

% ionisation = 1.8 × 10⁻⁹ M



So no. of mole of OH⁻ removed = [.01 - 0.001] = 0.009

I.

30. Sol (i) to (v)

$$\begin{array}{cccc} H_3PO_4 & & \longleftrightarrow & H_2PO_4^- & + & H^+ \\ 0.1-x & & x & & x \end{array}$$

$$K_{a1} = \frac{x^2}{0.1 - x} = 10^{-3}$$

$$\label{eq:constraint} \begin{split} x &= 0.01 = [H^+] = [H_2 P O_4^{-1}] \\ \text{and} \qquad [H P O_4^{-2-}] = 10^{-7} \, M \end{split}$$

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \Longrightarrow 10^{-12}$$

$$\frac{(0.01) [PO_4^{3-}]}{10^{-7}}$$
$$[PO_4^{3-}] = 10^{-17} M$$
$$[OH^{-}] = 10^{-12} M$$

32. pH of 0.1 M H₂S solution can be derived by : H₂S \longrightarrow H⁺ + HS⁻; K₁ = 1 × 10⁻⁷

$$\therefore [H^+] = C\alpha = C \sqrt{\frac{K_1}{C}} = \sqrt{K_1 \times C} = \sqrt{1 \times 10^{-7} \times 0.1}$$
$$= \sqrt{10^{-8}} = 10^{-4} \therefore pH = 4$$

34.
$$CH_3COOH(aq) \longrightarrow H^+(aq) + CH_3COO^-(aq)$$

 $t = 0 0.01$
 $t = eq 0.01 - x x x$
 $[H^+] = x + 0.01 \approx 0.01 M$

$$\therefore \quad \mathbf{K}_{a} = \frac{[\mathrm{H}^{+}][\mathrm{CH}_{3}\mathrm{COO}^{-}]}{[\mathrm{CH}_{3}\mathrm{COOH}]}$$

⇒
$$1.69 \times 10^{-5} = \frac{0.01 \times [CH_3COO^-]}{0.01}$$

∴ $[CH_3COO^-] = 1.69 \times 10^{-5} M$

So, degree of dissociation of CH₃COOH = $\frac{1.69 \times 10^{-5}}{0.01}$ = 1.69 × 10⁻³

35.
$$CH_{3}COOH + OH^{-} \longrightarrow CH_{3}COO^{-} + H_{2}O$$

$$t = 0 \qquad 20 \qquad 20$$

$$t = eq \qquad - \qquad - \qquad 20$$
So,
$$[CH_{3}COO^{-}] = \frac{20}{200} = 0.1 \text{ M}$$

pH = 7 +
$$\frac{1}{2}$$
 pK_a + $\frac{1}{2}$ log C = 7 + 2.37 + $\frac{1}{2}$ log 10⁻¹
= 7 + 2.37 - 0.5 = 8.87
36. For Na₂HPO₄, pH = $\frac{pK_{a_2} + pK_{a_3}}{2} = \frac{7.28 + 12}{2} = 9.6.$
For Na₂HPO₄, pH = $\frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.2 + 7.2}{2} = 4.7.$

37. Solution of HCl & NH_4Cl will be acidic, solution of NaCl neutral whereas solution of NaCN will be basic.

40. h=0.03 C=0.1 M

$$K_{h} = Ch^{2} = 9 \times 10^{-5}$$

 $K_{h} = \frac{K_{w}}{K_{a}} = 9 \times 10^{-5}$
 $\Rightarrow K_{a} = \frac{10^{-14}}{9 \times 10^{-5}} = 1.11 \times 10^{-10} \approx 1 \times 10^{-10}$

42. Initial pH = $\frac{1}{2}$ (pK_b - log C) = $\frac{1}{2}$ (5 - log 2 - log 0.1) = 2.85

After adding NaOH, pOH of solution = 1 Change in pOH = 1.85

Ionic product = $K_w = (2x)(x) = 10^{-14}$ $\Rightarrow 2x^2 = 10^{-14} \Rightarrow x = \sqrt{50} \times 10^{-8}$

46. m. moles of HCl = $0.1 \times 20 = 2$ m. moles of CH₃COOH = $0.1 \times 20 = 2$ After titration of HCl by NaOH

$$[CH_{3}COOH] = \frac{2}{40} = \frac{1}{20}M$$

:
$$pH = \frac{1}{2} (pK_a - \log C) = \frac{1}{2} [5 - \log 2 - \log (\frac{1}{20})] = 3.$$

- **47.** This is ostwald dilution law.
- **48.** The molecule shows three H atoms are replaceable, i.e., basicity of acid.
- 49. It is definition of Levelling effect,



50. Acid $\xrightarrow{-H^+}$ Conjugate base, Base $\xrightarrow{+H^+}$ Conjugate acid

51. K_{w} changes with temperature.

52. H₃BO₃ is weak, Lewis monobasic acid and shows the given equilibrium.
 H₃BO₃ + H₂O → B(OH)₄⁻ + H⁺

53. $CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$

$$\therefore [OH^{-}] = C.h = C \sqrt{\frac{K_{H}}{C}} = \sqrt{K_{H}.C} = \sqrt{\frac{K_{w}}{K_{a}}C}$$

or $-\log OH = -\frac{1}{2} [\log K_{w} + \log C - \log K_{a}]$ or
 $pOH = \frac{1}{2} [pK_{w} - \log C - pK_{a}]$
Now $pH + pOH = pK_{w}$
$$\therefore pH = \frac{1}{2} [pK_{w} + \log C + pK_{a}]$$

- 54. Higher is pH, lesser is acidic nature. Also $NH_4CI(aq)$ is acidic and NaCN(aq) is basic.
- 55. Meq. of HCI = $10 \times 10^{-1} = 1$ Meq. of NaOH = $= 10 \times 10^{-1} = 1$ Thus both are neutralised and 1 Meq. of NaCI (a salt of strong acid and strong base) which does not hydrolyse and thus pH = 7.
- 56. On heating water K_w increases and thus pH scale for neutrality changes from 7 to some lower value, i.e., 6.8 or 6.9 depending upon K_w values.

57.
$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$$
 (: [H^+] = [A^-]) and

$$K_{b} = \frac{[H^{+}][B^{-}]}{[HB]} = \frac{[H^{+}]^{2}}{[HB]} (:: [H^{+}] = [B^{-}])$$

Also H⁺ are same
$$\therefore \frac{K_a}{K_b} = \frac{[HB]}{[HA]} = \frac{4}{1} \qquad \frac{[HA]}{[HB]} = \frac{1}{4}$$

58.
$$H^+ + OH^- \longrightarrow H_2O.$$

59. New concentration of HCI =
$$\frac{10^{-6}}{100} = 10^{-8} \text{ M}$$

[H⁺] = $10^{-7} + 10^{-8}$ (approximately)
(Little less than 10^{-7} from water).

60. Meq. of HCI =
$$75 \times \frac{1}{5} = 15$$

Meq. of NaOH = $25 \times \frac{1}{5} = 5$
∴ Meq. of HCI left = $15 - 5 = 10$
Now [HCI] left = $\frac{10}{100} = 10^{-1}$
∴ pH = 1
61. Ca₃(PO₄)₂ + 6HCI → CaCI₂ + 2H₃PO₄

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52. HA
$$\longrightarrow$$
 H⁺ + A⁻ $K_a = \frac{[H^+][A^-]}{[HA]}$ (i)
Also HA + B⁺ + OH⁻ \rightarrow B⁺ +A⁻ + H₂O

Keq. =
$$\frac{[H_2O][A]}{[HA][OH]}$$
.....(ii)

By (i) and (ii),
$$\frac{K_{eq}}{K_a} = \frac{1}{[H^+][OH^-]} = \frac{1}{K_w}$$

$$K_{eq} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

3.
$$K_a = 10^{-6}$$
 for HA + H₂O \longrightarrow H₃O⁺ + A⁻
Thus K for reverse reaction is $\frac{1}{10^{-6}} = 10^{6}$

64. The degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of salt.

65.
$$\alpha = \sqrt{\frac{K_a}{C}}$$
 $\therefore \%\alpha = 100 \sqrt{\frac{K_a}{C}}$
Also $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+].C\alpha}{C(1-\alpha)} = \frac{[H^+].\alpha}{(1-\alpha)}$
 $\log K_a = \log H^+ + \log \frac{\alpha}{(1-\alpha)}$ or $pK_a = pH + \log \frac{1-\alpha}{\alpha}$
or $pK_a - pH = \log \frac{1-\alpha}{\alpha}$ $\therefore \frac{1-\alpha}{\alpha} = 10^{pK_a-pH}$
or $\frac{1}{\alpha} = 10^{pK_a-pH} + 1$ or $\alpha = \frac{1}{[1+10^{pK_a-pH}]}$



66.
$$HS^- + H_2O = H_2S + OH^-$$

 $\therefore [OH^-] = Ch = \sqrt{\frac{K_wC}{K_a}}$
 $\therefore [H^+] = \frac{K_w}{\sqrt{\frac{K_w.C}{K_a}}} = \sqrt{\frac{K_wK_a}{C}}$
or $pH = 1/2[pK + pK + logC]$

67. pH of 10^{-6} M HCI = 6; on dilution

$$[\text{HCI}] = \frac{10^{-6} \times 10}{100} = 10^{-7}$$

Thus new pH of HCI is not 7 because it is acid. For new solution pH:

 $[H^+] = 10^{-7} + 10^{-7} (\text{from H}_2\text{O}) = 2 \times 10^{-7}$ $\therefore \text{ pH} = 6.7$ (approximately)

68. Meq. of
$$H^+ = 10^{-3} \times 10 = 10^{-2}$$

:. Number of H⁺ ions =
$$\frac{10^{-2} \times 6.02 \times 20^{23}}{1000}$$

= 6.02 × 10¹⁸

- 69. On heating pure water the value of ionic product of water increases i.e., $K_w = 10^{-14}$ at 25°C and at 100°C $K_w = 10^{-12}$. Thus pH and pOH both becomes 6 at 100°C (pH and pOH = 7 at 25°C).
- 70. Given density of formic acid = 1.15 g/cm³
 ∴ Weight of formic acid in 1 litre solution = 1.15 × 10³ g

Thus, [HCOOH] =
$$\frac{1.15 \times 10^3}{46} = 25 \text{ N}$$

Since in case of auto ionisation

 $[HCOOH_2^+] = [HCOO^-]$ and

 $[\text{HCOO}^-][\text{HCOOH}_2^+] = 10^{-6} \implies [\text{HCOO}^-] = 10^{-3}$

Now % dissociation of HCOOH =
$$\frac{[\text{HCOO}^-] \times 100}{[\text{HCOOH}]}$$

$$=\frac{10^{-3}}{25}\times100=0.004\%.$$

71. [H⁺] after mixing = $\frac{10^{-2} \times 10 + 10^{-4} \times 990}{1000}$

$$= \frac{0.1 + 0.0990}{1000} = \frac{0.1990}{1000} = 1.99 \times 10^{-4}.$$

$$\therefore \quad pH = 4 - 0.3 = 3.7$$

- ¹ 72. At infinite weak electrolytes are 100% dissociated.
 - 73. $[H^+] = 10^{-6}$ at pH = 6 If $[H^+]$ are diluted to 10^2 times, the new $[H^+] > 10^{-7}$ as we get $[H^+]$ from water. Thus pH of solution will be in between 6 to 7 or approximately 6.95.
- 74. Initial pOH = $\frac{1}{2}$ (pK_b log C) = $\frac{1}{2}$ (4.7-log 0.1) = 2.85

Final pOH = 1 Change in pOH = Change in pH = 1.85

75. Follow text.

76. (C) [H⁺] =
$$\sqrt{K_{a1}C_1 + K_{a2}C_2} = \sqrt{5 \times 10^{-5}}$$

 $pH = \frac{5 - \log 5}{2} \approx 3 - \log 7$

2

7. Relative strengths of weak acids =
$$\sqrt{\left(\frac{K_a}{K_a}\right)^2}$$

Assume C_1 and C_2 are same (Although not given).

$$\therefore \text{ Relative strength} = \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)} = \sqrt{\left(\frac{2.1 \times 10^{-4}}{1.1 \times 10^{-5}}\right)}$$

Relative strength for HCOOH to $CH_3COOH = 4.37:1$.

78.
$$[OH^{-}] = Ca = C \sqrt{\frac{K_b}{C}}$$

= $\sqrt{K_b.C} = \sqrt{1.0 \times 10^{-12} \times 0.01} = 1.0 \times 10^{-7} M.$

79.
$$K_a = 5 \times 10^{-10}$$
 $pK_a = 10 \log 5 = 9.3$

$$pH = pK_{b} + \log\left[\frac{CN^{-}}{HCN}\right]$$

$$9 = 9.3 + \log \left[\frac{5 \times V_{ml}}{10 \times 2} \right] \quad \Rightarrow \quad -0.3 = \log \left[\frac{V_{ml}}{4} \right]$$
$$0.3 = \log \left[\frac{4}{V_{ml}} \right]$$
$$\Rightarrow \quad \frac{4}{V_{ml}} = 2 \quad \Rightarrow V_{ml} = 2 \text{ ml}$$

81.
$$pH = pK_a + \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

 $\Rightarrow 7 = 7 - \log 4 + \log \frac{[HCO_3^-]}{[H_2CO_3]}$
 $\Rightarrow \frac{[HCO_3^-]}{[H_2CO_3]} = 4$

% of Carbon in the form of HCO₃⁻⁼
$$\frac{[HCO_3^-]}{[HCO_3^-] + [H_2CO_3]} \times 100$$

$$=\frac{4}{1+4}$$
 × 100 = 80 %

Mole of NaOH is required for 1 lit solution = x82. : Mole of NaOH is required for 100 ml of solution = 0.1 xNow, $0.1x = 1 \times V \implies V = 0.1x \text{ lt} = 100x \text{ ml.}$

85.
$$pH = pK_a + \log \frac{[Ionised]}{[un \ Ionised]}$$

 $\Rightarrow 6 = 5 + \log \frac{[Ionised]}{[un \ Ionised]}$

$$\Rightarrow 1 = \log \frac{[\text{lonised}]}{[\text{un Ionised}]}$$

$$\Rightarrow \frac{[\text{Ionised}]}{[\text{un Ionised}]} = 10$$

$$\Rightarrow \frac{[\text{Ionised}]}{[\text{Ionised}] + [\text{un Ionised}]} = \left[\frac{10}{11}\right]$$

- 86. $pK_{HIn} = 5$ (a) CH₃COOH + NaOH, end point pH > 7 (b) Auillne hydrochloride + NaOH, end point pH > 7(c) NaHCO₃ + HCI, end point pH < 7(d) $Ba(OH)_2 + H_2C_2O_4$, end point pH > 7
- 88. (a) Initially pH will decrease fast, then slowly due to buffer formation and then will decrease fast as buffer action diminishes.
 - (b) For a weak electrolyte

$$K_{a} = \frac{C\alpha^{2}}{(1-\alpha)}$$

when $\alpha \ll 1$ then $\alpha = \sqrt{\frac{K_{a}}{C}}$

 $\Rightarrow \alpha$ decreases as C increases as C is tending to zero $\Rightarrow \alpha$ will be unity

(c) At 1/4th neutralisation
CH₃COOH + NaOH
$$\longrightarrow$$
 CH₃COONa + H₂O
 $\left(0.1 \times \frac{3}{4}\right)$ $\left(0.1 \times \frac{1}{4}\right)$
pH = pK_a + log $\frac{[CH_3COO^-]}{[CH_3COOH]}$ = pK_a + log $\left(\frac{1}{3}\right)$
At 3/4th neutralisation
pH = pK_a + log 3
so difference in pH = Δ (pH) = log 3 - log $\frac{1}{3}$ = 2 log 3
89. HCOOH + KOH \longrightarrow HCOOK + H₂O
milimole 20 10
10 - 10
pH = pK_a + log $\frac{[HCOO^-]}{[HCOOH]}$ = 3.74 + log $\left(\frac{10}{10}\right)$
 \Rightarrow pH = 3.74
91. (a) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.2 M 0.1 0 0 0
0.1 0 0.1 0.1
pOH = pK_b
(b) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.1 0.05 0 0.05
pOH = pK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.3 0.15
0.15 0 0.15
pOH = pK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.3 0.15
0.15 0 + pH = PK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.3 0.15
0.15 0 + pH = PK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.3 0.15
0.15 0 + pH = PK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.3 0.15
0.15 0 + pH = PK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow NH₄CI + H₂O
0.3 0.15
0.15 0 0.15
pOH = pK_b + log $\left(\frac{0.05}{0.05}\right)$ = pK_b
(c) NH₄OH + HCI \longrightarrow O(h₁ - h₂O) + H₂O
 $U = 0$ 2 1
 t_{eq} 1 - 1
 $U = 1$ - 2
 $U = 1$ -



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t_{eq}

t_{eq}

I.

I.

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97. For the buffer solution of $NH_3 \& NH_4^+$

$$pH = pK_{a} + \log \frac{[NH_{3}]}{[NH_{4}^{+}]}$$

$$\Rightarrow 8.26 = 9.26 + \log \frac{(500 \times 0.01)}{m.moles of NH_{4}^{+}}$$

$$\Rightarrow m. moles of NH_{4}^{+} = 50$$

$$\therefore moles of (NH_{4})_{2} SO_{4} required = 0.025.$$
99. $pK_{a} = 5.45$

$$pH = pK_{Hin} + \log \frac{[Base form]}{[Acid form]} \Rightarrow pH = pK_{Hin} = 5.45$$
For a Buffer solution
$$pH = pK_{a} + \log \frac{[CH_{3}COONa]}{[CH_{3}COOH]}$$

$$\Rightarrow 5.45 = 4.75 + \log \frac{[CH_{3}COONa]}{[CH_{3}COOH]}$$

$$0.7 = \log \frac{[CH_{3}COONa]}{[CH_{3}COOH]} \Rightarrow \frac{5}{1} = \frac{[CH_{3}COONa]}{[CH_{3}COOH]}$$
100. $CH_{3}COONa + HCI \longrightarrow NaCI + CH_{3}COOH$

$$t=0 \quad 20 \text{ meq.} \quad 20 \text{ meq.}$$

$$t_{eq.} - - 20 \text{ meq.}$$

$$[CH_{3}COOH] = \frac{20}{200} = 0.1 \text{ M}$$

$$pH = \frac{1}{2} [pK_{a} - \log C] = \frac{1}{2} [5 - \log 2 + 1]$$

$$= \frac{1}{2} [6 - \log 2] = 3 - \log \sqrt{2}$$
101. meq. of acid = meq of base $\Rightarrow 20 \times M = 20 \times 0.2 = 4$

$$Molarity of HA = 0.2 \text{ M}$$

$$HA + OH \longrightarrow A^{-} + H_{2}O$$

$$5 \quad 2 \qquad \text{m.mole}$$

$$\therefore pH = pK_{a} + \log \frac{[A^{-1}]}{[HA]} \Rightarrow 5.8 = pK_{a} + \log (\frac{2}{3})$$

$$\Rightarrow pK_{a} = 5.98$$

103. m. moles of HA taken = $27 \times 0.1 = 2.7$ $OH^- \longrightarrow A^- + H_0O$ HA + 2.7 t=0 1.2 1.5 _ 1.2 t_{ea} $pH = pK_a + \log \frac{[A^-]}{[HA]}$ $\Rightarrow 5 = pK_a + \log\left(\frac{1.2}{1.5}\right) = pK_a + \log\frac{4}{5}$ $\therefore pK_a = 5.1 \implies K_a = 8 \times 10^{-6}.$ 104. pOH = $pK_b + log \frac{[Salt]}{[Base]} = pK_b + log \frac{[Cation]}{[Base]}$ $[NH_{4}^{+}] = 2 \times \text{mole of}(NH_{4})_{2}SO_{4}$: $pOH = 5 + \log 2 = 5.3$ or pH = 8.7**105.** $\operatorname{NaH}_{2}\operatorname{PO}_{4} + \operatorname{H}_{3}\operatorname{PO}_{4}$; $\operatorname{NaH}_{2}\operatorname{PO}_{4} + \operatorname{NaHPO}_{4}^{-}$; $Na_{2}HPO_{4} + Na_{3}PO_{4}$. $HC_2H_3O_2 + NaOH \rightarrow C_2H_3O_2Na + H_2O$ 106.

This solution contains weak acid + its salt with strong base. and thus acts as buffer.

EXERCISE - 2 Part # I : Multiple Choice

2. (A) In 0.6 m M HCOOH solution

$$K_{a} = \frac{[H^{+}]^{2}}{C - [H^{+}]} \implies 8 \times 10^{-4} = \frac{[H^{+}]^{2}}{6 \times 10^{-4} - [H^{+}]}$$

 $\therefore [H^+] = 4 \times 10^{-4} \text{ M.}$ So solution in (A), (C) & (D) are ISOHYDRIC.

- On the basis of ostwald dilution law, number of H⁺ ions will increase but increase in volume will be more. Therefore, [H⁺] decreases, pH increases.
- Let BA be this salt BA→B⁺+A⁻
 A⁻ does not undergo hydrolysis because HA is strong acid. B⁺ undergoes hydrolysis

$$h = \sqrt{\frac{K_h}{c}}$$
 $h =$ degree of hydrolysis where



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or

 $K_{h} = Hydrolysis constant = \frac{K_{w}}{K_{b}}$.

 $h \propto \sqrt{K_h}$ greater the hydrolysis constant greater the h(degree of hydrolysis).

$$h \propto \frac{1}{\sqrt{K_b}}$$
 greater the K_b lesser the h.

Hydrolysis is endothermic, K_h increases with temperature and h also increase with temperature.

$$h \propto \sqrt{V} V =$$
 volume of salt solution hence h

increases with dilution. $K_{h} = \frac{K_{w}}{K_{h}}$

Both K_w and K_b change with temperature, hence K_h changes with temperature.

Hence, statement(**B**) is correct. h increases if K_{b} decreases, statement(**C**) correct.

It is found that as temperature increase, K_w and K_b increase but increase in K_w is greater than increase in K_b . Hence, h increases with increase in temperature. or h decrease in temperature., hence statement.

(D) is correct.

(D) is not correct from explanation of **(B)**.

6. (A) $[H^+] = 10^{-2}$ and $[OH^-] = 10^{-2}$

 $H^+ + OH^- \longrightarrow H_2O$

This leads complete neutralisation

so,
$$pH = 7 = \frac{2+12}{2}$$

(D) $[H^+] = 10^{-5} \text{ and } [OH^-] = 10^{-5}$

$$[\mathrm{H}^+] + [\mathrm{OH}^-] \longrightarrow \mathrm{H}_2\mathrm{O}$$

This leads complete neutralisation

so,
$$pH = 7 = \frac{5+9}{2}$$

- 7. Bronsted bases are proton acceptor and each Lewis base contain one or more electron pair and thus accept proton. On the other hand Bronsted acids are proton donor and may or may not be capable of accepting lone pair of electron, e.g., H₂SO₄ is Bronsted acid but not Lewis acid BF₃ is Lewis acid but not Bronsted acid. Also each cation is acid an each anion is base.
- 8. In a given mixture, the ionisation of two acids can be written as: Let α , β be degree of ionisation at same concentration.

$$\begin{array}{c} \text{CH}_{3}\text{COOH} \rightleftharpoons \text{CH}_{3}\text{COO}^{-} + \text{H}^{+} \\ 1-\alpha & \beta & \alpha+\beta - x \end{array}$$

$$C_{2}H_{5}COOH \xrightarrow{} C_{2}H_{5}COO^{-} + H^{+}$$
$$\frac{1-\beta}{\beta} \qquad \alpha+\beta-x$$
$$\therefore \quad K_{A,A} = \frac{[\alpha][\alpha+\beta-x].c}{[1-\alpha]} \qquad K_{P,A} = \frac{[\beta][\alpha+\beta-x].c}{[1-\beta]}$$

(where 'x' is equivalents of NaOH droped).

$$\therefore \quad \frac{K_{AA}}{K_{PA}} = \frac{\alpha}{1-\alpha} \times \frac{1-\beta}{\beta}$$
$$\frac{\alpha}{1-\alpha} = \frac{1.75}{1.3} \times \left[\frac{\beta}{1-\beta}\right]$$

9. Let α_1 and α_2 be the degree of dissociation of two acids and α_1 , α_2 are very small when compared to unity.

$$\frac{c\alpha_1^2}{1-\alpha_1} = K_{a_1} \qquad \frac{c\alpha_2^2}{1-\alpha_2} = K_{a_2}$$

$$\sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\alpha_1}{\alpha_2} = \text{relative strength.}$$

Hence choices (A) and (C) are correct while (B) and (D) are incorrect.

- (A) A buffer solution is a solution which contains weak acid and its conjugate base. it is acidic buffer.
 - (B) Basic buffer contains weak base and its conjugate acid.
 - (C) is wrong because it does not show change in pH on adding small amount of acid or base.
 - (D) is wrong; all the above statements are not correct.

16.
$$[A^{2-}] = K_{a_2} = 10^{-5}$$

$$\begin{split} pH &= 1 & pH = 3 \\ [H^+]_1 &= 10^{-1} & [H^+]_2 &= 10^{-3} \\ \hline \frac{[H^+]_1}{[H^+]_2} &= 100 \\ pH &= \frac{1}{2} (pK_w + pK_a - pK_b) \end{split}$$

pH is independent of dilution with in a limit since no concentration term in pH expression.

17. (B) is correct because $pH = pK_a + log \frac{[Salt]}{[Base]}$ for acidic

buffer.

If [Salt] increases, pH of acidic buffer will increase.

$$pOH = pK_b + log \frac{[Salt]}{[Acid]}$$
 for basic buffer.



Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141 If [Salt] increases, pOH will increase, pH will decrease as ¹ 25. $K_{sp} = 1.1 \times 10^{-11} = (1.4 \times 10^{-4})^{x+y} x^{x} \cdot y^{y}$ pH = 14 - pOH.

Therefore (C) is correct but (D) is wrong.

(A) is not correct
$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

If [Salt] increase, pH will increase.

19. (A) is buffer because it contains weak acid and its salt and they will also show common ion effect. (B) is also a buffer because it contains a weak acid and its salt. They will not show common ion effect. (C) is not buffer solution because they contains strong acids and its salt. They will not show common ion effect.

(D) is not a buffer solution because it contains strong acids and its salt. They will not show common ion effect.

20. (A)
$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$$

moles 1.5 1
 $0.5 - 1$
so it is a buffer solution.
(B) $H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$
moles 1.5 2
 $- 0.5 1.5$
 $HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$
moles 1.5 0.5
 $- - 0.5$
so it is a buffer solution.
(C) $NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$
moles 5 4
 $1 - 4$
so it is a buffer solution.

21. HIn \longrightarrow H⁺ + In⁻

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \implies \frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]} = \frac{10^{-9}}{10^{-9.6}} = 10^{0.6} = 4$$

$$\therefore \% \text{ of } [In^-] \text{ in solution} = \frac{4}{5} \times 100 = 80\%$$

so pink colour will be visible.

23.
$$CH_{3}COO^{-} + H_{2}O \implies CH_{3}COOH + OH^{-}.$$

 $0.1 (1-h)$ $0.1 h$ $0.1 h$.
 $K_{h} = \frac{(0.1 h)(0.1h)}{0.1(1-h)} = 0.1 h^{2} \implies 5.6 \times 10^{-10} = 0.1 h^{2}$
 $\implies h = 7.48 \times 10^{-5} \qquad [\therefore h <<<<1]$
 $[OH^{-}] = ch = 7.48 \times 10^{-5} \times 10^{-1} = 7.48 \times 10^{-6}.$
 $[H^{+}] = \frac{K_{w}}{[OH^{-}]} = \frac{10^{-14}}{7.48 \times 10^{-6}} = 1.33 \times 10^{-9}.$

pH = 8.8 approx.

so we have x + y = 3 (by comparing values)

so,
$$x^{x} \cdot y^{y} = \frac{1.1 \times 10^{-11}}{1.4 \times 1.4 \times 1.4 \times 10^{-12}} = \frac{110}{1.96 \times 1.4} = 4$$

Hence $x = 1, y = 2$ or $y = 1, x = 2$

26. It is factual.

27. $pH = pK_a + log \frac{[Salt]}{[Acid]}$

28. The salt hydrolysis in each case occurs execpt NaW because its. pH = 7. Thus HW is strongest acid.

29. pOH = pK_b + log
$$\frac{[Salt]}{[Base]}$$
 = 4 + log $\frac{0.2}{0.1}$
∴ pOH = 4 + log 2 and pH = 10 - log 2

30. $C_6H_5NH_3^+$ CI⁻; $C_6H_5NH_3^+$ + H_2O \subset $C_6H_5NH_3OH$ + H^+

Thus y is $C_{4}H_{5}NH_{3}^{+}$ and x is acidic.

32. Aspirin a weak acid is unionised in acid medium due to common ion effect and completely ionised in alkaline medium.

33.
$$CO_2(aq) + H_2O(aq) \implies HCO_3^-(aq) + H^+(aq).$$

34. $pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$

Let a mol litre⁻¹ be concentration of salt, then concentration of acid = (0.29 - a).

$$4.4 = -\log 1.8 \times 10^{-5} + \log \frac{a}{(0.29 - a)}.$$

- \therefore a=0.09. [Salt] = 0.09 M[Acid] = 0.29 - 0.09 = 0.20 M.
- **35.** For neutralisation : Total Meq. of acid = Meq. of base = $26.6 \times 0.1 = 2.66$. Now for partial neutralisation of acid.

HA+BOH ---- \rightarrow BA+H₂O Meq. before reaction 2.66 1.2 0 0 Meq. after reaction 1.46 0 1.2 1.2 The resultant mixture acts as a buffer and [HA] and [BA] may be placed in terms of Meq. sincen volume of mixture is constant.

pH =
$$-\log K_a + \log \frac{[Salt]}{[Acid]}$$
 or $5 = -\log K_a + \log \frac{1.2}{1.46}$
 $K_a = 8.22 \times 10^{-6}$.



K_{sp}

[C1⁻]

 $AgBr \longrightarrow Ag^+ + Br^-$

 $\begin{array}{cc} y & y \\ (x+y) & y \end{array}$

+ CI-

х

(x+y) y

=11.25

x = 11.25

36. NH₁ + HCl in 2: 1 will give NH₁ + NH₂Cl in 1: 1 ratio.
37. pH = − log K₁ + log
$$\frac{|Sal|}{|Acid|}$$
 = − log 10⁺⁺ log $\frac{1}{1}$ = 4
 $|Since K_1 \times K_{\infty} = 10^{-10}$ Given K₁ = 10⁺⁰ ∴ K₁ = 10⁻¹
38. Meq. of acetic acid = 50 × 2 − 100
Meq. of CH₂CONA = 10.0 × 1 = 10
pH = − log K₁ + log $\frac{|Sal|}{|Acid|}$ or pH = − log
10⁻² + log $\frac{10}{100}$ = 4
39. (a) NaF → Na⁺ + F
0.1 0.1 0.1 0.1
Cal² → Ca⁺ + 22⁺
(2x + 01) ≈ 0.1
Cal² → Ca⁺ + 22⁺
(2x + 01) ≈ 0.1
Cal² → Ca⁺ + 22⁺
(2x + 01) ≈ 0.1
Cal² → Ca⁺ + 22⁺
(2x + 01) ≈ 0.1
K₂ = 4x²(0.01)
K₂ = 4x²(0.01)
K₃ = 4x²(0.01)
K₄ = 4x²(0.01)
K₅ = 4x²(0.01)
K₆ = 4x²(0.01)
K₆ = 4x²(0.01)
K₆ = 4x²(0.01)
K₇ = 4x²(0.01)
K₆ = 4x²(0.01)
K₇ = 4x²(0.01)
K₆ = 4x²(0.01)
K₇ = 4x²(0.01)
K₈ = 4x²(0.01)
K₉ = 10.201
K₉ (AgCD) = 5x² = 10.201
(x + y) x
(x + y

54.
$$Ca(OH)_{2} \Longrightarrow Ca^{2+} + 2OH^{-}$$

 $t=0$ $\frac{1.48}{74} = 0.02$ 0 0
 t_{eq} 0 0.02 0.04
so, $pOH=2-\log 4 = 1.4$
so $pH=12.6$
56. Cd^{2+} + $H_{2}S \longrightarrow CdS \downarrow$ + $2H^{+}$
m.moles 0.1 0.2
Total m.moles of H⁺ in solution after the reaction
 $=0.2+0.8=1$
 $\therefore [H^{+}] = \frac{1}{100} = 0.01 \text{ M} \implies pH=2.$
57. $CaF_{2}(s) \Longrightarrow Ca^{2+} + 2F^{-}$
 $s 2s$
 $4s^{3}=K_{sp}=4 \times 10^{-11} \implies s=2.15 \times 10^{-4} \text{ M}$
So, amount of F⁻ in 20000 lt of water = 2s × 20000 = 8.6 mol.

- 58. For different salts such as AB, AB₂, AB₃,etc. $K_{sp} = s^2, 4s^3, 27s^4$ respectively. If K_{sp} is same for different salts, then s is more for the salt in which more number of ions.
- **59.** Let S is the solubility of BaF_2 in a solution of $BaNO_3$

Then $K_{SP} = [Ba^{2+}][F^{-}]^2$. Then $[F^{-}] = 2S;$

- Then $\frac{1}{2}[F^-] = S$
- 60. Find solubility for each separately by $S^2 = K_{sp}$ for MnS and ZnS. 108S⁵ = K_{sp} for Bi₂S₃ and 4S³ = K_{sp} for Ag₂S.

61.
$$CaCO_3 \implies Ca^{+2} + CO_3^{-2}$$

 $x \quad x$
 $(x+y) \quad x$
 $CaC_2O_4 \implies Ca^{+2} + C_2O_4^{-2}$
 $y \quad y$
 $(x+y) \quad y$
 $\frac{K_{SP}(CaCO_3)}{K_{SP}(CaC_2O_4)} = \frac{x}{y} = 3 \implies x = 3y$
 $(x+y) = 8 \times 10^{-5}$
 $(3y+y) = 8 \times 10^{-5} \implies y = 2 \times 10^{-5} \quad x = 6 \times 10^{-5}$
 $K_{SP}(CaCO_3) = [Ca^{+2}][CO_3^{-2}]$
 $= 8 \times 10^{-5} \times 6 \times 10^{-5}$
 $= 48 \times 10^{-10}$
 $K_{SP}(CaCO_3) = 4.8 \times 10^{-9}$

62. For AgCI precipitation

$$[Ag^{+}] = \frac{K_{SP}AgCI}{[CI^{-}]} = \frac{10^{-10}}{0.05} = 2 \times 10$$

For AgI precipitation

$$[Ag^{+}] = \frac{K_{SP}AgI}{[I]} = \frac{4 \times 10^{-16}}{0.05} = 8 \times 10^{-12}$$

Thus AgI will precipitate first. AgCI will precipitate only when,

$$[Ag^+] = 2 \times 10^{-9};$$
 Thus

$$[I^{-}]_{\text{Left}} = \frac{4 \times 10^{-16}}{2 \times 10^{-9}} = 2 \times 10^{-7} \,\text{M}$$

- 63. Solubility of Al(OH), is lesser than Zn(OH).
- 64. Presence of common ion decreases the solubility of salt.

65. For precipitation of Ag₂CO₃.

$$[CO_3^{2-}] = \frac{K_{SP}}{[Ag^+]^2} = \frac{6.9 \times 10^{-12}}{[10^{-5}]^2} = 6.9 \times 10^{-2}$$

and for precipitation of BaCO₃.

$$[CO_3^{2-}] = \frac{K_{SP}}{[Ba^{2+}]} = \frac{8.1 \times 10^{-9}}{10^{-4}} = 8.1 \times 10^{-5}$$

66.
$$K_{sp}$$
 of $PbCI_2 = 4s^3 = 4 \times (0.01)^3 = 4 \times 10^{-6}$
In NaCI solution for $PbCI_2$; $K_{sp} = [Pb^{2+}] [CI^{-}]^2$
or $4 \times 10^{-6} = [Pb^{2+}] [0.1]^2$ \therefore $[Pb^{2+}] = 4 \times 10^{-4} M$

67. Solubility of BaSO₄ =
$$\sqrt{K_{SP}}$$
 = $\sqrt{1.1 \times 10^{-10}}$
= 1.05 × 10⁻⁵ M

:. wt. of BaSO₄ =
$$1.05 \times 10^{-5} \times 233 = 244.37 \times 10^{-5} \text{ g/litre.}$$

 \therefore Volume of water needed to dissolve 1g BaSO₄ is equal to

$$\frac{1}{244.37 \times 10^{-5}} = 410$$
 litre

- **68.** $K_{sp} = 4 \times 10^{-12} = [M^+] [OH^-]^x = [10^{-4}] [x.10^{-4}]^x = x^x \cdot (10^{-4})^{1+x}$
 - \therefore Thus shows that x = 2

69.
$$K_{sp}$$
 of Ca(OH)₂ = 4s³ = 5.5 × 10⁻⁶

$$\therefore \quad s = 3\sqrt{\frac{5.5 \times 10^{-6}}{4}} = 1.11 \times 10^{-2}$$

- :. $[OH^{-}] = 2s = 2 \times 1.11 \times 10^{-2}$
- ∴ pOH=1.65 ∴ pH=12.35



70. $[Mg^{2+}][OH^{-}]^2 = 1 \times 10^{-12};$

:.
$$[OH^{-}] = \sqrt{\frac{10^{-12}}{0.01}} = 10^{-5}$$

or pOH = 5. and thus pH = 9.

- 71. The K_{sp} values are in the order : AgCl > AgBr > AgI.
- 72. $A_{3}B_{2} = 3A^{2+} + 2B^{3+}$ $K_{sp} = [A^{2+}]^{3}[B^{3+}]^{2}$. $K_{sp} = (3s)^{3}(2s)^{2} = 108s^{2}$
- **73.** $K_{sp} = [M^+]$ [anion]; $[M^+]$ required to precipitate MA is less and MA precipitate first.

74. AgCI \longrightarrow Ag⁺ + CI⁻; AgBr \longrightarrow Ag⁺ + Br⁻ x x y y In simultaneous solubility solution contains [Ag⁺]=[CI⁻]+[Br⁻]

75. Solubility of M(OH)₃ =
$$\sqrt[4]{\frac{K_{SP}}{27}} = \sqrt[4]{\frac{10^{-35}}{27}} = 7.8 \times 10^{-10}$$

Solubility of M (OH)₂ =
$$\sqrt[3]{\frac{K_{SP}}{4}} = 6.3 \times 10^{-1}$$

Solubility of MOH = $\sqrt{K_{SP}} = 10^{-14}$

76.	$MgCl_2$ +	2NaOH	\rightarrow Mg(OH) ₂	+ 2NaCl
mm before	e 10	20	0	0
reaction	0	0	10	20

Thus, 10 m mole of Mg(OH), are formed. The product

of
$$[Mg^{2+}][OH^{-}]^2$$
 is therefore $\left[\frac{10}{200}\right] \times \left[\frac{20}{200}\right]^2$

= 5 ×10⁻⁴ which is more than K_{sp} of Mg(OH)₂. Now solubility(s) of Mg(OH)₂ can be derived by

$$K_{sp} = 4s^{3}$$

: $s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.2 \times 10^{-11}}{4}} = 1.4 \times 10^{-4} M$

:. $[OH^{-}] = 2s = 2.88 \times 10^{-4} M$

Part # II : Assertion & Reason

1. Due to very strong extent of hydration of H^+ ion.

I.

- 3. Since K_a of HCN is less than that of HF, so CN⁻ is stronger base than F⁻
- 6. NH₃ acts as weak base in aqueous solution. HCl acts as strong acid in aqueous solution.
- 7. Due to common ion effect, [H⁺] increases therefore ionization of HCOOH decreased.
- 8. At 25°C, pH of any acidic solution can not be 7.
- 9. HA + OH⁻ \longrightarrow A⁻ + H₂O

At the half equivalent point, $[HA] = [A^{-}] \Rightarrow pH = pK_a$

10. Due to complex formation solubility of sparingly soluble salt increases.

1. (A) $[H^+]$ in HCl solution = 10^{-5} M

[H⁺] in H₂S solution = $\sqrt{K_a \times C} = 10^{-4} \text{ M}$

- so $[H^+]$ in HCl solution < $[H^+]$ in H₂S solution
- & $[OH^-]$ in HCl solution > $[OH^-]$ in H₂S solution

& degree of dissociation of water in HCl solution > degree of dissociation of water in H_2S solution

pH of HCl solution > pH of H₂S solution.

- (B) At pH = 4.74 in CH₃COOH solution, $[CH_3COO^-]$ =[CH₃COOH]
- \therefore degree of dissociation of CH₃COOH = $\frac{1}{2}$

At pH = 9.26 i.e. pOH = 4.74 in NH₄OH solution, [NH₄⁺] = [NH₄OH]

:. degree of dissociation of $CH_3COOH = degree$ of dissociation of NH_4OH

degree of dissociation of water in CH_3COOH solution > degree of dissociation of water in NH_4OH solution.

(C) [H⁺] in CH₃COOH solution = $\sqrt{1.8 \times 10^{-5} \times 0.1}$

 $= \sqrt{1.8} \times 10^{-3} \,\mathrm{M}$

[H⁺] in HCOOH solution = $\sqrt{1.8 \times 10^{-4} \times 1}$

$$=\sqrt{1.8} \times 10^{-2} \,\mathrm{M}$$

so, degree of dissociation of $CH_3COOH =$ degree dissociation of HCOOH.



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(b) [H'] in HA, solution =
$$\sqrt{10^{-5} \times 0.1} = 10^{-3} M$$

(H'] in HA, solution = $\sqrt{10^{-5} \times 0.01} = 10^{-4} M$
so [OH] in solution of HA, <[OH] in solution of HA,
pH in solution of HA, <[OH] in solution of HA,
degree of dissociation of water HA,
 2 degree of dissociation for model PK,
 3 degree dissociation for model PK,
 3 degreed for hydrolysis of C

$$[NH_4^+] = \frac{a \times 2}{500}$$
; Let a millimole of $(NH_4)_2 SO_4$ are added.

Comprehension # 3 :
1. For SrF₂ in pure water

$$4s_1^{3} = K_{sp}$$

For SrF₂ in 0.1 M NaF solution
 $s_2(0.1)^2 = K_{sp}$
 $\Rightarrow 4s_1^3 = s_1 \times \frac{256}{10^6} (0.01)$
 $\Rightarrow 4s_1^3 = s_1 \times \frac{256}{10^6} (0.01)$
 $\Rightarrow s_1 = 8 \times 10^{-4} M$
 $\therefore K_{sp} = 4s_1^3 = 2.048 \times 10^{-9}$
2. $[Sr^{2s}] = 0.0011 = 11 \times 10^{-4} M$
 $[Sr^{2s}]_{i}^{-} = 2 \times 10^{-4} M$
 $\therefore [Sr^{2s}]_{i}^{-} = 2 \times 10^{-4} M$
 $\therefore [Fi]_{i}^{-} = 3.2 \times 10^{-3} M$
 $\therefore Total [F-] needed for 100 ml solution = $\frac{5 \times 10^{-3} \times 42}{10} = 0.021 \text{ g}$
3. SrF₂ \longrightarrow Sr²⁺ + 2F⁻
 s 2s
F⁻ will react with H⁺ to produce HF
F⁻ + H⁺ \implies HF
 $K = \frac{1}{K_a} = \frac{[HF]}{[H^+][F^-]} = \frac{7}{10^{-5}}$
 $\therefore [HF] = 7 \times 10^5 [F^-][H^+]$ ($\Theta [H^+] = 10^{-5}; pH=5$)
 $= 7 \times 10^5 [F^-] \times 10^{-5} = 7 [F^-]$
Here, $[F^-] + [HF] = 2s$
 $\therefore [F^-] = \frac{8}{4}$
 $K_{sp} = s (\frac{8}{4})^2 = 2.048 \times 10^{-9}$
 $\therefore s = 3.2 \times 10^{-3} mol/L$
Comprehension # 4 :
1. Suppose volume of HCO₃⁻ = V mL
millimoles of HCO₃⁻ = 5V
millimoles of HCO₃⁻ = 5V mL$

I. 3. If CO_2 escapes, $[H^+]$ decreases, hence pH increases.

Comprehension # 5 :

- 1. Phosphoric acid with three ionisable hydrogens ions is a tribasic acid. H-atoms are attached to O-atoms,
- 2. If first step is only taken

$$pH = \frac{1}{2} [pK_{a_1} - logc] c = [H_3PO_4] = 0.05\%$$
$$= \frac{0.05 \times 10}{98} mol L^{-1} (M) = 5.1 \times 10^{-3} M$$
$$-log c = 2.3, pK_{a_1} = 2.12 pH = 2.21$$

3. $\frac{[\mathrm{H}^+]^3[\mathrm{PO}_4^{3-}]}{[\mathrm{H}_3\mathrm{PO}_4]} = \mathrm{K}_{\mathrm{a}_1}\mathrm{K}_{\mathrm{a}_2}\mathrm{K}_{\mathrm{a}_3}$ $3\log[H^+] + \log[PO_4^{3-}]$

 $= \log K_{a_1} + \log K_{a_2} + \log K_{a_3} - \log [H_3 PO_4]$

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

$$Zn_{3}(PO_{4})_{2} \stackrel{*}{\ddagger} \stackrel{\wedge}{\uparrow} 3Zn^{2+} + 2PO_{4}^{3-}$$

$$K_{sp} = [Zn^{2+}]^{3} [PO_{4}^{-3-}]^{2}$$

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

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

	EXERCISE - 4					
Subjective Type						
1.		HCI	H_2SO_4	NaOH		
	mili mole	20	40	$\frac{2}{40} \times 1000 = 50$		
	milieq. remair	20 1 milieq. o	80 of Acid = 50	50		
	$[H^+] = \frac{50 \times 10^{-3}}{5} = 10^{-2} \text{ M} \implies pH_1 = 2$ Now Total milieq. of Acid = $(50 + 10 \times 2) = 70$					
	milieq. of NaOH = $\frac{4 \times 10^3}{40} = 100$					
	As milieq of Base is greater than milieq. of Acid resulting solution is Basic Remaining milieq. of Base = 30					
	$[OH^{-}] = \frac{30}{2}$	$\frac{0 \times 10^3}{5} =$	$= 6 \times 10^{-3} \mathrm{M}$			



I. $pOH = 3 - \log 6 = 2.22 \implies pH_2 = 11.78$ So change in pH = 11.78 - 2 = 9.78**3.** (i) $CH_3COOH = 0.2 M$ $[{\rm H}^{\scriptscriptstyle +}] = \sqrt{{\rm K}_{\rm a} \times {\rm C}} \quad = \sqrt{2 \times 10^{-5} \times 0.2} = \sqrt{4 \times 10^{-6}}$ $= 2 \times 10^{-3}$ $pH = 3 - \log 2 = 2.7$ 7. $C \alpha = [H^+] \implies \alpha = \frac{2 \times 10^{-3}}{2 \times 10^{-1}} \implies \alpha = 0.01$ (ii) HCI \longrightarrow H⁺ + CI⁻ 0.1 0.1 0.1 $[H^+] = 0.1$ pH = 1 $CH_3COOH \Longrightarrow CH_3COO^- +$ H^+ Ō 0.2 0.1 $0.2(1-\alpha)$ 0.2 α $0.1 + 0.2 \alpha = 0.1$ $K_{a} = \frac{0.2\alpha \times 0.1}{0.2} = 2 \times 10^{-5} \qquad \alpha = 2 \times 10^{-4}$ (iii) $[CH_3COO^-] = 0.2 \times 2 \times 10^{-4} = 4 \times 10^{-5}$ (iv) % change in $\alpha = \frac{1 \times 10^{-2} - 2 \times 10^{-4}}{1 \times 10^{-2}} \times 100$ $= \left[1 - \frac{2}{100}\right] \times 100 = 98 \%$ 5. pH = 6 $[H^+] = 10^{-6}$ $N_1V_1 = N_1V_2$ $\Rightarrow 10^{-6} \times 1 = N_2 \left[1 + \frac{7}{3} \right] \qquad \Rightarrow 10^{-6} = N_2 \times \frac{10}{3}$ $N_2 = \frac{3}{10} \times 10^{-6} \qquad \Rightarrow N_2 = 3 \times 10^{-7}$ $[H^+] < 10^{-6}$ So [H⁺] of water is also added. as common ion effect on H₂O is neglected so $[H^+] = 3 \times 10^{-7} + 10^{-7} = 4 \times 10^{-7} M$ \Rightarrow pH = 7 - log 4 = 7 - 0.60 = 6.4 6. $HA + NaOH \rightarrow NaA + H_2O;$ or $HA + OH^- \rightarrow A^- + H_2O$ $K_{eq} = 10^9 = \frac{[A^-][H_2O]}{[HA][OH^-]}$ Also HA \longrightarrow H⁺+A⁻ $K_a = \frac{[H^+][A^-]}{[HA]}$:. $\frac{K_{eq}}{K_{eq}} = \frac{1}{K_{uv}}$ or $K_a = 10^9 \times 10^{-14} = 10^{-5}$ Thus for

$$A^{-} + H_{2}O \rightleftharpoons HA + OH$$

$$[OH] = Ch = C \sqrt{\frac{K_{H}}{C}} = \sqrt{\frac{K_{w}C}{K_{a}}} = \sqrt{\frac{10^{-14} \times 0.1}{10^{-5}}} = 10^{5}M$$

$$\therefore [H^{+}] = 10^{-} \text{ and } pH = 9$$

$$Asc^{-} + H_{2}O \rightleftharpoons HAsc + OH^{-}$$

$$\therefore [OH^{-}] = C.h = C \sqrt{\frac{K_{h}}{C}} = \sqrt{K_{h}.C} = \sqrt{\frac{K_{w}}{K_{a}}.C}$$

$$= \sqrt{\frac{10^{-14} \times 0.02}{5 \times 10^{-5}}} = 2 \times 10^{-6}$$

$$\therefore [H^{+}] = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9}M$$

$$Also \quad h = \sqrt{\left[\frac{K_{h}}{C}\right]} = \sqrt{\frac{K_{w}}{K_{a} \times C}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-5} \times 0.02}}$$

$$= 10^{-4} \text{ or } 0.01 \%$$

$$HA \quad + H_{2}O \quad \Longrightarrow \quad H_{3}^{+}O \quad + A^{-}$$

$$K_{a} = \frac{[H_{3}O^{+}][A^{-}]}{[HA]} = \frac{C^{2}\alpha^{2}}{C(1-\alpha)}$$
with in an error of 10% C(1-\alpha) or C - C\alpha = 0.90 C. or C - C\alpha = 0.90 C.

- $K_a = \frac{(0.10C)^2}{0.90C} = \frac{C}{90}$ or $C = 90 K_a$.
- 10. Let a mole of $Ca(OH)_2$ be dissoved in 250 mL solution to have pH = 10.65.

$$[Ca(OH)_2] = \frac{a \times 1000}{250} = 4a M$$

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH$$

Complete ionization

0

 $2 \times 4a M$

Initial moles 4a = 0Final moles 0 = 4a $\therefore [OH^{-}] = 8a M$

$$10^{-14}$$

$$[H^+] = \frac{10}{8a} \implies pH = -\log[H^+]$$

∴
$$10.65 = -\log \frac{10^{-14}}{8a} \implies \frac{10^{-14}}{8a} = 2.238 \times 10^{-11}.$$

∴ $a = 5.58 \times 10^{-5}$ mole.



11.
$$K_a = \frac{C\alpha^2}{1-\alpha}$$

 $40 \alpha^2 + \alpha - 1 = 0$
 $\alpha = 0.146$
 $[H^+] = C\alpha = 1.75 \times 10^{-3} M$
 $pH = 2.76$

12.
$$(CH_3)_2NH_2 + H_2O \longrightarrow (CH_3)_2NH_3^+ + OH^-$$

base acid

$$K_{b} = \frac{[(CH_{3})_{2}NH_{3}^{+}][OH^{-}]}{[(CH_{3})_{2}NH_{2}]} = \frac{c\alpha.c\alpha}{c(1-\alpha)} = \frac{c\alpha^{2}}{(1-\alpha)}$$

5.4 × 10⁻⁴ = 0.02 × α².
∴ α=0.164.

Since
$$\alpha > 0.1$$
, we will use $K_b = \frac{c\alpha^2}{(1-\alpha)}$ or

$$5.4 \times 10^{-4} = \frac{0.02 \times \alpha^2}{(1-\alpha)}$$

Now $\alpha = 0.151$

In presence of NaOH, the dissociation of diethylamine will decrease due to common ion effect. Thus $0.1 + ca = 0.1 + c\alpha \approx \text{ and } 0.1 \& (1-\alpha) \approx 1$

Thus
$$K_b = 5.4 \times 10^{-4} = \frac{c\alpha \times (0.1 + c\alpha)}{c(1 - \alpha)} = \alpha \times 0.1.$$

or $\alpha = 5.4 \times 10^{-3} = 0.0054.$

13. CH₃COOH
$$\rightleftharpoons$$
 CH₃COO⁻ + H⁺
1 0 0
 $1-\alpha$ α α
(pK_a = -logK_a = 4.74, \therefore K_a = 1.82 × 10⁻⁵)

$$K_{a} = \frac{c\alpha^{2}}{(1-\alpha)} = c\alpha^{2} \qquad (1-\alpha \approx 1).$$

$$\therefore \quad \alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = 0.019 \text{ or } 1.9\%.$$

Always calculate a first by $K_b = c\alpha^2$, if $\alpha > 10\%$ then use again.

$$K = \frac{c\alpha^2}{(1-\alpha)}$$

(a) If H⁺ are already present (due to HCl)

CH₃COOH
$$\rightleftharpoons$$
 CH₃COO⁻ + H⁺
1 0 0.01
c(1- α) c α [0.01 + c α].

$$\mathrm{K}_{\mathrm{b}} = \frac{[\mathrm{CH}_{3}\mathrm{COO}^{-}][\mathrm{H}^{+}]}{[\mathrm{CH}_{3}\mathrm{COOH}]} = \frac{\mathrm{c}\alpha \times (0.01 + \mathrm{c}\alpha)}{\mathrm{c}(1 - \alpha)}$$

Since prsence of H^+ will favour the reverse reaction or α will decrease.

i.e.,
$$0.01 + c\alpha = 0.01$$
 and $1 - \alpha = 1$

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(due to common ion effect).

∴
$$1.82 \times 10^{-5} = \frac{0.05 \times \alpha \times 0.01}{0.05}$$

∴ $\alpha = 1.82 \times 10^{-3} = 0.0018.$
(b) Similarly solve for 0.1 M HCl
 $\alpha = 0.00018.$

14.
$$C_6H_5OH + C_5H_5N \rightleftharpoons C_6H_5O^- + C_5H_5NH^+$$

$$K_n = \frac{K_a K_b}{K_w} = 2.34 \times 10^{-5}$$

 K_n being small and thus neutralisation does not proceed very far towards completion.

15.HCOONa+ HClHCOOH + NaClInitially mM6.250.2500Finally mM600.250.25

:.
$$pH = 3.75 + \log \frac{6}{0.25} = 3.75 + \log 24 = 5.13$$

Also [HCOOH] =
$$\frac{0.25}{60} = 4.17 \times 10^{-3} \,\mathrm{M}$$

5. HA
$$\longrightarrow$$
 H⁺ + A⁻
t=0 0.2 0.1
t_{eq.} 0.2-x x 0.1+x

$$\mathbf{K}_{a} = \frac{[\mathbf{H}^{+}][\mathbf{A}^{-}]}{[\mathbf{H}\mathbf{A}]} = \frac{\mathbf{x}(0.1 + \mathbf{x})}{(0.2 - \mathbf{x})}$$

$$\Rightarrow 0.05 = \frac{x^2 + 0.1x}{0.2 - x}$$

$$\Rightarrow 0.01 - 0.05 x = x^2 + 0.1 x$$

$$x^2 + 0.15 x - 0.01 = 0$$

$$x = 0.05 M$$

17. Given,
$$\frac{\text{wt. of } \text{NH}_3}{\text{wt. of solution}} = \frac{10}{100}$$

$$\therefore \quad 100 \text{ g dsolution contains } 10 \text{ g } \text{NH}_3$$

$$\therefore \quad M_{\text{NH}_3} = (10 \times 1000) / [17 \times (100/0.99)]$$

$$(\therefore \text{ V} = \text{mass } / \text{ density})$$

Now $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \xrightarrow{} \text{NH}_4^+ + \text{OH}^-$
Before dissociation $1 \qquad 0 \qquad 0$
After dissociation $(1-\alpha) \qquad \alpha \qquad \alpha$



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:.
$$[OH^{-}] = C.\alpha = C \sqrt{(K_b / C)} = \sqrt{(K_b . C)}$$

[:. $C = 5.82 \text{ M} \text{ and } K_b = k_w / K_a = 10^{-14} / (5 \times 10^{-10})$
 $= 2 \times 10^{-5}$]

:.
$$[OH^{-}] = \sqrt{[2 \times 10^{-5} \times 5.82]} = 1.07 \times 10^{-2} M$$

$$\therefore [H^+] = 10^{-14}/1.07 \times 10^{-2}$$

= 0.9268 × 10⁻¹² M
$$\therefore PH = -\log [H^+] = -\log 0.9268 \times 10^{-12} = 12.0330$$

18. Dissociation of H_2S can be represented as

(a)
$$H_2S \longrightarrow H^+ + HS^-$$

(b) $HS^- \longrightarrow H^+ + S^{2-}$

From the first ionisation of $H_2S = \frac{[H^+][HS^{-1}]}{[H_2S]} = K_{a_1}$

Since H_2S is weakly ionised and its ionisation is further decreased in presence of highly ionised HCl, concentration of H⁺ in solution will be mainly due to HCl. Thus [H⁺] = 0.2 M.

Substituting the value in the above reaction

$$\frac{0.2[\text{HS}^-]}{0.1} = 1 \times 10^{-7}$$
$$[\text{HS}^-] = 5 \times 10^{-8} \text{ M}$$

From the second ionisation of H₂S,

$$\frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \text{Ka}_2 \text{ or } \frac{0.2 \times [\text{S}^{2-}]}{5 \times 10^{-8}} = 1.3 \times 10^{-13}$$
$$[\text{S}^{2-}] = 3.25 \times 10^{-20} \text{ M}$$

19. HA \rightleftharpoons H⁺ + A $c(1-\alpha)$ $c\alpha$ $c\alpha$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = pK_a + \log \frac{c\alpha}{c(1-\alpha)}$$

$$\Rightarrow pH = pK_a + \log\left(\frac{\alpha}{1-\alpha}\right) = pK_a - \log\left(\frac{1-\alpha}{\alpha}\right)$$
$$\Rightarrow \log\left(\frac{1-\alpha}{\alpha}\right) = pK_a - pH.$$

$$\Rightarrow \left(\frac{1-\alpha}{\alpha}\right) = 10^{(pK_a-pH)}$$
$$\Rightarrow \alpha = \frac{1}{1+10^{(pK_a-pH)}}$$

20. HA
$$\implies$$
 H⁺ + A⁻
 $c-x$ x x
 $[H^+]=x=1.5 \times 10^{-3} M$
 $K_a = \frac{x^2}{c-x}$
 $2.5 \times 10^{-3} = \frac{(1.5 \times 10^{-3})^2}{c-1.5 \times 10^{-3}}$.
 $c = 2.4 \times 10^{-3} M$.
21. B₂H₆ + 6H₂O \longrightarrow 2H₃BO₃ + 6H₂.
concentration H₃BO₃ = $c = 2 \times \frac{1}{27.6} \times \frac{1000}{100} = 0.725$
HA \implies H⁺ + A⁻
 $[H^+] = \sqrt{K_a c} = \sqrt{7.3 \times 10^{-10} \times 0.725} = 2.3 \times 10^{-5}$.
 $pH = -\log[H^+] = 4.64$.

22. meq. of H⁺ = 10 × 0.1 + 40 × 0.2 × 2 = 17.
[H⁺] =
$$\frac{17}{50}$$
 = 0.34.
pH = 0.47

23.
$$[H^+] = \frac{10 - 9.9}{109.9} = \frac{0.1}{109.9} = 9.1 \times 10^{-4}$$

pH = 4.0 - log 9.1 = **3.04**

24.
$$pV = nRT$$

 $n = \frac{(740 - 23.7)}{760} \times 100 \times \frac{1}{0.0821 \times 298} \times 10^{-3}$
 $= 3.85 \times 10^{-3} M$
 $[HCl] = 3.85 \times 10^{-3} M = [H^+].$
 $pH = 3 - \log 3.85 = 2.41$

25.
$$C_{6}H_{5}NH_{2} + H_{2}O \longrightarrow C_{6}H_{5}NH_{3}^{+} + OH^{-}$$

Thus, $K_{b} = \frac{[C_{6}H_{5}NH_{3}^{+}][OH^{-}]}{[C_{6}H_{5}NH_{2}]}$

$$\frac{10^{-14}}{2.4 \times 10^{-5}} = \frac{10^{-8} \times [\text{OH}^{-}]}{0.24}$$

:. $[OH^{-}] = 10^{-2} M$ 26. pH of Final Solution = 1 pH = 1

$$[H^{+}] = 10^{-1}$$
Initial $\rightarrow M = \frac{P \times d \times 10}{M.W.} = \frac{36.5 \times 10 \times 1.25}{36.5} \quad M = 12.5$

$$N_1 V_1 = N_2 V_2 \implies 12.5 \times V_1 = 10^{-1} \times 2.5$$

$$V_1 = \frac{2.5}{125} \quad V_1 = .02 \text{ lit} = 20 \text{ ml}$$



27. $H_3PO_4 \qquad \longleftarrow \qquad H_2PO_4^- + H^+$. 0.1 - xx+y+z. $K_{a1} = \frac{(x-y)(x+y+z)}{0.1-x} = \frac{x^2}{0.1-x}$ y + z are very small compared to x) $7.5 \times 10^{-3} = \frac{x^2}{0.1 - x} \implies x = 0.024 \text{ M}$ $K_{a2} = \frac{(y-z)(x+y+z)}{x-y} = \frac{y.x}{x} = y.$ $y = 6.2 \times 10$ (here z < < y) $K_{a3} = \frac{Z(X+Y+Z)}{V-Z} = \frac{Z.X}{V}.$ $z = K_{a3} \cdot \frac{y}{x} = 9.3 \times 10^{-19} M$ \therefore [H,PO] = 0.1 - x = 0.076 M $[H^+] = [H_2PO_4^-] = x = 0.024 M$ $[HPO_4^{2-}] = 6.2 \times 10^{-8} M$ $[PO_{4}^{3-}] = z = 9.3 \times 10^{-19} M$ $[OH^{-}] = \frac{K_{W}}{[H^{+}]} = 4.17 \times 10^{-13} M$ 28. HA \longrightarrow H⁺ + A⁻ Co-x x+y x $H_2O = H^+ + OH^-$ x+y y $K_a = \frac{[H^+]x}{c_0 - x}$, $[H^+]y = 10^{-14} = K_w$ Where $[H^+] = x + y$. $y = \frac{K_W}{[H^+]}, x = \frac{K_a c_0}{K_a + [H^+]}.$ $[H^{+}] = x + y = \frac{K_{W}}{[H^{+}]} + \frac{K_{a}c_{0}}{K_{a} + [H^{+}]}$ $10^{-3} = 10^{-11} + \frac{0.1 \text{ K}_{a}}{\text{K}_{a} + 10^{-3}}$ $K_{a} + 10^{-3} = 100 K_{a}$ $K_{a} = \frac{10^{-3}}{99} \approx 10^{-5} .24$

29. HCI \longrightarrow H⁺ + CI⁻ 0.01 0.01 0.01 CHCI,COOH \rightleftharpoons CHCI,COO⁻ + H⁺ 0.01 0.01 $0.01(1-\alpha)$ 0.01α $0.01 + 0.01 \alpha$ $K_{a} = \frac{0.01\alpha \ [0.01+0.01\alpha]}{0.01(1-\alpha)} = 2 \times 10^{-2}$ $0.01 \alpha^2 + 0.01 \alpha = 2 \times 10^{-2}$ $10^{-2} \alpha^2 + 10^{-2} \alpha = 2 \times 10^{-2}$ $\alpha^2 + \alpha - 2 = 0$ $\alpha = \frac{-2 \pm \sqrt{1+8}}{2} = \frac{-2+3}{2} \Rightarrow \alpha = 0.56$ $[H^+] = 10^{-2} + 10^{-2} \times 0.56 = 1.56 \times 10^{-2} M$ $[CHCl_{,}COO^{-}] = 0.01 \alpha = 5.6 \times 10^{-3} M$ **30.** pH of $(Na_2C_2O_4)$ C = 0.5×10^{-3} $pH = 7 + \frac{1}{2} pK_{a2} + \frac{1}{2} \log C$ Here $pK_{a2} = [6 - \log 5]$ $pH = 7 + \frac{1}{2} [6 - \log 5] + \frac{1}{2} [\log 5 \times 10^{-4}]$ $=7+\frac{1}{2}[6-\log 5]+\frac{1}{2}[\log 5-4]=8$ $[H^+] = 10^{-8}$ So $[OH^-] = 10^{-6} M$ 31. AlCI, C = 0.15 M (AlCI₃ is SAWB) $[\mathsf{A} \bullet (\mathrm{H}_2\mathrm{O})_6]^{3+} + \mathrm{H}_2\mathrm{O} \rightleftharpoons [\mathsf{A} \bullet (\mathrm{H}_2\mathrm{O})_5\mathrm{OH}]^{2+} + \mathrm{H}_3\mathrm{O}^+$ At t = 00 0.15 Ο At $t = t_{eq} = 0.15$ (1- α) $K_a = 1.5 \times 10^{-5}$ 0.15α 0.15 α $K_{a} = \frac{0.15\alpha \times 0.15\alpha}{0.15[1-\alpha]} = 1.5 \times 10^{-5}$ \Rightarrow 1.5 × 10⁻¹ α^2 = 1.5 × 10⁻⁵ $\Rightarrow \alpha^2 = 10^{-4}$ $\Rightarrow \alpha = 10^{-2}$ $[H_3O^+] = 0.15 \times 10^{-2} = 1.5 \times 10^{-3} M$ \Rightarrow pH = 3 - log 1.5 = 3 - 0.18 = 2.82



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32.	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
	$K_{a} = 1.1 \times 10^{-22} = \frac{[H^{+}]^{2} [S^{2-}]}{[H_{2}S]}$ $[S^{-2}] = 1.1 \times 10^{-21} M$
33.	HSac \longrightarrow H ⁺ + Sac ⁻
	$\frac{0.002 \times 10^3}{250} \qquad 10^{-2} \qquad 0$
	$\begin{array}{lll} 8\times 10^{-3} & 10^{-2} & 0 \\ 8\times 10^{-3} \left(1-\alpha\right) & 10^{-2} & 8\times 10^{-3} \alpha \end{array}$
	$K_{a} = \frac{10^{-2} [8 \times 10^{-3} \alpha]}{8 \times 10^{-3} (1 - \alpha)} = 2 \times 10^{-12} \implies \alpha = 2 \times 10^{-10}$
	$[Sac^{-}] = 8 \times 10^{-3} \times 2 \times 10^{-10} = 16 \times 10^{-13} = 1.6 \times 10^{-12} M$
34.	$\begin{array}{ccc} C_{6}H_{5}OH \ (Phenol) & \longrightarrow & Weak \ acid \ K_{a} = 1 \times 10^{-10} \\ C_{6}H_{5}OH & & \frown & C_{6}H_{5}O^{-} & + & H^{+} \\ C & 0 & 0 \\ C - C \alpha & C \alpha & C \alpha \\ K_{a} = C \alpha^{2} & = 1 \times 10^{-10} \end{array}$
	$\alpha = \sqrt{\frac{1 \times 10^{-10}}{0.05}} = \sqrt{20 \times 10^{-10}} \qquad \alpha = 4.47 \times 10^{-5}$
	$\begin{bmatrix} C_6H_5O^{-} \end{bmatrix} = 4.47 \times 10^{-5} \times 0.05 \\ \begin{bmatrix} C_6H_5ONa \end{bmatrix} = 0.01 \text{ M} \\ \end{bmatrix}$
	$\begin{array}{ccc} C_6H_5ONa & \longrightarrow & C_6H_5O- & + & Na^+\\ 0.01 & & 0.01 & & 0.01 \end{array}$
	$\begin{array}{cccc} C_{6}H_{5}OH & \longrightarrow & C_{6}H_{5}O^{-} & + & H^{+} \\ 0.05 & & 0.01 & O \\ 0.05 (1-\alpha) & & 0.01 & 0.05 \alpha \end{array}$
	$\frac{[0.05\alpha]\ 0.01}{0.05} = 1 \times 10^{-10} \alpha = 10^{-8}$
36.	$H_3PO_4 = \frac{0.98}{98} = 10^{-2}$ Mole
	$\Rightarrow [H_3 PO_4] = \frac{10^{-2}}{100} \times 10^3 = 0.1 \text{ M}$
	$pH = 5$ $[H^+] = 10^{-5}$ $H_3PO_4 \& H_2PO_4^-$
	$pH = pK_{a1} + log \frac{[H_2PO_4^-]}{[H_3PO_4]}$

 $\Rightarrow 5 = 3 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \Rightarrow 10^2 = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$ $[H_2PO_4^-] = 10^2 [H_3PO_4] \implies But [H_3PO_4^-] + [H_2PO_4^-] = 0.1$ $H_3PO_4 + 10^2 [H_3PO_4] = 0.1 \implies [1 + 10^2] [H_3PO_4] = 0.1$ $[H_3PO_4] = 10^{-3} M$ \Rightarrow [H₂PO₄⁻] = 0.1 M For $H_2PO_4^- \& HPO_4^{2-} \Rightarrow pH = pK_{a2} + log \frac{[HPO_4^{2-}]}{[H_2PO_4^1]}$ $5 = 8 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2 \text{PO}_4^{-1}]} \Rightarrow -3 = \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2 \text{PO}_4^{1}]}$ $\frac{[\text{H PO}_4^{2-}]}{[\text{H}_2 \text{ PO}_4^{1}]} = 10^{-3} \implies [\text{H PO}_4^{2-}] = 10^{-3} [\text{H}_2 \text{ PO}_2^{-}]$ $[H_2PO_4^{-}] + [HPO_4^{2-}] = 0.1 \implies [H_2PO_4^{-}] + 10^{-3} [H_2PO_4^{-}]$ =0.1 $[1+10^{-3}]$ $[H_2PO_4^{-}] = 0.1 \implies [H_2PO_4^{-}] = 0.1 M \implies$ $[HPO_4^{2-}] = 10^{-4} M$ Again $pH = pK_{a3} + \log \frac{[PO_4^{-3}]}{[HPO_4^{-2}]} \implies 5 = 12 + \log \frac{[PO_4^{-3}]}{[HPO_4^{-2}]}$ $10^{-7} = \frac{[PO_4^{-5}]}{[HPO_4^{-2}]} \implies [PO_4^{-3}] = 10^{-7} [HPO_4^{-2}]$ $[\mathrm{H} \mathrm{PO}_{4}^{-2}] + [\mathrm{PO}_{4}^{-3}] = 10^{-4} \implies [1 + 10^{-7}] [\mathrm{H} \mathrm{PO}_{4}^{-2}] = 10^{-4}$ $[PO_4^{-3}] = 10^{-7} \Longrightarrow [HPO_4^{-2}] = 10^{-11} M$ 37. (a) At eq. point No. of milieq. of Base = No. of milieq. of HCI

$$\frac{0.252 \times 1000}{\text{Molarmass}} = 0.14 \times 40$$

$$\therefore \text{ Molar mass of base} = 45$$

(b) BOH + HCI \longrightarrow BCI + H₂O
t = 0 5.6 0.14 × 20
5.6 2.8 0 0
2.8 0 2.8
Basic buffer
pH = 10.7 So pOH = 3.3
pOH = pK_b = 3.3
K_b = Anti log (-3.3) = Anti log (1-0.3) × 10⁻⁴ = 5 × 10⁻⁴



38.
$$K_b (NH_3) = 1.8 \times 10^{-5}$$

 $CH_3 COOCH_3 (aq) + 2H_2O (aq) \longrightarrow CH_3COO^{-}(aq)$
 $+ H_3O^+(aq) + CH_3OH(aq)$
 $[NH_4^+]_0 = 0.1 M, [NH_3] = 0.06 M, [CH_3COOCH_3]_0 = 0.02 M$
 $pOH = pK_b + log \frac{[NH_4^+]}{[NH_3]} = 4.74 + log \left(\frac{0.1}{0.06}\right)$
 $(pOH)_{initial} = 4.74 + 0.22 = 4.96 \qquad (pH)_{initial} = 9.04$
 $NH_3 (aq) + H^+ (aq) \longrightarrow NH_4^+ (aq)$
 $0.06 \quad 0.02 \qquad 0.1 \qquad mole$
 $0.04 \qquad - \qquad 0.12 \qquad mole$
 $(pOH)_{final} = 4.74 + log \frac{0.12}{0.04} = 4.74 + log \left(\frac{0.12}{0.04}\right)$
 $= 4.74 + log 3 = 4.74 + 0.48 = 5.22$
 $\therefore (pH)_{final} = 8.78$
 $\Delta pH = 9.04 - 8.78 = 0.26$
Yes this is satisfactory buffer.

40. Let V mL of NH₄OH be mixed with NH₄Cl to have a buffer of pH 8.65.

The total volume after mixing becomes (V+30) mL. m mole of NH₄OH = $0.3 \times V$

$$\therefore [\mathrm{NH}_4\mathrm{OH}] = \frac{0.3 \times \mathrm{V}}{(\mathrm{V} + 30)}$$

m mole of $NH_4Cl = 0.2 \times 30$

$$\therefore [NH_4Cl] = \frac{0.2 \times 30}{(V+30)}$$

Also pOH of buffer mixture is given by :

$$pOH = pK_{b} + log \frac{[Salt]}{[Base]}$$

$$14-8.65=4.74+\log \frac{(0.2\times30)/(V+30)}{(0.3\times V)/(V+30)}$$
 (pOH=14-pH).

or

$$0.6 = \log \frac{6}{0.3 \mathrm{V}}.$$

 $\therefore V = 5 \text{ mL.}$ Similarly calculate

$$\left(14 - 10 = 4.74 + \log \frac{0.2 \times 30 / (V_1 + 30)}{0.3 \times V_1 / (V_1 + 30)}\right) \text{ for pH} = 10;$$

V=111.11 mL.

41. Initial pH of solution when,

$$[NH_{3}] = \frac{0.1}{1} \text{ and } [NH_{4}CI] = \frac{0.1}{1}$$
$$pOH = -\log 1.8 \times 10^{-5} + \log \frac{[Salt]}{[Base]}$$
$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.74$$
$$\therefore \quad pH = 9.26$$

(i) Now 0.02 mole of HCI are added then

 $\begin{array}{ccc} HCI + NH_4OH \longrightarrow NH_4CI + H_2O\\ Mole before & 0.02 & 0.1 & 0.1\\ reaction\\ Mole after & 0 & 0.08 & (0.1+0.02)\\ reaction & & & \end{array}$

 \therefore Volume = 1 litre

 $[NH_4OH] = \frac{0.08}{1}$

$$[NH_4CI] = \frac{0.12}{1}$$

$$pOH_1 = -\log 1.8 \times 10^{-5} + \log \frac{0.12}{0.08} = 4.92$$

and

.. $pH_1 = 9.08$ Change in $pH = pH - pH_1 = 9.26 - 9.08 = +0.18$ Change in pH = 0.18 and pH decreases

(ii) Now 0.02 mole of NaOH are added

	NaOH	+ NH₄CI —	\rightarrow NaCI +	NH₄OH
Mole before	0.02	0.1	0	0.1
reaction Mole after	0	0.08	0.02	0.12
reaction	0	0.08	0.02	0.12

.:
$$pOH_2 = -\log 1.8 \times 10^{-5} + \log \frac{0.08}{0.12} = 4.57$$

.: $pH_2 = 9.43$
Change in pH = pH - pH2 = 9.26 - 9.43 = -0.18
.: Change in pH = **0.18 unit** i.e., pH **increases.**

42. Let V mL of 0.1 M HCOONa be mixed to 50 mL of 0.05 M HCOOH.

$$\therefore \quad \text{In mixture [HCOONa]} = \frac{0.1 \times \text{V}}{(\text{V} + 50)}$$
$$[\text{HCOOH]} = \frac{50 \times 0.05}{\text{V} + 50}$$
$$\therefore \quad \text{pH} = -\log K_{\text{a}} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$
$$\therefore \quad 4.0 = 3.7 + \log \frac{(0.1 \times \text{V}) / (\text{V} + 50)}{2.5 / (\text{V} + 50)}$$
$$\therefore \quad \text{V} = 50 \text{ mL}$$



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43.	We know,	$pOH = -\log$	$K_{L} + \log$	[Salt]		
	-	[Base]				
		$5 = 4.7 + \log \frac{a}{b}$				
		$\frac{a}{b} = 2$		a = 2b		
	Given	a + b = 0.6 2b + b = 0.6				
	÷.	3b = 0.6				
	or $b = 0.2 \text{m}$	nole	or	$0.2 \times 17 = 3.4 \text{ g/L}$		
	\therefore a = 0.4 n	nole	or	$0.4 \times 53.5 = 21.4 \text{g/L}$		
	Thus, [Sa	[t] = 0.4 M	and	[Base] = 0.2 M		
44.	m. mole of C	$O_3^{2-} = \frac{31.8}{106} \times$	1000=30	00		
	m. mole of H	$^{+} = 150 \times 1 = 1$	50			
	CO	. ²⁻ + H ⁺ -	\longrightarrow H(<u>`</u> O		
	t=0 300	150				
	150	-	150	,		
			2			
	so pH=pK	$L_a + \log \frac{[CO_3]}{[HCO_3]}$	$\frac{2^{-}}{2_{3}^{-}} = 10$.3.		
45.	$K = c\alpha^2 = 0.$	$1 \times (0.01)^2 = 1$	0 ⁻⁵ .			
	$\mathbf{u}_{\mathbf{a}} \xrightarrow{\mathbf{u}_{\mathbf{b}}} \mathbf{u}_{\mathbf{b}} \xrightarrow{\mathbf{u}_{\mathbf{b}}} \mathbf{u}_{\mathbf{b}} \xrightarrow{\mathbf{b}_{\mathbf{b}}} \mathbf{u}_{\mathbf{b}}$					
	$0.1(1-\alpha)$ 0.1α $0.1\alpha+0.2$					
	$10^{-5} = \frac{0.10 \times (0.10 + 0.2)}{0.1}$					
	$a = 5 \times 10^{-5}$	0.1	Thomaford	0 louis maglastad)		
	$\alpha = 3 \times 10^{-5}$	C.	I nerelore	, 0.10 is neglected).		
46.	pH of CH ₃ CO	$OOH = \frac{1}{2} (pk)$	$(X_a - \log c)$			
	$3 = \frac{1}{2} (pK_a - \log 0.1)$: $pK_a = 5$					
	$\frac{1}{4}$ stage of neutralisation : pH = 5 + log $\frac{1/4}{3/4}$ = 4.52					
	$\frac{3}{4}$ stage of n	eutralisation :	pH = 5 +	$\log \frac{3/4}{1/4} = 5.48$		
47.	NaCN + HC	I is not a buffe	er but if H	ICI is in less amount		
	then, it gives a buffer as it produces HCN.					
		NaCN +	$\mathrm{HCI} \rightarrow$	NaCI + HCN		
	Mole added	0.01	a	0 0		

(0.01 - a) = 0

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Let a mole of HCI be used for this purpose $pH = -\log K_a + \log \frac{0.01 - a}{a}$... $8.5 = -\log(4 \times 10^{-10}) + \log \frac{0.01 - a}{2}$ а $a = 8.89 \times 10^{-3}$ mole of HCI ... $BOH + HCI \rightarrow BCI + H_{2}O$ 48. Case I: $0.1 \times 5 = 0.5$ 0 Millimole before a 0 reaction 0.5 Millimole after (a-0.5) 0 0.5 reaction .. pH=10.04 $pOH = -\log K_{b} + \log \frac{[BCI]}{[BOH]}$(1) : pOH=3.96 :. $3.96 = -\log K_b + \log \frac{0.5}{(a - 0.5)}$...(2) Case II: BOH + HCI \rightarrow BCI + H₂O Millimole before a $0.1 \times 20 = 2$ reaction Millimole after (a - 2)0 2 2 reaction ∴ pH=9.14 $\therefore \text{ pOH} = -\log K_{b} + \log \frac{[BCI]}{[BOH]}$...(3) .. pOH=4.86 $\therefore \quad 4.86 = -\log K_{\rm b} + \log \frac{2}{a-2}$...(4) $K_{L} = 1.81 \times 10^{-5}$ 49. Let Molarity of C_6H_4 (OH) COOH = M_1 $C_{6}H_{4}(OH)COOH + NaOH \longrightarrow C_{6}H_{5}(OH)COONa$ At end point No. of eq. of $C_6H_4(OH)COOH =$ No. of eq. of NaOH $= 16.24 \times .02$ $25 \times M_1 = 0.3248 \implies M_1 = \frac{0.3248}{25} = 0.013$ Half neutrilazation $C_6H_4(OH) COOH + NaOH \longrightarrow C_6H_5(OH) COONa$ 0.3248 0.1624 0 0 0.1624 0 0.1624 $pH = p\mathsf{K}_{\mathsf{a}_1} + \log \frac{[C_6H_5(OH)COONa]}{[C_6H_5(OH)COOH]} \Rightarrow 4.7 = p\mathsf{K}_{\mathsf{a}_1}$ \Rightarrow K_{a1} = 2 × 10⁻⁵

This is buffer of HCN + NaCN



Mole after

reaction

Complate Neutrilization C_6H_5 (OH)COOH + NaOH $\longrightarrow C_6H_5$ (OH)COONa + H_2O 0.3248 0.3248 0 0 0 0.3248 $[C_6H_5(OH) COONa] = \frac{0.3248}{41.24} = 7.88 \times 10^{-3}$ $C_{k}H_{s}(OH)COONa$ This species is amphiprotic species. So $pH = \frac{pK_{a1} + pK_{a2}}{2} \implies 7.5 = \frac{4.7 + pK_{a2}}{2}$ $15 - 4.7 = pK_{a2}$ $\Rightarrow K_{a2} = 5 \times 10^{-11}$ $\Rightarrow pK_{a2} = 10.3$ 50. Let Acid is H₂A $\begin{array}{ccc} H_2A & & \underbrace{K_{a1}} & HA^- & \underbrace{K_{a2}} & A^{-2} \\ For HA^-, & pK_{a2} = 9.7 \\ and & pK_b = 11.7 & So pK_{a1} = 14 - 11.7 = 2.3 \end{array}$ t = 0(10 - x)0 x х This solution Act as Buffer solution So $pH = pK_{al} + \log \frac{[HA^-]}{[H_2A]} \Rightarrow 2.6 = 2.3 + \log \frac{[HA^-]}{[H_2A]}$ $0.3 = \log \frac{(10-x)}{x} \Rightarrow 2 = \left\lceil \frac{10-x}{x} \right\rceil \Rightarrow 2x = 10$ $-\mathbf{x}$ \Rightarrow x=3.33 milimole 3x = 10**51.** pK = $11 - \log 4.7 = 11 - \log 4.7$ = $11 - \log 4.7$ = 11 - 0.672 = 10.328 $pH = pK_a + \log\left(\frac{n_{Na_2CO_3}}{0.3}\right)$ $10 = 10.328 + \log \left(\frac{n_{Na_2CO_3}}{0.3} \right)$ $\log \frac{0.3}{n_{\text{Na},\text{CO}}} = 0.328 \implies \frac{0.3}{n_{\text{Na},\text{CO}}} = 2.13$ $W_{Na_2CO_3} = \left| \frac{0.3}{2.13} \right| \times 106 = 14.94 \approx 15 \text{ gram}$ **52.** $pH_1 = pK_a + \log \frac{x}{a}$ $pH_2 = pK_a + \log \frac{y}{2}$. $pH_2 - pH_1 = 0.6 = \log \frac{y}{x}$. $y = x 10^{0.6} = 4x.$ x: y = 1:4.

53. We know that pH of a mixture of solution containing weak acid and strong base can be calculated as below

pH = 7 +
$$\frac{1}{2}$$
 pK_a + $\frac{1}{2}$ log c
= 7 + $\frac{1}{2} \times 4.72 + \frac{1}{2}$ log 0.05 = 7 + 2.36 - 0.65 = 8.71

54. Let NaHCO₃ + Na₂CO₃ + KCl xg yg At 1st equivalent point

$$Na_2CO_3 + HCI \longrightarrow NaHCO_3 + NaCI$$

Milimole HCI consumed = $0.15 \times 10 = 1.5$

$$\left[\frac{Y}{106}\right] \times 1 \times 10^3 = 1.5 \qquad y = \frac{1.5 \times 106}{1000} = 0.159 \,g$$

At IInd equivalent point

m. eq. of $Na_2CO_3 + m.$ eq. of $NaHCO_3 = m.$ eq. of $HCl = 35 \times 0.15$

$$\Rightarrow \left[\frac{x}{84}\right] + \left[\frac{y}{106}\right] \times 2 = 0.15 \times 35 \times 10^{-3}$$

$$\frac{x}{84} + (1.5 \times 10^{-3}) \times 2 = 5.25 \times 10^{-3}$$

$$\mathbf{x} = \frac{(2.25 \times 84)}{1000} = 0.189 \,\mathrm{g}$$

mass of KCI = 0.152 g

mass % of Na₂CO₃ =
$$\frac{0.159 \times 100}{0.5}$$
 = 31.8 %

mass % of NaHCO₃ =
$$\frac{0.189 \times 100}{0.5}$$
 = 37.8 %

mass % of KCI =
$$\frac{0.152 \times 100}{0.5}$$
 = 30.4 %

55. As the value of K_{sp} is very law so we.
(a) can assume that almost all the Mg(OH)₂ will Present in solid state.



	(b)	Mg^{+2}	+20H	I	\rightarrow Mg (OH), (s)
		01	0.0	1	- · · · · · ·
		0.1	0.0	+	
			_		0.04
		At the	e end o	f reaction	$[Mg^{+2}] = 0.1 - \frac{1}{2} = 0.08$
	IZ A		TT))	ГЪ (+21 г (2
	K _{sp} ((Mg(C	$(H)_{2} = $		$JH]^2 = 1.6 \times 10^{-12}$
			16.1	0^{-12}	
	[O]	$[-]^2 = 1$	1.0×1	$\xrightarrow{0}$	$[OH^{-}] = 4.47 \times 10^{-6}$
	-	-	0.0	8	
	. r	oOH=	6 - lo	g 4.47	=5.35
	pH=	= 14 -	5.35 =	8.65	
	r				
	(c)	Mg(C	$(PH)_2 +$	- 2HCI –	\longrightarrow Mg ⁺² +2Cl ⁻ + 2 H ₂ O
		0.1		0.04	0.1
		01_0	0.02	0	0.1 ± 0.02
	ГЛ <i>(</i>	+21 0	12 14	0	0.1 + 0.02
	liviê	g~-]=0	.12 IVI		
		$K_{sp}[N]$	Ag (OF	$[\mathbf{I}]_2] = [\mathbf{Mg}]$	g^{+2} [OH ⁻] ² = 1.6 × 10 ⁻¹²
			1	c 10-12	4
		[OH-	$l^2 = \frac{l}{l}$	6×10 ·-	$-=\frac{4}{-}\times 10^{-11} M^2$
		[011	1	0.12	3
			_		
		LOTT .	, 4	v10 ⁻¹¹	
	⇒	[OH-]	$ =\sqrt{3}$	·×10	M
		011	- 1 A		
	⇒	рОН	= 5.44	⇒	pH = 14 - 5.44 = 8.56
59	(a) r	V (C		(1) - 47	1
30.				///) = 4 ./-	
	[CH	,000	[H] = 0	23 M,	$[CH_3 COONa] = 0.15 M$
		K	$_{1}[CH_{3}]$	COOH]	
	$[H^+]$	=	СНС	00-1	
		L	C113C	100	
	1.	8×10	$^{-5} \times 0$.25	10.515
	=	0	15	=3	× 10 ⁻³ M
		0	.15		
				- 0	$[H^+]^2 [S^{-2}]$
	H_2S	_	$\ge 2 \mathrm{H}$	$+ S^{-2}$	\Rightarrow $K_a = [H_2S]$
		9	$\times 10^{-2}$	1×0.1	
	$[S^{2-}]$] = —	0 10	$\frac{10}{-10} =$	10 ⁻¹² M
			9×10	10	
	IP (l	MnS)=	= [Mn ⁺	$[S^{-2}] =$	$1.5 \times 10^{-2} \times 10^{-12} = 1.5 \times 10^{-14}$
	IP <	K	\rightarrow So N	o PPT is t	formed.
		sp			
	(b)]	For pro	ecipitat	ion of Mr	S the minimum concentration
	of [S	S ²⁻]			
	[Mr	$^{+2}][S^2$	-] = K		
	1.5	$\times 10^{-2}$	$\times [S^{2}]$	$= 2.4 \times 10$	\Rightarrow [S ²⁻] = 1.6 × 10 ⁻¹¹ M
	For	thic [S	1~ J		, [2] 110 10 111
	101	uns [c	. 1		
		K	[H ₂ S	9×1	$0^{-21} \times 0.10$
	$[H^+]$	$ ^2 = -$	[S ²⁻¹	= $-$	$\frac{10^{-10}}{10^{-11}} = 7.5 \times 10^{-6} \mathrm{M}$
			[2]	1.0	b×10
		K	ICH (COOHI	
	[H +]	$l = \frac{\kappa_a}{2}$			\rightarrow 75 × 10 ⁻⁶
	[11]		CH ₃ C	00 ⁻]	- 1.5 . 10

$$= \frac{1.8 \times 10^{-5} \times 0.25}{[CH_3 COO^-]}$$

[CH_3COONa] = **0.60 M**

59. Let solubility of CaC₂O₄ is s mole/lit
CaC₂O₄ (s)
$$\implies$$
 Ca⁺² (aq) + C₂O₄²⁻ (aq)
s s
C₂O₄²⁻ react with H⁺ to produce HC₂O₄⁻² & H₂C₂O₄
H⁺ + C₂O₄²⁻ \implies HC₂O₄⁻¹ K'₁ = $\frac{1}{K_2}$
 $\frac{1}{K_2} = \frac{[HC_2O_4^{-1}]}{[H^+][C_2O_4^{-1}]} \Rightarrow [HC_2O_4^{-1}] = \frac{[H^+][C_2O_4^{-1}]}{K_2}$
Again this HC₂O₄⁻ react with H⁺ as.
HC₂O₄⁻⁺ H⁺ \implies H₂C₂O₄ K₁' = $\frac{1}{K_1}$
 $\frac{1}{K_1} = \frac{[H_2C_2O_4]}{[HC_2O_4^{-1}][H^+]}$
 $\Rightarrow [H_2C_2O_4] = \frac{[HC_2O_4^{-1}][H^+]}{K_1}$
Puting the value of [HC₂O₄⁻¹]
 $\Rightarrow [H_2C_2O_4] = \frac{[H^+]^2 [C_2O_4^{2-1}]}{K_1 K_2}$
Now [C₂O₄²⁻] + [HC₂O₄⁻¹] + [H₂C₂O₄] = s
[C₂O₄²⁻] $\left[1 + \frac{[H^+]^+}{K_2} + \frac{[H^+]^2}{K_1 K_2}\right] = s$
[C₂O₄²⁻] $\left[1 + \frac{10^{-4}}{5 \times 10^{-5}} + \frac{10^{-8}}{25 \times 10^{-7}}\right] = s$
[C₂O₄²⁻] = $\left(\frac{8}{3}\right) \Rightarrow K_{sp} = [Ca^{s^2}] [C_2O_4^{2-}] = 2.7 \times 10^{-9}$
 $\frac{s^2}{3} = 2.7 \times 10^{-9} \Rightarrow s = 9 \times 10^{-5} M$
60. Initial moles of Ag⁺ = 0.01; Initial moles of IO₃⁻⁻ = 0.005

60. Initial moles of $Ag^+ = 0.01$; Initial moles of $IO_3^- = 0.005$ Initial moles of $CrO_4^{2-} = 0.1$ Ksp of $AgIO_3 < < Ksp$ of CrO_4^{2-} Ag^+ first combined with $IO_3^ Ag^+$ (aq) + IO_3^- (aq) $\longrightarrow AgIO_3(s)$



moles of Ag* left after the above reaction = 0.01 - 0.005
=0.005
Now
2Ag* (aq) + CrO₄²⁻ (aq)
$$\longrightarrow$$
 Ag₂CrO₄ (s)
0.005 0.1
moles of CrO₄²⁻ left after the above reaction = 0.1 - 0.0025
=0.0975
At equilibrium
[CrO₄²⁻] = **0.0975 M**
[Ag'] = $\sqrt{\frac{\text{Ksp of Ag_2CrO_4}}{[\text{CrO}_4^{2^-}]}} = \sqrt{\frac{10^{-8}}{0.0975}} = 3.2 \times 10^{-4} \text{ M}$
[Ag'] = $\sqrt{\frac{\text{Ksp of Ag_1O_3}}{[\text{Ag}^+]}} = \frac{10^{-13}}{3.2 \times 10^{-4}} = 3.125 \times 10^{-10} \text{ M}$
Total moles of precipitate formed = 0.005 + 0.0025
= **0.0075**
61. [Sr(OH)₂] \longrightarrow Sr²⁺ + 2OH⁻
[Sr(OH)₂] = $\frac{19.23}{121.62 \times 1} = 0.158 \text{ M}$
 \therefore [OH⁻] = 2 × 0.158 M = **0.316 M**
or pOH = 0.5. \therefore pH = **13.5**
[Sr²⁺] = **0.158 M**.
62. Co²⁺ + N₂H₄ \implies Co(N₂H₄)²⁺
t = 0 0.01 0.02
t_{eq}. 0.01 - x 0.02 - x x
= 0.06
 \therefore x = 4 × 10⁻³ M
 \therefore [N₂H₄] = 0.016 M
 \therefore K_r = $\frac{(4 \times 10^{-3})}{(0.006)(0.016)} = 41.67$
63. Cu²⁺ + 4NH₃ (•) \implies [Cu(NH₃)₄]²⁺
Initial mole 0.005 0.5 × 0.4 0
= 0.2
K_j = 5.6 × 10¹¹
K_j is large and thus all the Cu²⁺ will give [Cu(NH₃)₄]²⁺
Let Cu²⁺ left is a, than
[Cu(NH₃)₄]²⁺ = 0.005 mole = $\frac{0.005}{0.5} \text{ M}$ (0.005 >> a)
[Cu²⁺] = $\frac{a}{0.5} \text{ M}$ (Let)
[NH₃] = 0.2 - 4 × 0,005 + 2a
= 0.2 - 0.02 + 2a (0.18 >> 2a)
= 0.18 mole = $\frac{0.18}{0.5} \text{ M}$

$$\therefore K_{j} = 5.6 \times 10^{11} = \frac{[Cu(NH_{3})_{4}]^{2+}}{[Cu^{2+}][NH_{3}]^{4}}$$

$$= \frac{0.005}{0.5} = \frac{[Cu^{2+}] \times \left[\frac{0.18}{0.5}\right]^{4}}{[Cu^{2+}] \times \left[\frac{0.18}{0.5}\right]^{4}}$$

$$\therefore [Cu^{2*}] = 1.06 \times 10^{-12} M$$
64. BaSO₄ $\implies Ba^{2+} + SO_{4}^{2-}$
s s
(where s M/litre is soluble of BaSO₄)
(i) $K_{sp} = s \times s$

$$\therefore s = \sqrt{K_{SP}} = \sqrt{1.6 \times 10^{-9}} = 4 \times 10^{-5} \text{ mol litre}^{-1}$$
(ii) In presence of 0.10 M BaCl₂, let s mol/litre BaSO₄ is disolved
 $K_{sp} = [Ba^{2+}][SO_{4}^{2-}]$
 $1.6 \times 10^{-9} = (0.1 + s)(s) = [(0.1 + s) = 0.1 \text{ as } s <<<0.1]$

$$\therefore s = 1.6 \times 10^{-8} M$$
65. Pb^{2*} + 2Cl⁻ \implies PbCl₂.
 $\frac{10}{101} - x = \frac{1}{101} - 2x \approx 0.$
 $[Pb^{2+}] = \left(10 - \frac{1}{2}\right) \times \frac{1}{101} = \frac{9.5}{101} = 9.4 \times 10^{-2} M.$
66. BaSO₄ $\implies s + s' = s$
BaCrO₄ $\implies Ba^{2+} + SO_{4}^{2-}.$
 $[Ba^{2+}] = 1.4 \times 10^{-5} = \sqrt{K_{sp1} + K_{sp2}}$

$$\therefore K_{sp1} + K_{sp1} = (1.4 \times 10^{-5})^{2}$$
 $\& \frac{K_{sp1}}{K_{sp2}} = \frac{1}{2.5}$
On solving, $K_{sp1} = 5.6 \times 10^{-11} K_{sp2} = \frac{5.6 \times 10^{-11}}{0.01}$

 $= 5.6 \times 10^{-9}$ M.

Add. 41-42A, Ashok Park Main, New Rohtak Road, New Delhi-110035 +91-9350679141 67. Taking density of water to be 1 g/cc.

$$[\text{CaSO}_4] = \frac{136}{10^6} \times \frac{1000}{136} = 10^{-10} \text{ M}.$$

Concentration of CaSO₄ in saturated solution.

$$\begin{split} &= \sqrt{K_{SP}} = 3 \times 10^{-3}.\\ &M_1 V_1 = M_2 V_2.\\ &10^{-10} \times V_1 = 3 \times 10^{-3} \times V_2.\\ &\frac{V_2}{V_1} = \frac{1}{3} \qquad \Rightarrow \quad \frac{V_1 - V_2}{V_1} = 0.67. \end{split}$$

68. For the precipitation of $Mg(OH)_2$ $[Mg^{2+}][OH^{-}]^{2} = K_{sp}$ $[OH^{-}] = 5 \times 10^{-5}.$ For NH₃ - NH₄⁺ buffer solution,

$$K_{b} = \frac{[OH^{-}][NH_{4}^{+}]}{[NH_{3}]} \implies [NH_{3}] = \frac{(5 \times 10^{-6})(0.4)}{2 \times 10^{-5}} = 0.1 \,\mathrm{M}.$$

69. Let final concentration of SO_4^{2-} in solution = $[SO_4^{2-}]_{left} = x$ Mole balance equation for SO_4^{2-}

$$[SO_4^{2-}]_{initial} = [SO_4^{2-}]_{left} + [SO_4^{2-}]_{combined}$$
$$\frac{0.3 \times 10}{30} = 0.1 = [SO_4^{2-}]_{left} + [SO_4^{2-}]_{combined}$$

$$D.1 = x + [Ca^{2^{+}}]_{combined} + [Sr^{2^{+}}]_{combined}$$

$$\Rightarrow 0.1 = x + ([Ca^{2^{+}}]_{initial} - [Ca^{2^{+}}]_{left}) + ([Sr^{2^{+}}]_{initial} - [Sr^{2^{+}}]_{left})$$

$$\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{K_{sp} \text{ of } CaSO_4}{[SO_4^{2-}]_{left}}\right)$$

$$\left(\frac{0.2}{3} - \frac{\mathrm{K_{sp}\,of\,SrSO_4}}{[\mathrm{SO_4}^{2-}]_{\mathrm{left}}}\right)$$

$$\Rightarrow 0.1 = x + \left(\frac{0.2}{3} - \frac{2.4 \times 10^{-5}}{x}\right) + \left(\frac{0.2}{3} - \frac{7.6 \times 10^{-7}}{x}\right)$$

$$3x^{2}+0.1x+7.428 \times 10^{-5} = 0$$

on solving, $x = [SO_{4}^{2-}]_{left} = 7.26 \times 10^{-4} M$
$$[Ca^{2+}]_{left} = \frac{2.4 \times 10^{-5}}{7.26 \times 10^{-4}} = 0.033 M$$

$$[Sr^{2+}]_{left} = \frac{7.6 \times 10^{-7}}{7.26 \times 10^{-4}} = 1.05 \times 10^{-3} M$$

70. [Ag⁺] concentration =
$$\frac{100}{350} \times 2 \times \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}}$$

= 8.68 × 10⁻³.
[SO₄²⁻] concentration = $\frac{100}{350} \times \sqrt[3]{\frac{1.4 \times 10^{-5}}{4}}$
= 4.34 × 10⁻³.
[Pb²⁺] = $\frac{250}{350} \times \sqrt{2.8 \times 10^{-13}}$ = 3.78 × 10⁻⁷.
[CrO₄²⁻] = 3.78 × 10⁻⁷.
[Ag⁺]² [CrO₄²⁻] = 2.85 × 10⁻¹¹ > K_{SP} of Ag₂CrO₄.
[Pb²⁺] [SO₄²⁻] = 1.64 × 10⁻⁹ < K_{SP} of PbSO₄.
Only Ag₂CrO₄ will precipitate.

- 71. For $CaSO_4$, Let solubility be s mol/litre
 - Them s = $\sqrt{K_{SP}} = \sqrt{9 \times 10^{-6}} = 3 \times 10^{-3} \text{ mol litre}^{-1}$ Thus, 3×10^{-3} mole of CaSO₄ is soluble in water = 1 litre $\frac{1}{136}$ mole (1 g) of CaSO₄ is soluble in $\frac{1}{136 \times 3 \times 10^{-3}} = 2.45$ litre water

2. For
$$Ag_2CrO_4(s) \Longrightarrow 2Ag^+ + CrO_4^{2-}$$

 $2s \quad s$
 $K_{sp} = 4s^3 \Longrightarrow \quad s = 2 \times 10^{-4} \text{ mol/lt.}$
Now,

I.

$$CrO_4^{2-} + Pb^{2+} \longrightarrow PbCrO_4 (s)$$

m. moles of $CrO_4^{2-} = m$. moles of Pb^{2+}
 $50 \times 2 \times 10^{-4} = 20 X$

 $X = 5 \times 10^{-4} M.$...

73. Let solubility of $Mg(OH)_2$ be s mol litre⁻¹

$$Mg(OH)_2 \xrightarrow{} Mg^{2+} + 2OH^{-}$$
$$[Mg^{2+}] [OH^{-12} = K]$$

- $\therefore \quad [Mg^{2^{+}}] [OH^{-}]^{2} = K_{SP}$ $4s^3\,{=}\,8.9\,{\times}\,10^{{-}12}$
- :. $s = 1.305 \times 10^{-4} \text{ mol litre}^{-1}$
- :. $[OH^{-}] = 2 \times 1.305 \times 10^{-4} \text{ mol litre}^{-1}$
- : pOH=3.58
- ∴ pH = 10.42
- 74. Mole balance equation $[HCO_3^{-}]_0 = [H_2CO_3] + [HCO_3^{-}] + [CO_3^{2-}]$ \Rightarrow [HCO₃⁻]₀



$$= [H_{2}CO_{3}] + \frac{K_{a1}[H_{2}CO_{3}]}{[H^{+}]} + \frac{K_{a1}K_{a2}[H_{2}CO_{3}]}{[H^{+}]^{2}}$$

$$\Rightarrow [HCO_{3}^{-}]_{0} = [H_{2}CO_{3}] \left(1 + \frac{K_{a1}}{[H^{+}]} + \frac{K_{a1}K_{a2}}{[H^{+}]^{2}}\right)$$

$$\Rightarrow [HCO_{3}^{-}]_{0}$$

$$= [H_{2}CO_{3}] \left(1 + \frac{4.9 \times 10^{-7}}{10^{-8}} + \frac{4.9 \times 10^{-7} \times 10^{-12}}{(10^{-8})^{2}}\right)$$

$$\Rightarrow [HCO_{3}^{-}]_{0} = [H_{2}CO_{3}](1 + 49 + 4.9 \times 10^{-3})$$

$$\therefore [H_{2}CO_{3}] = \frac{[HCO_{3}^{-}]_{0}}{50}$$

$$\Rightarrow n_{H_{2}CO_{3}} = \frac{0.0005}{50} = 10^{-5} \text{ mole.}$$

$$[HCO_{3}^{-}] = \frac{K_{a1}[H_{2}CO_{3}]}{[H^{+}]}$$

$$\Rightarrow n_{HCO_{3}^{-}} = \frac{4.9 \times 10^{-7} \times 10^{-5}}{10^{-8}} = 4.9 \times 10^{-4} \text{ mole}$$

$$[CO_{3}^{-2}] = \frac{K_{a1}K_{a2}[H_{2}CO_{3}]}{[H^{+}]^{2}}$$

$$n_{CO_{3}}^{2-} = \frac{4.9 \times 10^{-7} \times 10^{-12} \times 10^{-5}}{(10^{-8})^{2}}$$

$$= 4.9 \times 10^{-8} \text{ mole}$$
75. PbBr₂ $\Longrightarrow 2 \times 0.8s$
 $8 \times 10^{-5} = 4 \times (0.8)^{3} \times s^{3} \Rightarrow s = 5 \times 10^{-3} \text{ mol/lt.}$
solubility of salt = $5 \times 10^{-3} \times 368 = 1.84 \text{ g/lt.}$
76. milli moles of $I^{-} = 25 \times 2 \times \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}}$
milli moles of $Ag^{+} = 13.3 \times M$.
 $Ag^{*} (aq) + I^{-} (aq) \longrightarrow AgI (s)$
Equating both M = 4.55 \times 10^{-3}.

77. [F⁻] concentration when [Sr²⁺] is 2.5×10^{-3} = $\sqrt{\frac{2.8 \times 10^{-9}}{2.5 \times 10^{-3}}}$ = 1.058 × 10⁻³ M. Total m. moles of F⁻ added = 100 × [1.058 × 10⁻³ + 2 (0.016 - 0.0025)] = 2.8 Mass of NaF added = 2.8 × 10⁻³ × 42 = 0.1776 g.

78.
$$[Ag^+][Cl^-] = 1.75 \times 10^{-10}$$

 $[Ag^+][Br^-] = 5.25 \times 10^{-13}$
 $\Rightarrow [Br^-] = \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times [Cl^-]$
 $= \frac{5.25 \times 10^{-13}}{1.75 \times 10^{-10}} \times (0.075) = 2.25 \times 10^{-4} M.$

79. 500 mL of 0.4 M NaOH are mixed with 500 mL of Ca(OH)₂ a saturated solution having Ca(OH), solubility as s M.

Then,

...

For

Ca(OH)₂
$$Ca^{2+} + 2OH^{-1}$$

 $K_{sp} = s \times (2s)^2 = 4s^3$
 $4s^3 = 4.42 \times 10^{-5}$

$$s = \sqrt[3]{\left(\frac{4.42 \times 10^{-5}}{4}\right)} = 0.0223M$$

Now Ca (OH)₂ + NaOH are mixed ∴ Solution has Ca²⁺ and OH⁻ out of which some Ca²⁺ are precipiated

On mixing,
$$[Ca^{2+}] = \frac{0.0223 \times 500}{1000} = 0.01115$$

= 111.5 × 10⁻⁴ M

$$[OH^{-}] = \frac{0.0223 \times 2 \times 500}{1000} + \frac{500 \times 0.4}{1000} = 0.2223 \text{ M}$$

[from Ca (OH)₂] [from NaOH]
[Ca²⁺] [OH^{-}]² = K_{SP}
[Ca²⁺] [0.2223]² = 4.42 \times 10^{-5}

$$\left[\text{Ca}^{2^+}\right]_{\text{left}} = \frac{4.42 \times 10^{-5}}{\left[0.2223\right]^2} = 8.94 \times 10^{-1} \text{ mol litre}^{-1}$$

:. Mole of $Ca(OH)_2$ precipitated = Mole of $[Ca^{2+}]$ precipitated

 $=\!111.5\!\times 10^{-\!4}\!-\!8.94\!\times 10^{-\!4}\!=\!102.46\!\times 10^{-\!4}$

 $\therefore \text{ Wt. of Ca(OH)}_2 \text{ precipitated from Ca(OH)}_2 \text{ solution} = 102.46 \times 10^{-4} \times 74 = 7582.04 \times 10^{-4} \text{ g} = 759 \text{ mg}$

80. For $CaSO_4 \longrightarrow Ca^{2+} + SO_4^{2-}$

 $[Ca^{2+}][SO_4^{2-}] = K_{SP}$

Let $[SO_4^{2-}] = a$, just sufficient to precipitate $CaSO_4$ from a solution having $[Ca^{2+}] = 0.005$ M

Then, $[0.005][a] = 2.4 \times 10^{-5}$ $\therefore a = \frac{2.4 \times 10^{-5}}{0.005}$ $[SO_4^{2-}] = 4.8 \times 10-3 \text{ mol litre}^{-1}$



81. Concentration of CaCO₃ =
$$\left[\frac{7 \times 10^{-3}}{100}\right]$$
 mole/lit

 $= 7 \times 10^{-5}$ mole/lit

 K_{sp} of CaCO₃ = 49 × 10⁻⁵ mole/lit

when only $[Ba^{+2}]$ is 90% precipitated then only $CaCO_3$ starts precipitation

then if & solution contain a mole/lit of $Ca^{\scriptscriptstyle +\!2}\,$ & $Ba^{\scriptscriptstyle +\!2}$

$$[Ca^{+2}][CO_{3}^{-2}] = 49 \times 10^{-10} [CO_{3}^{-2}] = \left[\frac{49 \times 10^{-10}}{a}\right]$$

Now for BaCO₃ $K_{sp} = [Ba^{+2}] [CO_3^{-2}]$

$$=\frac{a\times10}{100}\times\frac{49\times10^{-10}}{a}=4.9\times10^{-10}$$

82. Ca $F_2 = Ca^{+2} + 2F^{-1}$

Let Solubility is s mole/lit

$$CaF_{2} \xrightarrow{} Ca^{+2} + 2F^{-}$$
s 2 s
The F⁻ react with H⁺ to produce HF

$$F^- + H^+ = HF$$

$$K_1 = \frac{1}{K_a} = \frac{[HF]}{[F^-][H^+]}$$

$$\Rightarrow [HF] = \frac{[F^{-}][H^{+}]}{K_{a}} = \frac{[F^{-}][H^{+}]}{3.45 \times 10^{-4}}$$

 $[HF] = 2.9 \times 10^{3} [F^{-}] [H^{+}]$ (A) at pH = 7 [HF] = 2.9 × 10⁻⁴ [F⁻] But the solution contain [HF + F⁻] = 2 [Ca⁺²] [2.9 × 10⁻⁴ + 1] [F⁻] = 2s [F⁻] = 2s K_{sp} = 4s³ = 0.4 × 10⁻¹¹ s = (10 × 10⁻¹²)^{1/3} = 2.15 × 10⁻⁴ (b) At pH = s [HF] = 2.9 × 10³ [F⁻] × 10⁻⁵ = 2.9 × 10⁻² [F⁻] [F⁻] + HF = 2s \implies [F⁻] + 0.029 [F] = 2s

$$[F] [1.029] = 2s \implies [F^-] = \left(\frac{1}{1.029}\right) \times 2s$$

$$K_{sp} = 4 s^3 \left(\frac{1}{1.029}\right)^2 = 4 \times 10^{-11} \implies s^3 = (1.29)^2 \times 10^{-11}$$

$$s = (10.6 \times 10^{-12})^{\frac{1}{3}} = 2.2 \times 10^{-4}$$

83. Volume of both AgNO₃ & HCN are equal so. There concentration is half $[AgNO_3] = 0.01 M$ [HCN] = 0.01 M HCN \longrightarrow H⁺ + CN⁻ K_a = 4 × 40⁻¹⁰ (i) $Ag^+ + CN^- \Longrightarrow AgCN K = \frac{1}{K_a}$ (ii) on adding equation (i) & equation (ii) $Ag^+ + HCN \implies H^+ + AgCN$ $K' = 10^{6}$ As the volue of K' is very high so almost all Ag⁺ & HCN converted in product Ag⁺ + HCN \longrightarrow H⁺+AgCN(s) K'= $\frac{K_a}{K_{sp}} = 1 \times 10^6$ 0.01 0 0.01 Х $\approx 0.01 \approx 0.01$ х $K' = \frac{0.01}{(x)^2} = 10^6$ $X^2 = 10^{-8} \implies X = 10^{-4}$ Conc. of $[Ag^+] = 10^{-4}$

84. Given,

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$$\begin{split} & MBr_{2(g)} \longrightarrow MBr_{2(aq)} \rightarrow M^{2+} + 2Br^{-} \\ & MBr_{2} + H_{2}S \rightarrow MS + 2HBr \\ & K_{SP} \text{ of } MS = [M^{2+}] [S^{2-}] \\ & 6 \times 10^{-21} = [0.05] [S^{2-}] \\ & [S^{-2}] = 1.2 \times 10^{-19} M \end{split}$$

Thus, MS will be precipitated if H_2S provides 1.2×10^{-19} M ions of S^{2-}

Now for
$$H_2S$$
 $H_2S \Longrightarrow 2H^+ + S^{2-}$

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

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[H^+]^2 [1.2 \times 10^{-19}]}{[0.1]}$$
$$[H^+] = 1.04 \times 10^{-1} \text{ and } pH = 0.983$$

85. When Mg(OH)₂ starts precipitation, then, $[Mg^{2+}][OH^{-}]^2 = K_{ep} \text{ of } Mg(OH)_2$

$$[Mg] [OH] = K_{sp} \text{ of } Mg($$

$$[0.1] [OH^{-}]^{2} = 1 \times 10^{-11}$$

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

$$pOH = 5$$

$$pH = 14 - pOH$$

$$pH = 14 - 5 = 9$$

86. The minimum [OH⁻] at which there will be no precipitation of Mg(OH), obtained by

 $K_{SP} = [Mg^{2+}] [OH^{-}]^{2}$ 6.0 × 10^{-12} = [0.05][OH^{-}]^{2} [OH^{-}] = 1.34 × 10^{-5} M



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Thus, a solution having $[OH^-] = 1.34 \times 10^{-5}$ M will not show precipitation of Mg(OH), in 0.05 M Mg²⁺ solution. These hydroxyl ions are to be derived by a buffer of NH4CI and NH4OH i.e.,

$$NH_{4}OH = NH_{4}^{+} + OH^{-}$$

$$NH_{4}CI \longrightarrow NH_{4}^{+} + CI^{-}$$

$$H \qquad K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{4}OH]}$$

For NH₄OH

In presence of NH_4CI ; all the $[NH_4^+]$ are provided by NH4CI since common ion effect decreases dissociation of NH₄OH.

$$\therefore \quad 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][1.34 \times 10^{-5}]}{[0.05]}$$
$$\therefore \quad [\text{NH}_4^+] = 0.067 \text{ M or } [\text{NH}_4\text{CI}] = 0.067 \text{ M}$$

h,
$$\operatorname{AgI}_{(s)} \longrightarrow \operatorname{Ag}_{(aq)}^{+} + \operatorname{I}_{(aq)}^{-},$$

 $\operatorname{K}_{sp} = [\operatorname{Ag}^{+}] [I^{-}] = 1.2 \times 10^{-17}$ (1)
 $\operatorname{Ag}_{(aq)}^{+} + 2\operatorname{CN}_{(aq)}^{-} \longrightarrow [\operatorname{Ag}(\operatorname{CN})_{2}]_{(aq)}^{-};$
 $\operatorname{K}_{f} = \frac{[\operatorname{Ag}(\operatorname{CN})_{2}^{-}]}{[\operatorname{Ag}^{+}][\operatorname{CN}^{-}]^{2}} = 7.1 \times 10^{19}$ (2)

Let x mole of AgI be dissolved in CN⁻ solution then,

Now
$$\operatorname{AgI}_{(s)} + 2\operatorname{CN}^{-} \bigoplus [\operatorname{Ag}(\operatorname{CN})_{2}^{-}] + I^{-}$$

mole before reaction I 0 0
mole after reaction (1-2x) x x
By Eqs. (1) and (2), $\operatorname{K}_{eq} = \operatorname{K}_{sp} \times \operatorname{K}_{f}$
 $= \frac{[\operatorname{Ag}(\operatorname{CN})_{2}^{-}][\Gamma^{-}]}{[\operatorname{CN}^{-}]^{2}} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$
 $\operatorname{K}_{eq} = 8.52 \times 10^{2}$ (3)
 $\therefore \operatorname{K}_{eq} = 8.52 \times 10^{2} = \frac{x.x}{(1-2x)^{2}} = \frac{x^{2}}{(1-2x)^{2}}$ or
 $\frac{x^{2}}{1-2x} = 29.2$
Thus, $x = 29.2 - 52.4x$ or $x = 0.49$ mole
88. AgCI $\Longrightarrow \operatorname{Ag}^{+} + \operatorname{CI}^{-}$ AgI $\Longrightarrow \operatorname{Ag}^{+} + \operatorname{I}^{-}$
 $(x+y) x (x+y) y$
 $\approx x \times x$
 $\frac{\operatorname{K}_{sp}(\operatorname{AgCI})}{\operatorname{K}_{sp}(\operatorname{AgI})} = \frac{x}{y} = \frac{1 \times 10^{-10}}{8.5 \times 10^{-17}} = \frac{10}{8.5} \times 10^{+6}$
 $x = 1.8 \times 10^{6}$ y

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But
$$K_{sp} [Zn(OH)_2] = [Zn^{2+}] [OH^{-}]^2 = 1.2 \times 10^{-17}$$

 $\Rightarrow (1.2 \times 10^{-9}) [OH^{-}]^2 = 1.2 \times 10^{-17}$
 $[OH^{-}] = 10^{-4} M$

EXERCISE - 5 Part # I : AIEEE/JEE-MAIN

Conjugate base is formed by the removal of H' from acid 1.

 $H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$

2. MX_4 (solid) $\implies M^{4_+}(aq) + 4X^-(aq)$ Solubility product, $K_{sp} = s \times (4s)^4 = 256 s^5$

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

- 3. $MX_{2(s)} \implies M^{2+}(aq) + 2X^{-}(aq)$ $\Rightarrow 4 \times 10^{-12} = 4s^3$ $K_{sn} = s \cdot (2s)^2 = 4s^3$ \Rightarrow s³ = 1 × 10⁻¹² \Rightarrow s = 1 × 10⁻⁴ M \Rightarrow [M²⁺] = 1 × 10⁻⁴ M $OH^- \rightleftharpoons O^{2-} + H^+$ 4. Conjugate base of OH⁻
- $pH = -log[H^+]$ $[H^+] = antilog (-pH)$ 5. \Rightarrow = antilog (-5. 4) = 3.98 \times 10⁻⁶

6.
$$H_2A \implies H^+ + HA^-; \quad K_1 = \frac{[H^+][HA^-]}{[H_2A]} = 1 \times 10^{-5}$$

 $HA^- \implies H^+ + A^{2-}; \quad K_2 = 5 \times 10^{-10} = \frac{[H^+][H^{2-}]}{[HA^-]}$

$$\mathbf{K} = \frac{[\mathbf{H}^+]^2 [\mathbf{H}^{2-}]}{[\mathbf{H}_2 \mathbf{A}]} = \mathbf{K}_1 \times \mathbf{K}_2 = 1 \times 10^{-5} \times 5 \times 10^{-15}$$

- 7. For acidic buffer, pH = pKwhen the acid is 50% ionised, $[A^-] = [HA]$ or $pH = pK_{a} + \log 1$ or $pH = pK_{a}$ given $pK_{a} = 4.5$ $\therefore pH = 4.5$ \therefore pOH = 14 - 4.5 = 9.5.
- $AgIO_3(s) \Longrightarrow Ag^+(aq) + IO^-_3(aq)$ [s = Solubility]8. $K_{sp} = s^2$ or

 $s = 1.0 \times 10-4$ mol/lit = $1.0 \times 10^{-4} \times 283$ g/lt = 2.83×10^{-3} gm/100 ml.

9.
$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7 + \frac{4.8}{2} - \frac{4.78}{2} = 7.01$$

- 10. CO.2-Na₂CO₃ - $2Na^+$ 1×10^{-4} M 1×10^{-4} M $1 \times 10^{-4} M$ $K_{sn}[BaCO_3] = [Ba^{+2}][CO_3^{2-}]$ $5.1 \times 10^{-9} = [Ba^{+2}] \times 1 \times 10^{-4}$ $[Ba^{+2}] = 5.1 \times 10^{-5}M$
- 11. $K_{sp} = [Ag^+] [Br^-] = 5.0 \times 10^{-13}$ $[Ag^+] = 0.05 M$ [0.05] [Br⁻] = 5.0×10^{-13}

I.

$$[Br^{-}] = \frac{5.0 \times 10^{-13}}{0.05} = 1 \times 10^{-11} \,\mathrm{M}$$

moles of KBr = $M \times V = 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$ weight of KBr = $1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

- **12.** $K_{sp} = 1.0 \times 10^{-11} = (Mg^{+2}) (OH^{-})^2$ $1.0 \times 10^{-11} = (0.001) (OH^{-})^2$ $(OH^{-}) = 10^{-4}$ $P^{OH} = 4$ $P^{H} = 14 - 4 = 10.$
- **13.** In IInd equation $H_2PO_4^-$ give H^+ ion to the H_2O therefore in the IInd equation it act as an acid.

14.
$$H_2CO_3 \implies H^+ + HCO_3^ K_1 = 4.2 \times 10^{-7}$$

 $HCO_3^- \implies H^+ + CO_3^{2-}$ $K_2 = 4.8 \times 10^{-11}$
 $K_1 >> K_2$
 $\therefore [H^+] = [HCO_3^-]$
 $K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$
but $[H^+] = [HCO_3^-]$
 $[CO_3^{2-}] = K_2 = 4.8 \times 10^{-11}$
15. $pH = 1$ $[H^+] = 10^{-1} = 0.1 \text{ M}$;
 $pH = 2$ $[H^+] = 10^{-2} = 0.01 \text{ M}$
for dilution of HC1 $M_1V_1 = M_2V_2$
 $0.1 \times 1 = 0.01 \times V_2$
 $V_2 = 10 \text{ lt}$
Volume of water added = $10 - 1 = 9$ litre
16. $CH_3COOK + H_2O \longrightarrow CH_3COOH + KOH$
Weak acid Strong base
Hence nature of solution is basic

17.
$$[H_2S] = 0.10 M$$

 $[HCI] = 0.20 M \implies [H^+] = 0.2 M$



(1) $H_2S f HS^- + H^+ K_1 = 1.0 \times 10^{-7}$ (2) $HS^{-} f S^{2-} + H^{+}$ $K_2 = 1.2 \times 10^{-13}$ So, $H_{2}S f S^{2-}+2H^{+}$ $=K_1 \times K_2$ $=1.2 \times 10^{-20}$

So,

$$[\mathbf{S}^{2-}] = \frac{1.2 \times 10^{-20} \times [\mathbf{H}_2 \mathbf{S}]}{[\mathbf{H}^+]^2}$$

$$=\frac{1.2\times10^{-20}\times10^{-1}}{4\times10^{-2}}=3\times10^{-20}\,\mathrm{M}$$

* All the $[H^+]$ will come from strong acid [HCl] only.

Part # II : IIT-JEE ADVANCED

- 1. $NaX + H_2O \implies NaOH + HX$ In it HX is weak acid, so NaX is a salt of weak acid and strong base.
 - :. Hydrolysis constant of NaX is $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}}$ $= 1 \times 10^{-9}$

For this type of salt $K_h = Ch^2$ C = molar concentration, h = degree of hydrolysis $\therefore 1 \times 10^{-9} = 0.1 \times h^2$

or
$$h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8}$$
 $h = 1 \times 10^{-4}$

: percentage hydrolysis of NaX salt = $1 \times 10^{-4} \times 100$ $= 1 \times 10^{-2} = 0.01 \%$

2. HA + OH⁻
$$\longrightarrow$$
 A⁻ + H₂O
0.1 V 0.1 V
- - 0.1 V m. moles

$$[A^{-}] = \frac{0.1V}{2V} = \frac{0.1}{2} M,$$

pH = 7 + $\frac{1}{2}$ (pK_a + log c) = 7 + $\frac{1}{2}$ (6 - log 5.6) +

3.

Initial moles moles after

 $\frac{1}{2}\log\left(\frac{311}{2}\right)$

≈ 9

$$CH_{3}NH_{2} + HCI \longrightarrow CH_{3}NH_{3}^{+}$$

$$0.1 \quad 0.08$$

$$0.02 \quad 0$$

0.08 mole in 1 lt reaction

I.

+

$$K_{b} = \frac{[OH^{-}][CH_{3}NH_{3}^{+}]}{[CH_{3}NH_{2}]}$$

or, $5 \times 10^{-4} = \frac{[OH^{-}] \times 0.08}{0.02}$ or, $[OH^{-}] = \frac{5}{4} \times 10^{-4}$.

$$[H^+] = \frac{K_w}{[OH^-]} \quad \text{or,}$$
$$[H^+] = \frac{10^{-14} \times 4}{5 \times 10^{-4}} = 8 \times 10^{-11} \,\text{M}.$$

4. BOH + HCl \longrightarrow BCl + H₂O (in titration) $B^+ + H_2O \Longrightarrow BOH + H^+$ For titration $N_{acid} V_{acid} = N_{base} V_{base}$ $\frac{2}{15}$ xV=2.5 x $\frac{2}{5}$

$$V=3 \times 2.5 = 7.5 \text{ mL}$$

In resulting solution

$$[B^+] = \frac{\frac{2}{5} \times 2.5}{10} = \frac{2}{20} = 0.1$$
$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

or $K_h = \frac{0.1 h^2}{(1-h)} = 10^{-2}$ (solve quadratic equation to

get 'h', as we can't write $1 - h \approx 1$ since h is > 0.1) or h = 0.27

$$[H^{\scriptscriptstyle +}]\,{=}\,0.1\,{\times}\,0.27\,{=}\,2.7\,{\times}\,10^{{\scriptscriptstyle -}2}$$

5. MX MX₂ M₃X

$$s_1^2 = 4 \times 10^{-8}$$
 4 $s_2^3 = 3.2 \times 10^{-14}$ 27 $s_3^4 = 2.7 \times 10^{-15}$
 $s_1 = 2 \times 10^{-4}$ $s_2^3 = 8 \times 10^{-15}$ $s_3^4 = 10^{-16}$
 $\Rightarrow s_1 > s_3 > s_2$
 \Rightarrow MX > M₃X > MX₂
6. Given $K_a = 10^{-4}$
 $pK_a = 4$
 $C = 0.01 M$
 $pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C = 7 + \frac{1}{2} (4) + \frac{1}{2} (-2)$
 $= 8$ Ans.



 $+ CI^{-}$.

CHEMISTRY FOR JEE MAIN & ADVANCED

7. Basic solutions will convert red litmus blue.

KCN K_2CO_3 , their aqueous solution will be basic due to LiCN anionic hydrolysis.

8. (C) HNO₃ + CH₃COONa mixture can act as buffer solution if volume of HNO₃ solution taken is lesser than volume of CH₃COONa solution because of following reaction : CH₃COONa + HNO₃ → CH₃COOH + NaNO₃
 (D) CH₃COOH + CH₃COONa - mixture will act as buffer.

9. AgCl (s)
$$\implies$$
 Ag⁺ + Cl⁻ K_{sp}(AgCl) = 1.6 × 10⁻¹⁰
Z Z+Y
CuCl (s) \implies Cu⁺ + Cl⁻ K_{sp}(CuCl) = 10⁻⁶
Y Z+Y
Z(Z+Y) = 1.6 × 10⁻¹⁰
Y(Z+Y) = 10⁻⁶
 \Rightarrow (Z+Y)² = 1.6 × 10⁻¹⁰ + 10⁻⁶ \Rightarrow (Z+Y)² \approx 10⁻⁶
 \Rightarrow Z+Y = 10⁻³ \Rightarrow Z(Z+Y) = 1.6 × 10⁻¹⁰
 \Rightarrow Z × 10⁻³ = 1.6 × 10⁻¹⁰ \Rightarrow Z = 1.6 × 10⁻⁷
 \Rightarrow 1.6 × 10^{-x} = 1.6 × 10⁻⁷ \Rightarrow x=7

10. As ester hydrolysis is first order with respect to $[H^+]$.

$$\frac{R_{HA}}{R_{HX}} = \frac{[H^+]_{HA}}{[H^+]_{HX}}$$

$$\frac{1}{100} = [H^+]_{HA}$$

$$HA \longrightarrow H^+ + HA \longrightarrow H^+ + HA$$

$$1 - 0.01 \qquad 0.01 \qquad 0$$

$$\approx 1$$

$$K_a = \frac{0.01 \times 0.01}{1} = 10^{-4}$$

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

 $m_0(1-\alpha) \qquad m_0\alpha \ 2m_0\alpha \qquad ; \qquad m = m_0(1+2\alpha)$

A

0.01

$$\frac{(-\Delta T_{\rm f})_{\rm observed}}{(-\Delta T_{\rm f})_{\rm undissociated}} = i = \frac{m}{m_0} = 2$$

12. A, C, D

(C) $\operatorname{HClO}_{4} + \operatorname{H}_{2}O \longrightarrow \operatorname{ClO}_{4}^{-} + \operatorname{H}_{3}O \xrightarrow{\operatorname{weak base}} \operatorname{errong ac}_{(\operatorname{Resonance stable})} \operatorname{weak base}_{(\operatorname{Resonance stable})}$

AB $f A^+ + B^-$

13.Solubility

I.

x x x -y

$$2 \times 10^{-10} = x (x-y)$$
(1)
B⁻ + H⁺ f HB
x - y 10⁻³ y
 $10^8 = \frac{y}{(x-y)10^{-3}}$
 $\frac{y}{x-y} = 10^5$
x - y = 10⁻⁵ y(2)

$$From(1)\&(2)$$

$$2 \times 10^{-10} = x^{2} - 2 \times 10^{-5}$$
$$x^{2} = 2 \times 10^{-5}$$
$$x = \sqrt{20} \times 10^{-3}$$
$$= 4.47 \times 10^{-3}$$

(P) NaOH+CH₃COOH \longrightarrow CH₃COONa+H₂O M.Mole 1 2

Now solution contains 1 m mole $CH_3COOH \& 1 m$. mole CH_3COONa in 30 ml solution. It is a Buffer solution

 \therefore [H⁺] does not charge with dilution.

(Q) NaOH+CH₃COOH \longrightarrow CH₃COONa+H₂O M.Mole 2 2

Now solution contains 2 m mole CH₃COONa in 40 ml solution (salt of weak acid strong base)

$$[\mathrm{H}^{+}]_{\mathrm{initial}} = \sqrt{\frac{\mathrm{K}_{\mathrm{w}}\mathrm{Ka}}{\mathrm{C}}}$$

Now on dilution up to 80 ml, now can. Becomes $\frac{C}{2}$

$$\therefore \quad [\mathrm{H}^+]_{\mathrm{new}} = \sqrt{\frac{\mathrm{K}_{\mathrm{w}}\mathrm{K}_{\mathrm{a}}}{\mathrm{C}/2}} = [\mathrm{H}^+]_{\mathrm{initial}} \times \sqrt{2}$$



 $\frac{1}{5} \times 25 = 5$

(R) $HCl + NH_3 \longrightarrow NH_4Cl$ M.Mole 2 2

Now solution contain 2 m. mole of NH_4Cl in 40 ml solution (salt of SA & WB)

$$\left[H^{+}\right]_{initial} = \sqrt{\frac{K_{w}C}{K_{b}}}$$

Now on dilution up to 80 ml, new conc. becomes $\frac{C}{2}$

$$\therefore \quad [\mathrm{H}^+]_{\mathrm{new}} = \sqrt{\frac{\mathrm{K}_{\mathrm{w}}\mathrm{C}}{\mathrm{K}_{\mathrm{b}}\,2}} = \frac{[\mathrm{H}^+]_{\mathrm{initial}}}{\sqrt{2}}$$

(S) Ni(OH)2 (s)
$$\longrightarrow$$
 Ni²⁺ +2OH⁻

 \rightarrow it is sparingly soluble salt

 \therefore on dilution [OH⁻] conc. is saturated solution of Ni(OH) 2 remains const.

 $\therefore [\mathrm{H}^{+}]_{\mathrm{new}} = [\mathrm{H}^{+}]_{\mathrm{initial}}$

MOCK TEST

2. Conjugate acid base pair are differ by an proton (H⁺).

 $HF^{+} \xrightarrow{-H^{+}} HF$ (acid) (base)

- 6. $K = [HCOOH_2^+] [HCOO^-] = 10^{-3} \times 10^{-3} = 10^{-6}$
- 7. $K_a = 10^{-6}$ for HA+H₂O \longrightarrow H₃O⁺+A⁻ Thus K for reverse reaction is $\frac{1}{10^{-6}} = 10^{6}$
- 9. (A) At 25°C, [H⁺] in a solution of 10^{-8} M HCl > 10^{-7} M. (B) [H⁺] = 10^{-8} M. (C) [OH⁻] = 4×10^{-6} M \Rightarrow [H⁺] = 2.5×10^{-9} M. (D) [H⁺] = 10^{-9} M.
- 10. (a) HCI

No. of mili eq. = $\frac{1}{10} \times 100 = 10$ $\frac{1}{10} \times 100 = 10$

NaOH

So solution is Neutral

(b)
$$\frac{1}{10} \times 55 = 5.5$$
 $\frac{1}{10} \times 45 = 4.5$

$$[\mathrm{H}^+] = \frac{1}{100} = 10^{-2} \,\mathrm{M}, \ \mathrm{pH} = 2$$

(c)
$$\frac{1}{10} \times 10 = 1$$
 $\frac{1}{10} \times 90 = 9$ Basic

(d)
$$\frac{1}{5} \times 75 = 15$$

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- [H⁺]=0.1 M,pH=1
 12. Concentration of Solutions are same therefore [H⁺] depends only on Dissociation constant.
- 14. pH of 0.1 M H₂S solution can be derived by :

$$H_{2}S = H^{+} + HS^{-}; K_{1} = 1 \times 10^{-7}$$

$$[H^{+}] = C\alpha = C\sqrt{\frac{K_{1}}{C}} = \sqrt{K_{1} \times C} = \sqrt{1 \times 10^{-7} \times 0.1}$$

$$= \sqrt{10^{-8}} = 10^{-4} \quad \therefore \quad pH = 4$$

$$K_a = \frac{[H^+]^2}{C - [H^+]} \implies 8 \times 10^{-4} = \frac{[H^+]^2}{6 \times 10^{-4} - [H^+]}$$

 $\therefore [H^+] = 4 \times 10^{-4} \text{ M.}$ So solution in (A), (C) & (D) are ISOHYDRIC.

16. (A)
$$[H^+] = 10^{-2}$$
 and $[OH^-] = 10^{-2}$
 $H^+ + OH^- \longrightarrow H_2O$
This leads complete neutralisation

so,
$$pH = 7 = \frac{2+12}{2}$$

- (D) $[H^+] = 10^{-5}$ and $[OH^-] = 10^{-5}$ $[H^+] + [OH^-] \longrightarrow H_2O$ This leads complete neutralisation so, $pH = 7 = \frac{5+9}{2}$
- On the basis of ostwald dilution law, number of H⁺ ions will increase but increase in volume will be more. Therefore, [H⁺] decreases, pH increases.
- 20. Since $K_{_a}$ of HCN is less than that of HF, so CN- is stronger base than F^-
- 22. Due to common ion effect, [H⁺] increases therefore ionization of HCOOH decreased.
- 24. Since K_a of $CH_3COOH \& K_b$ of NH_4OH are same so degree of hydrolysis of $CH_3COO^- \& NH_4^+$ are exactly same.
- **25.** (A) $[H^+]$ in HCl solution = 10^{-5} M

[H⁺] in H₂S solution = $\sqrt{K_a \times C} = 10^{-4} \text{ M}$

- so $[H^+]$ in HCl solution $< [H^+]$ in H₂S solution
- & $[OH^-]$ in HCl solution > $[OH^-]$ in H₂S solution



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- (B) At pH = 4.74 in CH_3COOH solution, [CH_3COO^{-}]=[CH_3COOH]
- ∴ degree of dissociation of $CH_3COOH = \frac{1}{2}$ At pH = 9.26 i.e. pOH = 4.74 in NH₄OH solution,
- [NH₄⁺] = [NH₄OH]
 ∴ degree of dissociation of CH₃COOH = degree of dissociation of NH₄OH

degree of dissociation of water in CH_3COOH solution > degree of dissociation of water in NH_4OH solution.

(C) [H⁺] in CH₃COOH solution =
$$\sqrt{1.8 \times 10^{-5} \times 0.1}$$

= $\sqrt{1.8} \times 10^{-3}$ M

[H⁺] in HCOOH solution =
$$\sqrt{1.8 \times 10^{-4} \times 1}$$

= $\sqrt{1.8} \times 10^{-2} \text{ M}$

so, degree of dissociation of $CH_3COOH = degree dissociation of HCOOH.$

(**D**) [H⁺] in HA₁ solution =
$$\sqrt{10^{-5} \times 0.1}$$
 = 10⁻³ M

 $[H^+]$ in HA₂ solution = $\sqrt{10^{-6} \times 0.01} = 10^{-4} M$

- so $[OH^-]$ in solution of $HA_1 < [OH^-]$ in solution of HA_2 pH in solution of $HA_1 < pH$ in solution of HA_2
- & degree of dissociation of water HA₁ < degree of dissociation of water HA₂.

27. (i)
$$CH_3COOH = 0.2 M$$

 $[H^{+}] = \sqrt{K_{a} \times C} = \sqrt{2 \times 10^{-5} \times 0.2} = \sqrt{4 \times 10^{-6}}$ $= 2 \times 10^{-3}$ $pH = 3 - \log 2 = 2.7$

$$C \alpha = [H^{+}] \implies \alpha = \frac{2 \times 10^{-3}}{2 \times 10^{-1}} \implies \alpha = 0.01$$
(ii) HCI \longrightarrow H⁺ + CI-
0.1 0.1 0.1
[H⁺]=0.1 pH=1
CH₃COOH \implies CH₃COO⁻ + H⁺
0.2 0 0.1
0.2 (1-\alpha) 0.2 \alpha 0.1 + 0.2 \alpha = 0.1
 $K_{a} = \frac{0.2\alpha \times 0.1}{0.2} = 2 \times 10^{-5} \qquad \alpha = 2 \times 10^{-4}$

(iii) $[CH_3COO^-] = 0.2 \times 2 \times 10^{-4} = 4 \times 10^{-5}$

(iv) % change in $\alpha = \frac{1 \times 10^{-2} - 2 \times 10^{-4}}{1 \times 10^{-2}} \times 100$ = $\left|1 - \frac{2}{100}\right| \times 100 = 98\%$

28. HA+NaOH
$$\rightarrow$$
 NaA+H₂O; or HA+OH⁻ \rightarrow A⁻+H₂O

$$K_{eq} = 10^9 = \frac{[A^-][H_2O]}{[HA][OH^-]}$$

Also HA
$$\longrightarrow$$
 H⁺+A⁻ K_a = $\frac{[H^+][A^-]}{[HA]}$

$$\therefore \quad \frac{K_{eq}}{K_a} = \frac{1}{K_w} \text{ or } K_a = 10^9 \times 10^{-14} = 10^{-5} \text{ Thus for}$$
$$A^- + H_2O \longrightarrow HA + OH$$

OH⁻]=Ch=C
$$\sqrt{\frac{K_{H}}{C}} = \sqrt{\frac{K_{w}C}{K_{a}}} = \sqrt{\frac{10^{-14} \times 0.1}{10^{-5}}} = 10^{-5}$$
M

$$\therefore [H^+] = 10^- \text{ and } pH = 9$$

Asc⁻ + H.O \implies HAsc + OH⁻

$$[OH^{-}] = C.h = C \sqrt{\frac{K_{h}}{C}} = \sqrt{K_{h}.C} = \sqrt{\frac{K_{w}}{K_{a}}.C}$$

$$=\sqrt{\frac{10^{-14}\times0.02}{5\times10^{-5}}}=2\times10^{-6}$$

$$[\mathrm{H}^{+}] = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9} \,\mathrm{M}$$

Also
$$h = \sqrt{\left[\frac{K_h}{C}\right]} = \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-5} \times 0.02}}$$

= 10⁻⁴ or 0.01 %



30.

<u>.</u>