5 + \log \frac{\text{In}^-}{\text{HIn}}$

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

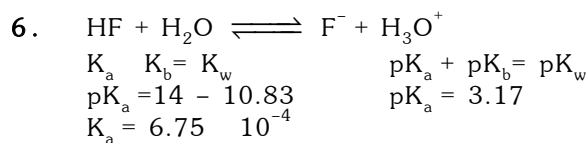
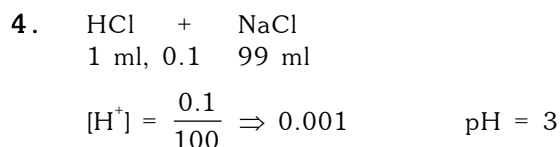
54. At Half way $[\text{HIn}] = \text{In}^-$

$$\text{pH} = 5.5 + \log \frac{[\text{salt}]}{[\text{acid}]} \quad 5.5 = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

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

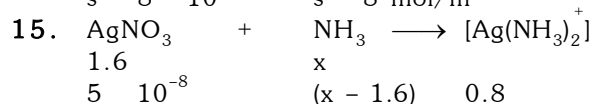
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EXERCISE # 2



9. $h = \sqrt{\frac{K_h}{C}} \quad h = \sqrt{\frac{K_w}{K_a \times C}}$
 $h = \sqrt{\frac{10^{-14} \times 8.0}{1.3 \times 10^{-9} \times 1}} \quad h = 2.48 \%$

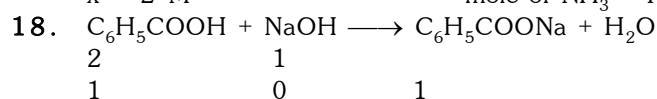
13. $K_{sp} = s^2 \quad s = \sqrt{K_{sp}} = \sqrt{6.4 \times 10^{-5}}$
 $s = 8 \times 10^{-3} \quad s = 8 \text{ mol/m}^3$



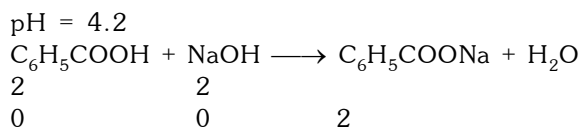
$$K_s = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{(\text{AgNO}_3)(\text{NH}_3)}$$

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

$$x = 2 \text{ M} \quad \text{mole of } \text{NH}_3 = 4$$



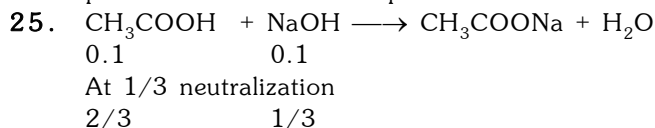
$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \quad \text{pH} = 4.2 + \log \frac{1}{1}$$



$$\text{pH} = 7 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log C$$

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

$$\text{pH} = 9.1 - 1 \quad \text{pH} = 8.1$$



$$\text{pH} = \text{p}K_a + \log \frac{(\text{salt})}{(\text{acid})}$$

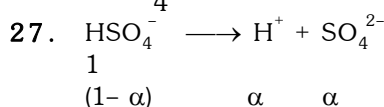
$$\text{pH}_1 = \text{p}K_a + \log \frac{1/3}{2/3} \quad \dots(1)$$

at 2/3 neutralization

$$\text{pH}_2 = \text{p}K_a + \log \frac{2/3}{1/3} \quad \dots(2)$$

$$\text{pH}_1 - \text{pH}_2 = \log \frac{1}{2} - \log 2$$

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



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

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EXERCISE # 3

COMPREHENSION BASED QUESTIONS

Comprehension # 1

1. Suppose volume of $\text{HCO}_3^- = V \text{ mL}$
 millimoles of $\text{HCO}_3^- = 5V$
 millimoles of $\text{H}_2\text{CO}_3 = 20$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

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

3. If CO_2 escapes, $[\text{H}^+]$ decreases, hence pH increases.
 (यदि CO_2 मुक्त होती है, तो $[\text{H}^+]$ घटते हैं अतः 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 हैं।)
 2. If first step is only taken (यदि केवल प्रथम पद को लिया जाये।)

$$\text{pH} = \frac{1}{2} [\text{p}K_{a1} - \log c] \quad c = [\text{H}_3\text{PO}_4] = 0.05 \%$$

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

$$-\log c = 2.3, \quad \text{p}K_{a1} = 2.12 \quad \text{pH} = 2.21$$

3. $\frac{[\text{H}^+]^3 [\text{PO}_4^{3-}]}{[\text{H}_3\text{PO}_4]} = K_{a1} K_{a2} K_{a3}$
 $3 \log [\text{H}^+] + \log [\text{PO}_4^{3-}]$

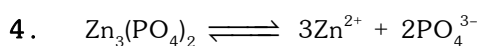
$$= \log K_{a1} + \log K_{a2} + \log K_{a3} - \log [\text{H}_3\text{PO}_4]$$

$$3 \text{pH} - \log [\text{PO}_4^{3-}] = \log [\text{H}_3\text{PO}_4] = \text{p}K_{a1} + \text{p}K_{a2} + \text{p}K_{a3}$$

$$21 - \log [\text{PO}_4^{3-}] - 3 = 2.12 + 7.21 + 12.32$$

$$\log [\text{PO}_4^{3-}] = -3.65$$

$$[\text{PO}_4^{3-}] = 2.24 \times 10^{-4} \text{ M}$$



$$K_{sp} = [\text{Zn}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

$$9.1 \times 10^{-33} = [\text{Zn}^{2+}]^3 (2.2 \times 10^{-4})^2$$

$$[\text{Zn}^{2+}]^3 = 1.88 \times 10^{-25} \quad [\text{Zn}^{2+}] = 5.73 \times 10^{-9} \text{ M}$$

$$1.(i) \quad \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{H}^+ + \text{OH}^-$$

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

$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{1000/8} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16}$$

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

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

$$3. \quad K_a = C\alpha^2$$

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}} = \sqrt{\frac{1.8 \times 10^{-5}}{6.2 \times 10^{-10}}}$$

$$4.(a) \quad \text{pH} = \frac{1}{2} \text{p}K_a - \frac{1}{2} \log C$$

$$4.50 \quad 2 = \text{p}K_a - \log (0.1)$$

$$9 - 1 = \text{p}K_a \quad \text{p}K_a = 8 \quad K_a = 10^{-8}$$

$$5.(c) \quad [\text{H}^+] = \sqrt{K_a C} = \sqrt{1.8 \times 10^{-6}} = 3 - \log 1.8 = 2.87$$

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

$$\text{pH} = 7 - \log 1.1 = 6.95$$

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

$$\text{POH} = 7 - \log 1.001 = 6.99$$

$$\text{pH} = 7.0004$$

$$(g) \quad [\text{H}^+] = \sqrt{K_a C} = \sqrt{1.8 \times 10^{-5} \times 10^{-6}}$$

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

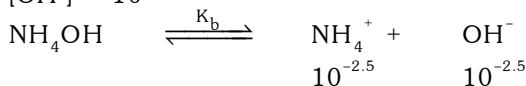
$$\text{pH} = 6 - \log 4.24 = 5.37$$

$$6. \quad \text{p}K_w = 14 - \log 2.56 = 13.59 \approx 13.6$$

$$\text{pH} = \frac{\text{p}K_w}{2} = 6.795$$

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

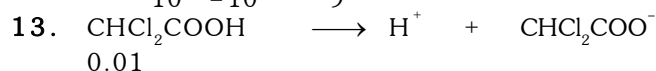
$$[\text{OH}^-] = 10^{-2.5}$$



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

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

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



$$0.01 - x \quad 0.01 + x \quad x$$

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

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

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

$$x = \frac{-0.355 \pm \sqrt{0.04775}}{2} = 1.1 \times 10^{-2}$$

$$\text{CHCl}_2\text{COO}^- = 6.126 \times 10^{-2}$$

14. For weak acid

$$[\text{H}^+] = \sqrt{K_1 C_1 + K_2 C_2 \dots + K_w}$$

$$= \sqrt{1.8 \times 10^{-5} \times 0.02 + 6.4 \times 10^{-5} \times 0.01 + 10^{-14}}$$

$$= \sqrt{100 \times 10^{-8}}$$

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

$$[\text{ACO}^-] = 3.6 \times 10^{-4}$$

$$\text{same } [\text{C}_2\text{H}_5\text{O}_2^\ominus] = 6.4 \times 10^{-4}$$

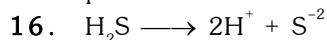
15. HCN is a weak acid so H^+ due to it can neglect
As comparison to HF

$$[\text{H}^+] = \sqrt{K C} = \sqrt{6.7 \times 10^{-4} \times 0.1} = \sqrt{67 \times 10^{-6}}$$

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

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

$$\text{pH} = 2.087$$



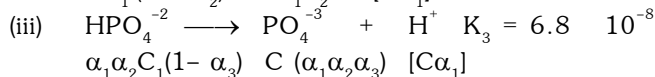
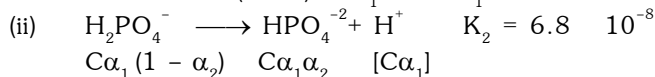
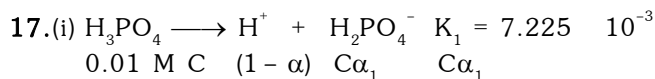
$$[\text{H}^+] = 2 \times 10^{-4}, \quad [\text{H}_2\text{S}] = 0.1 \text{ M}$$

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

$$K = 10^{-21}$$

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

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



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

RxN. (i)

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

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

$$\alpha_1 = 0.562$$

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

$$[\text{H}_2\text{PO}_4^\ominus] \approx 5.6 \times 10^{-3} \quad \text{RxN. (ii)}$$

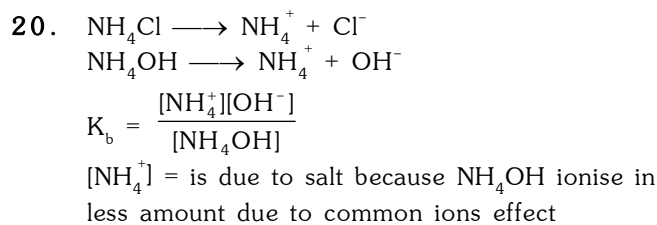
$$6.8 \times 10^{-8} = \frac{[\text{HPO}_4^{2-}][\text{H}^+]}{[\text{H}_2\text{PO}_4^-]} \quad \text{from [i] reaction.}$$

$$\Rightarrow [\text{HPO}_4^{2-}] = 6.8 \times 10^{-8} \text{ M} \quad \text{RxN. (iii)}$$

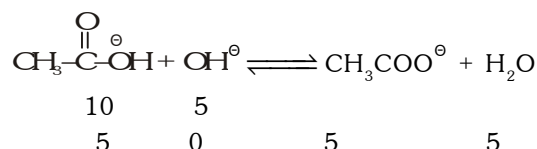
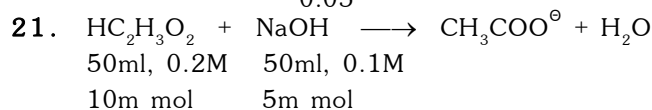
$$4.5 \times 10^{-13} = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{[\text{HPO}_4^{2-}]}$$

$$\frac{4.5 \times 10^{-13} \times 6.8 \times 10^{-8}}{5.6 \times 10^{-3}} = [\text{PO}_4^{3-}]$$

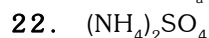
$$5.464 \times 10^{-18} = [\text{PO}_4^{3-}]$$



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



$$\text{pH} = \text{pK}_a = 5 - \log 1.8 \quad \text{pH} = 4.74$$



$$\text{Molarity } (\text{NH}_4)_2\text{SO}_4 = \left(\frac{x}{100} \right)$$

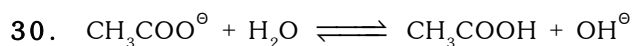
$$\text{Molarity of } \text{NH}_4^+ = \left(\frac{2x}{100} \right)$$

$$\text{Molarity of } \text{NH}_4\text{OH} = \left(\frac{0.1}{100} \right) = 10^{-3}$$

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

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

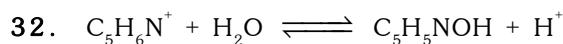
$$x = 1/20 \text{ mole} \quad x = 0.05 \text{ mole}$$



$$0.08 \quad K_b = \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$$\frac{x^2}{0.08} = \frac{10}{1.8} \times 10^{-10} \quad x^2 = \frac{0.8}{1.8} \times 10^{-10}$$

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



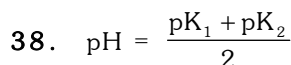
$$\text{pH} = \frac{1}{2} [\text{pK}_w - \text{pK}_b - \log C]$$

$$2.699 = \frac{1}{2} [14 - \text{pK}_b + 0.6]$$

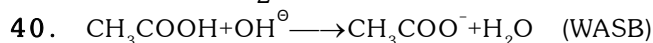
$$2.398 = 14.6 - \text{pK}_b$$

$$\text{pK}_b = 14.6 - 5.398 = 9.802$$

$$K_b = 10^{-9.802}$$



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



$$\text{pH} = \frac{1}{2} [\text{pK}_w + \text{pK}_a + \log C]$$

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

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

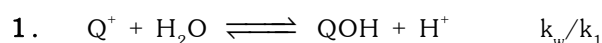
$$\text{pH} = \frac{1}{2} [19 - \log 20 - 1.9] = 8.78$$

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

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

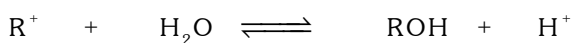
IONIC EQUILIBRIUM

EXERCISE # 4[B]



$$\frac{n_1}{V} = n_1'$$

$$n_1' - x \quad x \quad x + y$$



$$\frac{n_2}{V} = n_2'$$

$$n_2' - y \quad y \quad y + x$$

$$\frac{k_w}{k_1} = \frac{x(x+y)}{n_1' - x} \approx \frac{x(x+y)}{n_1'} \quad \dots\dots\dots(i)$$

$$\frac{k_w}{k_2} = \frac{y(x+y)}{n_2' - y} \approx \frac{y(x+y)}{n_2'} \quad \dots\dots\dots(ii)$$

$$\text{Assuming (माना)} \quad x \ll n_1' \text{ \& } y \ll n_2'$$

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

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

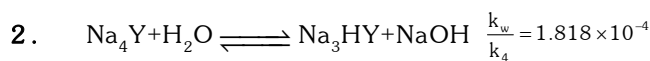
adding both (दोनों को जोड़ने पर)

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

$$[\text{H}^+] = (x+y) = \sqrt{\frac{k_w}{k_1 k_2 V} (k_2 n_1 + k_1 n_2)}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = \frac{1}{2} \log \left[\left(\frac{k_1 k_2}{k_w} \right) \frac{V}{(k_2 n_1 + k_1 n_2)} \right]$$

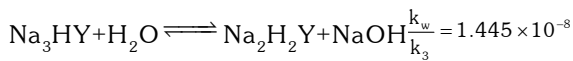


$$0.1$$

$$0.1 - x \quad x \quad x$$

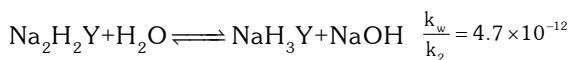
$$\frac{x^2}{0.1-x} = 1.818 \times 10^{-4} \Rightarrow 5500.55x^2 + x - 0.1 = 0$$

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



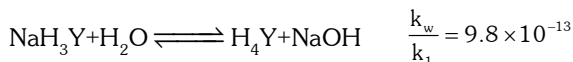
$$\begin{array}{ccc} x & & \\ x - y & y & y + x \\ \text{since } y \ll x & x - y \approx x, & x + y \approx x \end{array}$$

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



$$\begin{array}{ccc} y & & \\ y - z & z & z + x \\ y - z \approx y, & z + x \approx x \end{array}$$

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



$$\begin{array}{ccc} z & & \\ z - t & t & t + x \\ z - t \approx z, & t + x \approx x \end{array}$$

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

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

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

$$s = k_1 + \frac{k_1 k_2}{[\text{OH}^-]} + \frac{k_1 k_2 k_3}{[\text{OH}^-]^2} + k_1 k_4 [\text{OH}^-] + k_1 k_4 k_5 [\text{OH}^-]^2$$

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

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

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

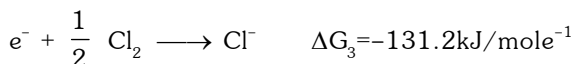
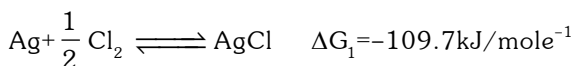
$$(b) \quad \text{pH} = 9, \text{pOH} = 5, [\text{OH}^-] = 10^{-5}$$

$$s = 10^{-6} + 10^{-8} + 10^{-7} + 10^{-8} + 10^{-12} = 1.12 \quad 10^{-6} \text{ M}$$

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

$$s = 10^{-6} + 10^{-12} + 10^{-15} + 10^{-4} + 10^{-4} = 2 \quad 10^{-4} \text{ M}$$

4. Given :



so for reaction (अतः अभिक्रिया के लिए)



$$\Delta G = 55.7 \text{ kJ/mole}$$

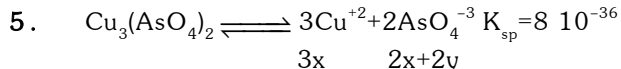
$$\Delta G = -RT \ln K_{sp}$$

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

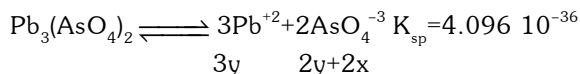
$$K_{sp} = 1.723 \quad 10^{-10}$$

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

$$s = 3.446 \quad 10^{-9} \text{ M}$$



$$3x \quad 2x+2y$$



$$3y \quad 2y+2x$$

Let solubility of $\text{Cu}_3(\text{AsO}_4)_2$ & $\text{Pb}_3(\text{AsO}_4)_2$ is x & y respectively. (माना $\text{Cu}_3(\text{AsO}_4)_2$ व $\text{Pb}_3(\text{AsO}_4)_2$ की विलेयता क्रमशः x व y है।)

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

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

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

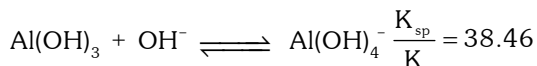
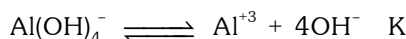
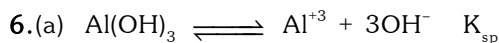
putting this in equation (ii) (इसे समीकरण(ii)में रखने पर)

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

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

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

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



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

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

$$\text{pOH} = 4.585$$

$$\text{pH} = 9.415$$

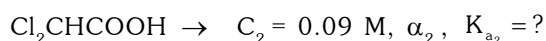
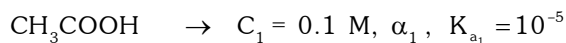
$$(b) \quad K_{sp} = [\text{Al}^{+3}] [\text{OH}^-]^3$$

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

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

$$\text{pOH} = 9.767$$

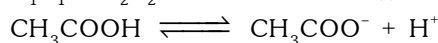
$$\text{pH} = 4.23$$



$$\text{pH} = 1, [\text{H}^+] = 0.1$$

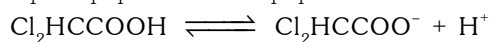
$$0.1 = 0.09 + \text{C}_1\alpha_1 + \text{C}_2\alpha_2$$

$$\text{C}_1\alpha_1 + \text{C}_2\alpha_2 = 0.01 \quad \dots(i)$$



$$\text{C}_1$$

$$\text{C}_1 - \text{C}_1\alpha_1 \quad \text{C}_1\alpha_1 \quad 0.1$$



$$\text{C}_2$$

$$\text{C}_2 - \text{C}_2\alpha_2 \quad \text{C}_2\alpha_2 \quad 0.1$$

$$K_{a1} = \frac{(\text{C}_1\alpha_1)(0.1)}{\text{C}_1(1-\alpha_1)} \approx \alpha_1 \quad 0.1 = 10^{-5}$$

$$\alpha_1 = 10^{-4}$$

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

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

$$\alpha_2 = 0.111$$

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

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

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

$$\alpha = 10^{-3}$$

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

$$\text{pOH} = 2.26, \quad \mathbf{\text{pH} = 11.74}$$

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

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

$$\Delta H = \mathbf{51952.6 \text{ J} = 51.95 \text{ kJ/mole}}$$

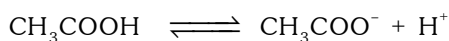
$$10. \quad \text{In beginning } [\text{H}^+] = \sqrt{K_a C}$$

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

$$\text{pH} = 2.372$$

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

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



C

$$C - C\alpha \qquad C\alpha \qquad C\alpha$$

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

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

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

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

$$V = \frac{1}{C} = \mathbf{2.77 \times 10^4 \text{ L}}$$

$$11.(a) \text{PV} = nRT$$

$$1 \times 0.959 = n \times 0.0821 \times 298$$

$$n = 0.03919$$

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

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

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

$$\text{p}K_b = 3.39 \Rightarrow K_b = 4 \times 10^{-4}$$

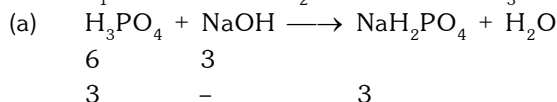
$$[\text{OH}^-] = \sqrt{K_b C} = 0.1252 \text{ M}$$

$$\text{pOH} = 0.9023$$

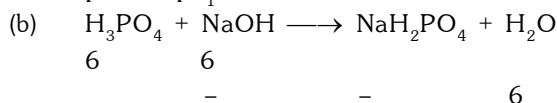
$$\mathbf{\text{pH} = 13.097}$$

$$(b) \quad M = \mathbf{0.1252} \text{ for NaOH (NaOH के लिए 0.1252)}$$

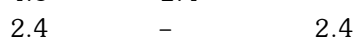
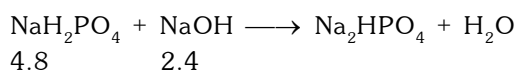
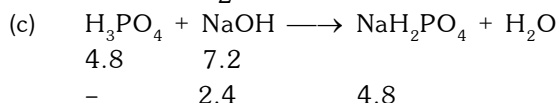
$$12. \quad k_1 = 7.5 \times 10^{-3}, \quad k_2 = 6.2 \times 10^{-8}, \quad k_3 = 10^{-12}$$



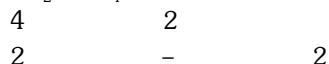
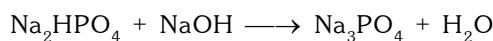
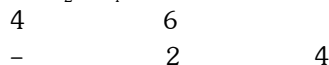
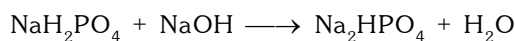
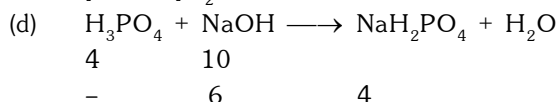
$$\text{pH} = \text{p}K_1 = \mathbf{2.12}$$



$$\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2} = \mathbf{4.66}$$



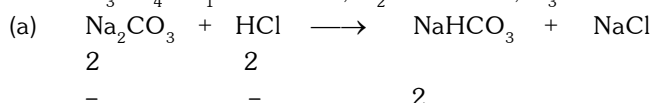
$$\text{pH} = \text{p}K_2 = \mathbf{7.2}$$



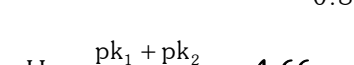
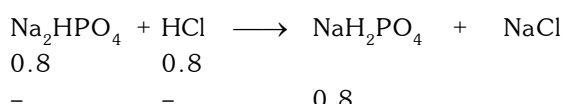
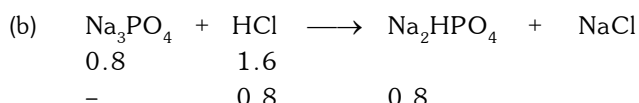
$$\text{pH} = \text{p}K_3 = \mathbf{12}$$

$$13. \quad \text{For } \text{H}_2\text{CO}_3 \rightarrow k_1 = 4.2 \times 10^{-7}, \quad k_2 = 4.8 \times 10^{-11}$$

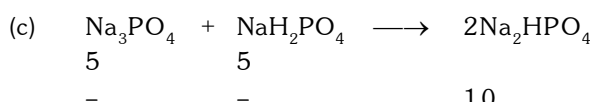
$$\text{H}_3\text{PO}_4 \rightarrow k_1 = 7.5 \times 10^{-3}, \quad k_2 = 6.2 \times 10^{-8}, \quad k_3 = 10^{-12}$$



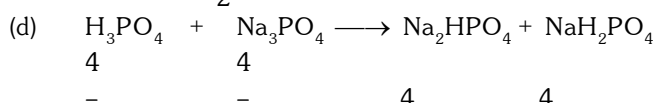
$$\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2} = \mathbf{8.347}$$



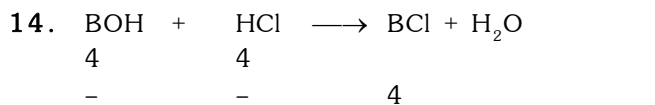
$$\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2} = \mathbf{4.66}$$



$$\text{pH} = \frac{\text{p}K_2 + \text{p}K_3}{2} = \mathbf{9.6}$$



$$\text{pH} = \text{p}K_2 = \mathbf{7.2}$$



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

$$0.16 \quad V = 4 \quad V = 25 \text{ mL}$$

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

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

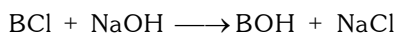
since BCl is SAWB

$$\text{pH} = 7 - \frac{1}{2} \text{pk}_b - \frac{1}{2} \log C$$

$$5.23 = 7 - \frac{1}{2} \text{pk}_b - \frac{1}{2} \log \frac{4}{65}$$

$$\text{pk}_b = 4.75$$

Now on further adding NaOH (अब पुनः NaOH को मिलाने पर)



$$\text{pOH} = \text{pk}_b + \log \frac{2.2}{1.8} = 4.837 \Rightarrow \text{pH} = 9.1628$$

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

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

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

$$[\text{HCOOH}] = 0.005, [\text{HCOONa}] = 0.006$$



$$0.005$$

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

$$\text{K}_a = 1.8 \times 10^{-4} = \frac{(0.005\alpha + 0.006)(0.005\alpha)}{0.005(1 - \alpha)}$$

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

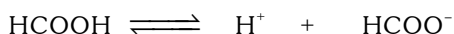
$$\Rightarrow 27.77\alpha^2 + 34.33\alpha - 1 = 0$$

$$\alpha = 0.0285$$

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

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

$$[\text{HCOOH}] = 0.0005, [\text{HCOONa}] = 0.0006$$



$$0.0005$$

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

$$\text{K}_a = 1.8 \times 10^{-4} = \frac{(0.0005\alpha + 0.0006)(0.0005\alpha)}{0.0005(1 - \alpha)}$$

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

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

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

$$\text{pH} = 3.9899$$

$$16. \text{Initial (प्रारम्भ में) } \text{pOH} = \text{pK}_b = 4.744$$

Let x mole of NaOH has been added so (माना NaOH के x मोल मिलाये हैं, अतः)

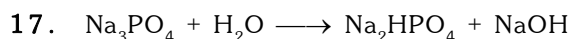
$$[\text{NH}_4^+] = 0.1 + x, [\text{NH}_3] = 0.1 - x$$

$$\text{pOH} = 5.744$$

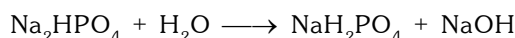
$$5.744 = 4.744 + \log \frac{0.1 + x}{0.1 - x}$$

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

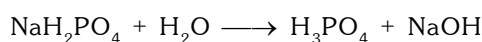
$$\frac{0.1 + x}{0.1 - x} = 10 \Rightarrow x = \frac{0.9}{11} = 0.0818 \text{ moles}$$



$$\text{K} = \frac{\text{K}_w}{\text{K}_3} = 0.0222$$



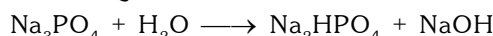
$$\text{K} = \frac{\text{K}_w}{\text{K}_2} = 1.58 \times 10^{-7}$$



$$\text{K} = \frac{\text{K}_w}{\text{K}_1} = 1.4 \times 10^{-12}$$

since equilibrium constant of 2nd & 3rd reaction is very less, [OH⁻] will mainly come from 1st reaction.

(चूँकि 2nd व 3rd अभिक्रिया का साम्य नियतांक बहुत कम है, [OH⁻] मुख्यतः 1st अभिक्रिया से प्राप्त होगा।)



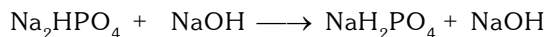
$$0.1$$

$$0.1 - x \quad x \quad x$$

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

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

$$[\text{OH}^-] = x = 3.73 \times 10^{-2} \text{ M}$$

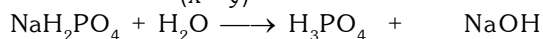


$$x$$

$$x - y \quad y \quad y + x$$

$$x - y \approx x, \quad y + x \approx x, \text{ so}$$

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



$$y$$

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

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

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

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

$$[\text{H}_3\text{PO}_4] = z = 5.93 \times 10^{-18} \text{ M}$$

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

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad K = 5 \times 10^{-13}$$

0.0005

0.0005-y-z 10^{-8} y

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^- \quad K = \frac{K_w}{K_1} = 2 \times 10^{-8}$$

0.0005

0.0005-y-z z 10^{-6}

since equilibrium constant for first reaction is very less $y \ll z$ (चूँकि प्रथम कोटि अभिक्रिया के लिए साम्य नियतांक बहुत कम है $y \ll z$)

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

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

$[\text{H}_2\text{CO}_3] = 9.8 \times 10^{-6} \text{ M}$

$[\text{HCO}_3^-] = 0.0005 - 9.8 \times 10^{-6} = 4.9 \times 10^{-4} \text{ M}$

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

$[\text{CO}_3^{2-}] = y = 2.45 \times 10^{-8} \text{ M}$

19. $\text{Fe}^{+3} + \text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})^{+2} + \text{H}^+ \quad k = 6.5 \times 10^{-3}$

x

0.95x 0.05x 0.05x

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

$[\text{H}^+] = 0.05x = 0.1235 \quad \text{pH} = 0.908$

20. $\text{pH} = \text{pK}_2 + \log \frac{\text{salt}}{\text{acid}}$

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

$y = 1.58 \times 10^{-3} \text{ mole}$

21. When indicator is half in ionic form pH (जब आधा सूचक आयनिक रूप में है $\text{pH} = \text{pK}_a = 7.2$)

$\text{pH} = 7.2 + \log 5 = 7.898$

now with this pH (अब इस pH में)

$$7.898 = \text{pK}_{a_1} + \log 4 = \text{pK}_{a_1} = 7.2959$$

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

$\text{pH} = \text{pK}_{a_1} = 7.2959$

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

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

$$\text{PO}_4^{3-} + \text{H}^+ \longrightarrow \text{HPO}_4^{2-} \quad \frac{1}{k_3}$$

0.02 0.04 0.08

- 0.02 0.1

$$\text{HPO}_4^{2-} + \text{H}^+ \longrightarrow \text{H}_2\text{PO}_4^- \quad \frac{1}{k_2}$$

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)

$$\text{pH} = \text{pK}_2 + \log \frac{0.08}{0.02} \quad (k_2 = 6.3 \times 10^{-8})$$

$\text{pH} = 7.2 + \log 4 = 7.8$

23. At equivalence point (तुल्यांक बिन्दु पर)

meq. of HA = meq. of NaOH = 3.612

$$\text{NaA} + \text{HCl} \longrightarrow \text{HA} + \text{HCl}$$

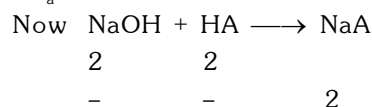
3.612 1.806

1.356 - 1.806

$$\text{pH} = \text{pK}_a + \log \frac{[\text{S}]}{[\text{A}]}$$

$$4.92 = \text{pK}_a + \log \frac{1.356}{1.806}$$

$$\text{pK}_a = 5.044$$

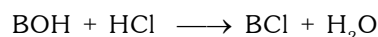


$$[\text{NaA}] = \frac{2}{20} = 0.1$$

$$\text{pH} = 7 + \frac{1}{2}\text{pK}_a + \frac{1}{2}\log C = 7 + \frac{5.044}{2} + \frac{1}{2}\log 0.1$$

$$\text{pH} = 9$$

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



x

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

$$\text{pOH} = \text{pK}_b + \log \frac{1}{3}$$

$$14 - 9.24 = \text{pK}_b - \log 3$$

$$\text{pK}_b = 5.237$$

$$k_b = 5.8 \times 10^{-6}$$



$$\begin{array}{ccc} \frac{x}{4} & 6 & \\ - & - & x \end{array}$$

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

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

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

$$\text{pOH} = 2.77$$

$$\text{pH} = 11.22$$

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

$$(\text{pH})_1 = \text{p}K_a + \log \frac{x/4}{3x/4} = \text{p}K_a + \log$$

$$\frac{1}{3}$$

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

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

$$3$$

$$\Delta \text{pH} = (\text{pH})_2 - (\text{pH})_1 = 2 \log 3 =$$

$$0.9542$$

$$(b) \quad 4.45 = \text{p}K_a + \log \frac{x/3}{2x/3} = \text{p}K_a - \log 2$$

$$\text{p}K_a = 4.751$$

$$(c) \quad \Delta \text{pH} = 2 \quad \text{i.e.}$$

$$(\text{pH})_1 = \text{p}K_a + 1, (\text{pH})_2 = \text{p}K_a - 1$$

$$\text{For } \text{p}K_a + 1 \Rightarrow \frac{[\text{S}]}{[\text{A}]} = 10$$

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

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

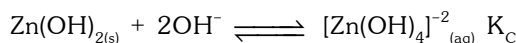
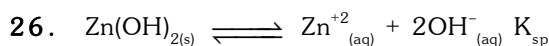
$$\text{i.e. } \frac{10^{\text{th}}}{11} \text{ stage}$$

$$\text{For } \text{p}K_a - 1 \Rightarrow \frac{[\text{S}]}{[\text{A}]} = \frac{1}{10}$$

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

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

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



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

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

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

$$\text{अतः विलेयता } s = [\text{Zn}^{+2}] + [\text{Zn(OH)}_4]^{-2}$$

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

For min. solubility (न्यूनतम विलेयता के लिए)

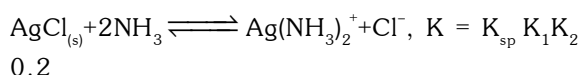
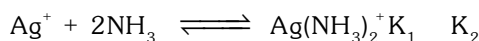
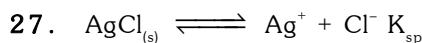
$$\frac{ds}{d[\text{OH}^-]} = 0 \Rightarrow \frac{-2K_{sp}}{[\text{OH}^-]^3} + 2K_C[\text{OH}^-] = 0$$

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

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

$$\text{pOH} = 4.00869$$

$$\text{pH} = 9.9913$$



$$0.2$$

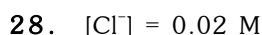
$$0.2-2x \quad x \quad x$$

$$K = \frac{x^2}{(0.2-2x)} = K_{sp} K_1 K_2 = 0.002828$$

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

$$x = 0.009613$$

$$\text{Solubility (विलेयता)} = 9.6 \times 10^{-3} \text{ M}$$



$$0.05$$

$$0.05-x \sim 0.05 \quad x \quad 2x$$

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

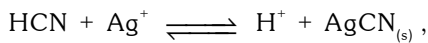
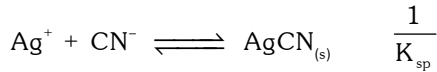
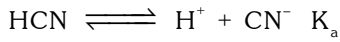
$$\frac{4x^3}{0.05} = 4 \times 10^{-19} \Rightarrow x = 1.7 \times 10^{-7}$$

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

so **AgCl will precipitate.** (अतः AgCl अवक्षेपित होगा।)

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

$$[\text{Ag}^+] = 0.01 \text{ M}, \text{HCN} = 0.01 \text{ M}$$



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

$$0.01 \quad 0.01$$

$$x \quad x \quad 0.01$$

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

(चूँकि K मान बहुत उच्च है लगभग सभी क्रियाकारक उत्पाद में परिवर्तित होंगे।)

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

$$[\text{Ag}^+] = 6.66 \times 10^{-5} \text{ M}$$

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

$$s \quad s$$

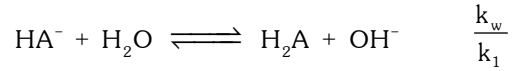
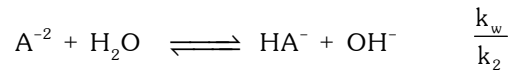
Let solubility is s. (माना विलेयता s है।)

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)



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

$$\frac{k_w}{k_1} = \frac{[\text{H}_2\text{A}][\text{OH}^-]}{[\text{HA}^-]} \Rightarrow [\text{H}_2\text{A}] = \frac{k_w[\text{HA}^-]}{k_1[\text{OH}^-]}$$

$$[\text{H}_2\text{A}] = \frac{k_w^2}{k_1 k_2} \frac{[\text{A}^{-2}]}{[\text{OH}^-]^2}$$

From mass balance (द्रव्यमान सन्तुलन से)

$$s = x + \frac{k_w}{k_2} \frac{[\text{A}^{-2}]}{[\text{OH}^-]} + \frac{k_w^2}{k_1 k_2} \frac{[\text{A}^{-2}]}{[\text{OH}^-]^2}$$

$$s = x + \frac{[\text{H}^+]x}{k_2} + \frac{[\text{H}^+]^2 x}{k_1 k_2}$$

$$x = \frac{s}{1 + \frac{[\text{H}^+]}{k_2} + \frac{[\text{H}^+]^2}{k_1 k_2}}$$

$$k_{sp} = [\text{M}^{+2}][\text{A}^{-2}] = s \cdot x = \frac{s^2}{1 + \frac{[\text{H}^+]}{k_2} + \frac{[\text{H}^+]^2}{k_1 k_2}}$$

$$s = \sqrt{k_{sp} \left(1 + \frac{[\text{H}^+]}{k_2} + \frac{[\text{H}^+]^2}{k_1 k_2} \right)}$$

1. $\therefore \text{pH} = 1 ; \text{H}^+ = 10^{-1} = 0.1 \text{ M}$
 $\text{pH} = 2 ; \text{H}^+ = 10^{-2} = 0.01 \text{ M}$
 $\therefore \text{M}_1 = 0.1 \quad \text{V}_1 = 1$
 $\text{M}_2 = 0.01 \quad \text{V}_2 = ?$

From

$$\text{M}_1 \text{V}_1 = \text{M}_2 \text{V}_2$$

$$0.1 \quad 1 = 0.01 \quad \text{V}_2$$

$$\text{V}_2 = 10 \text{ litre}$$

$$\therefore \text{volume of water added} = 10 - 1 = 9 \text{ litre.}$$

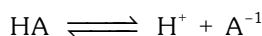
2. $\text{H}^+ = \text{C}\alpha ; \alpha = \frac{[\text{H}^+]}{\text{C}} \quad \text{or} \quad \alpha = \frac{10^{-3}}{0.1} = 10^{-2}$

$$\text{K}_a = \text{C} \alpha^2 = 0.1 \quad 10^{-2} \quad 10^{-2} = 10^{-5}$$

3. $\text{Cr}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq.}) + 3\text{OH}^-(\text{aq.})$
 $27\text{S}^4 = \text{K}_{\text{sp}}$

$$\text{S} = \left(\frac{\text{K}_{\text{sp}}}{27} \right)^{1/4} = \left(\frac{1.6 \times 10^{-30}}{27} \right)^{1/4}$$

4. $\text{pH} = 5$ means
 $[\text{H}^+] = 10^{-5}$



$$t = 0 \quad \text{c} \quad 0 \quad 0$$

$$\text{teq} \quad \text{c}(1 - \alpha) \quad \text{c}\alpha \quad \text{c}\alpha$$

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

But, $[\text{H}^+] \ll \text{C}$

$$\therefore \text{K}_a = (10^{-5})^2 = 10^{-10}$$

5. $\text{AgBr} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$

$$\text{K}_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$$

For precipitation to occur

Ionic product > Solubility product

$$[\text{Br}^-] = \frac{\text{K}_{\text{sp}}}{[\text{Ag}^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

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}

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

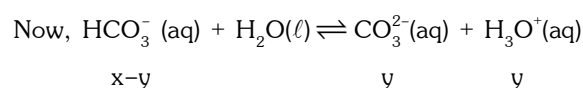
6. $\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 $0.034 - x \quad \quad \quad x \quad \quad \quad x$

$$\text{K}_1 = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} = \frac{x \times x}{0.034 - x}$$

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

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

$$x = [\text{H}^+] = [\text{HCO}_3^-] = 1.195 \quad 10^{-4}$$



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

$$\text{K}_2 = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} = \frac{y \times (x + y)}{(x - y)}$$

Note : $[\text{H}_3\text{O}^+] = \text{H}^+$ from first step(x) and from second step(y) = (x + y)

[As $x \gg y$ so $x + y \approx x$ and $x - y \approx x$]

$$\text{So, } \text{K}_2 \approx \frac{y \times x}{x} = y$$

$$\Rightarrow \text{K}_2 = 4.8 \quad 10^{-11} = y = [\text{CO}_3^{2-}]$$

So the concentration of $[\text{H}^+] \approx [\text{HCO}_3^-]$ = concentrations obtained from the first step. As the first step. As the dissociation will be very low in second step so there will be no change in these concentrations.

$$[\text{H}^+] = [\text{HCO}_3^-] = 1.195 \quad 10^{-4} \quad \& \quad [\text{CO}_3^{2-}] = 4.8 \quad 10^{-11}$$

7. $\text{AgBr} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$

$$\text{K}_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$$

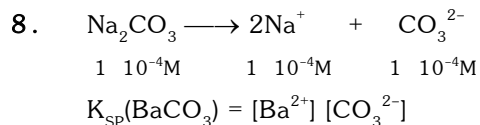
For precipitation to occur Ionic product > Solubility product

$$[\text{Br}^-] = \frac{\text{K}_{\text{sp}}}{[\text{Ag}^+]} = \frac{5 \times 10^{-13}}{0.05} = 10^{-11}$$

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

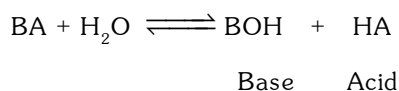
∴ Number of moles of Br⁻ needed from KBr = 10⁻¹¹

∴ Mass of KBr = 10⁻¹¹ × 120 = 1.2 × 10⁻⁹ g



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

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



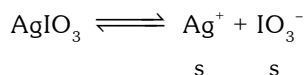
Now pH is given by

$$\text{pH} = \frac{1}{2} \text{pK}_w + \frac{1}{2} \text{pK}_a - \frac{1}{2} \text{pK}_b$$

Substituting given values, we get

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

10. Let s = solubility



$$K_{\text{sp}} = [\text{Ag}^+] [\text{IO}_3^-] = s \times s = s^2$$

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

$$\therefore s = \sqrt{K_{\text{sp}}} = \sqrt{1 \times 10^{-8}}$$

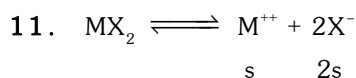
$$= 1.0 \times 10^{-4} \text{ mol/lit}$$

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

(∵ Molecular mass of Ag IO₃ = 283)

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000} \text{ gm/100ml}$$

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



Where s is the solubility of MX₂

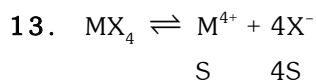
$$\text{then } K_{\text{sp}} = 4s^3; (2s)^2 = 4 \times 10^{-12} = 4s^3; s = 1 \times 10^{-4}$$

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

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

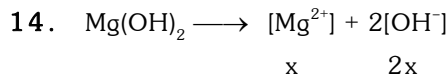
$$5.4 = \log \frac{1}{[\text{H}^+]}$$

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

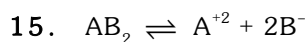


$$K_{\text{sp}} = [s] [4s]^4 = 256 s^5$$

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



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



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

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