

## LECTURE # 1

### Introduction :

All the substances can be classified into

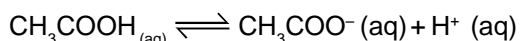
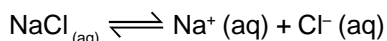
Non electrolytic substances

\* Will not dissociate into ions on dissolving in solvent like water.  
eg.  $C_6H_6$ , diethyl ether

Electrolytic substances

\* Will dissociate on dissolving in water into ions.  
\* Solution will be conductor of electricity.  
Eg. Salt like  $NaCl$ ,  $BaCl_2$   
\*  $Hg_2Cl_2$  dissolve but dissociate negligible.

When an electrolyte is dissolved in a solvent(water), it spontaneously dissociates into oppositely charged ions, partially or sometimes fully



The degree of dissociation of an electrolyte ( $\alpha$ ) is the fraction of one mole of the electrolyte that has dissociated under the given conditions. The value of  $\alpha$  depends on

- (A) nature of the electrolyte      (B) nature of the solvent  
(C) the dilution      (D) temperature

#### (a) Nature of electrolyte :

Electrolytes 100% dissociated at all reasonable concentrations under normal temperatures - **strong electrolytes**.

Strong acids(generally  $HClO_4$ ,  $HI$ ,  $HBr$ ,  $HCl$ ,  $H_2SO_4$ ,  $HNO_3$ ), strong bases (generally ( $NaOH$ ,  $KOH$ ,  $RbOH$ ,  $CsOH$  and  $Ba(OH)_2$ )) and all type of salts (SASB, SAWB, WASB, or WAWB) are all examples of strong electrolytes.

electrolytes not 100% dissociated - **weak electrolytes**. weak acids ( $CH_3COOH$ ,  $HCN$ ), weak bases( $NH_3$ ,  $Zn(OH)_2$ ) are examples.

#### Electrolytic substances :

1. For strong electrolyte  $\alpha$  is considered to be unity because of 100% ionisation.
2. For weak electrolyte In most practical cases  $\alpha \ll 10\%$  or  $\alpha < 0.1$  (generally valid if  $K_{eq} < 10^{-3}$ )

#### (b) Nature of solvent :

A solvent having high value of **dielectric constant** and high **solvation**(in water **hydration**) will favour dissociation.

#### (c) Temperature :

On increasing temperature generally degree of dissociation increases.

#### (d) Dilution :

For some electrolytes degree of dissociation increases by dilution (**Ostwald's dilution law**)

## ACIDS BASES AND SALTS :

### 1. Arrhenius concept :

**Arrhenius Acid** : Substance which generate  $H^+$  ion on dissolving in water ( $H^+$  generator)  
eg.  $HNO_3$ ,  $HClO_4$ ,  $HCl$ ,  $HI$ ,  $HBr$ ,  $H_2SO_4$ ,  $H_3PO_4$  etc.

If acid release only one  $H^+$  ion is known as mono basic/monoprotic symbol -  $H.A$ .

If two  $H^+$  ion releases then known as dibasic/diprotic symbol  $\rightarrow H_2A$

If triprotic / tribasic eg.  $H_3PO_4$  (symbol  $H_3A$ )

\*  $H_3BO_3$  is not Arrhenius acid.

\* Due to high charge density,  $H^+$  ion in water is extremely hydrated (in form of  $H_3O^+$ ,  $H_5O_2^+$ ,  $H_7O_3^+$ )

\* The structure of solid  $HClO_4$  is studied by X-ray, It is found to be consisting of  $H_3O^+$  and  $ClO_4^-$ .  
 $HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$  (better representation)

**Arrhenius base :**

Any substance which releases  $\text{OH}^-$  ion in water ( $\text{OH}^-$  ion generator)

→ mono acidic base :  $\text{CsOH}$ ,  $\text{RbOH}$ ,  $\text{NH}_4\text{OH}$  symbol  $\text{BOH}$

→ diacidic base :  $\text{Ba}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  symbol  $\text{B}(\text{OH})_2$

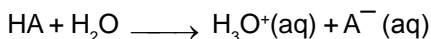
→ Tri-basic base :  $\text{Fe}(\text{OH})_3$

\*  $\text{OH}^-$  ion also in hydrated form of  $\text{H}_3\text{O}_2^-$ ,  $\text{H}_7\text{O}_4^-$ ,  $\text{H}_5\text{O}_3^-$

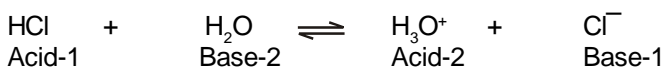
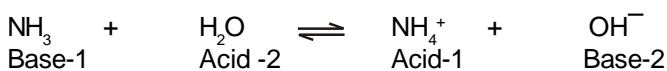
**2. Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)**

Acid :  $\text{H}^+$  doner

Base :  $\text{H}^+$  acceptor



Hydronium ion



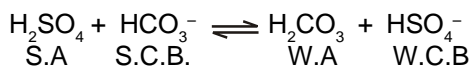
\*\* Congugate acid - base pair

Acid - base which differ only in one proton.

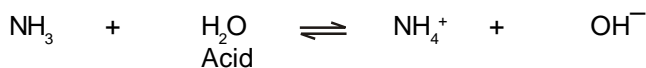
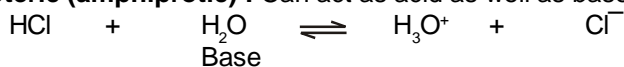


(i) Strong acid will have weak conjugate base.

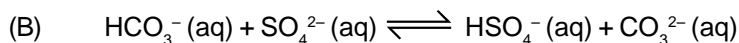
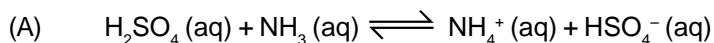
(ii) Reaction will always proceeds from strong acid to weak acid or from strong base to weak base.



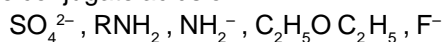
**Amphoteric (amphiprotic) :** Can act as acid as well as base.



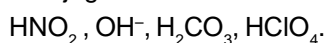
**Q.** If equal concentrations are mixed (of products & reactants) then which of the reaction will proceed to the right and which will proceed to the left.



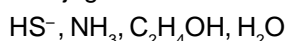
**Q.** (a) Write conjugate acids of



(b) Write conjugate basis of



(c) Write conjugate acids and conjugate basis of amphoteric species.

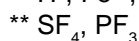
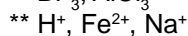
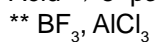


### 3. Lewis concept (electronic concept) :

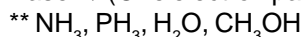
An acid is any molecule/ion which can accept an electron pair with the formation of a coordinate bond.

A base is any molecule/ion which has a lone pair of electrons which can be donated.

⇒ Acid → e<sup>-</sup> pair acceptor



⇒ Base → (One electron pair donate)



Ex. In the reaction

- (A) C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> + HI ⇌ (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sup>+</sup> I<sup>-</sup>. which reactant would be considered as Bronsted acid, is it also an Arrhenous acid is it also a lewis acid.

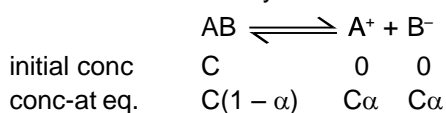
Ans. [HI, yes, no]

- (B) What about the other species (C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>) in the above reaction is it Arrhenius base is it Bronsted base, is it lewis base.

Ans. [No, yes, yes]

### Ostwald's Dilution Law (for weak electrolyte's)

When a weak electrolyte A<sup>+</sup>B<sup>-</sup> is dissolved in water and if α is the degree of dissociation then

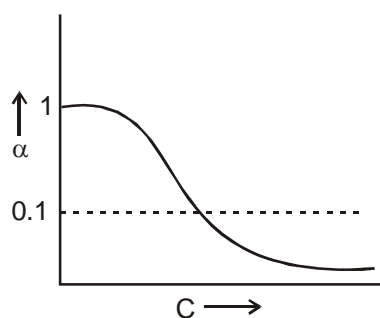


Then according to law of mass action,

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = \text{dissociation constant of the weak electrolyte}$$

$$[C = \frac{1}{V}, \text{ then } V = 1/C (\text{volume of solution in which 1 mole is present}) \text{ is called } \textbf{dilution}, \text{ so } k_{eq} = \frac{\alpha^2}{(1-\alpha)V}]$$

If α is negligible in comparison to unity 1 - α ≈ 1.      so  $k_{eq} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{k_{eq}}{C}} = \sqrt{k_{eq} \cdot V}$



as **concentration increases** ⇒ α **decreases** ⇒ **dilution decreases** and at **infinite dilution** α **reaches its maximum value, unity**.      C ↓, α ↑ but (Cα) ↓

## LECTURE # 2

### Acidity and pH scale :

Acidic strength means the tendency of an acid to give  $\text{H}_3\text{O}^+$  or  $\text{H}^+$  ions in water and basic strength means the tendency of a base to give  $\text{OH}^-$  ions in water. So more the tendency of the substance to give  $\text{H}^+$  or  $\text{OH}^-$  ions, more will be the acidic or basic strength of the substance.

The concentration of  $\text{H}^+$  ions is written in a simplified scale introduced by Sorenson known as pH scale. pH is negative logarithm of activity of  $\text{H}^+$  ions.

$$\therefore \text{pH} = -\log a_{\text{H}^+} \quad (\text{where } a_{\text{H}^+} \text{ is the activity of } \text{H}^+ \text{ ions})$$

Activity of  $\text{H}^+$  ions is the concentration of free  $\text{H}^+$  ions or  $\text{H}_3\text{O}^+$  ions in a solution.

For dilute solutions  $[\text{H}^+] \leq 1\text{M}$  concentration can be taken as activity of  $\text{H}^+$  ions while for higher concentrations the activity would be much less than the concentration itself, so is calculated experimentally.

The pH scale was marked from 0 to 14 with central point at 7 at  $25^\circ\text{C}$  taking water as solvent. If the temperature and the solvent are changed, the pH range of the scale will also change. For example

0 – 14	at $25^\circ\text{C}$
0 – 13	at $80^\circ\text{C}$ ( $K_w = 10^{-13}$ )

[Note : pH can also be negative or  $> 14$ ]

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] ; & [\text{H}^+] &= 10^{-\text{pH}} \\ \text{pOH} &= -\log [\text{OH}^-] ; & [\text{OH}^-] &= 10^{-\text{pOH}} \\ \text{pKa} &= -\log K_a ; & K_a &= 10^{-\text{pKa}} \\ \text{pKb} &= -\log K_b ; & K_b &= 10^{-\text{pKb}} \end{aligned}$$

### PROPERTIES OF WATER :

#### 1. Acid/base nature:

Water - an acid as well as base according to Arrhenius and Bronsted-Lowry theory but according to Lewis concept it can only be taken as base only.

In pure water  $[\text{H}^+] = [\text{OH}^-]$  so it is Neutral.

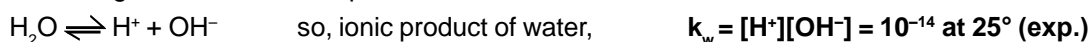
#### 2. Molar concentration / Molarity of water :

$$\text{No. of moles/liter of water} = \frac{\text{mass of 1-litre water in grams}}{\text{molecular mass of water}}$$

$$\text{Molarity} = \text{No. of moles/litre} = \frac{1000\text{gm}}{18\text{gm}} = 55.55 \text{ mole /litre} = \mathbf{55.55 \text{ M}} \quad (\text{density} = 1 \text{ gm/cc})$$

#### 3. Ionic product of water :

According to Arrhenius concept



increasing temp  $\Rightarrow K_w$  increases (dissociation of water, is endothermic, so on increasing temperature  $K_{\text{eq}}$  increases)

Now  $\text{pH} = -\log[\text{H}^+] = 7$  and  $\text{pOH} = \log[\text{OH}^-] = 7$  for water at  $25^\circ$  (exp.)

$\text{pH} = 7 = \text{pOH} \Rightarrow$  neutral

$\text{pH} < 7$  or  $\text{pOH} > 7 \Rightarrow$  acidic

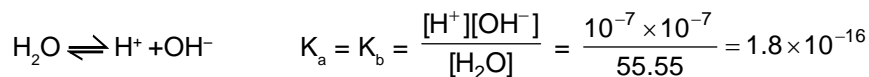
$\text{pH} > 7$  or  $\text{pOH} < 7 \Rightarrow$  Basic

**Note.** Ionic product of water is always a constant whatever has been dissolved in water since its an equilibrium constant so will be dependent only on temperature.

#### 4. Degree of dissociation of water :

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad \Rightarrow \quad \alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\%$$

**5. Absolute dissociation constant of water :**



So,  $\text{p}K_a = \text{p}K_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$

**Note:** For a conjugate acid base pair prove that

$$\text{p}K_a + \text{p}K_b = \text{p}K_w \quad (\text{p}K_w = -\log K_w) = 14 \quad \text{or} \quad K_a \times K_b = K_w$$

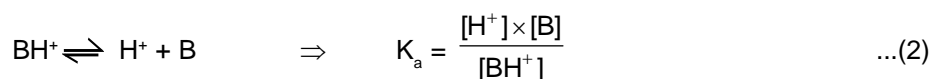
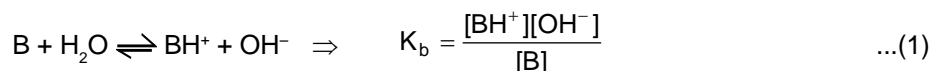
**Note:**  $\text{p}K_a$  of  $\text{H}_3\text{O}^+$  ions = -1.74

**Note:**  $\text{p}K_b$  of  $\text{OH}^-$  ions = -1.74

**Q.** ✍ For a conjugate acid base pair prove that

$$\text{p}K_a + \text{p}K_b = \text{p}K_w \quad (\text{p}K_w = -\log K_w) = 14 \quad \text{or} \quad K_a \times K_b = K_w$$

**Sol.** let B is Bronsted-lowry Base



$$K_a \times K_b = [\text{H}^+][\text{OH}^-] = K_w$$

$$\Rightarrow -\log K_a - \log K_b = -\log K_w \Rightarrow \text{p}K_a + \text{p}K_b = \text{p}K_w = 14 \text{ at } 25^\circ\text{C}$$

**2.** At a temperature under high pressure  $K_w(\text{H}_2\text{O}) = 10^{-10}$ , A solution of pH 5.4 under these conditions is said to be:

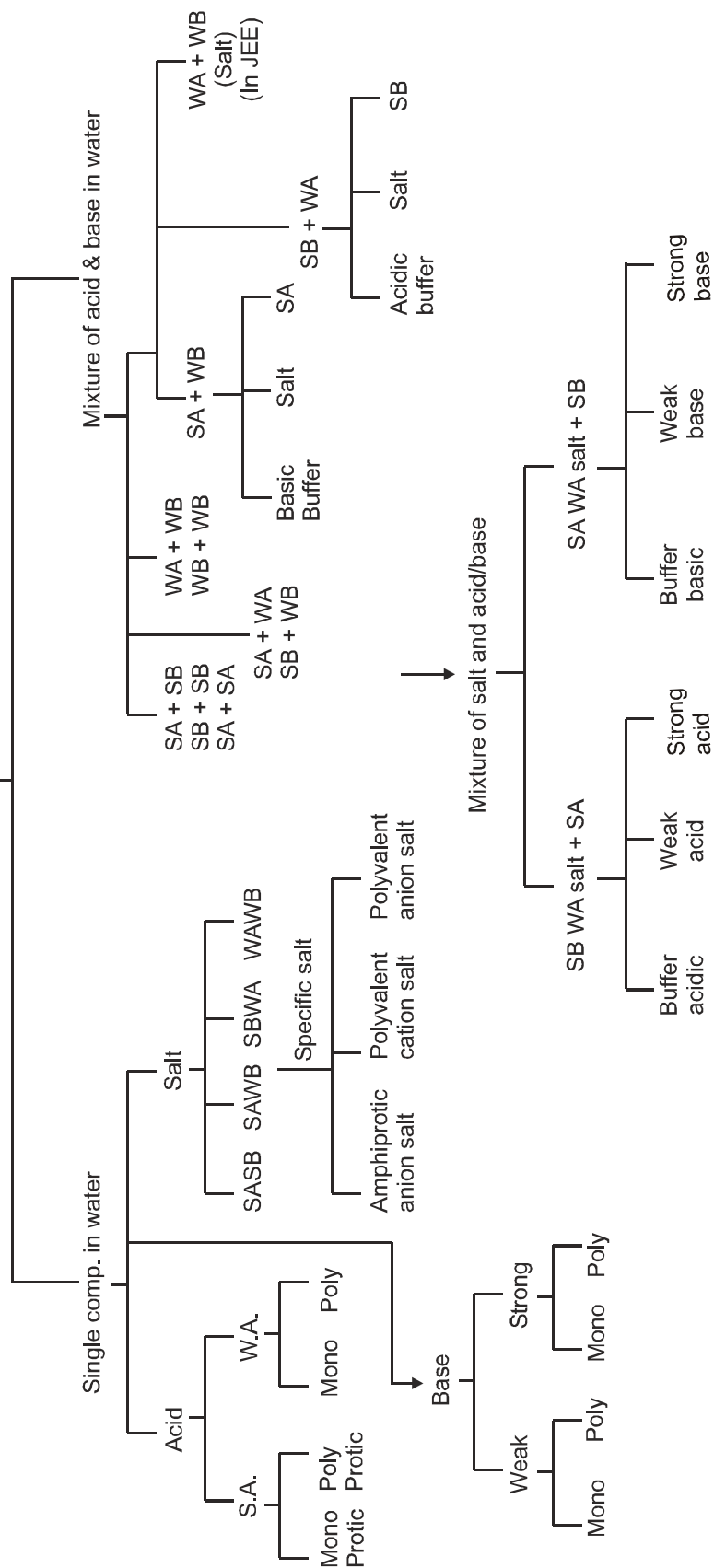
- (A) acidic                      (B) basic                      (C) neutral                      (D) amphitonic

**Q.** ✍ Which is stronger acid  $\text{H}_3\text{O}^+$  or acetic acid ( $K_a = 1.8 \times 10^{-5}$ )

$$\therefore \text{p}K_a(\text{H}_3\text{O}^+) < \text{p}K_a(\text{acetic acid})$$

so,  $\text{H}_3\text{O}^+$  is stronger acid than acetic acid

## pH Calculation



## pH Calculations of Different Types of Solutions :

(a) Strong acid solution :

(i) If concentration is greater than  $10^{-6}$  M

In this case  $H^+$  ions coming from water can be neglected,  
so  $[H^+] = \text{normality of strong acid solution}$

(ii) If concentration is less than  $10^{-6}$  M

In this case  $H^+$  ions coming from water cannot be neglected and since water is a weak electrolyte so its dissociation equilibrium will be disturbed much more than dissociation equilibrium of strong acid.

So  $[H^+] = \text{normality of strong acid} + H^+$  ions coming from water in presence of this strong acid

(b) Strong base solution :

Using similar method as in part (a) calculate first  $[OH^-]$  and then use  $[H^+] \times [OH^-] = 10^{-14}$

**Q.** Calculate pH of a solution obtained by dissolving 490 mg of  $H_2SO_4$  in water, so total volume of solution becomes 100 ml.

**Sol.** 
$$\text{Molarity} = \frac{490 \times 10^{-3}}{98 \times 100} \times 1000 = \frac{1}{20} = 0.05$$

Normality =  $2 \times \text{molarity} = 0.1$

$$pH = -\log 10^{-1} = 1$$

**Q.** Calculate pH of  $10^{-7}$  M of NaOH solution

**Sol.**  $[OH^-]$  from NaOH =  $10^{-7}$

$[OH^-]$  from water =  $x < 10^{-7}$  M (due to common ion effect)



—  $(x + 10^{-7})$      $x$

$K_w = [H^+][OH^-] = 10^{-14} = x(x + 10^{-7})$

$x^2 + 10^{-7}x - 10^{-14} = 0$

$$\Rightarrow x = \frac{\sqrt{5} - 1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$$

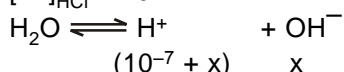
$[OH^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$

$pOH = 7 - \log(1.618) = 6.8$

$pH = 14 - 6.8 = 7.2$

**Ex.** Calculate the  $\alpha$  of water and pH of  $10^{-7}$  M HCl solution.

**Sol.**  $[H^+]_{HCl} = 10^{-7}$  M



$(10^{-7} + x)$      $x$

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

$10^{-14} = x(10^{-7} + x)$

$\Rightarrow x^2 + 10^{-7}x - 10^{-14} = 0$

$x = 0.618 \times 10^{-7}$

Net  $[H^+] = 10^{-7} + x$

$= 10^{-7} + 0.618 \times 10^{-7}$

$= 1.618 \times 10^{-7}$

$\therefore pH = 7 - \log 1.618$

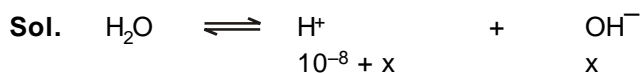
$$= 7 - 0.2 = 6.8 \quad \alpha = \frac{x}{\frac{1000}{18}} \times 100\%$$

$$= 0.618 \times 1.8 \times 10^{-9} / 0.618 \times 1.8 \times 10^{-7} \%$$

% change in  $\alpha$  of water

$$= \frac{(1 - 0.618) \times 1.8 \times 10^{-9}}{1.8 \times 10^{-9}} \times 100\% = 38.2\%$$

**Ex.** ✎ Calculate pH of  $10^{-8}$  M HCl solution.



$$K_w = [\text{H}^+][\text{OH}^-]$$

$$10^{-14} = x(x \times 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2}$$

$$= \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2}$$

$$= \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[\text{pH}] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

$$[\text{pH}] = 7 - \log 1.05 \approx 6.98$$

$$10^{-9} \text{ M HCl pH} \approx 7$$

$$10^{-16} \text{ M HCl pH} \approx 7$$

**Ex.** ✎ Calculate amount of water added to the solution of pH = 2.1. So that pH may get increased to

$$4(\log 2 = 0.3)$$

**Sol.**  $[\text{H}^+]_f = 10^{-4} \text{ M}$

$$[\text{H}^+]_i = 8 \times 10^{-3} \text{ M}$$

$$V_i = 1 \text{ Lt.} = 1000 \text{ ml}$$

$$\text{no. of moles} = (8 \times 10^{-3}) \times (1)$$

of water initially

$$\text{Finalley no. of moles} = 10^{-4} \times V_f$$

$$8 \times 10^{-3} = 10^{-4} V_f$$

$$\Rightarrow 80 = V_f$$

$$\text{Volume of water added} = 80 - 1 = 79 \ell$$



## LECTURE # 3

**(c) pH of mixture of two strong acids :**

If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of another strong acid solution of normality  $N_2$ , then

Number of  $H^+$  ions from I-solution =  $N_1 V_1$

Number of  $H^+$  ions from II-solution =  $N_2 V_2$

If final normality is  $N$  and final volume is  $V$ , then

$$NV = N_1 V_1 + N_2 V_2$$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[H^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

**(d) pH of mixture of two strong bases :**

similar to above calculation

$$[OH^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

**Q.** Calculate pH of mixture of  $(400\text{ml}, \frac{1}{200} \text{ M } H_2SO_4) + (400\text{ml}, \frac{1}{100} \text{ M } HCl) + (200 \text{ ml of water})$

**Sol.**  $N_1 V_1 = \frac{1}{100} \times \frac{400}{1000} = \frac{4}{1000}$ ,  $N_2 V_2 = \frac{4}{1000}$ ,  $H^+$  ions from water will be neglected

$$N_1 V_1 + N_2 V_2 = 8 \times 10^{-3}$$

$$[H^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$$

$$pH = 3 - \log 8 = 2.1$$

**Q.** A 200 ml of 0.1 M HCl solution is added to a 500 ml solution of  $H_2SO_4$  containing 4.9 gm/lit and water is added to the resultant solution so that the final volume becomes one litre. Calculate the pH of resultant solution. ( $\log 7 = 0.84$ )

**Sol.**  $N_{HCl} = 0.1 \text{ N}$ ,  $V_{HCl} = 200 \text{ ml}$   
 $\Rightarrow$  me. of HCl = 20

$$\text{me. of } H_2SO_4 = \frac{4.9}{49} \times 500 = 50$$

$$\therefore [H_3O^+] = \frac{20 + 50}{1000} = 0.07$$

$$pH = -\log (0.07) = 1.16$$

**Ex.** 500 ml of  $10^{-5} \text{ M } NaOH$  is mixed with 500 ml of  $2.5 \times 10^{-5} \text{ M}$  of  $Ba(OH)_2$ . In resultant solution 99 L water is added. Calculate pH.

**Sol.**  $[OH^-] = \frac{.500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{.1000}$   
 $= 3 \times 10^{-5} \text{ M}$

$$M_1 = 3 \times 10^{-5} \text{ M}$$

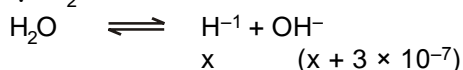
$$V_1 = 1 \text{ L}$$

$$V_2 = 100 \text{ L}$$

no. of moles of  $[OH^-]$  initially = no. of moles of  $[OH^-]$  of

$$3 \times 10^{-5} = M_2 \times 100$$

$$\therefore M_2 = .3 \times 10^{-7} < 10^{-6}$$



$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left( \frac{\sqrt{13} - 3}{2} \right) \times 10^{-7}$$

$$[\text{OH}^-]_{\text{Net}} = \left[ 3 + \frac{\sqrt{13} - 3}{2} \right] \times 10^{-7}$$

$$= \left[ \frac{3 + \sqrt{13}}{2} \right] \times 10^{-7} = 2.36 \times 10^{-7}$$

**(e) pH of mixture of a strong acid and a strong base :**

There will be neutralisation of the acid and the base, and the solution will be acidic or basic depending on which component has been taken in excess.

If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of a strong base solution of normality  $N_2$ , then

Number of  $\text{H}^+$  ions from I-solution =  $N_1 V_1$

Number of  $\text{OH}^-$  ions from II-solution =  $N_2 V_2$

If  $N_1 V_1 > N_2 V_2$ , then solution will be acidic in nature and

$$[\text{H}^+] = N = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

If  $N_2 V_2 > N_1 V_1$ , then solution will be basic in nature and

$$[\text{OH}^-] = N = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$

**Q.** Calculate pH of mixture of (400ml,  $\frac{1}{200}$  M  $\text{Ba}(\text{OH})_2$ ) + (400ml,  $\frac{1}{50}$  M  $\text{HCl}$ ) + (200ml of Water)

**Sol.**  $[\text{H}^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$ , so  $\text{pH} = 3 - 2 \log 2 = 2.4$

**Q.** 560 ml of  $\text{HCl}$  gas (measured at STP) is added to a 500 ml solution of 0.01 M  $\text{NaOH}$ . Calculate pH of resulting solution. ( $\log 2 = 0.3$ )

**Sol.** moles of  $\text{HCl} = \frac{560}{22400} = \frac{1}{40}$ ,

$$\text{m eq of HCl} = \frac{1}{40} \times 1000 = 25$$

$$\text{meq. of NaOH} = 500 \times 0.01 = 5$$

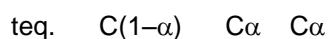
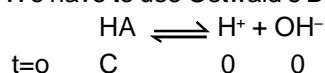
$\therefore$  Resulting solution is acidic

$$[\text{H}^+] = \frac{25 - 5}{500} = \frac{20}{500} = \frac{1}{25}$$

$\therefore \text{pH} = \log (25) = 1.4$

**(f) pH of a weak acid(monoprotic) solution :**

We have to use Ostwald's Dilution law(as have been derived earlier)



$$K_a = \frac{[\text{H}^+][\text{OH}^-]}{[\text{HA}]} = \frac{C\alpha^2}{1-\alpha}$$

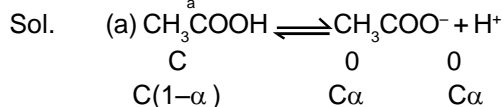
$$\text{if } \alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$[H^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \quad \text{So } \text{pH} = \frac{1}{2}(\text{p}K_a - \log C)$$

$$\text{on increasing the dilution} \Rightarrow C \downarrow \Rightarrow \alpha \uparrow \quad \text{and } [H^+] \downarrow \Rightarrow \text{pH} \uparrow$$

**Q.** Calculate pH of (a)  $10^{-1}$  M  $\text{CH}_3\text{COOH}$  (b)  $10^{-3}$  M  $\text{CH}_3\text{COOH}$  (c)  $10^{-6}$  M  $\text{CH}_3\text{COOH}$

Take  $K_a = 2 \times 10^{-5}$ .



$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

$$\text{So, } [H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$$

$$(b) \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$$

So we have to do the exact calculations

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\%$$

$$[H^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8$$

$$(c) \text{ If approximation is used then, } \alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20} > 1,$$

$$\text{so we have to do the exact calculation, } 2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95 \text{ or } 95\%$$

$$[H^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \Rightarrow \text{pH} = 7 - \log(9.5) = 6.022$$

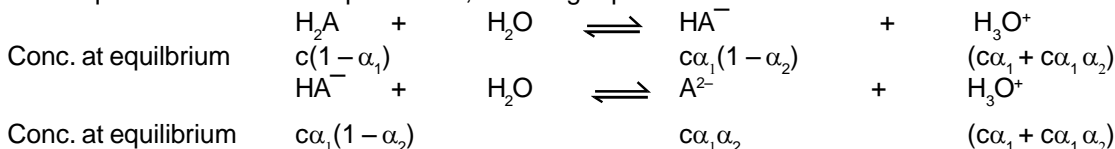
**\*\* At very low concentration ( $\infty$  dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte**

$$[\text{pH of } 10^{-6} \text{ M HCl} \approx \text{pH of } 10^{-6} \text{ M CH}_3\text{COOH} \approx 6; \quad \text{pH of } 10^{-8} \text{ M HCl} = \text{pH of } 10^{-8} \text{ M CH}_3\text{COOH}]$$

**(g) pH of a solution of a polyprotic weak acid :**

Let us take a weak diprotic acid ( $\text{H}_2\text{A}$ ) in water whose concentration is c M. Diprotic acid is the one, which is capable of giving 2 protons in water.

In an aqueous solution of a diprotic acid, following equilibria exist.



where  $\alpha_1$  is the degree of ionization (dissociation) of  $\text{H}_2\text{A}$  in presence of  $\text{HA}^-$  and  $\alpha_2$  is the degree of ionisation of  $\text{HA}^-$  in presence of  $\text{H}_2\text{A}$ .

Knowing the values of  $K_{a_1}$ ,  $K_{a_2}$  and c, the values of  $\alpha_1$  and  $\alpha_2$  can be calculated using equations (i) and (ii).

After getting the values of  $\alpha_1$  and  $\alpha_2$   $[\text{H}_3\text{O}^+]$  can be calculated as.

$$[\text{H}_3\text{O}^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

### Approximation

For diprotic acids,  $K_{a2} < K_{a1}$  and  $\alpha_2$  would be even smaller than  $\alpha_1$ .  
 $\therefore 1 - \alpha_2 \approx 1$  and  $1 + \alpha_2 \approx 1$

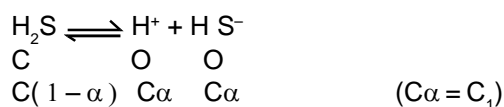
Thus, equation (i) can be reduced to  $K_{a1} = \frac{C\alpha_1 \times \alpha_1}{1 - \alpha_1}$  So  $[H^+] = C\alpha_1$

This is an expression similar to the expression for a weak monoprotic acid. Hence, even for a diprotic acid (or a polyprotic acid) the  $[H_3O^+]$  can be calculated from its first equilibrium constant expression along provided  $K_{a2} \ll K_{a1}$ .

Finally, if the total  $[H_3O^+]$  from the acid is less than  $10^{-6}$  M, the contribution of  $H_3O^+$  from water should be taken into account for calculating pH while if it is  $> 10^{-6}$  M, then  $[H_3O^+]$  contribution from water can be ignored. Using this  $[H_3O^+]$ , pH of the solution can be calculated.

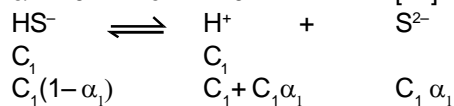
Q.. calculate pH of 0.1M  $H_2S$  solution that  $K_{a1} = 10^{-7}$

$$\alpha = \sqrt{\frac{K_a}{C}}$$



$$\alpha = \sqrt{\frac{K_{a1}}{C}} = \sqrt{\frac{10^{-7}}{10^{-1}}} = 10^{-3}$$

$$\alpha = 10^{-3} \times 10^{-1} = 10^{-4} \quad \therefore [H^+] = 10^{-4} \quad \text{and} \quad pH = 4$$



$$K_{a2} = \frac{C_1(1 + \alpha_1)C_1\alpha_1}{C_1(1 - \alpha_1)} \quad 1 + \alpha \approx 1$$

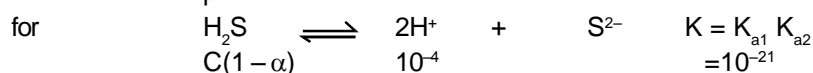
$$1 - \alpha \approx 1$$

$$\alpha_1 = \frac{10^{-14}}{10^{-4}} = 10^{-10}$$

$$\text{net } [H^+] = C_1 + C_1\alpha_1$$

$$= 10^{-4} + 10^{-4} \times 10^{-10} = 10^{-4} + 10^{-14}$$

$$pH = 4$$

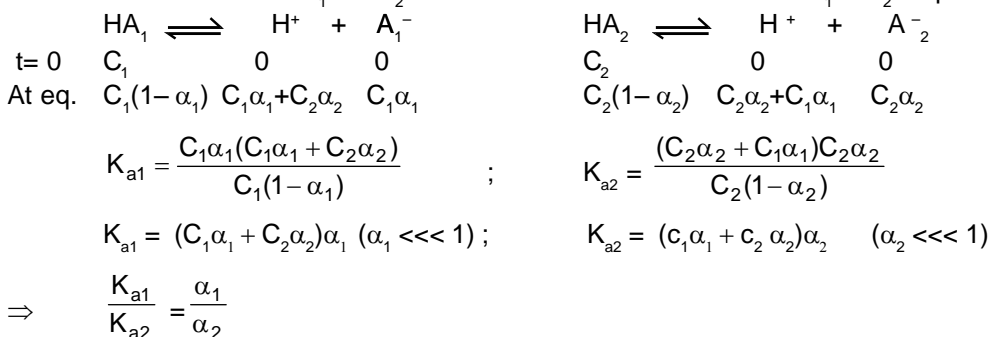


$$K = 10^{-21} = \frac{[S^{2-}] \times 10^{-8}}{10^{-1}}$$

## LECTURE # 4

(h) pH of a mixture of two weak acid(both monoprotic) solutions :

let the acid are  $HA_1$  &  $HA_2$  and their final concentrations are  $C_1$  &  $C_2$  respectively, then



$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a1}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} + \frac{C_2K_{a2}}{\sqrt{C_1K_{a1} + C_2K_{a2}}} \Rightarrow [H^+] = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

So,  $[H^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$

**\*\* If water is again considered third weak acid in solution of two weak acid then**

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2 + K_w}$$

$$C_w = \frac{1000}{18} = 55.5$$

$$K_{aw} = 1.8 \times 10^{-16}$$

$$C_w K_{aw} = 10^{-14} = K_w$$

$$[H^+] = \sqrt{C_1K_{a1} + C_2K_{a2} + 10^{-14}}$$

**Ex.** Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M  $CH_3COOH$  solution given that  $K_{a1}(HOCl) = 2 \times 10^{-4}$  (log2 = 0.3)

$$K_{a2}(CH_3COOH) = 2 \times 10^{-5}$$

also calculate  $OH^-$ ,  $OCI^-$ ,  $CH_3COO^-$

**Sol.** Final solution volume become double

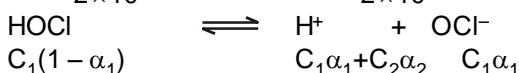
$$C_1 = 0.01, \quad C_2 = 0.1$$

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2}$$

$$= \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1} = \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$pH = 3 - \log 2 = 3 - 0.3 = 2.7$$

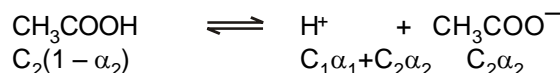
$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} ; \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[OCI^-] = C_1\alpha_1$$

$$= 0.01 \times 10^{-1}$$

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



$$[CH_3COO^-] = C_2\alpha_2$$

$$= 0.1 \times 10^{-2}$$

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

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}$$

$$[HOCl] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M}$$

$$[CH_3COOH] = 10^{-1}(1 - 0.01) \approx 10^{-1}$$

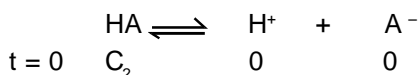
(I) **pH of a mixture of weak acid(monoprotic) and a strong acid solution :**

For the first approximation we can neglect the  $H^+$  ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

To be precise we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If  $[SA] = C_1$  and  $[WA] = C_2$ , then  $[H^+]$  from SA =  $C_1$  and  $[H^+]$  from WA =  $C_2$

Let HA is a weak acid



$$t = t_{(eq)} \quad C_2(1-\alpha) \quad C_2\alpha + C_1 \quad C_2\alpha \quad K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha \ll 1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid)

$$K_a = (C_2\alpha + C_1)\alpha$$

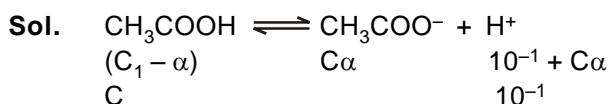
Finally, if the total  $[H^+]$  from the acid is greater than  $10^{-6}$  M, then contribution from the water can be neglected, if not then we have to take  $[H^+]$  from the water also.

**\*\* If a strong acid of low conc is added in water then  $[H^+]$  of solution can be calculated as**

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_w}}{2}$$

$K_a C = K_w$  for water and this solution can be treated as SA + WA solution.

**Ex.** Calculate pH  $10^{-1}$  M HCl if  $10^{-3}$  M  $CH_3COOH$  [ $K_a = 2 \times 10^{-5}$ ]



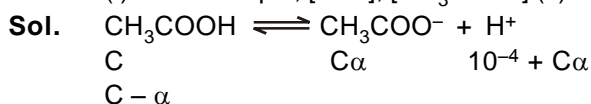
$H^+$  ion can be treated completely from HCl due to less dissociation of  $CH_3COOH$  and its low conc.

$$2 \times 10^{-5} = \frac{C\alpha \times 10^{-1}}{C} \Rightarrow \alpha = 2 \times 10^{-4}$$

$$[H^+]CH_3COOH = C\alpha = 2 \times 10^{-7}$$

**Ex.** In mixture  $[HCl] = 10^{-4}$  M &  $[CH_3COOH] = 10^{-2}$  M,  $K_a(CH_3COOH) = 2 \times 10^{-5}$

(i) Calculate pH,  $[OH^-]$ ,  $[CH_3COO^-]$  (ii) %  $[H^+]$  from  $CH_3COOH$  (iii) %  $[H^+]$  from  $H_2O$ .



$$K_a = 2 \times 10^{-5} = \frac{C\alpha(C\alpha + 10^{-4})}{C}$$

$$10^{-2}\alpha^2 + 10^{-4}\alpha - 2 \times 10^{-5} = 0$$

$$\alpha^2 + 10^{-2}\alpha - 2 \times 10^{-3} = 0$$

$$\Rightarrow \alpha = \frac{-10^{-2} + \sqrt{10^{-4} + 8 \times 10^{-3}}}{2} = \frac{9 \times 10^{-2} - 10^{-2}}{2} = 4 \times 10^{-2} = 0.04 < 0.1$$

$$[H^+]CH_3COOH = C\alpha = 10^{-2} \times 4 \times 10^{-2}$$

$$[H^+]_{net} = 5 \times 10^{-4} \Rightarrow pH = 4 - \log 5 = 3.3$$

$$[OH^-] = 2 \times 10^{-11}; [CH_3COO^-] = 4 \times 10^{-4}$$

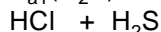
$$\% [H^+] \text{ from } [CH_3COOH] = \frac{4 \times 10^{-4}}{5 \times 10^{-4}} \times 100 = 80\%$$

$$\% [H^+] \text{ from } H_2O = \frac{2 \times 10^{-11}}{5 \times 10^{-4}} \times 100 = 4 \times 10^{-6} \%$$

**Ex.** Calculate pH  $[\text{HS}^-]$ ,  $[\text{S}^{2-}]$ ,  $[\text{Cl}^-]$  in a solution which is 0.1 M HCl & 0.1 M  $\text{H}_2\text{S}$  given that

$$K_{a1}(\text{H}_2\text{S}) = 10^{-7} \quad K_{a2}(\text{H}_2\text{S}) = 10^{-14}. \text{ Also calculate } \alpha_1 \text{ \& } \alpha_2$$

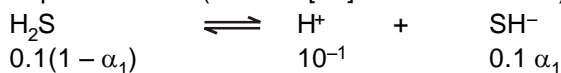
**Sol.**



$$0.1 \quad 0.1$$

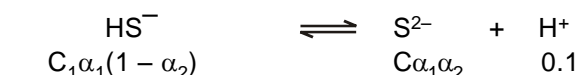
$$C_1 = C_2 = 0.1$$

$$\therefore \text{pH} = 1 \quad (\text{most of } [\text{H}^+] \text{ comes from HCl})$$



$$0.1(1 - \alpha_1) \quad 10^{-1} \quad 0.1 \alpha_1$$

$$K_{a1} = \frac{C\alpha_1 \times 10^{-1}}{C(1 - \alpha_1)} \Rightarrow \frac{10^{-7}}{10^{-1}} = \alpha_1 \Rightarrow \alpha_1 = 10^{-6}$$



$$C_1\alpha_1(1 - \alpha_2) \quad C\alpha_1\alpha_2 \quad 0.1$$

$$10^{-14} = 0.1 \times \alpha_2$$

$$\Rightarrow \alpha_2 = 10^{-13}$$

$$[\text{S}^{2-}] = C\alpha_1 \alpha_2 = 10^{-6} \times 10^{-1} \times 10^{-13} = 10^{-20} \text{ M}$$

**Ex.**

Calculate pH,  $[\text{H}^+]$ ,  $[\text{OH}^-]$ ,  $[\text{CH}_3\text{COO}^-]$   $[\text{CH}_3\text{COOH}]$   $[\text{OH}^-]$ ,  $[\text{H}_2\text{S}]$

$[\text{S}^{2-}]$  in a solution obtained by mixing equal vol. of 0.2 M  $\text{H}_2\text{S}$  & 0.02 M acetic acid given that

$$K_a(\text{CH}_3\text{COOH}) = 2 \times 10^{-5}$$

$$K_a(\text{H}_2\text{S}) = 10^{-7}$$

$$K_a(\text{H}_2\text{S}) = 10^{-14}$$

**Sol.**

$$[\text{H}^+] = \sqrt{10^{-1} \times 10^{-7} + 10^{-2} \times 2 \times 10^{-5}}$$

$$= \sqrt{(0.1 + 2) \times 10^{-7}}$$

$$= \sqrt{2.1 \times 10^{-7}} = \sqrt{21} \times 10^{-4}$$

$$\text{pH} = 4 - \frac{1}{2} \log 21$$

$$[\text{H}_2\text{S}] = 0.1$$

$$[\text{CH}_3\text{COOH}] = 0.01 \text{ in new solution}$$

\* The only first  $[\text{H}^+]$  of  $\text{H}_2\text{S}$  is considered.

$$(\alpha) \text{ acetic acid} = \frac{2 \times 10^{-5}}{\sqrt{21} \times 10^{-4}} = \frac{2}{\sqrt{21}} \times 10^{-1} = 0.0436$$

$$(\alpha_1)_{\text{H}_2\text{S}} = \frac{10^{-7}}{[\text{H}^+]} = \frac{10^{-7}}{\sqrt{21} \times 10^{-4}} = 0.218 \times 10^{-3}$$

$$[\text{HS}^-] = C\alpha_1 = 0.1 \times 0.218 \times 10^{-3} = 2.18 \times 10^{-5} \text{ M}$$



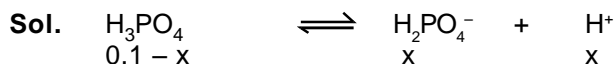
$$10^{-14} = \frac{\sqrt{21} \times 10^{-4}}{2.18 \times 10^{-5}} = \frac{[\text{S}^{2-}]}{10^{-1}}$$

$$[\text{S}^{2-}] = \frac{2.18 \times 10^{-15}}{4.56}$$

$$2.18 \times 10^{-5} \times \alpha_2 = \frac{2.18 \times 10^{-15}}{4.56} = \frac{10^{-10}}{4.56}$$

**Ex.** Calculate conc. of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{H}_2\text{PO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $[\text{H}^+]$ ; pH,  $[\text{OH}^-]$  of 0.1 M  $\text{H}_3\text{PO}_4$  acid solution

given  $K_{a1} = 10^{-3}$ ,  $K_{a2} = 10^{-7}$ ,  $K_{a3} = 10^{-12}$



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

and  $x = 0.01 = [\text{H}^+] = [\text{H}_2\text{PO}_4^-]$   
 $[\text{HPO}_4^{2-}] = 10^{-7} \text{ M}$

$$K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \Rightarrow 10^{-12} = \frac{(0.01)[\text{PO}_4^{3-}]}{10^{-7}}$$

$$[\text{PO}_4^{3-}] = 10^{-17} \text{ M}$$

$$[\text{OH}^-] = 10^{-12} \text{ M}$$

## LECTURE # 5

(k) pH of a mixture of a weak acid/ weak base with weak/strong base/acid respectively.

For this type of mixtures there can be two cases in general,

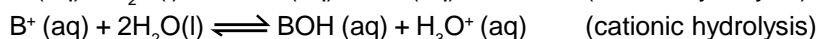
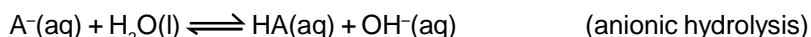
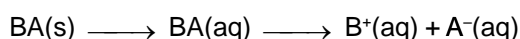
- (i) if the acids and bases are mixed in equal amounts(equivalents)
- (ii) if the acids and bases are mixed in different amounts(equivalents)

First case will lead to phenomenon of **SALT HYDROLYSIS** and second case will lead to formation of **BUFFER SOLUTIONS**.

### **Salt Hydrolysis (Reverse of neutralisation) Salt + Water $\rightleftharpoons$ acid + base**

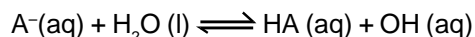
When acids and bases are mixed in equal amounts(equivalents), then we will be having salt solutions only in the water and we have to calculate pH of salt solutions.

When a salt is added to water, the solid salt first dissolves and breaks into ions completely(unless otherwise specified). The ions of the salt may or may not react with water, the cations when react with water will always produce  $\text{H}_3\text{O}^+$  ions and the anions on reaction with water will produce  $\text{OH}^-$  ions. Depending on the extent of hydrolysis and on the amounts of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions the solution can be acidic, basic or neutral. If salt is BA, then



#### **ANIONIC HYDROLYSIS**

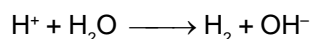
Anions can function as a base on reaction with water and hydrolyze as follows :



The extent of hydrolysis of a given anion depends on its basic strength

#### **(a) Complete hydrolysis**

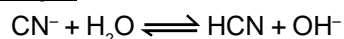
The anions, which are stronger base than  $\text{OH}^-$  and the conjugate acids of the anions are weaker acid than  $\text{H}_2\text{O}$ , they will show complete hydrolysis in aqueous medium. For example



#### **(b) Hydrolysis to a limited extent**

The anions, which are weaker base than  $\text{OH}^-$  and the conjugate acids are stronger acid than  $\text{H}_2\text{O}$  but weaker acid than  $\text{H}_3\text{O}^+$  will hydrolyse to a limited extent in aqueous medium

#### **For Example**

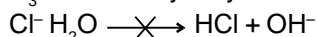


Other examples are  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$  etc.



**(c) No hydrolysis**

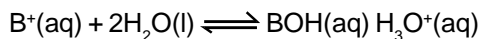
The anions that are weaker base than  $\text{OH}^-$  and the conjugate acids are stronger than both  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  do not hydrolyse at all.



Other examples include  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  etc.

**CATIONIC HYDROLYSIS**

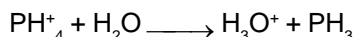
Cations can function as acid on reaction with water and hydrolyze as follows.



The extent of hydrolysis of a given cation depends on its acidic strength.

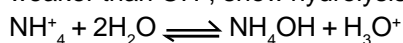
**(a) Complete hydrolysis**

The cations, which are stronger acid than  $\text{H}_3\text{O}^+$  and their conjugate bases are very much weaker than  $\text{H}_2\text{O}$  will show complete hydrolysis. Example is  $\text{PH}_4^+$  ion.



**(b) Hydrolysis to a limited extent**

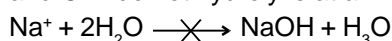
The cations, which are weaker acid than  $\text{H}_3\text{O}^+$  ion and their conjugate bases are stronger than  $\text{H}_2\text{O}$  but weaker than  $\text{OH}^-$ , show hydrolysis to a limited extent. For example



Other ions showing hydrolysis to limited extent are  $\text{C}_6\text{H}_5\text{NH}_3^+$ ,  $\text{CH}_3\text{NH}_3^+$  etc.

**(c) No hydrolysis**

The cations, which are weaker acid than  $\text{H}_3\text{O}^+$  and their conjugate bases are stronger than both  $\text{H}_2\text{O}$  and  $\text{OH}^-$  do not hydrolyze at all. Example is alkali and alkaline earth metal ions.



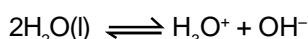
**There are four types of salt.**

- (i) Salt of strong acid and strong base
- (ii) Salt of strong acid and weak base
- (iii) Salt of weak acid and strong base
- (iv) Salt of weak acid and weak base

Salts of first type does not undergo hydrolysis and rest three types undergo hydrolysis.

**(I) Salt of strong acid and strong base**

Neither of the ions will undergo hydrolysis so the solution contain only the equilibrium of ionization of water.

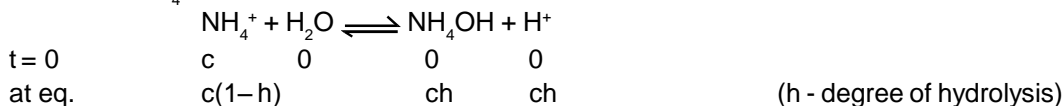


Thus, **the pH of solution will be 7(neutral solution).**

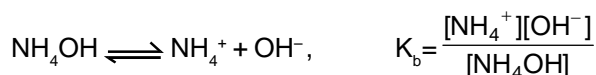
**(II) Salt of strong acid and weak base**

The examples can be  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{C}_6\text{H}_5\text{NH}_4^+\text{Cl}^-$ ,  $\text{CuSO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ .

Only the cation will undergo hydrolysis and the solution will be acidic in nature. for example in the solution of  $\text{NH}_4\text{Cl}$  of concentration  $c$ , we will have



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \text{called hydrolysis constant of the salt}$$



From above equations we can get

$$K_h \times K_b = K_w$$

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)} \quad (\text{generally } 1-h \approx 1) \text{ so we get, } \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

$$\Rightarrow [H^+] = ch = \sqrt{K_h \times c} = \sqrt{\frac{K_w}{K_b} \times c}$$

$$\Rightarrow pH = -\log [H^+] = -\frac{1}{2} [\log K_w - \log K_b + \log c] = \frac{1}{2} [pK_w - pK_b - \log c]$$

**(III) Salt of weak acid and strong base**

The examples can be  $CH_3COONa$ ,  $KCN$ ,  $Na_2C_2O_4$ ,  $K_3PO_4$

Similar to above analysis we will get

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)} \quad (\text{generally } 1-h \approx 1) \text{ so we get, } \Rightarrow h = \sqrt{\frac{K_h}{c}}$$

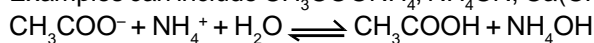
$$K_h \times K_a = K_w$$

$$[OH^-] = ch = \sqrt{K_h \times c} = \sqrt{\frac{K_w}{K_a} \times c}$$

$$pH = -\log [H^+] = -\frac{1}{2} [\log K_w + \log K_a - \log C] = \frac{1}{2} [pK_w + pK_a + \log C]$$

**(IV) Salt of weak acid and weak base**

Examples can include  $CH_3COONH_4$ ,  $NH_4CN$ ,  $Ca(CH_3COO)_2$ ,  $MgC_2O_4$



t = 0	c	c	0	0
at eq.	c - ch	c - ch	ch	ch

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \quad \dots\dots(i)$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+, \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad \dots\dots(ii)$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-, \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \dots\dots(iii)$$

$$H_2O \rightleftharpoons H^+ + OH^-, \quad K_w = [H^+][OH^-] \quad \dots\dots(iv)$$

So,  $K_h \times K_a \times K_b = K_w$ ,

$$\Rightarrow K_h = \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \left(\frac{h}{1-h}\right)^2 \Rightarrow \left(\frac{h}{1-h}\right) = \sqrt{K_h}$$

from (ii) equation

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = K_a \frac{ch}{c(1-h)} = K_a \times \frac{h}{1-h} = K_a \times \sqrt{K_h} = K_a \times \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}}$$

$$pH = -\log [H^+] = \frac{1}{2} [pK_w + pK_a - pK_b]$$

**Ex.** ✎ Equal vol. of 0.2 M  $NH_4OH$  (or ammonia) of 0.1 M  $H_2SO_4$  are mixed calculate pH of final solution.

Given :  $K_b$  of  $NH_3 = 1.8 \times 10^{-5}$

**Sol.**  $pH = \frac{1}{2} [14 - 4.7 + 1] = \frac{10.26}{2} = 5.13$

**Ex.** Calculate pH of 0.01 M ammonium chlorate solution given that  $K_b$  ( $\text{NH}_3 = 1.8 \times 10^{-5}$ ).

**Sol.**  $\text{pH} = \frac{1}{2} (14 - 4.74 + 2)$   
 $= \frac{1}{2} (16 - 4.74) = \frac{11.26}{2} = 5.63$

**Q.** Calculate pH of solution obtained by mixing 400 mL of 0.01 M  $\text{C}_6\text{H}_5\text{NH}_2$  + 400 mL of 0.01 M  $\text{HCl}$  + 1200 mL of  $\text{NaOH}$ . Equilibrium constant of  $\text{C}_6\text{H}_5\text{NH}_2$  with any strong acid is  $10^4$ .

**Q.** Calculate degree of hydrolysis (h) and pH of solution obtained by dissolving 0.1 mole of  $\text{CH}_3\text{COONa}$  in water to get 100 mL of solution (take  $K_a$  of acetic acid =  $2 \times 10^{-5}$ ), ( $\log 2 = 0.3$ )

**Sol.**  $C = \frac{0.1}{100} = 1 \times 10^{-3}$

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}, \Rightarrow h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5 \times 10^{-10}}{2 \times 10^{-3}}} = 5 \times 10^{-3} = 0.5\%$$

$$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C] = \frac{1}{2} [14 + 5 - \log 2 + \log (10^{-3})] = \frac{1}{2} (15.7) = 7.85$$

**Q.** Calculate pH of  $10^{-2}$  M  $\text{Ba}(\text{Lac})_2$ , given that  $K_a$  of lactic acid =  $10^{-4}$ .

**Sol.**  $C = 2 \times 10^{-2}$  M (concentration of lactate ion, as it is the one which will be hydrolysed)  
 $\text{Lac}^- + \text{H}_2\text{O} \rightleftharpoons \text{Lactic acid} + \text{OH}^-$   
 $2 \times 10^{-2}$

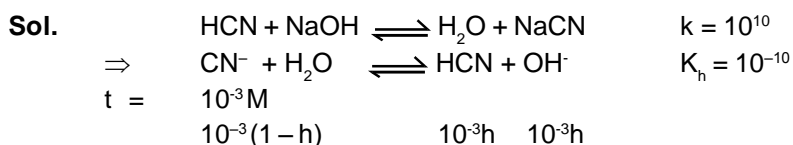
$$\text{pH} = \frac{1}{2} [14 + 4 + \log (2 \times 10^{-2})] = \frac{1}{2} [16 + \log 2] = 8.15$$

**Q.** Calculate pH of  $10^{-2}$  M  $\text{NH}_4\text{CN}$  solution given  $K_a$  of  $\text{HCN} = 5 \times 10^{-10}$  and  $K_b$  of  $\text{NH}_3(\text{aq.}) = 2 \times 10^{-5}$ .

**Sol.**  $\text{pH} = \frac{1}{2} [14 + \text{p}K_a - \text{p}K_b] = \frac{1}{2} [14 + 10 - \log 5 - 5 + \log 2] = \frac{1}{2} [18.6] = 9.3$

$$\frac{h}{1-h} = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-10} \times 2 \times 10^{-5}}} = 1 \Rightarrow 2h = 1 \Rightarrow h = \frac{1}{2} = 0.5$$

**Q.** If the equilibrium constant for reaction of  $\text{HCN}$  with  $\text{NaOH}$  is  $10^{10}$ , then calculate pH of  $10^{-3}$  M  $\text{NaCN}$  solution.



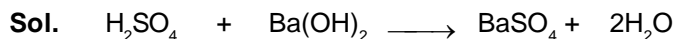
$$K_h = 10^{-10} = \frac{10^{-3}h \times 10^{-3}h}{10^{-3}(1-h)} \Rightarrow h = \sqrt{\frac{K_h}{C}} = \sqrt{10^{-7}}, \Rightarrow [\text{H}^+] = \frac{10^{-14}}{10^{-3}\sqrt{10^{-7}}}$$

$$\text{pH} = 7 + \frac{1}{2} \log 10 = 7.5$$

**Q.** Calculate pH of solution obtained by mixing equal volumes of 0.02 M  $\text{CH}_3\text{COOH}$  and 0.02 M  $\text{NaOH}$   
 0.02 M  $\text{CH}_3\text{COOH}$  and 0.02 M  $\text{NaOH}$   
 given that  $\text{p}K_a$  of  $\text{CH}_3\text{COOH} = 4.74$

**Sol.**  $\text{pH} = \frac{1}{2} [14 + \text{p}K_a + \log c] = \frac{1}{2} [14 + 4.74 + \log (10^{-2})] = 8.37$

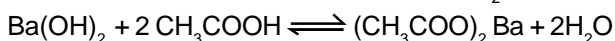
**Q.** 10 ml of 0.2 M  $\text{H}_2\text{SO}_4$  is mixed with 20 ml of 0.2 M  $\text{Ba}(\text{OH})_2$  solution, the solution obtained is filtered and the obtained solution after filtering is reacted with some of 20 ml of 0.2 M  $\text{CH}_3\text{COOH}$  solution. Calculate pH of final solution. (given that  $\text{pK}_a$  of  $\text{CH}_3\text{COOH} = 4.74$ )



t = 0      2 mmole          4 mmole          0          -

at eq.      0                  2 mmole          2 mmole

Solution is containing 2 mmole of  $\text{Ba}(\text{OH})_2$  in 30ml volume,



t = 0      2 mmole          4 mmole          0          -

at eq.      0                  0                  2 mmole

Finally it is a solution of a salt of type SBWA, having concentration of the anion being hydrolysed equal to

$$[\text{CH}_3\text{COO}^-] = \frac{4 \times 10^{-3}}{50} \times 1000 = 8 \times 10^{-2}, \text{ so}$$

$$\text{pH} = \frac{1}{2} [14 + 4.74 - 2 + 3 \log 2] = 8.82$$

## LECTURE # 6

### Hydrolysis of polyvalent anions or cations

The hydrolysis of these species will take place in steps (just like dissociation of weak acids). Out of different steps generally first step hydrolysis dominates mainly because of two reasons

- (a) The hydrolysis constant of second and further steps is generally negligible in comparison to first step hydrolysis constant.
- (b) The second and further step hydrolysis will be suppressed in presence of ions produced due to first step hydrolysis.

For a polyprotic acid ( $\text{H}_2\text{S}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ) we already know that the dissociation always takes place in steps, so for example for  $\text{H}_3\text{PO}_4$



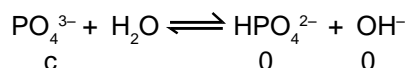
For all acids we always have  $K_{a1} \gg K_{a2} \gg K_{a3}$

pH of the solution can be calculated from I<sup>st</sup> step only because  $[\text{H}^+]$  from II<sup>nd</sup> & III<sup>rd</sup> step can be neglected as

- (a)  $K_{a1} \gg K_{a2} \gg K_{a3}$
- (b)  $[\text{H}^+]$  from I<sup>st</sup> dissociation will suppress the dissociation of II<sup>nd</sup> & III<sup>rd</sup> step.

Now for the hydrolysis of polyvalent ions (of salts like  $\text{K}_3\text{PO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{ZnSO}_4$ ,  $\text{FeCl}_3$ ,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  or ions like  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$  etc.)

Consider the hydrolysis in steps



$$\underset{c(1-h)}{\quad} \quad \quad \underset{ch}{\quad} \quad \quad \underset{ch}{\quad} \quad K_{h1} = \frac{[\text{OH}^-][\text{HPO}_4^{2-}]}{[\text{PO}_4^{3-}]} \quad \dots (4)$$



From above equations we get,

$$K_{a1} \times K_{h3} = K_w$$

$$K_{a1} \times K_{h2} = K_w$$

$$K_{a3} \times K_{h1} = K_w$$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{\text{Ch} \cdot \text{Ch}}{\text{C}(1-h)} = \frac{\text{Ch}^2}{1-h} \approx \text{Ch}^2$$

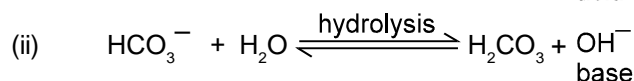
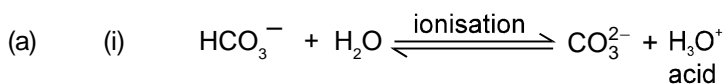
$$h = \sqrt{\frac{K_{h1}}{\text{C}}} \Rightarrow [\text{OH}^-] = \text{ch} = \sqrt{K_{h1} \times \text{C}} \Rightarrow [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = K_w \sqrt{\frac{K_{a3}}{K_w \text{C}}} = \sqrt{\frac{K_w \times K_{a3}}{\text{C}}}$$

So  $\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_{a3} + \log \text{C}]$

#### Hydrolysis of Amphiprotic Anion.

(Cation is not Hydrolysed)

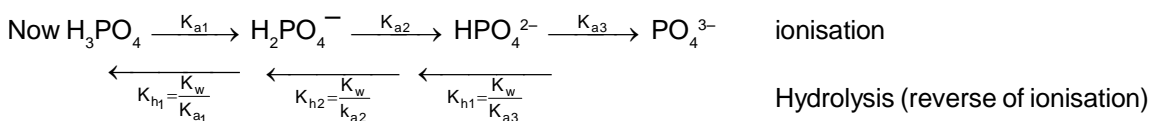
$\text{NaHCO}_3$ ,  $\text{NaHS}$ , etc., can undergo ionisation to form  $\text{H}^+$  ion and can undergo hydrolysis to form  $\text{OH}^-$  ( $\text{Na}^+$  ion is not hydrolysed)



$$\text{pH}(\text{HCO}_3^-) = \left( \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} \right)$$

(b) Similarly for  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  amphiprotic anions.

$$\text{pH}_{(\text{H}_2\text{PO}_4^-)} = \left( \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} \right) \quad \text{and} \quad \text{pH}_{(\text{HPO}_4^{2-})} = \left( \frac{\text{p}K_{a2} + \text{p}K_{a3}}{2} \right)$$



The  $\text{pH}$  of  $\text{H}_3\text{PO}_4 = \frac{1}{2}(\text{p}K_{a1} - \log \text{C})$   $\therefore K_{a1} \gg K_{a2} \gg K_{a3}$

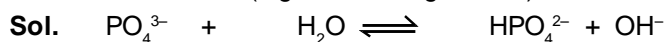
$$\text{pH} \text{ of } \text{NaH}_2\text{PO}_4 = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$$

$$\text{pH} \text{ of } \text{Na}_2\text{HPO}_4 = \frac{1}{2}(\text{p}K_{a2} + \text{p}K_{a3}) \quad \therefore \text{sec ionisation can neglect}$$

$$\text{pH} \text{ of } \text{Na}_3\text{PO}_4 = \frac{1}{2}(\text{p}K_w + \text{p}K_{a3} + \log \text{C}) \quad \therefore \text{Sec hydrolysis can neglect}$$

$$= 7 + \frac{1}{2} \text{p}K_{a3} + \frac{1}{2} \log \text{C}$$

**Q.** Calculate the pH of a 0.1 M  $K_3PO_4$  solution. The third dissociation constant of orthophosphoric acid is  $1.5 \times 10^{-12}$ . ( $\log 3 = 0.48$ ,  $\log 2 = 0.3$ )



$$pH = 7 + \frac{1}{2} pK_{a3} + \frac{1}{2} \log C = 7 + \left( \frac{12 - \log 1.5}{2} \right) + \frac{1}{2} (\log 0.1)$$

$$= 7 + 5.91 - 0.5 = 12.41$$

## LECTURE # 7

### Buffer Solution :

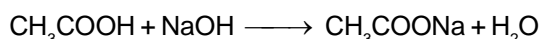
(if the acids and bases are mixed in different amounts (equivalents))

Buffer solutions are those, which resist a change in pH upon addition of small amount of acid or base. this does not mean that the pH will not change, and all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

#### BUFFER CAN BE FORMED IN THREE WAYS.

##### Acidic buffer :

- (i) Mixing of SAWB salt and weak acid.  $CH_3COOH + CH_3COONa$
- (ii) Mixing of WA and strong base [Condition  $[WA] > [SB]$ ]

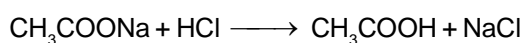


1	0.5		
0.5	0	0.5	0.5



buffer

- (iii) Mixture of SBWA salt and strong [condition  $[Salt] > [SA]$ ]

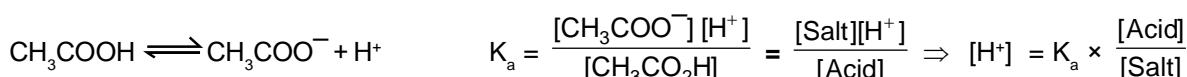


1	0.5	0.5	0.5
0.5	0	0.5	0.5



buffer

To calculate the pH of a buffer solution made up of a weak acid and its salt with a strong base. We have



Taking log of both sides.  $\log [H^+] = \log K_a + \log \frac{[Acid]}{[Salt]}$

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

This is known as the **Henderson's equation of a buffer.**

For a buffer made up of weak base and its salt with a strong acid the Henderson's equation looks like this :

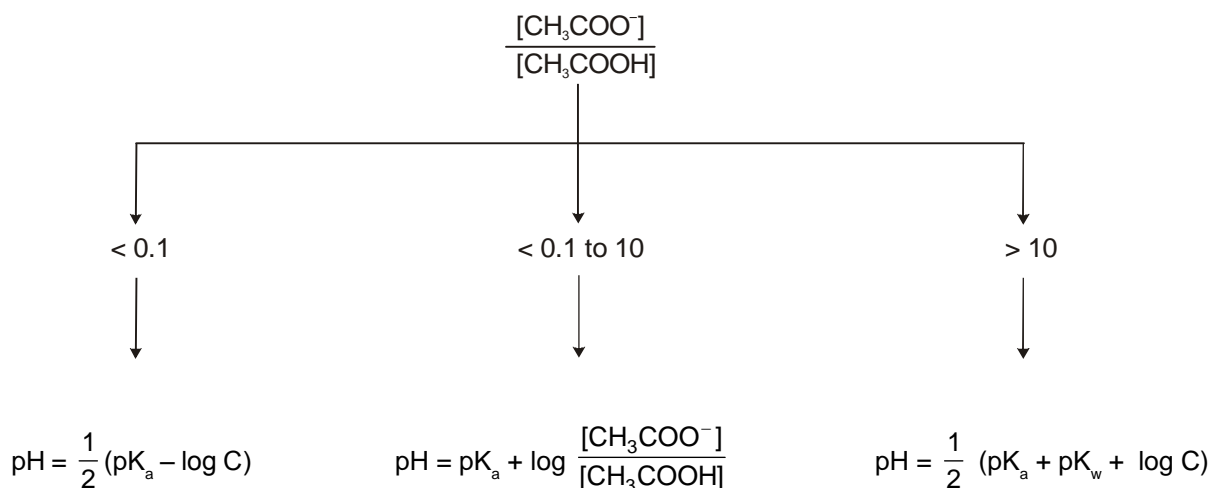
$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

#### Use of various relations :

Let us consider three situations, (i) a solution of  $CH_3COOH$  (ii) a solution of  $CH_3COONa$  and (iii) a solution of  $CH_3COOH$  and  $CH_3COONa$  (buffer). In all the three solutions, there will be some  $CH_3COO^-$  and  $CH_3COOH$ . But the relations used for calculating the pH differs. For (i), the relation used is :  $pH = \frac{1}{2} (pK_a - \log c)$  ; for (ii)

the relation used is :  $\frac{1}{2} (pK_w + pK_a + \log c)$  and for (iii), the relation used is  $pH = pK_a + \log \frac{[Salt]}{[Acid]}$ .

To understand as to when a particular relation is to be used, the following chart should be kept in mind.



Although it is difficult to give an exact limit up to which a buffer can be used, it is generally accepted that a buffer solution can be used for practical purposes when its [Salt]/[Acid] lies within the range of 0.1 to 10 (as shown above).

Therefore, it can be concluded that a particular weak acid (or base) can be employed for making useful buffer solution of pH (or pOH) lying within the range of  $(\text{pK}_a \pm 1)$  or  $(\text{pK}_b \pm 1)$ . For example, acetic acid ( $\text{pK}_a = 4.75$  at  $25^\circ\text{C}$ ) and sodium acetate mixture can be used for preparing buffer solutions whose pH values are roughly in the range of 3.75 to 5.75. Outside this range, the buffer capacity of acetic acid–sodium acetate solution is too small to be used for any practical purpose.

#### Effect of dilution on the pH of buffer solution :

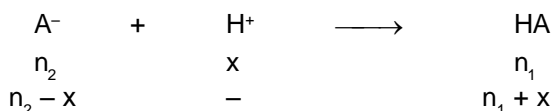
For acidic buffer of HA and  $\text{A}^-$ .

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

On increase in dilution  $[\text{A}^-]$  and  $[\text{HA}]$  decreased upto equal extent, so there will be no effect on dilution (generally).

#### Effect of addition of small amount of strong acid :

In acidic buffer of HA ( $n_1$  moles) and  $\text{A}^-$  ( $n_2$  moles),  $x$  moles of strong acid ( $\text{H}^+$ ) is added.

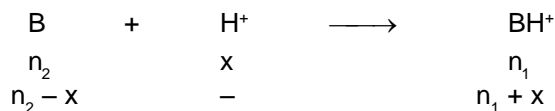


$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Before addition of strong acid,  $\text{pH}_1 = \text{pK}_a + \log \frac{[n_2]}{[n_1]}$

After addition of strong acid,  $\text{pH}_2 = \text{pK}_a + \log \frac{[n_2 - x]}{[n_1 + x]}$

In basic buffer of B ( $n_2$  moles) and  $\text{BH}^+$  ( $n_1$  moles),  $x$  moles of strong acid ( $\text{H}^+$ ) is added.



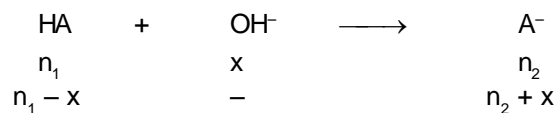
$$\text{pOH} = \text{pK}_b + \log \frac{[\text{BH}^+]}{[\text{B}]}$$

Before addition of strong acid,  $\text{pOH}_1 = \text{pK}_b + \log \frac{[n_1]}{[n_2]}$

After addition of strong acid,  $pOH_2 = pK_b + \log \frac{[n_1 + x]}{[n_2 - x]}$

**Effect of addition of small amount of strong base :**

In acidic buffer of  $HA$  ( $n_1$  moles) and  $A^-$  ( $n_2$  moles),  $x$  moles of strong base ( $OH^-$ ) is added.

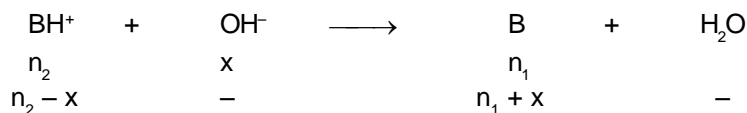


$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Before addition of strong base,  $pH_1 = pK_a + \log \frac{[n_2]}{[n_1]}$

After addition of strong base,  $pH_2 = pK_a + \log \frac{[n_2 + x]}{[n_1 - x]}$

In basic buffer of  $B$  ( $n_2$  moles) and  $BH^+$  ( $n_1$  moles),  $x$  moles of strong base ( $OH^-$ ) is added.



$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

Before addition of strong base,  $pOH_1 = pK_b + \log \frac{[n_2]}{[n_1]}$

After addition of strong base,  $pOH_2 = pK_b + \log \frac{[n_2 - x]}{[n_1 + x]}$

**Q.** Calculate the amount of  $(NH_4)_2SO_4$  in grams which must be added to 500ml of 0.2 M  $NH_3$  to yield a solution of  $pH = 9.3$ . Given  $pK_b$  for  $NH_3 = 4.7$

**Sol.**  $pOH = pK_b + \log \frac{[Conjugate\ acid]}{[Base]}$

$$4.7 = 4.7 + \log \frac{x}{0.2} \Rightarrow x = 0.2, \text{ so concentration of } (NH_4)_2SO_4 \text{ required} = 0.1 \text{ M}$$

$$\therefore \text{ moles of } SO_4 \text{ needed} = 0.05$$

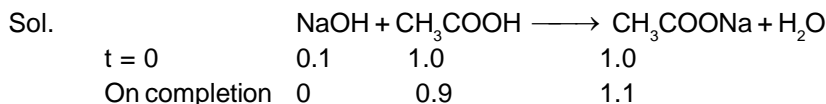
$$\therefore \text{ weight of } (NH_4)_2SO_4 \text{ needed} = 132 \times 0.05 = 6.6 \text{ gm}$$

**Q.** The pH of a blood stream is maintained by a proper balance of  $H_2CO_3$  and  $NaHCO_3$ . What volume of 5 M  $NaHCO_3$  solution should be mixed with 10 ml of a sample of solution which is 2.5 M in  $H_2CO_3$  (assume no  $NaHCO_3$ ), in order to maintain a  $pH = 7.4$ . ( $pK_a$  for  $H_2CO_3 = 6.7$ ,  $\log 2 = 0.3$ )

**Sol.**  $pH = pK_a + \log \frac{[HCO_3^-]}{[H_2CO_3]} \Rightarrow 7.4 = 6.7 + \log \frac{[HCO_3^-]}{[H_2CO_3]} \Rightarrow \frac{[HCO_3^-]}{[H_2CO_3]} = 5 \Rightarrow \frac{n_{HCO_3^-}}{n_{H_2CO_3}} = 5$   
 $\Rightarrow 5 \times 2.5 \times 10 \times 10^{-3} = 5 \times V \Rightarrow \text{required volume} = 25 \text{ ml}$



- Q.** 4 gm of NaOH were dissolved in 1 litre of a solution containing 1 mole of  $\text{CH}_3\text{COOH}$  and 1 mole of  $\text{CH}_3\text{COONa}$ . Calculate  $[\text{H}^+]$  in the resultant solution. (Given  $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ).



$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \times \frac{0.9}{1.1} = 1.47 \times 10^{-5} \text{ M}$$

## LECTURE # 8

- Q.** The total phosphate conc. in a blood sample is determined to be  $3 \times 10^{-3} \text{ M}$ . If the pH of the blood sample is 7.4. What are the conc. of  $\text{H}_2\text{PO}_4^-$  &  $\text{HPO}_4^{2-}$  in the blood? ( $K_{a2}$  of  $\text{H}_3\text{PO}_4 = 8 \times 10^{-8}$ ,  $\log 2 = 0.1$ ).

- Sol.** Let  $[\text{H}_2\text{PO}_4^-] = y$  &  $[\text{HPO}_4^{2-}] = x \Rightarrow x + y = 0.003$

$$\text{pH} = \text{p}K_{a2} + \log \left( \frac{x}{y} \right)$$

$$\Rightarrow 7.4 = 7.1 + \log \left( \frac{x}{y} \right) \Rightarrow y = \left( \frac{x}{2} \right)$$

$$\therefore x = 0.002 \text{ M} = [\text{HPO}_4^{2-}] \quad \& \quad y = 0.001 \text{ M} = [\text{H}_2\text{PO}_4^-]$$

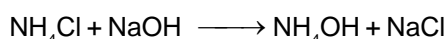
- Q.** A buffer solution of  $\text{pH} = 9.56$  was obtained by mixing 2 mole of  $\text{NH}_3(\text{eq.})$  and 1 mole of  $\text{NH}_4\text{Cl}$  to form 1 liter solution. To 200ml of this solution, 10 ml of 10 M NaOH is added. Calculate pH of this resulting solution.

**Sol.**  $\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$

$$\Rightarrow \text{pOH} = 14 - 9.56 = 4.44 = \text{p}K_b + \log \frac{1}{2} \Rightarrow \text{p}K_b = 4.74$$

In 200 ml of this solution, no. of moles  $\text{NH}_4\text{Cl} = 0.2$  and no. of moles of  $\text{NH}_3(\text{eq}) = 0.4$

no. of moles of NaOH added = 0.1

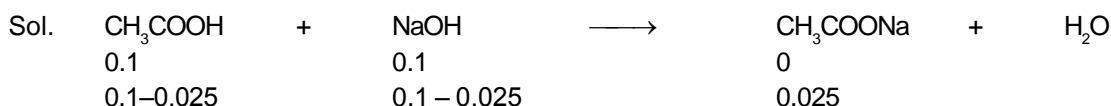


0.2	0.1		0.4
-----	-----	--	-----

0.1	0	0.5	$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.74 + \log \frac{0.1}{0.5} = 4.04$
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$$\text{pH} = 14 - 4.04 = 9.96$$

- Q.** You are given 0.1 M  $\text{CH}_3\text{COOH}$  in a beaker and to that 0.1 M solution NaOH is gradually added from a burette. Calculate the pH of the solution in a beaker when acid is 25% neutralized. (Given  $\text{p}K_a$  (acetic acid) = 4.74)



$$\text{pH} = \text{p}K_a + \log \frac{\text{salt}}{\text{acid}} = 4.74 + \log \frac{0.025}{0.075} = 4.263$$

If HA is neutralized by SB then at any stage of neutralization

$$\text{pH} = \text{p}K_a + \log \frac{\alpha}{1-\alpha}, \text{ where } \alpha \text{ is \% neutralization}$$

$\therefore$  for any weak acid at his half equivalence point,  $\text{pH} = \text{p}K_a$ ,

Similarly for a weak base, at 50% neutralization,  $\text{pOH} = \text{p}K_b$ .

**Q.** A 40ml solution of a weak base(BOH) is titrated with 0.1 M HCl the pH of the solution is found to be 10.04 and 9.14 after adding 5ml and 20 ml of the acid respectively. Calculate  $pK_b$  of base. ( $\log 2 = 0.3$ )

**Sol.** In first case  $pOH = 14 - 10.04 = 3.96$  and in second case  $pOH = 14 - 9.14 = 4.86$

number of mmoles of salt = 5 mmole

number of mmoles of base =  $(40C - 0.5)$  mmole

$$(i) 3.96 = pK_b + \log \frac{0.5}{40C - 0.5}$$

$$(II) 4.86 = pK_b + \log \frac{2}{40C - 2}$$

$$\Rightarrow 3.96 - \log \frac{0.5}{40C - 0.5} = 4.86 - \log \frac{2}{40C - 2} \Rightarrow \log \left( \frac{2}{40C - 2} \times \frac{40C - 0.5}{0.5} \right) = 0.9 = \log 8$$

$$\Rightarrow 40C - 0.5 = 2(40C - 2) \Rightarrow C = 0.0875$$

$$\Rightarrow 3.96 = pK_b + \log (0.0875) \Rightarrow pK_b = 5.02$$

### Buffer Capacity :

It is defined as the amount of a strong acid or strong base required to change the pH of a buffer by one unit. Let there be a buffer solution of volume 1 L with 'b' mole of salt and 'a' mol of acid. The pH of the buffer would be given by

$$pH = pK_a + \log \frac{b}{a}$$

On adding x mole of a strong acid (monobasic), the pH changes to  $pH = pK_a + \log \frac{b-x}{(a+x)}$ .

$$\therefore \Delta pH = \log \frac{b}{a} - \log \frac{b-x}{(a+x)}$$

Differentiating with respect to x we get

$$\begin{aligned} \frac{d\Delta pH}{dx} &= \frac{1}{2.303} \frac{1}{\frac{b}{a} \times \left( \frac{a+x}{b-x} \right)} \times \frac{b(a+b)}{a} \times \frac{1}{(b-x)^2} \\ &= \frac{1}{2.303} \frac{a+b}{(a+x)(b-x)} \end{aligned}$$

Taking the inverse

$$\frac{dx}{d\Delta pH} = 2.303 \frac{(a+x)(b-x)}{a+b}$$

This is defined as buffer capacity. It is the ratio of the small amount of acid or base added to the change in pH caused in the buffer.

### Maximum buffer capacity :

It can be proved that the maximum buffer is achieved when the salt and acid or base concentration is equal. Differentiating buffer capacity with respect to 'b', the amount of salt present in the and equating it to zero, gives

$$\frac{d}{db} \left( \frac{dx}{d\Delta pH} \right) = 2.303 \frac{[-1 \times (b-x)] + [1 \times (a-b+x)]}{a} = 0$$

$a - b + 2x = 0$  ; since x is very small we ignore 2x and we get

$$a - b = 0$$

$$\therefore b = a \Rightarrow [\text{Acid}] = [\text{Conjugate base}]$$

The buffer shows maximum buffer capacity when the amount of acid or base and the salt are same.

**Q.** Calculate the buffer capacity of 1L of

(i) 0.1M  $\text{CH}_3\text{COOH}$  and 0.1M  $\text{CH}_3\text{COONa}$

(ii) 0.2M  $\text{CH}_3\text{COOH}$  and 0.2M  $\text{CH}_3\text{COONa}$

$$pK_a \text{ CH}_3\text{COOH} = 4.74$$

which will you buy a better buffer

## Solution

$$\frac{\delta x}{dph} = 2.303 \frac{(a+x)(b-x)}{a+b} = 2.303 \frac{ab}{a+b} \quad x \ll a, b$$

$$(i) \text{ Buffer capacity} = \frac{0.1 \times 0.1}{0.1 + 0.1} = 0.05 \times 2.303 \quad (ii) \text{ Buffer capacity} = \frac{0.2 \times 0.2}{0.2 + 0.2} = 0.1 \times 2.303$$

Second buffer solution can be said better buffer

## ACID-BASE TITRATION :

(A) Titration of SA us SB :

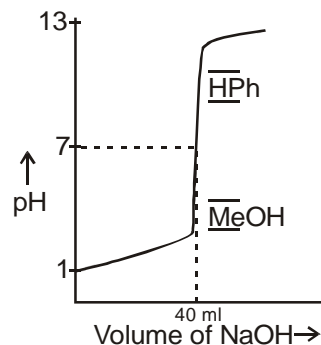
40 ml 0.1 M HCl,

Volume of NaOH added

NaOH 0.1 M

pH of solution

0 ml	1
10 ml	1.22
20 ml	1.48
30 ml	1.48
39 ml	1.84
39.9 ml	2.90
40.0 ml	3.90
40.1 ml	7
41 ml	10.1
50 ml	11.1
60 ml	12.05
60 ml	12.30



⇒ Indication should change its colour sharply for indication of reaction to be complete so its pH - range should lie perfectly with in sharp change to avoid experimental error.

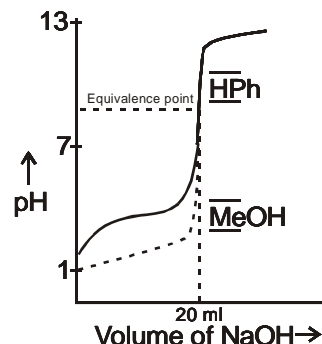
⇒ MeOH and HPh both can use for titration of SA and SB.

(B) Titration of SB is WA :

Volume of NaOH

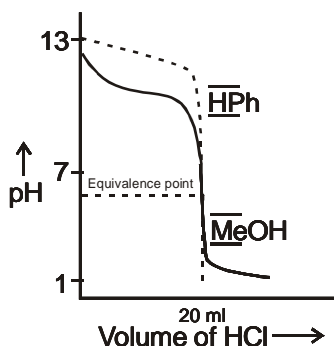
pH value

0	2.5
5 ml	4.23
10 ml	4.7
15 ml	$4.7 \log 3 = 5.17$
19 ml	$4.7 + \log 19/1 = 6$
20 ml	$7 + 1/2 (4.7) + 1/2 \log (1/4) = 9.05$
21 ml	12.4
30 ml	13.23



- \* In sharp change of titration HPh is suitable indicator.
- \* Initially fast change in pH is due to free ions available from weak acid.
- \* Slow down of pH change is due to Buffer formation, which is maximum at pH = pKa.
- \* Near equivalence point pH again increases fastly due to salt formation.
- \* After equiv. point pH changes very sharply due to presence of strong base.

(C) Titration of SA + wB



Sharp change between 4 to 7

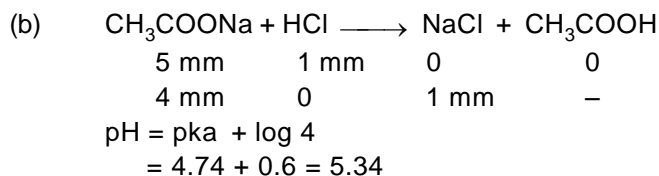
(D) Titration of W.A. S.B. salt + S.A.

50 mL of 0.1 M  $\text{CH}_3\text{COONa}$  is titrated with 0.1 M  $\text{HCl}$ . Calculate pH when Vol. of  $\text{HCl}$  added is.

- (a) 0 mL      (c) 25 mL      (e) 50 mL      (g) 75 mL  
 (b) 10 mL      (d) 40 mL      (f) 60 mL

$\text{pK}_a$  of  $\text{CH}_3\text{COOH} = 4.74$

(a)  $\text{pH} = 1/2 (\text{pK}_w + \text{pK}_a + \log c)$   
 $= 1/2 (14 + 4.74 - 1) = 8.87$



(c)  $\text{pH} = \text{pK}_a = 4.74$

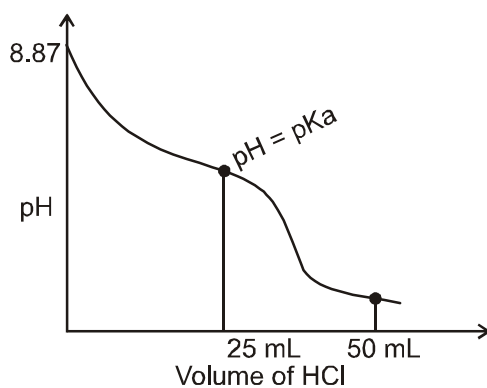
(d)  $\text{pH} = \text{pK}_a + \log 1/4 = 4.14$

(e) equivalent point, WA'S solution  
 $[\text{CH}_3\text{COOH}] = 5/100 = 1/20$

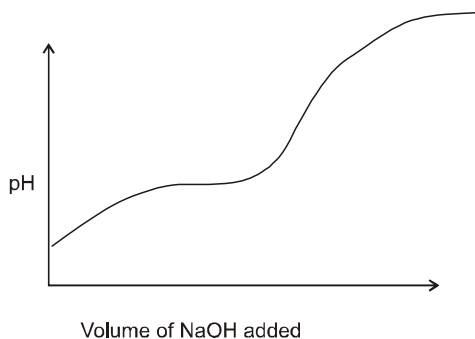
$\text{pH} = 1/2 (\text{pK}_a - \log C) = 1/2 (4.74 + 2 - 0.7)$   
 $= \frac{6.04}{2} = 3.02$

(f)  $[\text{HCl}] = 1/100$        $\text{pH} = 2.1$

(g)  $[\text{HCl}] = \frac{2.5}{125}$        $\text{pH} = 1.7$



(E) W.B.S.A salt + S.B.  
 $(\text{NH}_4\text{Cl}) + \text{NaOH}$



- Q.** 25 ml;  $10^{-4}$  M  $\text{NH}_4\text{OH}$  solution is titrated against  $10^{-3}$  M solution of  $\text{HCl}$ . Calculate the pH of solution at equivalent point. Also calculate the % of  $\text{NH}_4\text{OH}$  present in the form of  $\text{NH}_4^+$  ion at this point. ( $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ )



For equivalent point

$$N_1 V_1 = N_2 V_2$$

$$V_2 = 2.5 \text{ ml}$$

$\therefore$  total vol. of solution at equivalent point

$$= 25 + 2.5 = 27.5 \text{ ml}$$

$\therefore [\text{NH}_4^+] = 9.7 \times 10^{-5} \text{ M}$

$$K_h = \frac{10^{-14}}{1.8 \times 10^{-5}} = ch^2$$

$$h = 2.47 \times 10^{-3}$$

$\therefore [\text{H}^+] = ch = 2.247 \times 10^{-7} \text{ M}$

$$\text{pH} = 6.65 \quad \text{Ans.}$$

% of  $\text{NH}_4\text{OH}$  as  $\text{NH}_4^+ = 99.7753$ . **Ans.**

## LECTURE # 9

**(F) Titration of Poly protic acid v/s S.B. :**

50 mL of 0.1 M  $\text{H}_3\text{PO}_4$  agent 0.1 M  $\text{NaOH}$ . Calculate pH when vol. of  $\text{NaOH}$  added is

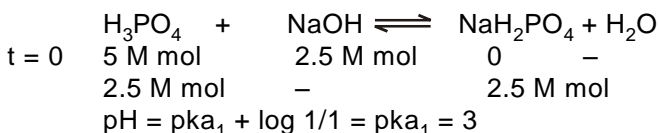
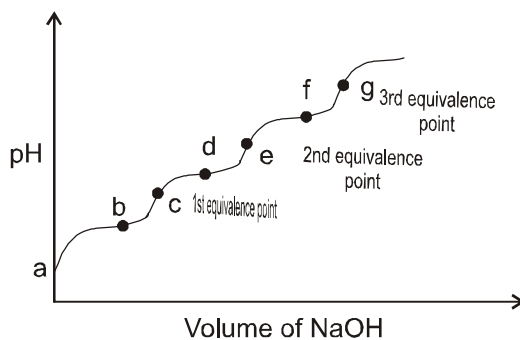
- (a) 0 mL      (b) 25 mL      (c) 50 mL      (d) 75 mL      (e) 100 mL  
(f) 125 mL      (g) 150 mL      (h) 200 mL      (i) 90 mL

$$\text{p}K_{a1} = 3 \quad \text{p}K_{a2} = 7, \text{p}K_{a3} = 11$$

(a)  $\text{pH} = 1/2 (\text{p}K_{a1} - \log C)$

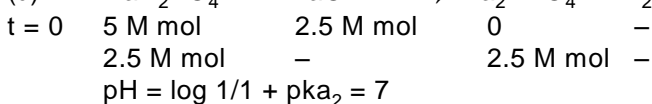
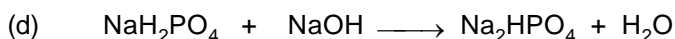
$$= 1/2 (3 + 1) = 2$$

(b)



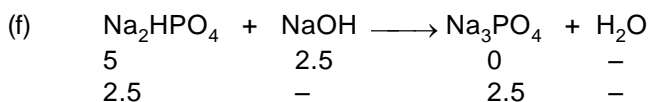
(c) solution of  $\text{H}_2\text{PO}_4^-$  amphoteric species

$$\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} = \frac{3 + 7}{2} = 5$$



(e)  $\text{HPO}_4^{2-}$  solution (amphoteric species)

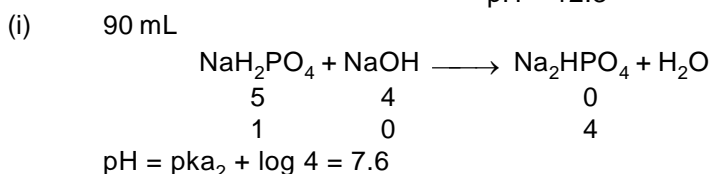
$$\text{pH} = \frac{\text{pK}_{a2} + \text{pK}_{a3}}{2} = 9$$



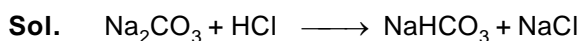
$$\text{pH} = \text{pK}_{a3} + 10 \log \frac{1}{1} = 0$$

(g) 3<sup>rd</sup> eq. pt  $\text{Na}_3\text{PO}_4$  solution  
 $[\text{Na}_3\text{PO}_4] = 5/200 = 1/40$   
 $\text{pH} = 1/2\{\text{pK}_w + \text{pK}_3 + \log C\}$   
 $= 1/2 (14 + 11 - 2 + 0.4) = 11.7$

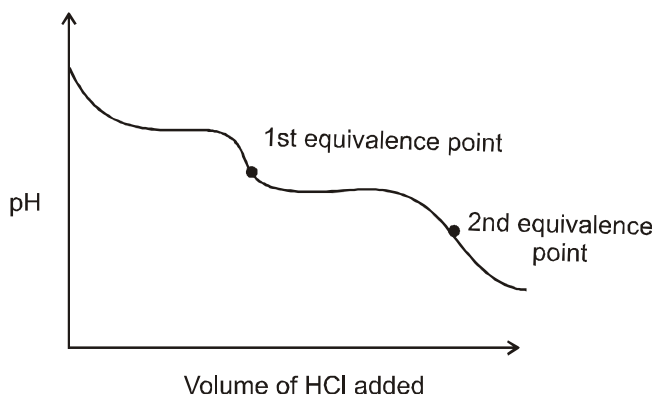
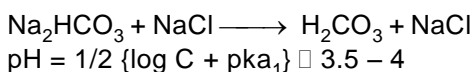
(H) 200 mL  
 hydrolysis of  $\text{Na}_3\text{PO}_4$  can be neglected in Presence of NaOH  
 $[\text{NaOH}] = 5/250 = 1/50$        $\text{pOH} = 1.7$   
 $\text{pH} = 12.3$



**Ex.** Predict graph for  $(\text{Na}_2\text{CO}_3 + \text{HCl})$ . (W.A.S.B Vs S.B.)



$$\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} \approx 9$$



**Q.** 1.06 gm of  $\text{Na}_2\text{CO}_3$  is dissolved in 100 ml water. This solution is titrated against a 0.05 M HCl. Calculate the pH when.

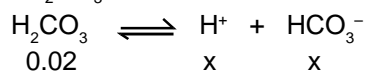
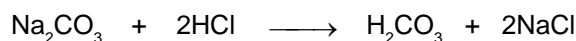
- (a) 200 ml of HCl is added       $K_1 = 4.2 \times 10^{-7}$   
 (b) 400 ml of HCl is added       $K_2 = 4.8 \times 10^{-11}$

**Sol.** m mole of  $\text{Na}_2\text{CO}_3$  taken =  $\frac{1.06}{106} \times 1000 = 10$

(a) m mole of HCl taken =  $200 \times 0.05 = 10$

$$\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} = \frac{6.38 + 10.32}{2} = 8.35 \quad \text{Ans.}$$

(b) m moles of HCl =  $400 \times 0.05 = 20$



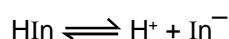
$$\frac{x^2}{0.02 - x} = 4.2 \times 10^{-7}$$

$$\Rightarrow x = 9.165 \times 10^{-5} \text{ M} = [\text{H}^+] \quad \Rightarrow \text{pH} = 4.04 \quad \text{Ans.}$$

## INDICATOR :

Indicators are the substance, which indicates the end-point of a titration by changing their colour. They are in general, either weak organic acids or weak organic bases having characteristically different colours in the ionised and unionised forms. For example, methyl orange is a weak base (having red colour in ionised form and yellow colour in the unionised form) and phenolphthalein is a weak acid (having pink colour in the ionized form while its unionised form is colourless)

Let us consider the equilibrium between the ionised and unionised form of an acid indicator (HIn)



$$\therefore K_{\text{HIn}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad [K_{\text{HIn}} = \text{indicator constant or dissociation constant of indicator}]$$

or  $[\text{H}^+] = K_{\text{HIn}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$

Taking negative logarithm of both sides

$$- \log [\text{H}^+] = \log K_{\text{HIn}} - \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\therefore \text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{In}^-]}{[\text{HIn}]} \quad \Rightarrow \quad \text{pH} = \text{p}K_{\text{HIn}} + \log \frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

In general, the intensity of a coloured solution depends on the concentration of the colour imparting species. If the solution contains two coloured species, then the colour of the solution depends on the relative concentration of the colour imparting species. When the solution contains two coloured species as HIn and  $\text{In}^-$ , then it is seen that the solution acquires a distinct colour of  $\text{In}^-$  only when the concentration of  $\text{In}^-$  is approximately at least 10 times greater than the concentration of HIn and vice versa.

Let us consider two cases.

### Case-I

In order for the solution to show colour due to  $\text{In}^-$  the minimum ratio of  $\frac{[\text{In}^-]}{[\text{HIn}]}$  should be 10.

$$\therefore \text{pH} = \text{p}K_{\text{HIn}} + \log (10) = \text{p}K_{\text{HIn}} + 1$$

At this stage, the percentage of the indicator in  $\text{In}^-$  form would be given by

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{10}{10 + 1} \times 100 \approx 91.$$

Thus, nearly 91% of the indicator has been present in the ionised form ( $\text{In}^-$ ). In fact  $\text{pH} = \text{p}K_{\text{HIn}} + 1$  is the minimum pH up to which the solution has a distinct colour characteristic of  $\text{In}^-$ . At pH greater than this value, some more indicator will be present in the ionised form. Thus at  $\text{pH} \geq \text{p}K_{\text{HIn}} + 1$ , the solution has a colour characteristic of  $\text{In}^-$ .

### Case - II

In order for the solution to show colour due to HIn, the minimum ratio of  $\frac{[\text{In}^-]}{[\text{HIn}]}$  should be  $\frac{1}{10}$ .

$$\therefore \text{pH} = \text{pK}_{\text{HIn}} + \log \frac{1}{10} = \text{pK}_{\text{HIn}} - 1.$$

At this stage, the percentage of the indicator in  $\text{In}^-$  form would be given by

$$\frac{[\text{In}^-]}{[\text{In}^-] + [\text{HIn}]} \times 100 = \frac{1}{10 + 1} \times 100 \approx 9.1$$

Thus, nearly 9.1% of the indicator has been present in the ionised form ( $\text{In}^-$ ) and  $\approx 91\%$  of the indicator is present in the unionised form ( $\text{HIn}$ ). In fact  $\text{pH} = \text{pK}_{\text{HIn}} - 1$  is the maximum pH up to which the solution has a distinct colour characteristic of  $\text{HIn}$ . At pH smaller than this value, some more indicator will be present in the unionised form. Thus at  $\text{pH} < \text{pK}_{\text{HIn}} = 1$ , the solution has a colour characteristic of  $\text{HIn}$ .

### Universal Indicator :

A mixture of the following indicator can be used to determine the approximate pH of the solution in the range 4 to 11. Methyl red,  $\alpha$ -naphtholphthalein, thymolphthalein, phenolphthalein and bromothymol blue.

This mixture gives different colour at different pH values of the solution. These are :

pH	4	5	6	7	8	9	10	11
colour	Red	Orange red	Yellow	Green yellow	Green	Blue green	Blue violet	Red violet

- Q.** A weak acid type indicator was found to be 60% dissociated at  $\text{pH} = 9$ . What will be the percent dissociation at  $\text{pH} = 8$ .

**Sol.**  $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} = \frac{10^{-9} \times 60}{40}$$

$$K_{\text{In}} = \frac{10^{-8} \times x}{1 - x} = \frac{10^{-9} \times 60}{40} = \frac{10^{-9} \times 3}{2}$$

$$\therefore \text{Percent dissociation} = \frac{300}{23} = 13.04.$$

- Q.** In indicator  $\text{HIn}$  has a standard ionisation constant of  $10^{-10}$ . The acid form of the indicator is yellow and the alkaline form is red. The yellow colour is visible when the ratio of yellow form to red form is 30 to 1 and the red colour is predominant when the ratio of red form to yellow form is 2 to 1. What is the pH range of indicator. ( $\log 2 = 0.3$ ,  $\log 3 = 0.48$ )

**Sol.**  $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

When yellow : red = 30 : 1

$$\Rightarrow [\text{H}^+]_1 = 10^{-10} \times \frac{[\text{HIn}]}{[\text{In}^-]} = 30 \times 10^{-10} \Rightarrow \text{pH}_1 = 8.52$$

When red : yellow = 2 : 1

$$10^{-10} = [\text{H}^+]_2 \left( \frac{2}{1} \right) \Rightarrow \text{pH}_2 = 10.3$$

- Q.** pH of 0.1 M solution of NaA is 8.92. Calculate  $\text{pK}_a$  of HA if a drop of HPh ( $\text{pK}_a = 9.52$ ) be added to the above solution predict whether the pink colour will visible or not under the medical fact our eyes can see the pink color if the molar % ionised form of indicator is 25% or more .

**Sol.**  $\text{pH} = \frac{1}{2} (\text{pK}_a + \text{pK}_w + \log c)$

$$8.92 = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} (-1)$$



$$\frac{1}{2} pK_a = 8.92 - 6.5 = 2.42$$

$$pK_a = 4.84$$

$$pH = pK_a(\text{indicator}) + \log \frac{\text{ionised}}{\text{unionised}}$$

$$8.92 = 9.52 + \log \frac{\text{ionised}}{\text{unionised}}$$

$$\frac{[IN^-]}{[HIN]} = \frac{\text{ionised}}{\text{unionised}} = \frac{1}{4}$$

Since  $[IN^-] = 20\%$  Colour will not be visible.

## SIGNIFICANCE OF INDICATORS :

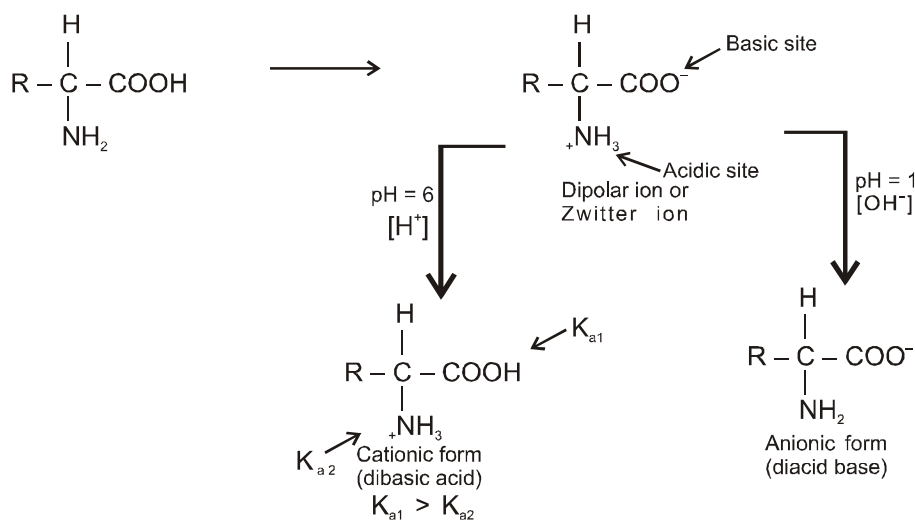
Indicators work in specific pH range i.e. they change their colour distinctly once a specific pH range is crossed. e.g. phenolphthalein works in pH range 8–10 while methyl orange in the range 3 to 4.4



Extent of reaction of different bases with acid (HCl) using these two indicators is summarised below

	Phenolphthalein	Methyl Orange
NaOH	100% reaction is indicated	100% reaction is indicated
	$NaOH + HCl \rightarrow NaCl + H_2O$	$NaOH + HCl \rightarrow NaCl + H_2O$
$Na_2CO_3$	50% reaction upto $NaHCO_3$ stage is indicated	100% reaction is indicated
	$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3$	No reaction is indicated	100% reaction is indicated
		$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

## Isoelectric Point of amino acids :



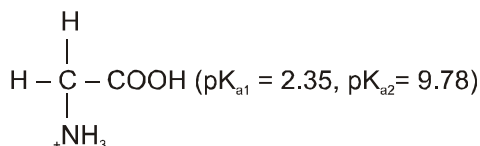
**Isoelectric point is the point when the net charge is equal to zero :**

⇒ At isoelectric point ,  $[Anionic\ form] = [Cationic\ form]$

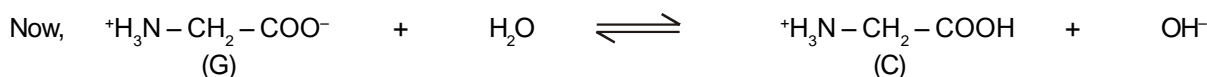
$$[H^+] = \sqrt{K_{a1} K_{a2}}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

- Q.** Calculate the pH of glycine at its isoelectric point what % of 0.01 M neutral solution of glycine is present in its cationic form.



**Sol.** At isoelectric point,  $\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2} = \frac{2.35 + 9.78}{2} = 6.065$ .



$$K_h = \frac{K_w}{K_{a1}} = \frac{[\text{C}][\text{OH}^-]}{[\text{G}]}$$

$$\Rightarrow \frac{[\text{C}]}{[\text{G}]} \times 100 = \frac{K_w \times 100}{K_{a1}[\text{OH}^-]} = \frac{K_w [\text{H}^+] \times 100}{K_{a1} \times K_w} = \frac{10^{-6.065} \times 100}{10^{-2.35}} = 0.0193\%$$

## LECTURE # 10

### Solubility(s) and Solubility Product( $K_{sp}$ )

This is generally used for sparingly soluble salts, We will be dealing with the solubilities in the following type of solutions

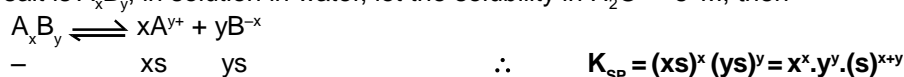
1. Simple solution in  $\text{H}_2\text{O}$
2. Effect of common ions on solubility
3. Simultaneous solubility
4.  $\text{Precipitate}_1 + \text{electrolyte}_1 \longrightarrow \text{Precipitate}_2 + \text{electrolyte}_2$
5. Condition for precipitation
6. Solubility in a buffer solution
7. Solubility due to complex formation

**Solubility product( $K_{sp}$ ) is a type of equilibrium constant, so will be dependent only on temperature for a particular salt.**

Following examples will illustrate the different type of solubilities and the effects of different factors or situations on solubility of a salt.

#### 1. Simple Solubility

Let the salt is  $\text{A}_x\text{B}_y$ , in solution in water, let the solubility in  $\text{H}_2\text{O}$  = 's' M, then



**Q.** Calculate  $K_{sp}$  of  $\text{Li}_3\text{Na}_3[\text{AlF}_6]_2$

**Sol.**  $K_{sp} = 3^3 \cdot 3^3 \cdot 2^2 (s)^8 = 3^6 \cdot 4 \cdot (s)^8 = 2916 s^8$

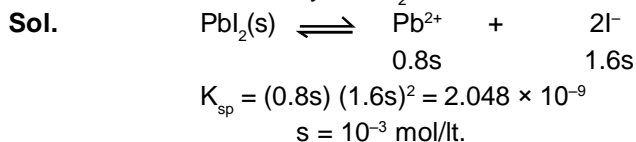
**Q.** Solubility product of  $\text{CaCO}_3$  is  $9 \times 10^{-8}$  calculate its solubility in gm/lit.

**Sol.**  $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$

$$K_{sp} = s^2 = 9 \times 10^{-8}$$

$$s = 3 \times 10^{-4} \text{ mol/lit.} = 3 \times 10^{-4} \times 100 = 0.03 \text{ gm/lit.}$$

**Q.** Calculate solubility of  $\text{PbI}_2$  in water at  $25^\circ\text{C}$  which is 80% dissociated  $K_{\text{sp}}[\text{PbI}_2] = 2.048 \times 10^{-9}$



## 2. Effect of common ions on solubility :

Because of the presence of common ion the solubility of the salt decreases.

**Q.** Calculate solubility of silver oxalate in  $10^{-2} \text{ M}$  potassium oxalate solution. Given that  $K_{\text{sp}}$  of silver oxalate =  $10^{-10}$ .

**Sol.**  $[\text{C}_2\text{O}_4^{2-}] = 10^{-2} + x$ , where  $x$  is the solubility of silver oxalate, this can be neglected in comparison to  $10^{-2}$ . So,

$$K_{\text{sp}} = 10^{-10} = 10^{-2} \times (2x)^2 \Rightarrow \frac{10^{-8}}{2 \times 2} = x^2 \Rightarrow x = 5 \times 10^{-5}$$

**Q.** If  $K_{\text{sp}}$  of  $\text{SrF}_2 = 8 \times 10^{-10}$ . Calculate its solubility in  $0.1 \text{ M NaF}$  solution.

**Sol.** If  $x$  be the solubility of  $\text{SrF}_2$  in presence of  $\text{NaF}$ , then



$$K_{\text{sp}} = x(2x + 0.1)^2 = 8 \times 10^{-10}$$

Neglecting  $2x$  with respect to  $0.1$ , as we have solubility of  $\text{SrF}_2$  in pure water in the range of  $10^{-3}$ , in presence of common ions from  $\text{NaF}$  the solubility will get further decreased so we can easily neglect  $\text{F}^-$  ions from  $\text{SrF}_2$ , then we will have

$$\Rightarrow \frac{K_{\text{sp}}}{[\text{F}^-]^2} = [\text{Sr}^{2+}] \Rightarrow \frac{K_{\text{sp}}}{(0.1)^2} = x = \text{solubility of } \text{SrF}_2 = 8 \times 10^{-8}$$

## 3. Calculation of simultaneous Solubility

**Q.** Calculate simultaneous solubility of silverthiocyanate and silver bromide in water given that  $K_{\text{sp}}$  of silver thiocyanate =  $10^{-12}$  and  $K_{\text{sp}}$  of silver bromide =  $5 \times 10^{-13}$  respectively.

**Sol.** Let the solubility of  $\text{AgSCN}$  be  $x$  and that of  $\text{AgBr}$  is  $y$ , then



$$10^{-12} = x(x + y) \quad \text{------(i)}$$

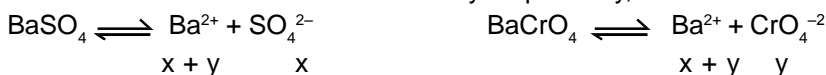
$$5 \times 10^{-13} = y(x + y) \quad \text{------(ii)}$$

On solving we get,  $x = 2y$

$$\text{So, } y = 4.08 \times 10^{-7} \text{ and } x = 8.16 \times 10^{-7}$$

**Q.** The ratio of solubility products of barium sulphate and barium chromate is  $1 : 2.4$ . When pure water is saturated with both the solids simultaneously the total  $[\text{Ba}^{2+}]$  is found to be  $1.85 \times 10^{-5}$ . Calculate  $K_{\text{sp}}$  of the compounds.

**Sol.** Let the solubilities of the salts be  $x$  and  $y$  respectively, then



$$x + y = 1.85 \times 10^{-5}$$

$$K_{\text{sp1}} = x(x + y)$$

$$K_{\text{sp2}} = y(x + y)$$

$$\frac{1}{2.4} = \frac{x}{y}$$

$$y = 2.4x$$

$$x = \frac{1.8 \times 10^{-5}}{3.4} \Rightarrow K_{\text{sp1}} = \frac{(1.85)^2}{3.4} \times 10^{-10} = 1 \times 10^{-10} \text{ and } K_{\text{sp2}} = 2.4 \times 10^{-10}$$

## LECTURE # 11

### 4. Condition of precipitation

**For precipitation ionic product should be greater than  $K_{sp}$**

**Q.** You are given  $10^{-5}$  M NaCl solution and  $10^{-8}$  M  $\text{AgNO}_3$  solution, they are mixed in 1 : 1 volume ratio, predict whether AgCl will be precipitated or not, if solubility product of AgCl is  $= 10^{-10}$  mole per litre.

**Sol.** Ionic product  $= \frac{10^{-5}}{2} \times \frac{10^{-8}}{2} = 25 \times 10^{-15} < K_{sp}$

Hence no precipitation will take place.

### 5. Selective Precipitation

**Q.**  $2 \times 10^{-4}$  moles of  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  each is present in one litre solution of  $10^{-3}$  M  $\text{HClO}_4$ , which is saturated with  $\text{H}_2\text{S}$ . Whether or not each of the ions will be precipitated? Given that concentration of  $\text{H}_2\text{S}$  in its saturated solution is  $= 0.1$  M, net dissociation constant of  $\text{H}_2\text{S} = 10^{-21}$ ,  $K_{sp}$  for  $\text{MnS} = 2.5 \times 10^{-10}$  and  $K_{sp}$  for  $(\text{CuS}) = 8.5 \times 10^{-36}$

**Sol.**  $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$   
 $\frac{10^{-1}}{10^{-1}} \rightleftharpoons \frac{10^{-3}}{10^{-3}} \times x$

$$K = \frac{x \times (10^{-3})^2}{10^{-1}} = 10^{-21} \Rightarrow [\text{S}^{2-}] = 10^{-16} \text{ M}$$

Ionic Product of  $\text{CuS} = [\text{Cu}^{2+}][\text{S}^{2-}] = 2 \times 10^{-4} \times 10^{-16} = 2 \times 10^{-20} > K_{sp}$  of  $\text{CuS}$

Ionic Product of  $\text{MnS} = 2 \times 10^{-20} < K_{sp}$  of  $\text{MnS}$

$\text{CuS}$  will be precipitated

**Ex.** A solution containing  $[\text{Cl}^-] = [\text{Br}^-] = [\text{I}^-] = 10^{-2}$  M (initially) to this solution  $[\text{AgNO}_3]$  is added gradually. Calculate

(a) which can will get ppt. final

(b) concentration of  $\text{Ag}^+$  ion when 1<sup>st</sup> ion start ppting.

(c) conc. of  $[\text{I}^-]$  &  $[\text{Cl}^-]$  ion when  $\text{AgBr}$  start ppting.

(d) conc. of  $[\text{Br}^-]$  &  $[\text{I}^-]$  ion when  $\text{AgCl}$  start ppting.

$K_{sp}$  of  $[\text{AgI}] = 10^{-17}$ ,  $K_{sp}$  of  $[\text{AgBr}] = 10^{-13}$ ,  $K_{sp}$  of  $[\text{AgCl}] = 10^{-10}$

(a) For the precipitation of  $\text{I}^-$  ion

$$[\text{Ag}^+][\text{I}^-] = K_{sp} [\text{AgI}]$$

$$[\text{Ag}^+] = \frac{10^{-17}}{10^{-2}} = 10^{-15}$$

For the precipitation of  $\text{Br}^-$  ion

$$[\text{Ag}^+] = \frac{10^{-13}}{10^{-2}} = 10^{-11}$$

For the precipitation of  $\text{Cl}^-$  ion

$$[\text{Ag}^+] = \frac{10^{-10}}{10^{-2}} = 10^{-8}$$

$\therefore$  1<sup>st</sup>  $\text{AgI}$  will be precipitated

(b)  $[\text{Ag}^+] > 10^{-15}$

(c)  $[\text{Ag}^+] = 10^{-11}$

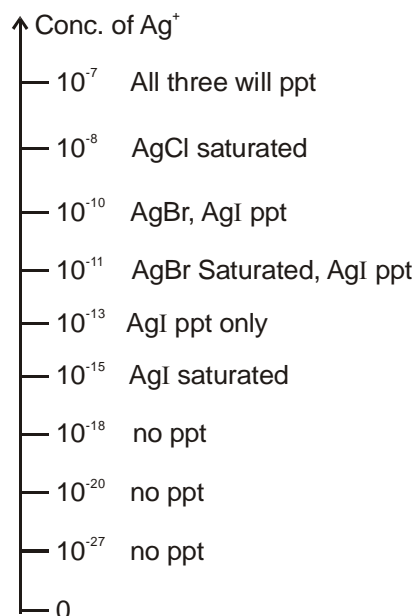
$[\text{Cl}^-] = 10^{-2}$  ( $\therefore$  ppt. is not formed)

$[\text{Ag}^+] = [\text{I}^-] = K_{sp} (\text{AgI})$

$$\Rightarrow 10^{-10} [\text{I}^-] = 10^{-17}$$

$$[\text{I}^-] = 10^{-6} \text{ M}$$

$$\% \text{ remaining iodide} = \frac{10^{-6}}{10^{-2}} \times 100 = 10^{-2} \% = 0.01 \%$$



% ppt. of  $[I^-] = 99.99\%$

(d)  $[Ag^+] = 10^{-8}$  ;  $[Ag^+][I^-] = K_{sp}$  of AgI

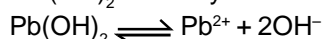
$$\Rightarrow [I^-] = \frac{10^{-17}}{10^{-8}} = 10^{-5} \text{ M} ; [Br^-] = \frac{10^{-13}}{10^{-8}} = 99.9\%$$

## 6. Solubility in appropriate buffer solutions.

Appropriate buffer means that the components of buffer should not interfere with the salt or only  $H^+$  or  $OH^-$  ions should be interacting with the ions of the salt.

**Q.1** The Solubility of  $Pb(OH)_2$  in water is  $6.7 \times 10^{-6} \text{ M}$ . Calculate its solubility in buffer solution of pH = 8

**Sol.**  $Pb(OH)_2$  solubility in water =  $6.7 \times 10^{-6}$ ,  $K_{sp} = 4s^3 = 4 \times 300 \times 10^{-18} = 1.2 \times 10^{-15}$



Let  $[Pb^{2+}] = x$ , then  $K_{sp} = x [OH^-]^2$

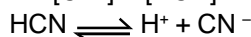
$$1.2 \times 10^{-15} = x \times 10^{-12} \Rightarrow x = 1.2 \times 10^{-3} \text{ M}$$

**Q.2** Calculate solubility of AgCN in a buffer solution of pH = 3, given that  $K_{sp}(AgCN) = 1.2 \times 10^{-15}$ ,  $K_a$  for HCN =  $4.8 \times 10^{-10}$ .

**Sol.** let the new solubility be = x

$[Ag^+] = x = [CN^-]$ , but some of  $CN^-$  ions will react with  $H^+$  ions from the buffer so,

$$x = [CN^-] + [HCN]$$



$$K_a = 4.8 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} \Rightarrow [HCN] = \frac{10^{-3}[CN^-]}{4.8 \times 10^{-10}} = \frac{[CN^-] \times 10^7}{4.8}$$

$$x = \frac{[CN^-] \times 10^7}{4.8} + [CN^-] \quad (CN^- \text{ concentration can be neglected in comparison to first term.})$$

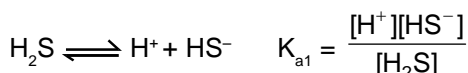
$$K_{sp} = x \cdot \frac{4.8x}{10^7} = 1.2 \times 10^{-15} \Rightarrow x = 5 \times 10^{-5}$$

**Q.3** Calculate solubility of MnS in a buffer of pH = 6. Given that for  $H_2S$ ,  $K_{a1} = 10^{-7}$  &  $K_{a2} = 10^{-14}$  and solubility of MnS in water is  $10^{-8} \text{ M}$ .

**Sol.** let the solubility be = x

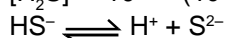
$$[Mn^{2+}] = x = S^{2-}, \text{ but free } [S^{2-}] < x$$

$$x = [S^{2-}] + [HS^-] + [H_2S]$$



$$[H_2S] = [H^+][HS^-] K_{a1}^{-1}$$

$$[H_2S] = 10^{-6} \times (10^{-7})^{-1} [HS^-] = 10 [HS^-]$$



$$K_{a2} = \frac{[H^+][S^{2-}]}{[HS^-]}, \quad [HS^-] = 10^{-6} \times [S^{2-}] \times 10^{+14} = 10^8 [S^{2-}]$$

$$[H_2S] = 10 [HS^-] = 10^{+9} [S^{2-}]$$

$$x = [S^{2-}] (1 + 10^8 + 10^9)$$

1 can be neglected

$$[S^{2-}] = \frac{x}{11 \times 10^8} = \frac{x}{11} \times 10^{-8}$$

$$K_{sp} = 10^{-16} = \frac{x^2}{11} \times 10^{-8} \Rightarrow x^2 = 11 \times 10^{-8} \Rightarrow x = 3.32 \times 10^{-4}$$

**Ex.** What must be  $[H^+]$  in a saturated  $H_2S$  solution, so as to precipitate  $Pb^{2+}$  ions but not  $Zn^{2+}$  ions from a solution in which each ion is present at a concentration of 0.1 M. Given that  $K_a$  for  $H_2S = 1.1 \times 10^{-21}$ ,  $K_{sp}$  for  $ZnS = 1.0 \times 10^{-21}$

## LECTURE # 12

7.  $\text{Precipitate -1} + \text{Ion-2} \rightleftharpoons \text{Precipitate -2} + \text{Ion-1}$

**Q.** 2M solution of  $\text{Na}_2\text{CO}_3$  is boiled in a closed container with excess of  $\text{CaF}_2$ . Very little amount of  $\text{CaCO}_3$  and  $\text{NaF}$  are formed. If the solubility product of  $\text{CaCO}_3$  is  $x$  and molar solubility of  $\text{CaF}_2$  is  $y$ . Find the molar concentration of  $\text{F}^-$  in resulting solution after equilibrium is attained.

**Sol.**  $\text{Na}_2\text{CO}_3(\text{aq}) + \text{CaF}_2(\text{s}) \rightleftharpoons 2\text{NaF}(\text{aq}) + \text{CaCO}_3(\text{s})$

$$\begin{array}{lcl} t = 0 & 2 & \\ t_{eq} & 2 - a & - \quad 2a \end{array}$$

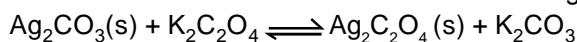
where  $a$  is very small

For  $\text{CaCO}_3$ ,  $K_{\text{SP}} = x = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$

$$[\text{Ca}^{2+}] = \frac{x}{2}$$

$$\text{For } \text{CaF}_2, K_{\text{SP}} = 4y^3 = \left(\frac{x}{2}\right) [\text{F}^-]^2 \Rightarrow [\text{F}^-] = \sqrt{\frac{8y^3}{x}}$$

**Q.** The solubility product of  $\text{Ag}_2\text{C}_2\text{O}_4$  at  $25^\circ\text{C}$  is  $1.3 \times 10^{-12}$ . A solution of  $\text{K}_2\text{C}_2\text{O}_4$  containing 0.15 moles in 500 ml water is shaken at  $25^\circ\text{C}$  with excess  $\text{Ag}_2\text{CO}_3$  till the following equilibrium is reached.



At equilibrium, the solution contains 0.02 mole of  $\text{K}_2\text{CO}_3$ . Assuming the degree of dissociation of  $\text{K}_2\text{CO}_3$  and  $\text{K}_2\text{C}_2\text{O}_4$ .

**Sol.**  $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

$0.3 \quad \quad \quad 0.3 - x \quad \quad \quad x = 0.04$

$$\therefore K = \frac{K_{SP} (\text{Ag}_2\text{CO}_3)}{K_{SP} (\text{Ag}_2\text{C}_2\text{O}_4)} = \frac{[\text{CO}_3^{2-}]}{[\text{C}_2\text{O}_4^{2-}]}$$

$$\Rightarrow \frac{K_{SP}}{1.3 \times 10^{-11}} = \frac{0.04}{0.26} \Rightarrow K_{SP} = 2 \times 10^{-12}$$

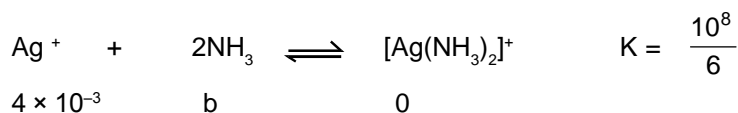
### 8. Effect on solubility because of complex formation

**Q.** What must be the concentration of aq.  $\text{NH}_3(\text{aq.})$  which must be added to a solution containing  $4 \times 10^{-3} \text{ M}$   $\text{Ag}^+$  and  $0.001 \text{ M}$   $\text{NaCl}$ , to prevent the precipitation of  $\text{AgCl}$ . Given that  $K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$  and the

formation constant of  $[\text{Ag}(\text{NH}_3)_2]^+$  is  $K_{\text{formation}} = \frac{10^8}{6}$ .

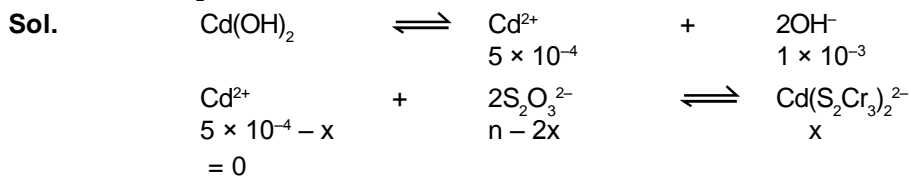
**Sol.** Calculate silver ion concentration which can be allowed to remain in the solution,  
 $1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} \text{ M}, \quad \text{This quantity is so small that almost all the Ag}^+ \text{ ion will be consumed.}$$



$$1.8 \times 10^{-7} \quad (b - 8 \times 10^{-3}) \quad 4 \times 10^{-3} \quad K = \frac{10^8}{6} = \frac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2} \Rightarrow b = 0.0445$$

- Q.** How much solid  $\text{Na}_2\text{S}_2\text{O}_3$  should be added to 1 L of water so that  $5 \times 10^{-4}$  mol  $\text{Cd}(\text{OH})_2$  would just barely dissolve.  $K_1$  &  $K_2$  for  $\text{S}_2\text{O}_3^{2-}$  complexation with  $\text{Cd}^{2+}$  are  $8.3 \times 10^3$  and  $2.5 \times 10^2$  respectively.  $K_{\text{sp}}$  of  $\text{Cd}(\text{OH})_2 = 4.5 \times 10^{-15}$



$$K_1 K_2 = (8.3 \times 10^3) (2.5 \times 10^2) = \frac{5 \times 10^{-4}}{[\text{Cd}^{2+}](n - 2x)^2}$$

$$\& \quad K_{\text{sp}} = 4.5 \times 10^{-15} = [\text{OH}^-]^2 [\text{Cd}^{2+}]$$

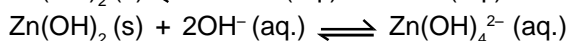
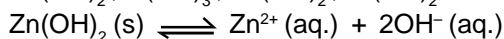
$$\Rightarrow (8.3 \times 10^3 \times 2.5 \times 10^2) \times (4.5 \times 10^{-15}) = \frac{(10^{-3})^2 \times (5 \times 10^{-4})}{(n - 2x)^2}$$

$$\Rightarrow n - 2x = 0.2314$$

$$n = 0.2314 + 2(5 \times 10^{-4}) = \mathbf{0.2324}$$

- 6. Amphoterism :** The hydroxides of certain metals can function as both bases and acids.

eg.  $\text{Zn}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Sn}(\text{OH})_2$ ,  $\text{Cr}(\text{OH})_2$

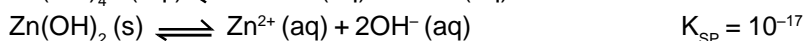
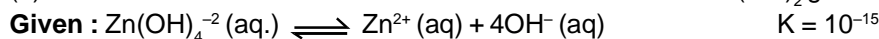


If the  $[\text{OH}^-]$  is very small, then  $\text{Zn}^{2+}$  is present in high concentration.

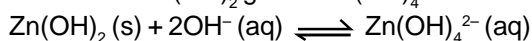
On the other hand at high hydroxide concentration  $\text{Zn}(\text{OH})_4^{2-}$  is present in high concentration.

In other words, solubility at  $\text{Zn}(\text{OH})_2$  is greater in an acidic or basic solution than in neutral water.

- Q.** (a) At what minimum concentration  $\text{OH}^-$  will  $10^{-3}$  mole of  $\text{Zn}(\text{OH})_2$  go into solution as  $\text{Zn}(\text{OH})_4^{2-}$  in 1 L solution.  
(b) At what maximum concentration of  $\text{OH}^-$  with  $10^{-3}$  moles of  $\text{Zn}(\text{OH})_2$  go into solution as  $\text{Zn}^{2+}$  in 1 L solution.

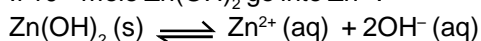


- Sol.** (a) If  $10^{-3}$  mole  $\text{Zn}(\text{OH})_2$  go into  $\text{Zn}(\text{OH})_4^{2-}$ .



$$10^{-2} = \frac{10^{-3}}{[\text{OH}^-]^2} \quad \Rightarrow \quad [\text{OH}^-] = 0.316 \text{ M}$$

- (b) If  $10^{-3}$  mole  $\text{Zn}(\text{OH})_2$  go into  $\text{Zn}^{2+}$ .



$$10^{-17} = 10^{-3} \times [\text{OH}^-]^2 \quad \Rightarrow \quad [\text{OH}^-] = 10^{-7} \text{ M}$$



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**COURSE : VIJAY (R)**  
**(LECTURE No. 1 TO 12)**

**TOPIC : IONIC EQUILIBRIUM**  
**(2012-13)**