

IONIC EQUILLINCE

Ionic

Equilibrium

# Ionic Equilibrium

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## • A/B Theories :

### ① Arrhenius A/B Theory :

Acid - It produces  $H^+$  when dissolved in  $H_2O$

Base - It produces  $OH^-$  when dissolved in  $H_2O$

### ② B/L - A/B Theory :

Acid -  $H^+$  donor

Base -  $H^+$  acceptor

Conjugate acid - add of  $H^+$

Conjugate base - Removal of  $H^+$

### • conjugated A/B pair :

A/B pair which

differ by only one  $H^+$

### ③ Lewis A/B Theory :

Acid : -  $e^-$  pair acceptor

To accept  $e^-$  pair [L.P] = Vacant orbital required.

Base :-  $e^-$  pair donor

To donate  $e^-$  pair [L.P] = L.P on central atom

of molecule/ion required

### • Lewis Acid :

- ①  $BF_3$
  - ②  $AlCl_3$
- } All Group-13 elements.  
B, Al, Ga, In, Tl



- ③  $Al^{+3}$  } All most all cations.  $[+1]$   $[+1]$   $[+1]$  ①
- ④  $Fe^{+2}$  }  $[+1]$   $[+1]$   $[+1]$  ①
- ⑥  $SF_6$  }  $sp^3d$ ,  $sp^3d^2$ ,  $sp^3d^3$
- ⑥  $PCl_5$  }  $4V \cdot 0$   $3V \cdot 0$   $2V \cdot 0$
- ⑦  $CO_2$  — multiple bonds within dissimilar atoms.
- ⑧  $O$  — Group -16 [elements]. ①
- α ⑨  $NH_4^+$  /  $H_3O^+$  /  $PH_4^+$  ①
- ⑩  $Cl_2O_7$  — multiple bonds within dissimilar atoms.

• Lewis Base :  $G-15$  /  $G-16$  /  $G-17$

1LP      2LP      3LP

- ①  $NH_3$
- ②  $C_6H_5NH_2$
- ③  $H-O-H$
- ④  $R-O-H$
- ⑤  $R-SH$
- ⑥  $SO_4^{-2}$  }  $[+1]$   $[+1]$   $[+1]$  ①
- ⑦  $N^{-3}$  } All most all anions.  $[+1]$   $[+1]$   $[+1]$  ①
- ⑧  $CN^-$  }  $[+1]$   $[+1]$   $[+1]$  ①
- ⑨  $CH_2 = CH_2$
- ⑩  $CH \equiv CH$   $[+1]$   $[+1]$   $[+1]$  ①

• Ionic product of water:

- ①  $K_w = [H^+][OH^-]$
- ② At room temperature /  $25^\circ C \rightarrow [H^+] = [OH^-] = 10^{-7} M = 10^{-7} mol/L$
- ③  $K_w = 10^{-14} M^2$  at  $25^\circ C$

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

Ostwald dilution law for weak electrolyte:  $[W.A/W.B] : 1$

① strong electrolytes [S.A / S.B / salt] undergo 100% dissociation  $[\alpha = 100\%]$

② Weak electrolytes [W.A / W.B]

Degree of dissociation = very very less

$\alpha$  = degree of dissociation or ionisation

$K_a$  = dissociation constant of W.A.

$K_b$  = dissociation constant of W.B.

W.A	W.B
① $[H^+] = c \cdot \alpha$	① $[OH^-] = c \cdot \alpha$
② $K_a = c \alpha^2$	② $K_b = c \alpha^2$
$\alpha = \sqrt{\frac{K_a}{c}}$	$\alpha = \sqrt{\frac{K_b}{c}}$
③ $[H^+] = \sqrt{K_a \cdot c}$	③ $[OH^-] = \sqrt{K_b \cdot c}$

$p^H$  scale:

①  $p^H = -\log [H^+]$       a)  $p^H + p^{OH} = [H^+] = K_w$

②  $p^{OH} = -\log [OH^-]$        $[H^+] \cdot [OH^-] = 10^{-14}$

③  $p^{K_a} = -\log [K_a]$

④  $p^{K_b} = -\log [K_b]$       b)  $p^{K_a} + p^{K_b} = 14$

⑤  $[H^+] = \text{Antilog} [-p^H]$       c)  $K_a \cdot K_b = 10^{-14}$

c) For Acids  $p^H < 7$

$$\log 1 = 0$$

For Base  $p^H > 7$

$$2 = 0.30$$

For neutral  $p^H = 7$

$$3 = 0.47$$

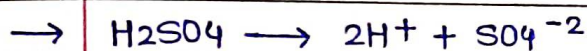
$$4 = 0.60$$

$$5 = 0.69$$

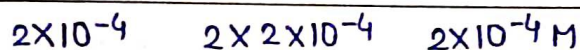
Q.  $2 \times 10^{-4}$  M  $H_2SO_4$  soln  $p^H$  value is

$$6 = 0.77$$

$$7 = 0.84$$



$$8 = 0.90$$



$$9 = 0.95$$

$$4 \times 10^{-4}$$

$$10 = 1$$

$$p^H = 4 - \log 4$$

$$= 4 - 0.60$$

$$= 3.40.$$

Q. 0.005 M NaOH soln  $p^H$  value is



$$5 \times 10^{-3} \text{ M}$$

$$5 \times 10^{-3} \text{ M}$$

$$p^{OH} = 3 - \log 5$$

$$p^H = 14 - p^{OH}$$

$$= 3 - 0.69$$

$$p^H = 14 - 2.31$$

$$= 2.31$$

$$p^H = 11.69.$$

Q. 0.01 M  $CH_3COOH$  undergo 0.01 % dissociation  $p^H = ?$

$$\rightarrow C = 0.01 \text{ M} \quad \alpha = 0.01 \%$$

$$= 10^{-2}$$

$$= 10^{-4}$$

$$[H^+] = C\alpha$$

$$p^H = \underline{\underline{6}}$$

$$= 10^{-2} \times 10^{-4}$$

$$= 10^{-6}$$

Q. 0.56 g of KOH dissolved in 200 ml of H<sub>2</sub>O pH = ?

→ 0.56 g KOH ——— [OH<sup>-</sup>] = N<sub>Base</sub>.

$$N = \frac{\text{wt}}{\text{E.wt}} \times \frac{1000}{\text{Vml}}$$

$$= \frac{0.56}{56} \times \frac{1000}{200}$$

$$\text{E.wt} = \text{M.wt} \times \alpha\text{-factor}$$

$$= \frac{56}{1}$$

$$N_{\text{Base}} = [\text{OH}^-] = 0.05$$

$$= 5 \times 10^{-2}$$

$$p^{\text{OH}} = 2 - \log 5$$

$$= 2 - 0.69$$

$$= 1.31.$$

$$pH = 14 - 1.31$$

$$= 12.69.$$

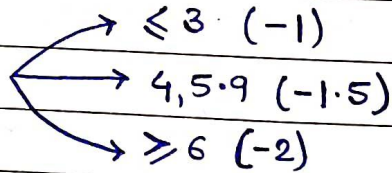
Q. pH of 0.1 M HCN is 2.34 Then calculate K<sub>a</sub> and α values ?

→ pH = 2.34

$$[\text{H}^+] = \text{Antilog} [-2.34]$$

$$-3 + 0.64$$

6.4



$$[\text{H}^+] = 4.4 \times 10^{-3}$$

①  $[\text{H}^+] = \alpha c$

$$4.4 \times 10^{-3} = 10^{-1} \times \alpha$$

$$\alpha = 4.4 \times 10^{-2}$$

$$\alpha = 4.4\%$$

②  $[\text{H}^+] = \sqrt{K_a \cdot c}$

$$4.4 \times 10^{-3} = \sqrt{K_a \cdot 10^{-1}}$$

$$4.4 \times 4.4 \times 10^{-6} = K_a \cdot 10^{-1}$$

$$K_a = 4.4 \times 4.4 \times 10^{-5} //$$

Q. K<sub>a</sub> (HCN) = 1 × 10<sup>-5</sup>

pH = ?

conc. of HCN = 0.05 M

→  $K_a = 1 \times 10^{-5}$  At room temperature  
 $c = 0.05$  conc. of Hydronium ion =  $1 \times 10^{-10}$   
 Then  $pOH$  of solution: ←

$$[H^+] = \sqrt{K_a \cdot c}$$

$$= \sqrt{10^{-5} \times 5 \times 10^{-2}} \rightarrow [H_3O]^+ = [OH^-] = ?$$

$$= \sqrt{5 \times 10^{-7}} \quad [H^+] = 10^{-10}$$

$$= \sqrt{50 \times 10^{-8}}$$

$$= 7 \times 10^{-4} \text{ (app)}$$

$$K_w = [H^+][OH^-]$$

$$1 \times 10^{-14} = 10^{-10} [OH^-]$$

$$[OH^-] = 10^{-4}$$

$$pOH = 4 - 1 = 3$$

$$pH = 4 - \log 7$$

$$= 4 - 0.84 = 3.16$$

• If equal volume of two acids mixed  
 $pH = \text{lower } pH + 0.30$

• If equal volume of two bases mixed  
 $pH = \text{higher } pH - 0.30$

Q. 4g of NaOH dissolved in 1000 ml of  $H_2O$  conc. of  $H^+$  ions is

$$\rightarrow [OH^-] = N_{\text{base}} = \frac{wt \times 1000}{E_{wt} \cdot V_{ml}}$$

$$[OH^-] = \frac{4 \times 1000}{40 \cdot 1000}$$

$$[OH^-] = 10^{-1}$$

$$K_w = [H^+][OH^-]$$

$$1 \times 10^{-14} = 10^{-1} [H^+]$$

$$[H^+] = 1 \times 10^{-13}$$

Q. 100 ml of 0.2 M HCl; 100 ml of 0.4 M HNO<sub>3</sub> are mixed pH = ?

→ If two or more only acids or only bases are mixed

$$pH = [-\log [H^+]] \quad NRS = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

$$[H^+] = \frac{0.2 \times 100 + 0.4 \times 100}{100 + 100}$$

$$[H^+] = \frac{60}{200} = 0.3 = 3 \times 10^{-1}$$

$$pH = 1 - \log 3 = 0.47$$

Normality = Molarity  $\times$  x-factor

Q. 200 ml of 0.2 M HCl and 400 ml of 0.1 M NaCl are mixed.

→ When A and B Both are mixed

$$\textcircled{1} \quad N_aV_a > N_bV_b \text{ [Acidic]} \rightarrow [H^+]_{RS} \rightarrow NRS = \frac{N_aV_a - N_bV_b}{V_a + V_b}$$

$$\textcircled{2} \quad N_bV_b > N_aV_a \text{ [Basic]} \rightarrow [OH^-]_{RS} \rightarrow NRS = \frac{N_bV_b - N_aV_a}{V_a + V_b}$$

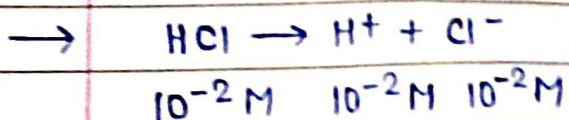
$$\textcircled{3} \quad N_aV_a = N_bV_b \text{ [Neutral]} \rightarrow pH = 7$$

$$N_aV_a = 0.2 \times 200 = 40$$

$$N_bV_b = 0.1 \times 400 = 40$$

$$pH = 7$$

Q. 1 ml of  $10^{-2}$  M is diluted upto 100 ml pH = ?



$$[H^+] = 10^{-2}$$

$$pH = 2$$



• pH = 2 (Acid)

10 times diluted pH inc. by 1 unit (3)

100 times diluted pH inc. by 2 unit (4)

1000 times diluted pH inc. by 3 unit (5)

• pH = 13 (Basic)

10 times diluted pH dec by 1 unit (12)

100 times diluted pH dec by 2 units (11)

1000 times diluted pH dec by 3 units (10)

• solubility product concept:

Solubility: The maxi. amount [moles or g] salt that can be dissolved in 1L of solvent (H<sub>2</sub>O).

• Solubility depends upon:

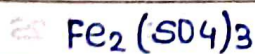
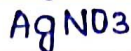
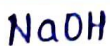
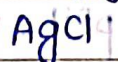
① Nature of salt.

② Nature of solvent (H<sub>2</sub>O)

③ Temp.

④ Common-Ion effect.

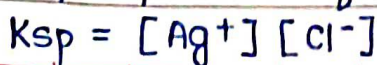
• Soluble salts  $\propto$  sparingly soluble salt ✓



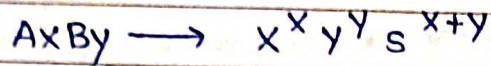
• Solubility  $\propto \frac{1}{\text{Temp}}$

• Solubility  $\propto \frac{1}{\text{C.I. effect}}$

• K<sub>sp</sub>: product of molar conc of ions which is soluble in H<sub>2</sub>O.

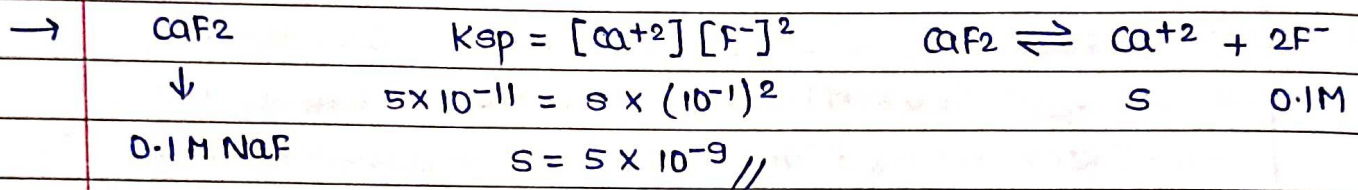


I. Relation Between  $K_{sp}$  and  $s$ :

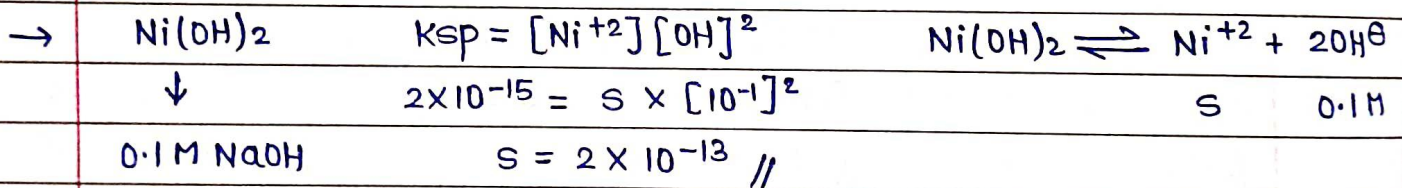


- solubility = Molarity =  $n \times \frac{1}{V_L} = \text{mole/L}$

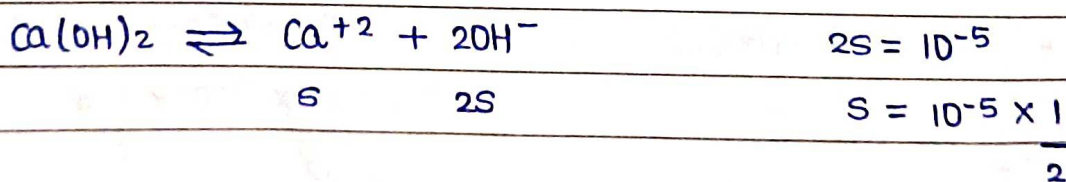
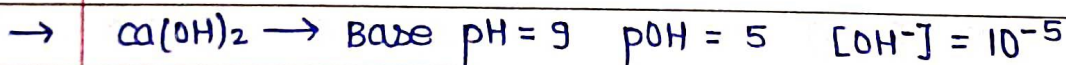
Q. The solubility of  $CaF_2$  in 0.1 M NaF solution. If  $K_{sp} = 5.3 \times 10^{-11}$  ( $CaF_2$ )



Q. Find out solubility of  $Ni(OH)_2$  in 0.1 M NaOH If  $K_{sp}(Ni(OH)_2) = 2 \times 10^{-15}$



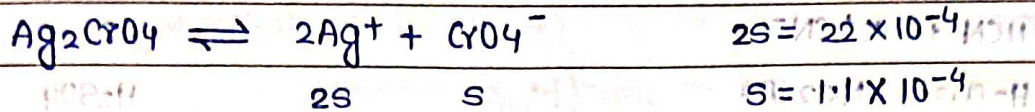
Q. pH of salt soln of  $Ca(OH)_2 = 9$  The  $K_{sp}$  of  $Ca(OH)_2$  is



$$\begin{aligned}
 K_{sp} &= [Ca^{+2}][OH^-]^2 \\
 &= \frac{1}{2} \times 10^{-5} \times 10^{-5} \times 10^{-5} \\
 &= 0.25 \times 10^{-15}
 \end{aligned}$$

Q. Conc. of  $\text{Ag}^+$  ions in  $\text{Ag}_2\text{CrO}_4 = 2.2 \times 10^{-4} \text{ mol/L}$   
 Then  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4 = ?$

→



$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$K_{sp} = (2.2 \times 10^{-4})^2 (1.1 \times 10^{-4}) //$$

• Concept :-

① unsaturated sol<sup>n</sup> →  $K_{IP} < K_{SP}$

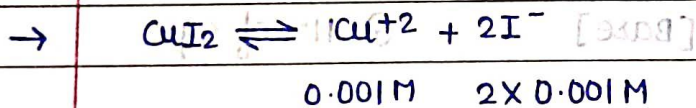
② saturated sol<sup>n</sup> →  $K_{IP} = K_{SP}$

③ super saturated sol<sup>n</sup> →  $K_{IP} > K_{SP}$  (ppt)

Q. Eq. vol of 0.002 M  $\text{NaI}$  and  $\text{Cu}(\text{ClO}_3)_2$  are mixed. If  $K_{sp}$  of

$$\text{Cu}(\text{ClO}_3)_2 = 7.4 \times 10^{-8}$$

In this  $\text{CuI}_2$  salt get ppt or not?



$$0.001 \text{ M} \quad 2 \times 0.001 \text{ M}$$

$$K_{IP} = [\text{Cu}^{2+}] [\text{I}^-]^2$$

$$= (10^{-3}) (2 \times 10^{-3})^2$$

$$K_{IP} = 4 \times 10^{-9}$$

$$K_{SP} = 7.4 \times 10^{-8}$$

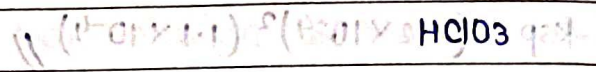
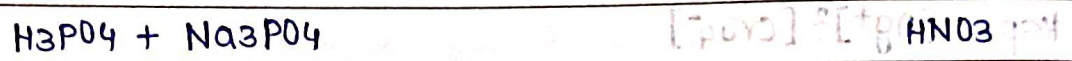
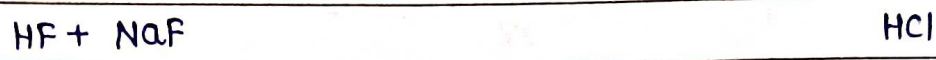
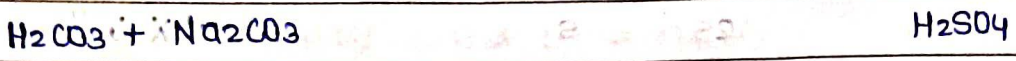
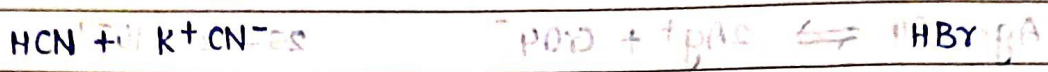
[Here  $K_{IP} < K_{SP}$  → unsaturated sol<sup>n</sup>

[Hence] No precipitation.

• Buffer solution - The solution can't change its pH upon addition of small amount of A/B.

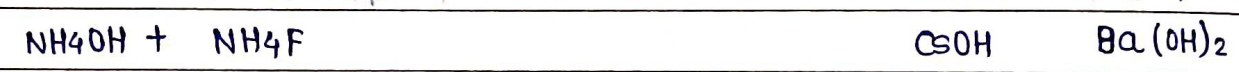
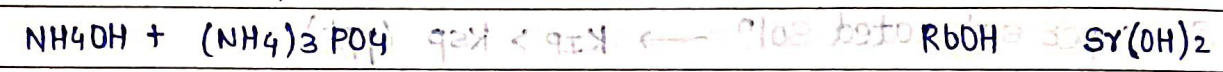
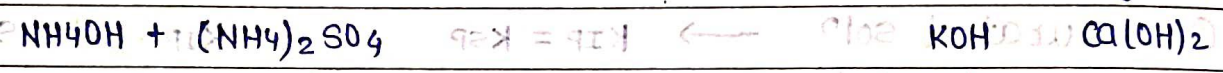
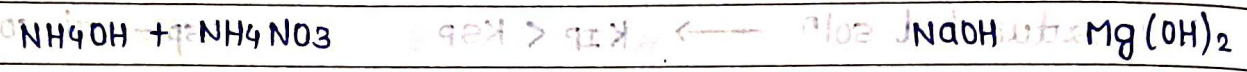
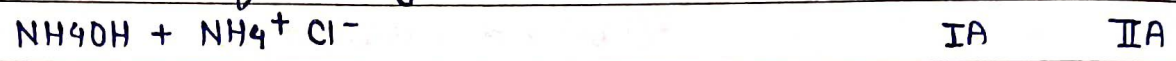
① Acidic B.S

WA + salt of its conjugate Base =  $HClO_4$



② Basic B.S

WB + salt of its conj. Acid



• ABS  $\rightarrow pH = pK_a + \log \frac{[salt]}{[Acid]}$  ① N/M

BBS  $\rightarrow pOH = pK_b + \log \frac{[salt]}{[Base]}$  ② NV/MV

③ n ④ No. of eq.

Q. A vessel contain 0.8 moles  $NH_4Cl$  and 0.2 moles of  $NH_4OH$

If  $K_b = 2 \times 10^{-5}$  pH of solution is

$\rightarrow$

BBS  $\rightarrow pOH = pK_b + \log \frac{[salt]}{[Base]}$   $pK_b = 5 - \log 2$

$pOH = 4.70 + \log \frac{0.8}{0.2} = 4.70$

$pOH = 5.30$

$pH + 5.30 = 14$

$pH = 14 - 5.30 //$

Q.  $K_a$  of HCN =  $5 \times 10^{-10}$  To main pH = 9 The volume of 5M KCN solution required to add 10 ml of 2M HCN.

$K_a = 5 \times 10^{-10}$

→  $pH = pK_a + \log \left( \frac{[salt]}{[Acid]} \right)$   
 $pK_a = 10 - \log 5 = 10 - 0.69 = 9.31$

$9 = 9.31 + \log \frac{5 \times V_s}{2 \times 10}$   
 $-0.31 = \log \frac{5 \times V_s}{20}$

$\log 2 = \log \frac{5 \times V_s}{20}$

- ① Neutral salt + Acid
- ② WA + SA salt
- ③ SA + WB salt
- ④ WA + SB salt

Q. The dissociation constant of WB =  $10^{-4}$  The ratio of salt and WB to main pH = 9.

→  $pH = 9$   $pOH = 5$   $K_b = 10^{-4}$

BBS →  $pOH = pK_b + \log \left( \frac{[salt]}{[Base]} \right)$

$5 = 4 + \log \left( \frac{S}{B} \right)$

$1 = \log \left( \frac{S}{B} \right)$   $\log 10 = \log \left( \frac{S}{B} \right)$   
 $\log(B) = \log(S)$

Q. In an acidic B.S (pH = 4.4) and (salt) = 2:1 Value of  $K_a$  ?

→  $pH = pK_a + \log \left( \frac{[salt]}{[Acid]} \right)$

$4.4 = pK_a + \log 2$

$pK_a = 4.4 - 0.30$

$pK_a = 4.10$

$K_a = 7 \times 10^{-5}$

$9.0 \left( \begin{array}{l} \leq 4 \text{ (-1)} \\ 4 \text{ to } 6 \text{ (-1.5)} \\ \geq 6 \text{ (-2)} \end{array} \right)$

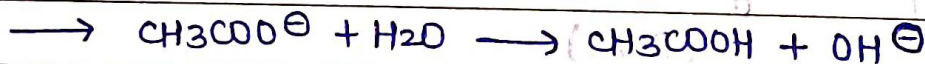
• Buffer capacity :- The no. of moles of A or B added to 1L of B.S to change the pH value.

B.C = no. of moles of A/B added to 1L B.S / change (in pH) value.

• Salt hydrolysis  $\rightarrow$  salt + H<sub>2</sub>O  $\rightarrow$  A + B

- ① SA + SB salt  $\rightarrow$  Neutral pH=7 Both H<sup>+</sup> or OH<sup>-</sup> ions
- ② WA + SB salt  $\rightarrow$  Basic pH > 7 OH<sup>-</sup> ions anionic
- ③ SA + WB salt  $\rightarrow$  Acidic pH < 7 H<sup>+</sup> ions cationic
- ④ WB + WA salt  $\rightarrow$  Neutral pH=7 No H<sup>+</sup> or OH<sup>-</sup> ions

① CH<sub>3</sub>COONa + H<sub>2</sub>O  $\rightarrow$  CH<sub>3</sub>COOH + NaOH



1) CH<sub>3</sub>COONa is a salt of WA and SB

2) Nature of salt  $\rightarrow$  OH<sup>-</sup> (Basic) [pH > 7]

3) It undergoes anionic hydrolysis

4) This salt gives OH<sup>-</sup> ion.

Q. pH of NH<sub>4</sub>CN [K<sub>a</sub> = 1.9 × 10<sup>-10</sup> K<sub>b</sub> = 2 × 10<sup>-5</sup>]

$\rightarrow$  WA + WB  $\rightarrow$  pH = 7 +  $\frac{1}{2}$  (pK<sub>a</sub> - pK<sub>b</sub>)

$$\text{pH} = 7 + \frac{1}{2} (9.05 - 4.70)$$

2

Q. The hydrolysis constant of 0.5 M NaCN [Ka of HCN =  $2 \times 10^{-6}$ ]

→ ①  $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 0.5 \times 10^{-8} = 5 \times 10^{-9}$

②  $h = ?$       ③  $pH = 7 + \frac{1}{2} (pK_a + \log c)$

$K_h = ch^2$

$5 \times 10^{-9} = 5 \times 10^{-1} h^2$

$h^2 = 10^{-8}$

$h = 10^{-2} \%$

$pH = 7 + \frac{1}{2} (5.70 + 0.31) //$

	$K_h$ value	$h$ value	$[H^+]$ or $[OH^-]$	pH Value
SA + SB	No hydrolysis	—	Neutral	$pH = 7$
SA + WB	Cationic $K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_w}{K_b \cdot c}}$	$[H^+] = ch$ $[H^+] = \sqrt{\frac{K_w \cdot c}{K_b}}$	Acidic nature $pH < 7$ $pH = 7 - \frac{1}{2} (pK_a + \log c)$
WA + SB	Basic Anionic $K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_w}{K_a \cdot c}}$	$[OH^-] = ch$ $[OH^-] = \sqrt{\frac{K_w \cdot c}{K_a}}$	Basic nature $pH > 7$ $pH = 7 + \frac{1}{2} (pK_b + \log c)$
WA + WB	Neutral $K_h = \frac{K_w}{K_a \cdot K_b}$	$h = \sqrt{\frac{K_w}{K_a \cdot K_b}}$	$[H^+] = K_a \cdot h$ $[H^+] = \sqrt{\frac{K_w \cdot K_a}{K_b}}$	$pH = 7 + \frac{1}{2} (pK_a - pK_b)$

$h$  = degree of hydrolysis  
 $K_h$  = Hydrolysis constant.