TOPIC : IONIC EQUILIBRIUM EXERCISE # 1

SECTION (A)

- **2.** H_2SO_4 is a mineral acid.
- 4. Because it gain and also lose the proton

 $H_2O + H_2O = H_3O^+ + OH^-$

- **5.** H_3PO_3 is dibasic so $NaH_2PO_3 \& Na_2HPO_3$ both exist.
- 6. The molecule shows that three H atoms are replaceable, i.e., basicity of acid.
- 9. Conjugate acid base pair are differ by a proton (H⁺).

 $\begin{array}{ccc} H_2F^+ & \overset{-H^+}{\longrightarrow} & HF \\ \text{(acid)} & \text{(base)} \end{array}$

10. $CH_3COOH + HF \Longrightarrow CH_3COOH_2^+ + F^-$.

HF gives H⁺ to the CH₃COOH & forms F⁻. So it is a conjugate base of HF.

11.
$$H_3BO_3 = HO - B$$

electron deficient
species

So it will behave as Lewis acid.

12. Those substance which accept the proton are called Bronsted base and which donate the proton are called Bronsted acid.

 $HCO_3^- + H^+ \longrightarrow H_2CO_3$ (as Bronsted base)

 $HCO_3^- = H^+ + CO_3^{--}$ (as Bronsted acid)

- 13. Amphoteric means species which can accept as well as lose H⁺.
- **14.** Because it is conjugate base of weak acid. $CH_3COOH \longrightarrow CH_3COO^- + H^+$.

SECTION (B)

- 1. In weak electrolyte, the degree of dissociation, $\alpha = \sqrt{\frac{K}{C}}$. So it increases with increasing dilution.
- 2. According to Ostwald's dilution law, because degree of ionization is directly proportional to the dilution.
- 3. Ostwald's dilution law is valid for weak electrolytes.

4.
$$\alpha \propto \frac{1}{\sqrt{c}}$$
.

- 5. $pH = -log[H^+]$; 7.4 = $-log[H^+]$; $[H^+] = 4 \times 10^{-8} M$
- **7.** T ↑, [H⁺] ↑, pH ↓
- 8. When increasing the temperature the value of ionic product also increases.
- **9.** More is K_a , lesser is pK_a ($pK_a = -\log K_a$), more is acidic strength.
- **10.** The value of pK_a for stronger acid is less.

11. $[H^+] = y \times 10^{-x}$

 $\Rightarrow \qquad \mathsf{pH} = -\log[\mathsf{H}^+] \qquad \Rightarrow \qquad -\log\left[\mathsf{y} \times 10^{-\mathsf{x}}\right] \ \Rightarrow \qquad -\log \mathsf{y} - \log \mathsf{10}^{-\mathsf{x}}$

 $\Rightarrow \qquad \mathsf{xlog}_{10}\mathsf{10} - \mathsf{log} \; \mathsf{y} \qquad \Rightarrow \qquad \mathsf{x} - \mathsf{log} \; \mathsf{y}.$

(2)
$$[H^{*}] = \frac{1}{y} \times 10^{-x}$$

 $\Rightarrow pH = -\log \left[\frac{1}{y} \times 10^{-x}\right] \Rightarrow x - \log \frac{1}{y} \Rightarrow x + \log y.$
(3) $[H^{*}][OH^{-}] = ^{-14}$
 $\Rightarrow -\log[H^{+}][OH^{-}] = -\log 10^{-14} \Rightarrow -\log H^{*} - \log OH^{-} = 14$
 $pH = -\log[H^{+}] = 1.$
2. Millimole of $H^{+} = 0.3 \times 500 = 150$
Millimole of $OH^{-} = 0.1 \times 500 = 50$
After neutralization Millimole of H^{+} left = 150 - 50 = 100.
So, $[H^{+}] = \frac{100}{500 + 500} = \frac{1}{10}$
 $pH = -\log \left(\frac{1}{10}\right) = 1.$
3. $pOH = 4 \Rightarrow pH = 14 - 4 = 10.$
5. $[OH^{-}] = 10^{2} M; pOH = 2$
 $pH + pOH = 14; pH = 14 - pOH$
 $pH = 14 - 2 = 12$
6. pH of the solution $A = 3$
 $[H^{+}]_{a} = 10^{2} M.$
 $[H^{+}] = 10^{-3} + 10^{2} = 10^{-3} H \cdot 10^{-3} = \frac{11 \times 10^{-3}}{2} pH = 2.26$
7. $Initial \Rightarrow [OH^{-}] = \frac{2}{200} = 10^{-2} M \therefore pH = 12$
Final $\Rightarrow [OH^{-}] = 10^{-2} + \frac{0.04}{40 \times 0.1} = 2 \times 10^{-2} \therefore pH = 12.3$
So, change $= 12.3 - 12 = +0.3$
8. As the solution is acidic, pH < 7. This is because [H^{-}] from H_{2} C cannot be neglected in comparison to $10^{-4} M.$
9. $10^{-7} M AOH$ means $[OH^{-}] = 10^{-7} + 0^{-7} (10^{-7} (from water, approximately)$
 $\therefore pOH = 7 - \log 2 = 6.7 \therefore pH = 7.3$
Sectomot (D)
4. CO_{2} is acidic oxide, which on dissolution in water develops acidic nature.
5. $\alpha \% = \sqrt{\frac{K_{a}}{C}} \times 100 \Rightarrow \sqrt{\frac{1(8 \times 10^{-3}}{0.2}} \times 100 = 0.950.$

7.
$$[H^+] = \alpha.C = \frac{2}{100} \times .02$$
; $[H^+] = 4 \times 10^{-4} M$
pH = -log $[H^+] = 4 - \log 4$; pH = 3.3979

8.
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$\begin{array}{rcrcrcrcrc} t=0 & 0.1 & 0 & 0 \\ t=t_{eq} & 0.1-0.001 & 0.1 & 0.001 & 0.001 \\ K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]} = \frac{(0.001)(0.001)}{(0.1)} & \Rightarrow & K_{a} = 10^{-5}. \\ K_{a} \propto \alpha^{2} \\ \frac{K_{a_{1}}}{K_{a_{2}}} = \left(\frac{4}{9}\right)^{2} = \frac{16}{81} \\ \end{array}$$
On adding the 3 ionisation reactions, ionisation constants will get multipled.

$$\begin{array}{r} K_{a} = 10^{-4} \times 10^{-6} \times 10^{-8} = 10^{-18} \\ \text{or, } 10^{-18} = \frac{[H^{+}]^{3} \left[PO_{4}^{3-} \right]}{[H_{3}PO_{4}]} & \Rightarrow [H^{+}] = 10^{-5} \Rightarrow pH = 5 \\ \end{array}$$

$$\begin{array}{r} HA \rightleftharpoons H^{+} & + & A^{-} \\ 0.01 & 0.1\alpha & 0.1\alpha \\ HCI & \longrightarrow & H^{+} & + & CI^{-} \\ \end{array}$$

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} = \frac{(0.1\alpha + 0.01) \quad (0.1\alpha)}{0.01}$$

$$\Rightarrow \quad 1.44 \times 10^{-5} = \frac{0.01 \times 0.1 \quad \alpha}{0.01} \quad [\because 0.1 \quad \alpha < < 0.01]$$

$$[A^{-}] = 0.1 \quad \alpha = 1.44 \times 10^{-5} \text{ M}$$

SECTION (E)

9.

12.

13.

14.

 $\textbf{1.} \qquad \textbf{H}^{+} + \textbf{O}\textbf{H}^{-} \rightarrow \textbf{H}_2\textbf{O}.$

- **6.** Anion of weak acid will undergo hydrolysis. So, PO_4^{3-} .
- **7.** NaClO₄ is a salt of strong acid HClO₄.
- 8. Anionic hydrolysis results in basic solution.

9.
$$pH = 7 + \frac{1}{2} (pK_a - pK_b) = 7 + \frac{1}{2} [0]$$

 $pH = 7.$

10. $pK_b > pK_a$ i.e. $K_a > K_b$ i.e. acidic.

- **11.** $pOH = 7 0.5 \, pK_a + 0.5 \, pK_b$ or $pH = 7 + 0.5 \, pK_a 0.5 \, pK_b$ is valid for salt of WA and WB.
- **12.** Salt is of WAWB

$$\sqrt{K_{h}} = \frac{h}{1-h}$$

$$\sqrt{6.25 \times 10^{-6}} = \frac{h}{1-h}$$

$$25 \times 10^{-4} = \frac{h}{1-h}$$
%h = 25 × 10^{-2} = 0.25

13. NaZ is a salt of weak acid & strong base.

 $pH = 7 \times \frac{1}{2} pK_{a} + \frac{1}{2} logC$ $8.9 = 7 \times \frac{1}{2} pK_{a} + \frac{1}{2} log(0.1)$ $8.9 - 7 + 0.5 = \frac{1}{2} pK_{a}.$ $pK_{a} = 4.8$ $-log K_{a} = 4.8$ $log Ka = -4.8 = \overline{5}.2$ $Ka = 1.6 \times 10^{-5}$

14.
$$pH = \frac{1}{2} \left[pK_w + pK_a + \log_{10}C \right] = \frac{1}{2} \left[14 + 5 - \log 2 + \log_{10} 10^{-2} \right] = 8.35.$$

SECTION (F)

- 3. Acetic acid will dissociate less due to common ion effect of CH₃COO⁻
 - So, H⁺ concentration will decrease hence pH will increase.
- 4. On adding small amount of acid (H⁺) and base (OH⁻), weak acid or weak base will form respectively.
- 5. Weak base should be in excess.

0.

6.
$$HC_2H_3O_2 + NaOH \rightarrow C_2H_3O_2Na + H_2O$$

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

9.
$$pH = pK_a + \log \frac{[HA]}{[NaA]} = 3.346 + \log \frac{[0.20]}{500} \times \frac{[500]}{[0.05]} = 3.95$$

10.
$$pH = -\log K_{b} + \log \frac{[Salt]}{[Acid]}$$

 $pH = -\log [1.8 \times 10^{-5}] + \log \frac{[Salt]}{1.0}$
 $9 = 4.7 + \log \frac{[Salt]}{1.0}$; $\log \frac{[Salt]}{1.0} = 4.7 - 9 = -4.3$
 $\frac{[Salt]}{1.0} = Antilog \frac{1}{1.0}$; $[Salt] = 1.8 \text{ mole/L}$

pOH = pK_b + log
$$\frac{[salt]}{[base]}$$

When [salt] = [base], $pOH = pK_{b}$

13.
$$pH = -\log K_b + \log \frac{[\text{salt}]}{[\text{acid}]} \Rightarrow \qquad 5 = -\log 10^{-4} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

 $\log \frac{[\text{salt}]}{[\text{acid}]} = 1 \qquad \Rightarrow \qquad \frac{[\text{salt}]}{[\text{acid}]} = \text{antilog1} = 10:1$

SECTION (G)

11.

2. Fact.

- **4.** pH = pK_a = 4.75
- 6. $CH_3COOH + NaOH \longrightarrow CH_3Na + H_2O$

10 milimol 5 mili mol 5 5 $P^{H} = 4.74 + \log \frac{5}{5} = 4.74$ SECTION (H) $Ag_2CrO_4 \longrightarrow [2Ag^+] + [CrO_4^{--}]$ 1. Hence $K_{sp} = [Ag^+]^2 \left[CrO_4^{--} \right]$ $K_{SP}(CaF_2) = (2x)^2(x) = 4x^3.$ 2. $PbCl_2 \longrightarrow Pb^{2+}_{S} + 2Cl^{-}_{S}$ 3. K_{sp} of $PbCl_2 = [Pb^{2+}] \times [Cl^{-}]^2$; $K_{sp} = S \times (2S)^2$ $K_{sp} = S \times 4S^2$; $S^3 = \frac{K_{sp}}{4}$; $S = \sqrt[3]{\frac{K_{sp}}{4}}$ $MnS \implies Mn^{+2} + S^{2-}$ 4. S S $S^2 = 1.1 \times 10^{-21}$ $S = 10^{-11} \sqrt{11}$ $ZnS \implies Zn^{+2} + S^{2-}$ S S $S^2 = 1.1 \times 10^{-23}$ $S = 10^{-12} \sqrt{11}$ $PbS \implies Pb^{+2} + S^{2-}$ S S $S^2 = 1.1 \times 10^{-35}$ $S = 10^{-18} \sqrt{11}$ $CuS \rightleftharpoons Cu^{+2} + S^{2-}$ S S $S^2 = 1.1 \times 10^{-30}$ $S = 10^{-15} \sqrt{11}$ So, concentration is maximum in MnS $AaCrO > 2Aa^+ + CrO^{--}$ 5

AgCrO₄
$$\rightarrow 2 \operatorname{Ag}_{2S} + \operatorname{CrO}_{4}$$

 $K_{sp} = (2S)^2 S = 4S^3$
 $S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{32 \times 10^{-12}}{4}\right)^{\frac{1}{3}} = 2 \times 10^{-4} M.$

6. The solubility of $BaSO_4$ in g/litre is given 2.33×10^{-3}

∴ in mole/litre.= $n = \frac{W}{m.wt} 1 \times 10^{-5} = \frac{2.33 \times 10^{-3}}{233}$ Because BaSO₄ is a compound $K_{sp} = S^2 = [1 \times 10^{-5}]^2 = 1 \times 10^{-10}$

8. $CaF_2 \rightleftharpoons Ca^{2+}(s) + 2F^{-}(2s)$ $K_{sp} = 4s^3$

 $1.6 \times 10^{-10} = 4s^3$ $\sqrt[3]{\frac{16}{4} \times 10^{-11}} = s$ $(4 \times 10^{-11})^{1/3} = s$ $3.4 \times 10^{-4} = M$ mole of salt = $3.4 \times 10^{-4} \times 2 = 6.8 \times 10^{-4}$. 9. Let S is the solubility of BaF_2 in a solution of $Ba(NO_3)_2$ Then $K_{SP} = [Ba^{2+}] [F^{-}]^2$. Then [F[−]] = 2S; Then $\frac{1}{2}$ [F⁻] = S $CaF_2 \longrightarrow Ca^{2+} +$ 2F-10. S 2S $BaF_2 \longrightarrow Ba^{2+} +$ 2F-2×0.005 0.005 $K_{sp} = [Ca^{2+}] [F^{-}]^2 = S (2S + 0.01)^2$ 2S < < 0.01 $3.4 \times 10^{-11} = S \times 10^{-4}$ \Rightarrow $S = 3.4 \times 10^{-7} M.$ AgCl <u></u>→ Ag⁺ + Cl⁻ 11.

$$\begin{array}{cc} S & S \\ K_{sp} = S^2 = S = \sqrt{K_{sp}} \end{array} \implies \qquad S = \sqrt{10^{-10}} = 10^{-5}. \end{array}$$

- 12. 0.01 M CaCl₂ gives maximum Cl⁻ ions to keep K_{sn} of AgCl constant, decrease in [Ag⁺] will be maximum.
- **14.** Solubility is directly proportional to the K_{sp}.

18. Ionic product of AgBr

(1)
$$K_i(AgBr) = 0.1 \times 5 \times 10^{-12} = 5 \times 10^{-13}$$

(2)
$$K_i(AgBr) = 5 \times 10^{-12} \times 0.1 = 5 \times 10^{-13}$$

- (3) $K_i(AgBr) = 2 \times 10^{-6} \times 4 \times 10^{-8} = 8 \times 10^{-14}$
- (4) $K_i(AgBr) = 2 \times 10^{-6} \times 4 \times 10^{-6} = 8 \times 10^{-12}$
 - $K_i > K_{sp} \Rightarrow$ precipitate formed.

EXERCISE # 2

- **1.** Acid $\xrightarrow{-H^+}$ Conjugate base, $\xrightarrow{+H^+}$ Base Conjugate acid
- Acidic NH₄⁺, CH₃COOH₂⁺ (can donate H⁺ forming NH₃ & CH₃COOH, cant accept H⁺ due to existing positive charge). Basic – H₂PO₂⁻, HPO₃²⁻ (can accept H⁺ forming H₃PO₂ and H₂PO₃⁻, but cannot donate H⁺ as H is not directly attached to O, so non-acidic). Amphiprotic – H₂PO₃⁻, H₂PO₄⁻, HPO₄²⁻ (can accept H⁺ forming H₃PO₃, H₃PO₄ and H₂PO₄⁻ & can donate H⁺ forming HPO₃²⁻, HPO₄²⁻ & PO₄³⁻ respectively).
- **3.** H_3BO_3 is weak, Lewis monobasic acid and shows the given equilibrium. $H_3BO_3 + H_2O \Longrightarrow B(OH)_4^- + H^+$
- 4. For an acid solution pH < 7, pOH > 7, $OH^- < 10^{-7}$.
- 5. $K = [HCOOH_2^+] [HCOO^-] = 10^{-3} \times 10^{-3} = 10^{-6}$

(i) $HPO_4^{2-} \implies H^+ + PO_4^{3-}$; $K_{eq} = K_{a3}$ of $H_3PO_4 = 10^{-12}$ 6. (ii) $K_a(H_2PO_4^{-}) \times K_b(HPO_4^{2-}) = K_w = 10^{-14}$. So, $10^{-8} \times K_b(HPO_4^{2-}) = 10^{-14}$. Therefore, $K_b(HPO_4^{2-}) = 10^{-6}$. (iii) $K_a(H_3PO_4) \times K_b(H_2PO_4^{-}) = K_w = 10^{-14}$. So, $10^{-3} \times K_b(H_2PO_4^{-}) = 10^{-14}$. Therefore, $K_b(H_2PO_4^{-}) = 10^{-11}$. (iv) K_b of $PO_4^{3-}(K_{b_3}) = \frac{K_w}{K_{a_1}}$, K_b of $HPO_4^{2-}(K_{b_2})$ $\frac{K_w}{K_{a_2}} = and K_b$ of $H_2PO_4^{--}(K_{b_1}) = \frac{K_w}{K_{a_2}}$. Since order of K_a is K_{a1} > K_{a2} > K_{a3}, so order of K_b is K_{b1} < K_{b2} < K_{b3}. (i) 0.001 M HNO₃ : 7. $HNO_3 \longrightarrow H^+$ NO₃⁻ 10[–]3 M 0 t=00 10⁻³ 10-3 t=eq $pH = -\log 10^{-3} = 3.$ *.*.. $H_2SO_4 \longrightarrow SO_4^{2-}$ + (ii) 0.005 M H_2SO_4 : 2H+ 0.005 M 0 0 t=00.005 10-2 t=eq 0 $pH = -\log(10^{-2}) = 2.$ *.*.. (iii) 10⁻⁸ M NaOH : NaOH \longrightarrow Na⁺ OH-10⁻⁸ M 0 t=0 0 10⁻⁸ 10⁻⁸. t=ea 0 $H^+ + OH^$ t=ea H₂O х So, in solution, $[OH^{-}] = (10^{-8} + x) M and [H^{+}] = x$ $x(10^{-8} + x) = 10^{-14}$ $K_w = 10^{-14} = [H^+] [OH^-] \implies$ $x = 9.5 \times 10^{-8} = [H^+]$ \Rightarrow • pH = 7.022 (iv) 0.0008 M Ba(OH)₂ : Ba(OH)₂ Ba²⁺ 20H- $8 \times 10^{-4} \,\mathrm{M}$ 0 0 t=0 0 8×10^{-4} $2 \times 8 \times 10^{-4}$. t=ea

pOH = 2.8.

..

pH = 11.2.

9. By changing concentration 10 times, pH change by 1 unit.

...

11. New concentration of; $HCI = \frac{10^{-6}}{100} = 10^{-8} M$ [H⁺] = 10⁻⁷ + 10⁻⁸ (approximately) (Little less than 10⁻⁷ from water).

 $[OH^{-}] = 16 \times 10^{-4} M.$

12. (1)
$$[H^+] = c \times \alpha = 0.1 \times \frac{30}{100} = 0.03 \text{ M}$$

14. $\alpha = \sqrt{\frac{K_b}{C}}$ (C is same for both)

...

15.
$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \sqrt{\frac{3.14 \times 10^{-4}}{1.6 \times 10^{-5}}} = 4:1$$

17. (2) Due to common ion effect of H⁺.

18. (2)
$$H_2CO_3 + H_2O \implies HCO_3^- + H_3^+O$$
; $K_{a1} = 4.3 \times 10^{-7}$
 $HCO_3^- + H_2O \implies CO_3^{-2} + H_3^+O$; $K_{a2} = 4.8 \times 10^{-11}$
Given, $[H_2CO_3] = 0.037$ M

Now from Ostwald's dilution law, $[H_{3}O^{+}] = [HCO_{3}^{-}] = \sqrt{K_{a_{1}} \times C} = \sqrt{4.3 \times 10^{-7} \times 0.037} = 1.26 \times 10^{-4} \text{ M}$

As $K_{a2} < < K_{a1}$, hence the 2nd step ionisation is very small and $[HCO_3^-]$ remains nearly constant.

$$\Rightarrow \qquad \mathsf{K}_{a2} = \frac{[\mathsf{H}_3\mathsf{O}^+] \ [\mathsf{CO}_3^{-2}]}{[\mathsf{HCO}_3^{-1}]} = [\mathsf{CO}_3^{-2}] \Rightarrow \qquad [\mathsf{CO}_3^{-2}] = 4.8 \times 10^{-11} \, \mathrm{M}$$

- $\therefore \qquad \text{In a saturated solution of 0.037 M} \\ \text{nH}_2\text{CO}_3, \text{ the conc. of CO}_3^{2-} \text{ ion is 4.8 \times 10^{-11} M}.$
- **19.** $Na_2HPO_4 \implies Na_2PO_4^- + H^+$ Acidic salt Conjugate base $NaHSO_3$, $NaHSO_4 \& NaH_2PO_4$ also contain replacable H atom
- **20.** $K_a \cdot K_h = K_w \implies K_a \downarrow \Rightarrow K_h \uparrow$.
- 21. Higher is pH, lesser is acidic nature. Also NH₄CI(aq) is acidic and NaCN(aq) is basic.

25. Cationic hydrolysis result in acidic solution. So, $AI^{3+} + 3H_2O AI(OH)_3 + 3H^+$

acidic solution

- **26.** A strong acid is not used to make a buffer.
- **28.** Buffer action of above solution will vary when moles of HCI added to the solution one equal to moles of CH_3COONa .

	CH ₃	COONa +	HCI	\longrightarrow	CH ₃ COOH +	NaCl
t = 0	а	а		0	0	
after reaciton	0	0		а	а	

29.
$$K_a = 5 \times 10^{-10}$$
 pK_a = 10 log 5 = 9.3
pH = pK_b + log $\left[\frac{CN^{-}}{HCN}\right]$
9 = 9.3 + log $\left[\frac{5 \times V_{ml}}{10 \times 2}\right] \Rightarrow -0.3 = log \left[\frac{V_{ml}}{4}\right]$
0.3 = log $\left[\frac{4}{V_{ml}}\right] \Rightarrow \frac{4}{V_{ml}} = 2 \Rightarrow V_{ml} = 2 \text{ ml}$

- **30.** Millimoles of acetic acid = $50 \times 2 = 100$ Millimoles of CH₃COONa = $10 \times 1 = 10$ pH = $\frac{[Salt]}{[Acid]} - \log K_a + \log$ or pH = $-\log 10^{-5} + \log \frac{10}{100} = 4$
- 33. Strong acid can be used titrate both strong and weak base.

34.
$$\operatorname{NaH}_2\operatorname{PO}_4 + \operatorname{H}_3\operatorname{PO}_4$$
; $\operatorname{NaH}_2\operatorname{PO}_4 + \operatorname{Na}_2\operatorname{HPO}_4$; $\operatorname{Na}_2\operatorname{HPO}_4 + \operatorname{Na}_3\operatorname{PO}_4$.

37. (1) NaF \longrightarrow Na⁺ + F⁻ 0.1 0.1 0.1 0.1 CaF₂ \longrightarrow Ca⁺² + 2F⁻

	(2x + 0.1) 0.1 $K_{sp} = x (0.1)^2 = 3.4 \times 10^{-11}$ $x = 3.4 \times 10^{-9}$
38.	$Pb(OH)_2 \longrightarrow Pb^{2+} + OH^- \longrightarrow H_2O$ So solubility will increase.
39.	Order will be $4 > 2 > 1 = 3$. OH ⁻ combine with H ⁺ from acid to increase solubility of Fe(OH) ₃ .
42.	$\begin{split} &Ag_2CO_3\\ &K_{sp} = (2s_1)^2(s_1) = 4s_1^{-3} = 4 \times 10^{-12} \qquad \Rightarrow \qquad s_1 = 10^{-4}\\ &FeCO_3\\ &K_{sp} = (s_2) \; (s_2) = s_2^{-2} = 2.5 \times 10^{-11} = 5 \times 10^{-6}\\ &\frac{s_1}{s_2} = \frac{10^{-4}}{5 \times 10^{-6}} = \frac{100}{5} = 20:1. \end{split}$
44.	$\begin{split} &K_{sp}(SnS) = 10^{-25} = (0.01)(S) \\ \Rightarrow \qquad S = 10^{-23} \\ &K_{sp}(ZnS) = 1.6\times10^{-24} = 0.2\timesS \\ &S = 8\times10^{-24} \\ &So \text{ solubility of ZnS is less, so it will precipitate first.} \end{split}$
45.	$K_{sp} = 1.8 \times 10^{-10}$ Precipitation of AgCI will occur only where $K_{IP} (AgCI) > K_{sp}$ $K_{IP} = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = 2.5 \times 10^{-9}$ $K_{IP} > K_{SP}$ PPt is formed. EXERCISE # 3
	PART - I
1.	$\begin{array}{rcl} CH_3COOH & \overleftarrow{\longrightarrow} & CH_3COO^- & + & H^+ \\ C-3.4 \times 10^{-4} & & 3.4 \times 10^{-4} & & 3.4 \times 10^{-4} \\ & & K_a = \frac{(3.4 \times 10^{-4})(3.4 \times 10^{-2})}{(C-3.4 \times 10^{-4})} = 1.7 \times 10^{-5} = 10^{-1} \\ & \Rightarrow & 10^{-1} C = 6.8 \times 10^{-4} & \Rightarrow & 10^{-1} C = 6.8 \times 10^{-4} & \Rightarrow & C = 6.8 \times 10^{-4} \end{array}$
2	K (M S) - 4S ³ - 4 × (3.5 × 10 ⁻⁶) ³ - 1.7 × 10 ⁻¹⁶
2.	$N_{SP}(M_2O) = 4O = 4 \times (0.0 \times 10^{-1}) = 1.7 \times 10^{-1}$
3.	$K_{SP} = 4S^3 = 4 \times (0.5 \times 10^{-4})^3 = 5 \times 10^{-13}$
4.	$pOH = pK_{b} + \log\left(\frac{NH_{4}CI}{NH_{4}OH}\right)$ $14 - 9.25 = pK_{b} + \log\left(\frac{0.1}{2.4}\right) \implies pK_{b} = 4.75.$
	~ (U.1) ~

5. Anionic hydrolysis give basic solution.

6.
$$K_{SP} = 4S^3 = 3.2 \times 10^{-11} = 8 \times 10^{-12} \implies S = 2 \times 10^{-4}$$

7.
$$K_{SP}(AgI) = (Ag^+)(1) = S(10^{-4}) = 1 \times 10^{-16}$$
 \Rightarrow $S = 10^{-12}.$

8. $pH = pK_{ln} + log \frac{[ln^-]}{[Hln]}$

9. Acidity of sodium salt of oxygen family increases down the group. So pH decrease. $pH_1 > pH_2 > pH_3 > pH_4$.

10. Weak acid and its conjugate base form a buffer.

11.
$$H_2O = H^+ + OH^-$$

 $x+10^{-8} \times X$
 $\Rightarrow (x+10^{-8})(x) = 10^{-14}$
 $\Rightarrow x^2 + 10^{-8}x - 10^{-14} = 0$
 $\Rightarrow x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{10^{-8}(\sqrt{40} - 1)}{2}$
 $\Rightarrow x = \frac{10^{-8}(20 - 1)}{2} = \frac{19}{2} \times 10^{-8} = 9.5 \times 10^{-8}.$
 $\Rightarrow [H^+] = x + 10^{-8} = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}.$

12.
$$pH = -\log[H^+] = 10$$

 $pOH = 14 - 10 = 4.$

13.
$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.1}} = \sqrt{10^{-4}} = 10^{-2} = 1\%.$$

14.
$$[H^+]_{\text{final}} = \frac{V \times 10^{-3} + V \times 10^{-4} + V \times 10^{-5}}{V + V + V}$$
$$[H^+]_{\text{final}} = \frac{10^{-5}(100 + 10 + 1)}{3} = \frac{111}{3} \times 10^{-5} = 3.7 \times 10^{-4}$$

So solubility order will be $MX > M_3X > MX_2$.

16.
$$K_{h} = \frac{K_{w}}{K_{a}} = \frac{10^{-14}}{1.77 \times 10^{-5}} = \frac{10^{-9}}{1.77} = 5.65 \times 10^{-10}.$$

17.
$$[OH^{-}] = \frac{30 \times 0.10 \times 2 - 20 \times 0.05 \times 1}{20 + 30} = \frac{6 - 1}{50} = \frac{5}{50} = 0.1 \text{ M}.$$

18. Given, pH of Ba(OH)₂ = 12

$$\therefore \qquad [H^+] = [1 \times 10^{-12}] \text{ and } \qquad [OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} \qquad [\because \qquad [H^+] [OH^-] = 1 \times 10^{-14}]$$

$$= 1 \times 10^{2} \text{ mol/L}$$

$$Ba(OH)_{2} \longrightarrow Ba^{2x} + 2OH^{2}$$

$$s = 2s$$

$$K_{w} = [Ba^{2x}] [OH]^{2} = [s] [2s]^{2} = \left[\frac{1 \times 10^{-2}}{2}\right] (1 \times 10^{-2})^{2} = 0.5 \times 10^{-6} = 5.0 \times 10^{-7} \text{ M}^{3}$$
19. CH_xCOOH (weak acid) and CH_zCOONa (conjugated salt) form acidic buffer and for acidic buffer,

$$pH = pK_{x} + \log \frac{[salt]}{[acid]} \text{ and } [H^{2}] = -\text{ antilog } pH$$

$$pH = -\log (K_{x} + \log \frac{[salt]}{[acid]} \text{ [pK_{x}} = -\log K_{y}]$$

$$= -\log (1.8 \times 10^{-6}) + \log \frac{(0.20)}{(0.10)} = 4.74 + \log 2 = 4.74 + 0.3010 = 5.041$$
Now, $[H^{2}] = \text{ antilog } (-5.045) = 9.0 \times 10^{-6} \text{ mol/L}$
20. (i) For basic buffer

$$pOH = pK_{x} + \log \frac{[salt]}{[base]}$$
(ii) pH + pOH = 14
Given, $K_{y} = 1 \times 10^{-6}$, $[salt] = [base]$

$$pOH = -\log K_{y} + \log \frac{[salt]}{[base]} \therefore pOH = -\log (1 \times 10^{-6}) + \log 1$$

$$= 10$$

$$pH + POH = 14$$

$$pH = 14 \cdot 10 = 4$$
21. $K_{w} = [Ag^{2}] [CH]$

$$1.8 \times 10^{-6} = [Ag^{2}] [0.1]$$

$$[Ab^{2}] = 1.8 \times 10^{-6} \text{ M}$$

$$K_{w} = [Fb^{-2}] [0.1]^{2}$$

$$[Fb^{-1}] = 1.7 \times 10^{-6} \text{ M}$$

$$K_{w} = 1.8 \times 10^{-6} \text{ M}$$

$$K_{w} = 1.4 \times 56 = 9.436$$
23. $Ba(OH)_{z} \implies Ba^{2x} + 2 OH^{2}$

$$s = 2s$$

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

$$s = \frac{10^{2}}{2}$$

Ksp = 4s³ = 4 ×
$$\left(\frac{10^{-2}}{2}\right)^3$$
 = 5 × 10⁻⁷

- **24.** (AICl₃, LiCl & BeCl₂) all these solution are acidic due to cationic Hydrolysis, where BaCl₂, is salt of strong base & strong acid.
- 25. On adding small amount of acid (H⁺) and base (OH⁻), weak acid or weak base will be form respectively.
- **26.** $H_{\underline{C}IO_4}^{\prime}$ with highest oxidation number and its conjugate base is resonance stabilised, hence it is most acidic.
- **27.** Na_2CO_3 is basic due to hydrolysis of CO_3^{2-} ion

$$CO_3^{2-} + H_2O \implies HCO_3^- + OH^-$$

28. $K_{sp} \text{ of } Ag_2CrO_4 = 1.1 \times 10^{-12}$ $K_{sp} \text{ of } AgCI = 1.8 \times 10^{-10}$ $K_{sp} \text{ of } AgBr = 5.0 \times 10^{-13}$ $K_{sp} \text{ of } AgI = 8.3 \times 10^{-17}$ $[Ag^+]^2[C] = 1.1 \times 10^{-12}$ $[Ag^+] = \sqrt{\frac{1.1 \times 10^{-12}}{[C]}}$ If we take [C] = 1 then the map

If we take [C] = 1 then the maximum requirement of [Ag⁺] will be in case of Ag_2CrO_4 .

29. MY $K_{SP} = S_1^2 = 6.2 \times 10^{-13} = 62 \times 10^{-14}$ $S_1 = 7.9 \times 10^{-7}$ mole/lt = Solubility in pure water $MY_3 K_{SP} = 27 = S_2^4 = 6.2 \times 10^{-13} = 62 \times 10^{-14}$ $S_2 \simeq 10^{-3.5}$ mole/lt = Solubility in pure water Solubility of NY₃ > solubility of MY so 3rd statement is true Addition of KY will decrease the solubility due to common ion effect.

30.
$$C_5H_5N + H_2O = C_5H_5N^+H + OH^-$$

0.1
 $\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{\frac{1.7 \times 10^{-9}}{0.1}} = \sqrt{1.7 \times 10^{-8}} = 1.3 \times 10^{-4}$
% $\alpha = 1.3 \times 10^{-4} \times 100 = 1.3 \times 10^{-2} = 0.013.$

31. AgCl
$$\implies$$
 Ag+ + Cl-
S S + 0.1
Ksp = [Ag+] [Cl-]
1.6 × 10-10 = S × (S + 0.1) = S × 0.1
1.6 × 10-9 = S
32. Ag₂C₂O₄ (s) \implies 2Ag+ + C₂O₄²⁻
2s s
2s = 2.2 × 10⁻⁴
s = 1.1 × 10⁻⁴
K_{sp} = 4s³ = 4 (1.1 × 10⁻⁴)³ = 5.3 × 10⁻¹²
33. (a) [H⁺] = $\frac{6-4}{100} = \frac{2}{100}$ pH \neq 1
(b) [H⁺] = $\frac{5.5 - 4.5}{100} = \frac{1}{100} = 10^{-2}$ pH = 2
(c) [H⁺] = $\frac{15-5}{100} = \frac{10}{100} = 10^{-1}$ pH = 1

(d) $[H^+] = \frac{10 - 10}{200} = 0$ Neutral Solubility (S) = $\frac{2.42 \times 10^{-3}}{233}$ = $\frac{242}{233} \times 10^{-5}$ 34. = 1.039 x 10⁻⁵ $K_{sp}(BaSO_4) = (S)^2 = (1.039 \times 10^{-5})^2$ $= 1.0787 \times 10^{-10}$ $= 1.08 \times 10^{-10} M$ 35. Acid-Base Titration : HCI + $NH_4OH \longrightarrow NH_4CI$ 10 m mole 20 m mole 10 m mole 20 - 10HCI is limiting reagent Solution contain NH₄OH & NH₄CI (WB) (SAWB) The basic buffer will form. 36. pH of saturated solution of $Ca(OH)_2 = 9$ pOH of saturated solution of $Ca(OH)_2 = 5$ $OH^{-} = 10^{-5}$ $Ca(OH)_2 \rightleftharpoons Ca^{2+}$ 20H-S 2S ½ × 10^{−5} 10-5 solubility (s) = $\frac{1}{2} \times 2 \ 10^{-5}$ $K_{sp} = [Ba2+] [OH^{-}]^{2}$ [1/2 x 10⁻⁵] [10⁻⁵]² $= 0.5 \times 10^{-15}$ 37. Bronsted acid Conjugate base H_2O OH-HF F-38. $[OH] = 10^{-2}$ $P^{OH} = -\log(OH^{-})$ $P^{OH} = -\log(10^{-2})$ POH = 2 $PH = 14 - P^{OH}$ = 14 - 2= 12 39. HCI can not accept H⁺ ion. 40. Let molar solubiling of CaF₂ in 0.1 molar NaF is S¹ mole/L. NaF

Na⁺ + F⁻ С С $CaF_2 \rightleftharpoons Ca^{2+} + 2F^ S^1$ 2S1 + C $K_{sp} = [S^1] [2S^1 + C]^2$ neglect Higher power of S¹ $K_{sp} = S^1 C^2$ $S^{1} = \frac{Ksp}{C^{2}} = \frac{5.3 \times 10^{-11}}{10^{-2}} = 5.3 \times 10^{-9} \text{ mole/L}$ PART - II $pH = pK_a + \log \frac{(CH_3COO^-)}{(CH_3COOH)} = 4.57 + \log \left(\frac{0.10}{0.03}\right) = 4.57 + \log 10 - \log 3 = 5.57 - 0.48 = 5.09.$ 1. $K_w = [H^+] [OH^-] = (10^{-6}) (10^{-6}) = 1.0 \times 10^{-12}$ 2. $K_{SP}[AgCI] = [Ag^+] [CI^-] = (S) (0.2)$ 3.

$$S = \frac{1.8 \times 10^{-10}}{0.2} = 9 \times 10^{-10} \text{ M}.$$

- ${\rm HClO_4}$ is a strong acid so cannot behave as a buffer. 4.
- 5. pH > 8 for wA vs sB titration.
- 6. K_{SP} (AgCl) > K_{SP} (AgBr).
- 7. At equivalence point solution will be neutral.

8.

$$pH = \frac{1}{2} (pK_w - pK_b + pK_a) = \frac{1}{2} (14) = 7.$$
8. NH₃ + HCl \longrightarrow NH₄Cl + H₂O
t=0 40x0.1 20x0.1 0 -
=4mmol =2mmol
after reaction 2mmol 0 2mmol
pOH = pK_b = 4.74
pH = 14 - 4.74 = 9.26.
9. 10.8 × 10⁻⁹ = (0.5S × 2)² (0.5S) \implies S³ = $\frac{10.8 \times 10^{-9}}{0.25 \times 0.5}$
11. K_{SP} is least for BaSO₄. So it will precipitate first.
12. [OH⁻] = Ca = C $\sqrt{\frac{K_a}{C}} = \sqrt{5 \times 10^{-4} \times 2.5 \times 10^{-6}}$
[OH⁻] = $\sqrt{1.25 \times 10^{-3}}$
[OH⁻] = $\sqrt{1.25 \times 10^{-4}}$
pOH = 4 - $\frac{1}{2}$ log1.25
pH = 14 - pOH = 10 + $\frac{1}{2}$ log1.25 = 10.05.
13. pH = 10 \implies [H⁺] = 10⁻¹⁰ M \implies [OH⁻] = 10⁻⁴ M.
Number of ions [OH⁻] in 100 ml = 10⁻⁴ × 100 × 10⁻³ × N_A = 10⁻⁵ × 6.023 × 10²³ = 6.023 × 10¹⁸.
14. K_{SP}(M₂X₃) = 4S₃⁻², 8S₄⁻³ = 2.2 × 10⁻²⁰
 \implies S₁⁻⁵ = $\frac{2}{32}$ × 10⁻²⁰ \implies S₁ = $\frac{\sqrt[5]{2.2}}{2}$ × 10⁻⁴
K_{SP}(M₂X₃) = 4S₂⁻³ = 32S₁⁻³ = $\frac{32}{8}$ (2.2)³⁵ × 10⁻¹² = 4 × (2.2)³⁵ × 10⁻¹² = 3 × 10⁻¹².
15. Concentration of mixture = $\frac{\text{millequivalent of NaOH - milliequivalent of HCl}{\text{total volume}}$
 $= \frac{V \times \frac{1}{10} - V \frac{1}{20}}{(V + V)} = \frac{V(0.1 - 0.05)}{2V} = 0.025$
Since, NaOH is in excess,
[OH⁻] = 0.025
pOH = 1.6
pH = 14 - 1.6 = 12.4
16. Number of millimoles of base (i.e., Ca(OH)₂) = N, V, = 2 × 0.2 × 25 = 10 = 10 × 1 = 10
As, no. of millimoles of acid = no. of millimoles of base

... Acid is completely neutralised by base forming

 \therefore pH of the resulting solution = 7.

17. Blood contains serum protein which acts as buffer.

18. Normality of oxide acid =
$$\frac{6.3 \times 1000}{63 \times 250}$$
 = 0.4N
N₁V₁ = N₂V₂ or 10 ×0.4 = V×0.1 or V = 40 mL
20. K_n = $\frac{10^{-14}}{4.99 \times 10^{-19} \times 1.77 \times 10^{-6}}$ = 1.132
It can be seen that hydrolysis constant (K_n) is not small and for calculating h, the equation used is
h = $\frac{\sqrt{K_n}}{1+K_n} = \frac{\sqrt{1.132}}{1+\sqrt{1.113}} = \frac{1.06}{1+1.06} = \frac{1.06}{2.06} = 0.51$
Using the formula
pH = pK_a - log h + log 1 (1-h) = -log(4.99 × 10^{-10}) -log (0.51) + log (1-0.51) = 9.3
25. NH₃ + HCl → NH₄Cl
Initial 50 × 0.1 10× 0.1
5 mmol 1 mmol
Rem. 4 mmol 0 1 mmol
Rem. 4 mmol 0 1 mmol
pOH = pk_b + log salt = 4.75 + log $\frac{1}{4}$ = 4.15
pH = 14 - pOH = 14 - 4.15 = 9.85
26. CH₃COOCH₃ $\frac{HO}{H}$ → CH₃COOH + CH₃OH
HCl + NaOH → NaCl + H₂O
CH₃COOCH = $\frac{HO}{H}$ → CH₃COOH = CH₃OH
HCl + NaOH → NaCl + H₂O
CH₃COOCH₃ $\frac{HO}{H}$ → 24^{*} + 22^B
 $\frac{1}{5}$ 0.001
+S S
 $\frac{1}{5}$ 0.001
K₃₀ = 4x3 = S × (0.001)²
S = 4x³ × 10⁶
27. In pure water:
XB₂ → $\frac{2}{3}$ × $\frac{2}{3}$ 0.001
 $\frac{1}{4}$ S S
 $\frac{1}{5}$ 0.001
 $\frac{1}{5}$ S = $\frac{1}{5}$ 2.5 olution is acidic in nature but not a buffer solution.
3. Mg(OH)₂ Mg²⁺ 2.0H K₉ = [Mg²⁺] [OH²⁺]² K₉₀ = s (25)² = 4s³.
4. We know that for acids at 25⁵C, pH must be less than 7.
5. When rain is accompanied by a thunderstorm, N₂ + O_2 → NO → NO₂ = $\frac{1}{10}$ → HO₅ HNO₅
6. AB₂ ⇒ A²⁺ 2B⁻ S = 1.0 × 10⁻⁵ (2.0 × 10⁻⁵) = 4.0 × 10⁻⁵

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

)^{1/5}

8	MX (solid) $\longrightarrow M^{4+} \rightarrow 4X^{-} \rightarrow 50$ solubility product $K \rightarrow s \times (4s)^4 - 256 s^5 \rightarrow s - \left(\frac{K_{ps}}{2s}\right)^4$
0.	$\operatorname{Wix}_{4}(\operatorname{solid}) = \operatorname{Wix}_{(\operatorname{aq})} + 4 \operatorname{X}_{(\operatorname{aq})} $ Solubling product, $\operatorname{N}_{\operatorname{sp}} = 3 \operatorname{X}(43) = 230 \operatorname{S}^{\circ} \ldots $ $S = \left(\frac{256}{256}\right)$
9.	Conjugate base of OH ⁻ $OH- \implies O^{2-} + H^+$
10.	$pH = -\log[H^+] \implies [H^+] = antilog (-pH) = antilog (-5. 4) = 3.98 \times 10^{-6}$
11.	$\begin{array}{l} MX_{2(s)} & \longrightarrow & M^{2+} \left(aq \right) + 2X^{-} \left(aq \right) \\ K_{sp} = s . (2s)^2 = 4s^3 \qquad \Rightarrow \qquad 4 \times 10^{-12} = 4s^3 \qquad \Rightarrow \qquad s^3 = 1 \times 10^{-12} \\ \Rightarrow s = 1 \times 10^{-4} M \qquad \Rightarrow \qquad [M^{2+}] = 1 \times 10^{-4} M \\ \mathbf{H}^{+1} [H \wedge ^{-1}] \end{array}$
12.	$H_2A \implies H^+ + HA^- \implies K_1 = \frac{[1^+ j^-] [1^+ K^-]}{[H_2A]} = 1 \times 10^{-5}$
	$HA^{-} \rightleftharpoons H^{+} + A^{2-}; \qquad \Rightarrow \qquad K_{2} = 5 \times 10^{-10} = \frac{[H^{+}]^{-} [H^{2-}]}{[HA^{-}]}$
	$K = \frac{[H^+]^2 [H^{2-}]}{[H_2A]} = K_1 \times K_2 = 1 \times 10^{-5} \times 5 \times 10^{-15}$
13.	For acidic buffer, pH = pK _a + $\frac{\left[A^{-}\right]}{\left[HA\right]}$
	when 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 $pOH = 14 - 4.5 = 9.5$.
14.	AgIO ₃ (s) \longrightarrow Ag ⁺ (aq) + IO ⁻ ₃ (aq) [s = Solubility] $K_{sp} = s^2$ or $s = 1.0 \times 10-4$ mol/lit = 1.0 × 10 ⁻⁴ × 283 g/lt = 2.83 × 10 ⁻³ gm/100 ml.
15.	$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2}pK_b = 7 + \frac{4.8}{2} - \frac{4.78}{2} = 7.01$
16.	$\begin{array}{rcl} Na_{2}CO_{3} & \longrightarrow & 2Na^{+} & + & CO_{3}^{2-} \\ 1 \times 10^{-4}M & & 1 \times 10^{-4}M & 1 \times 10^{-4}M \\ K_{sp}[BaCO_{3}] = [Ba^{+2}] [CO_{3}^{2-}] \\ 5.1 \times 10^{-9} = [Ba^{+2}] \times 1 \times 10^{-4} \\ [Ba^{+2}] = 5.1 \times 10^{-5}M \end{array}$
17.	In II nd equation $H_2PO_4^-$ gives one H ⁺ ion to H_2O therefore in the II nd equation it act as an acid.
18.	$\begin{array}{l} H_{2}CO_{3} \longleftrightarrow H^{+} + HCO_{3}^{-} \qquad K_{1} = 4.2 \times 10^{-7} \\ HCO_{3}^{-} \longleftrightarrow H^{+} + CO_{3}^{2-} \qquad K_{2} = 4.8 \times 10^{-11} \\ K_{1} >> K_{2} \\ \therefore \qquad [H^{+}] = [HCO_{3}^{-}] \\ K_{2} = \frac{[H^{+}][CO_{3}^{2-}]}{[HCO_{3}^{-}]} \text{ but } \qquad [H^{+}] = [HCO_{3}^{-}] \implies \qquad [CO_{3}^{2-}] = K_{2} = 4.8 \times 10^{-11} \end{array}$
19.	For precipitation to start, $K_{sp} = IP$ $K_{sp} = [Ag^+] [Br^-] But, [Ag^+] = 0.05 M \therefore [0.05] [Br^-] = 5.0 \times 10^{-13}$ $[Br^-] = \frac{5.0 \times 10^{-13}}{0.05} = 1 \times 10^{-11} M$ moles of KBr required = M × V = 1 × 10^{-11} × 1 = 1 × 10^{-11}
20.	weight of KBr required = $1 \times 10^{-11} \times 120 = 1.2 \times 10^{-9} \text{ g}$ $K_{sp} = 1.0 \times 10^{-11} = [Mg^{+2}] [OH^{-}]^2$ $1.0 \times 10^{-11} = (0.001) [OH^{-}]^2$ $[OH^{-}] = 10^{-4}$ pOH = 4 pH = 14 - 4 = 10.

- **21.** O^{2-} (base) + H_2O (acid) $\longrightarrow OH^-$ (C.B) + OH^- (C.A.) O^{2-} acts as Lewis base.
- 22. HQ _ + H⁺ + Q⁻ 0.1 0.1 – x х х x = 10⁻³ pH = 3, $[H^+] = 10^{-3}$, $K_a = \frac{(x) \times (x)}{(0.1-x)} = \frac{(10^{-3})^2}{0.1-10^{-3}} \simeq \frac{10^{-6}}{0.1} = 10^{-5}$ 23. $pH = 1 \Rightarrow$ $[H^+] = 10^{-1} = 0.1 \text{ M}$ $pH = 2 \Rightarrow$ [H⁺] = 10⁻² = 0.01 M for dilution of HCI $M_1V_1 = M_2V_2$ $0.1 \times 1 = 0.01 \times V_2$ $V_{2} = 10 L$ Volume of water added = 10 - 1 = 9 litre
- 24. Salt of weak acid and weak base

$$pH = \frac{1}{2}(pk_w + pK_a - pK_b) = \frac{1}{2}(14 + 3.2 - 3.4) = 6.9$$

- **25.** Most basic salt in aq. solution is CH₃COOK it is salt of WASB and have pH = 7+ $\frac{(pK_a + logc)}{2}$ i.e. pH > 7
- $\begin{array}{rcl} \mbox{26.} & \mbox{NH}_4\mbox{OH} & + & \mbox{HCI} & \longrightarrow & \mbox{NH}_4\mbox{CI} + \mbox{H}_2\mbox{O} \\ & \mbox{Weak base} & \mbox{Strong acid} \end{array}$

At end point pH will be less than 7 as strong acid weak base salt have pH = 7 - $\frac{(pK_b + logc)}{2}$. \therefore Methyl orange will change colour from yellow to pinkish red at the end point.

27.
$$Ba^{+2} + SO_4^{2-} \longrightarrow BaSO_{4(s)}$$

final conc. of $[SO_4^{2-}] = \frac{MV_1}{V_1 + V_2} = \frac{1 \times 50}{500} = 0.1M$
Final conc. of $[Ba^{+2}]$ when $BaSO_4$ start precipitating
 $K_{SP} = Q_{SP} = [Ba^{+2}][SO_4^{2-}]$
 $10^{-10} = [Ba^{+2}](0.1M)$
 $[Ba^{+2}] = 10^{-9}M$
initial conc. $[Ba^{+2}]$; initial volume was = 500 -50 =450ml
 $M_1V_1 = M_2V_2$
 $M_1 = \frac{M_2V_2}{V_1} = \frac{10^{-9} \times 500}{450}$
 $M_1 = 1.1 \times 10^{-9} M$

 $HCI \longrightarrow H^+ +$ 28. CI-(0.2 + x + y)0.2 $H_2S \longrightarrow H^+ +$ HS⁻: Ka₁ =10⁻⁷ (x –y) 0.1-x (0.2 + x + y) HS- ← → H+ + S²⁻: Ka₂ =1.2×10⁻¹³ (x-y) (0.2 + x + y)(y) $[H^+] = (0.2 + x + y)M = 0.2M$ $K_{a1} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{0.2 \times [HS^-]}{0.1 - x} = \frac{0.2[HS^-]}{0.1}$ (x = negligible) $[HS^{-}] = \frac{Ka_1 \times 0.1}{0.2} = \frac{1}{2} \times 10^{-7}$ $K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{[0.2M][S^{2-}]}{\frac{1}{2} \times 10^{-7}}$ $[S^{2-}] = \frac{Ka_2 \times \frac{1}{2} \times 10^{-7}}{0.2} = \frac{1.2 \times 10^{-13} \times \frac{1}{2} \times 10^{-7}}{0.2}$

$$= 3 \times 10^{-20} \,\mathrm{M}$$

- 29. $H_2SO_4 + 2NH_4OH \longrightarrow (NH_4)_2 SO_4 + 2H_2O$ 2m.m 6m.m. - 2mm 2mm $pOH = 4.7 + \log \frac{4}{2} = 5$ pH = 14 - 5 = 9
- **30.** $8 \times 10^{-12} = (2S' + 0.1)^2 S'$ or S' = $8 \times 10^{-10} M$