



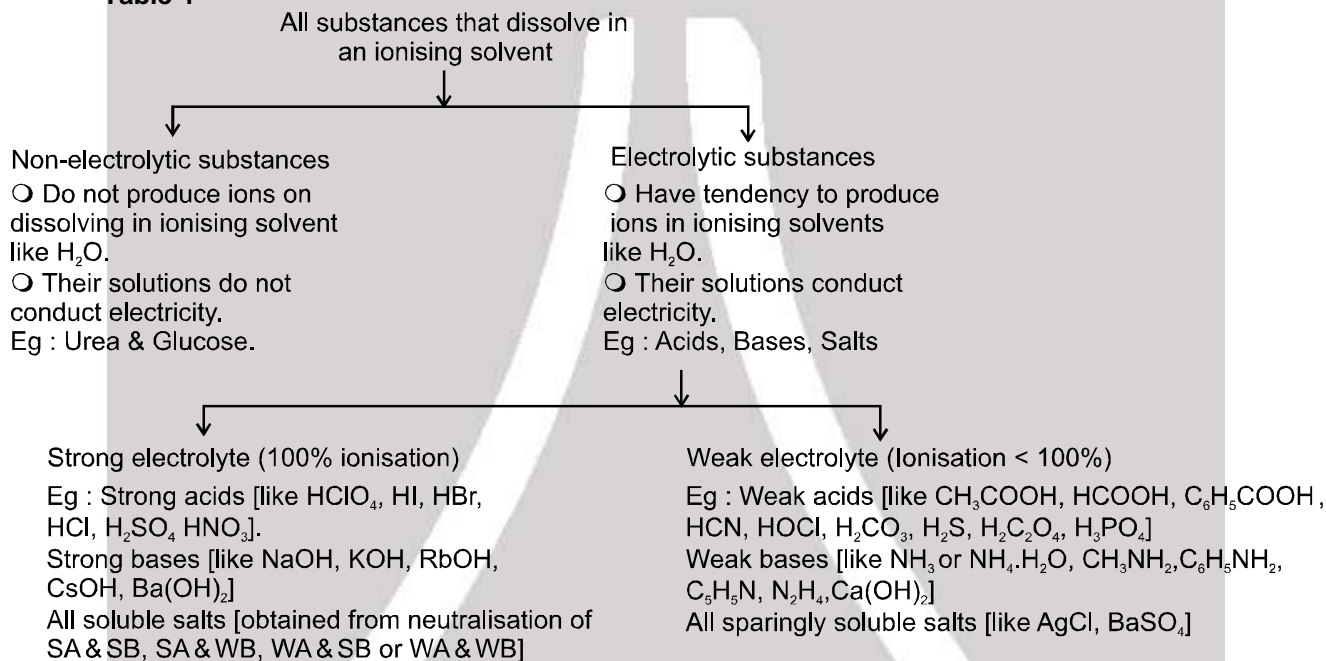
# Ionic Equilibrium (Elementary)

## Ionic Equilibrium-I

### Introduction :

Here we deal with the equilibria of species which are ionic in nature. Generally the concentration of  $H^+$  and  $OH^-$  ions is of importance. Also the concentration of ions forming precipitates is focused upon. As like dissolves like, the solvent for production of these ions should be polar. It is generally water.

**Table-1**



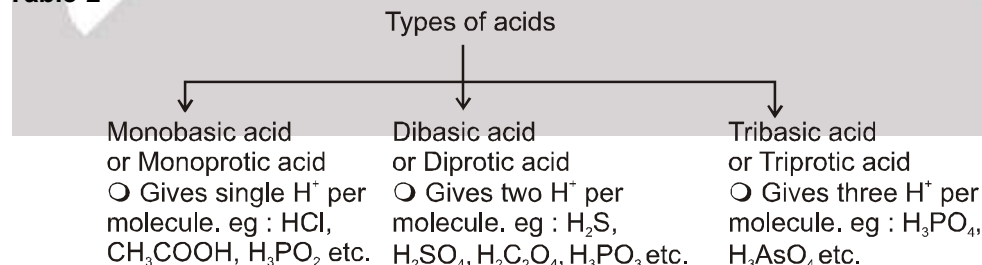
**SA : Strong Acid ; SB : Strong Base ; WA : Weak Acid ; WB : Weak Base**

### (A) Acid-Base concepts Arrhenius Concept

**D1 : Arrhenius Acid :** Substance which gives  $H^+$  ion from its own molecule on dissolving in an ionising solvent.

Eg :  $HCl$ ,  $H_2SO_4$ ,  $CH_3COOH$  etc.

**Table-2**



○  $H_3BO_3$  is not Arrhenius acid as it does not give  $H^+$  from its own molecule.

○  $H^+$  ion in water is extremely hydrated (in form of  $H_3O^+$ ,  $H_7O_2^+$ ,  $H_9O_4^+$ ) due to its high charge density.

○ The structure of solid  $HClO_4$  is studied by X-ray. It is found to consist of  $H_3O^+$  &  $ClO_4^-$  as :

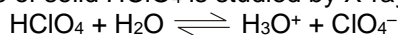
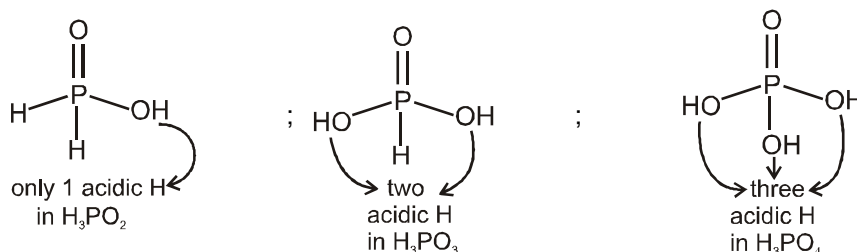




Figure-1



**D2 : Arrhenius Base :** Substance which gives  $\text{OH}^-$  ion from its own molecule on dissolving in an ionising solvent.

Eg :  $\text{NaOH}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{NH}_4\text{OH}$  etc.

Table-3

## Types of bases

### Mono acidic base

○ Gives single  $\text{OH}^-$  per molecule.

eg :  $\text{NaOH}$ ,  $\text{KOH}$

$\text{NH}_3 \cdot \text{H}_2\text{O}$

### Diacidic base

○ Gives two  $\text{OH}^-$  per molecule.

eg :  $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$

### Triacidic base

○ Gives three  $\text{OH}^-$  per molecule.

eg :  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$

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

○ First group elements of modern periodic table (except Li) form strong bases.

○ Insoluble hydroxides - like  $\text{Fe}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Cr}(\text{OH})_3$ .

## Bronsted-Lowry concept (Conjugate acid-base concept / Protonic concept)

**Bronsted Lowry Acid** : Species which donate  $\text{H}^+$  are Bronsted Lowry acids ( $\text{H}^+$  donor).

**Bronsted Lowry Base** : Species which accept  $\text{H}^+$  are Bronsted Lowry bases ( $\text{H}^+$  acceptor).

$$\begin{array}{ccccccc}
 \text{HX} & + & \text{B} & \rightleftharpoons & \text{HB}^+ & + & \text{X}^- \\
 \text{Acid} & & \text{Base} & & \text{Conjugate acid} & & \text{Conjugate base} \\
 & & \uparrow & & \uparrow & & \uparrow \\
 & & \text{Conjugate pair of acid-base} & & \text{Conjugate pair of acid-base} & & \\
 & & \text{Conjugate pair of acid-base} & & & & 
 \end{array}$$

**Conjugated acid-base pairs** : In a typical acid-base reaction,

**Forward reaction** : Here HX, being a proton donor is an acid. Here HB, being a proton acceptor is a base.

**Backward reaction** : Here  $\text{HB}^+$ , being a proton donor is an acid. Here  $\text{X}^-$ , being a proton acceptor is a base.

### Acid

$\text{HCl}$

+

### Base

$\text{H}_2\text{O}$

### Conjugate acidConjugate base

$\text{H}_3\text{O}^+$

+

$\text{Cl}^-$

$\text{HSO}_4^-$

+

$\text{NH}_3$

$\text{NH}_4^+$

+

$\text{SO}_4^{2-}$

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

$+$

$\text{H}_2\text{O}$

$\text{H}_3\text{O}^+$

+

$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$

○ Conjugate acid-base pair differ by only one proton ( $\text{H}^+$ ).

○ Strong acid will have weak conjugate base. This can be explained as the strong electrolyte will move the equilibrium where it is in dissociated form.

○ Weak acid/base will also have weak conjugate base/acid, because weak electrolyte has tendency to be in undissociated form.

○ Reaction will always proceed in a direction from stronger acid to weaker acid or from stronger base to weak base.



Table-4

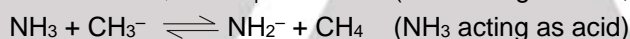
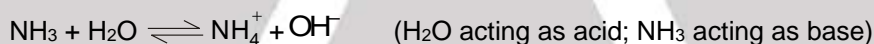
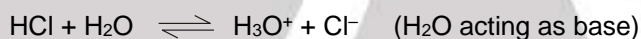
## Some Acid-Base Conjugate Pairs

Acid	Conjugate base = Acid - H <sup>+</sup>	Base	Conjugate acid = Base + H <sup>+</sup>
HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
HI	I <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> OH <sub>2</sub> <sup>+</sup>
HBr	Br <sup>-</sup>	NH <sub>3</sub> or NH <sub>3</sub> .H <sub>2</sub> O	NH <sub>4</sub> <sup>+</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	R-NH <sub>2</sub>	R-NH <sub>3</sub> <sup>+</sup>
HCl	Cl <sup>-</sup>	CN <sup>-</sup>	HCN
HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> OH
H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	NH <sub>2</sub> <sup>-</sup>	NH <sub>3</sub>
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CH <sub>3</sub> <sup>-</sup>	CH <sub>4</sub>
HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>		
H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>		
CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>		
H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>		
H <sub>2</sub> S	HS <sup>-</sup>		
NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>		
HCN	CN <sup>-</sup>		
C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>		
H <sub>2</sub> O	OH <sup>-</sup>		
C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>		
NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>		
CH <sub>4</sub>	CH <sub>3</sub> <sup>-</sup>		

**Note :** In polyprotic acids, the tendency of release of subsequent H<sup>+</sup> decreases.

eg : Order of acidic strength: H<sub>3</sub>PO<sub>4</sub> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > HPO<sub>4</sub><sup>2-</sup>.

**D5 : Amphiprotic/Amphoteric Species :** Species which can act as an acid as well as a base. eg : H<sub>2</sub>O, NH<sub>3</sub>.

**Lewis Concept (Electronic Concept)**

**D6 : Lewis Acid :** An Lewis acid is a species which can accept an electron pair with the formation of coordinate bond.

**Acid** ← Electron pair donor ⇒ **Acid** : Electron pair acceptor.

eg : Electron deficient molecules : BF<sub>3</sub>, AlCl<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, BeCl<sub>2</sub>

**Cations :** H<sup>+</sup>, Fe<sup>3+</sup>, Na<sup>+</sup>

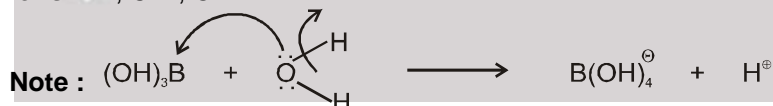
**Molecules with vacant orbitals :** SiCl<sub>4</sub>, SO<sub>2</sub>.

**D7 : Lewis Base :** A Lewis base is a species which has a lone pair of electrons available for donation.

**Base** → Electron pair acceptor ⇒ **Base** : Electron pair donor

eg : Molecules with donatable lone pairs :  $\ddot{\text{N}}\text{H}_3$ ,  $\text{H}_2\ddot{\text{O}}$ ,  $\text{CH}_3\ddot{\text{O}}\text{H}$

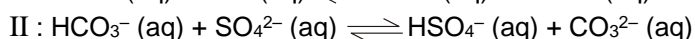
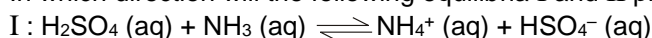
**Ions :** X<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>.



Here, Boric acid [i.e. B(OH)<sub>3</sub>] accepts a lone pair. So, it is a Lewis acid.

## Solved Examples

**Ex-1.** In which direction will the following equilibria I and II proceed ?



(A) I forward & II backward

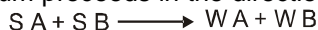
(B) I backward & II forward

(C) Both forward

(D) Both backward

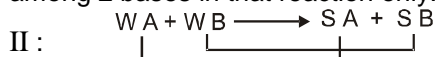


**Sol.** Equilibrium proceeds in the direction from strong (Acid/Base) to weak (Acid/Base).



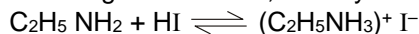
I :

Here, acidic strength is compared among the 2 acids in the reaction & basic strength is compared among 2 bases in that reaction only.



**Ans. (A)**

**Ex-2.** For the given reaction, identify the true (T) & false (F) statements.



S<sub>1</sub> : HI is bronsted base.

S<sub>2</sub> : HI is bronsted acid.

S<sub>3</sub> : HI is arrhenius acid.

S<sub>4</sub> : HI is lewis acid.

S<sub>5</sub> : HI is arrhenius base.

S<sub>6</sub> : HI is lewis base.

(A) T F F F T T

(B) F T T T F F

(C) F T T F F F

(D) T F F F T F

**Sol.** HI has donated H<sup>+</sup> in the above reaction. So it acts as an Arrhenius acid as well as a Bronsted acid.

**Ans. (C)**

**Ex-3.** In the above question, identify the true (T) & false (F) statements if HI is replaced with C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> in each statement.

(A) T F F F T T

(B) T F F F F T

(C) F F T T F F

(D) F T T T F F

**Sol.** Lewis base donates a lone pair to an electron deficient species. Arrhenius base releases OH<sup>-</sup>. Bronsted base accepts H<sup>+</sup> from a species.

**Ans. (B)**

**Ex-4.** Ammonium ion is :

(A) Lewis acid

(B) Lewis base

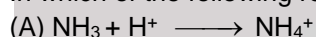
(C) Bronsted acid

(D) Bronsted base

**Sol.**  $NH_4^+ \longrightarrow NH_3 + H^+ \Rightarrow$  Bronsted Acid

**Ans. (C)**

**Ex-5.** In which of the following reactions, does NH<sub>3</sub> act as an acid ?



**Sol.** In the reaction, NH<sub>3</sub> changes to NH<sub>2</sub><sup>-</sup>. So, NH<sub>3</sub> has donated a proton (H<sup>+</sup>) and hence acts as an acid.

**Ans. (B)**

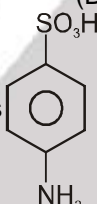
**Ex-6.** Sulphanilic acid is a/an :

(A) Arrhenius acid

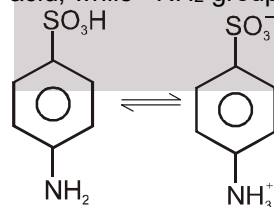
(B) Lewis base

(C) Neither (A) or (B)

(D) Both (A) & (B)

**Sol.** Sulphanilic acid is . Its -SO<sub>3</sub>H group is capable of donating H<sup>+</sup>, and hence it acts as arrhenius

acid, while -NH<sub>2</sub> group's nitrogen has lone pair of electron which can be donated as :

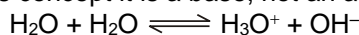


**Ans. (D)**



**(B) Properties of Water, pH scale, autoprotolysis****Properties of water :****Amphoteric Acid / Base Nature :**

Water acts as an acid as well as base according to Arrhenius & Bronsted - Lowry theory, but according to Lewis concept it is a base, not an acid.



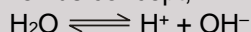
In pure water,  $[\text{H}^+] = [\text{OH}^-]$ , so it is always neutral

**○ Molar concentration / Molarity of water :**

$$\begin{aligned} \text{Molarity} &= \text{No. of moles} / \text{litre} = \frac{1000/18}{1} = 55.55 \text{ moles / litre} \\ &= 55.55 \text{ M (taking density} = 1 \text{ g / cc)} \end{aligned}$$

**Ionic product of water :**

According to arrhenius concept,



Ionic product of water is defined as :

**F1 :  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$  at 25°C (experimental data)**

∴ at 25°C pure water contains  $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$

Dissociation of water is endothermic, so on increasing temperature,  $K_{eq}$  increases. So,  $K_w$  increases with increase in temperature & decreases with decrease in temperature.

For eg. at 25°C,  $K_w = 1 \times 10^{-14}$  ; at 40°C,  $K_w = 2.916 \times 10^{-14}$  ; at 90°C,  $K_w = 10^{-13}$

Ionic product of water is always a constant whatever may be dissolved in water. As it is an equilibrium constant, it will depend only on temperature.

**Der1 : Degree of dissociation of water :**

$$\begin{aligned} \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow \alpha &= \frac{\text{no. of moles dissociated}}{\text{no. of moles initially taken}} = \frac{10^{-7}}{55.55} \\ \alpha &= 1.8 \times 10^{-9} \text{ or } 1.8 \times 10^{-7} \% \text{ (at 25°C)} \end{aligned}$$

**Der2 : Absolute dissociation constant of water :**

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow K_a = K_b = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

So,  $\text{p}K_a \text{ of } \text{H}_2\text{O} = \text{p}K_b \text{ of } \text{H}_2\text{O} = -\log(1.8 \times 10^{-16}) = 15.74 \text{ (at 25°C)}$

**pH Scale :**

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

○ Basic strength means the tendency of a base to give  $\text{OH}^-$  ions in water.  
So greater the tendency to give  $\text{OH}^-$  ions, more will be basic strength of the substance.

**D8 :** The concentration of  $\text{H}^+$  ions is written in a simplified form introduced by Sorenson known as pH scale.  
pH is defined as negative logarithm of activity of  $\text{H}^+$  ions.

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

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

○ The pH scale was marked from 0 to 14 with central point at 7 at 25°C taking water as solvent.

$$\text{F2 : } \text{pH} = -\log [\text{H}^+] \text{ or } \text{pH} = \log \frac{1}{[\text{H}^+]} \text{ or } \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{F3 : } \text{pOH} = -\log [\text{OH}^-] \text{ or } \text{pOH} = \log \frac{1}{[\text{OH}^-]}$$



**Der3 :** From,  $K_w = [H^+][OH^-] = 10^{-14}$  (at 25°C)

Taking negative log both sides,

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

$$\Rightarrow \mathbf{pH + pOH = pK_w = 14 \text{ (for an aqueous solution at 25°C)}}$$

- If the temperature and the solvent are changed, the pH range of the scale will also change.

For example :

0 – 14 at 25°C

Neutral point pH = 7

0 – 13 at 80°C ( $K_w = 10^{-13}$ )

Neutral point pH = 6.5

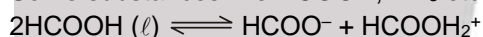
- pH can also be negative or greater than 14.

- Now,  $pH = -\log [H^+] = 7$  and  $pOH = -\log [OH^-] = 7$ , for water at 25°C (experimental)

$pH = 7 = pOH$	$\Rightarrow$	neutral	}	at 25° C only
$pH < 7$ or $pOH > 7$	$\Rightarrow$	acidic		
$pH > 7$ or $pOH < 7$	$\Rightarrow$	basic		

### Autoprotolysis :

**D9 :** Some substances like HCOOH, NH<sub>3</sub> etc are observed to be self ionised in pure liquid state as follows :



This phenomena is called Self-Ionisation or Autoprotolysis and equilibrium constant corresponding to above is called Autoprotolysis constant defined as follows :

$$K_{eq} = [HCOO^-][HCOOH_2^+]$$

### (C) Relation between $K_a$ and $K_b$ for conjugate acid-base pair

**Der4 :** For any conjugate acid-base pair (HA & A<sup>-</sup>) in aqueous solution :

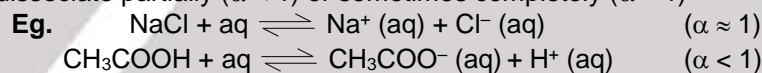


$$\text{Now, } K_a \times K_b = K_w \Rightarrow \mathbf{pK_a + pK_b = pK_w = 14 \text{ (at 25°C)}}$$

$$\text{Eg. } pK_a(CH_3COOH) + pK_b(CH_3COO^-) = pK_w = 14 ; pK_a(NH_4^+) + pK_b(NH_3) = pK_w = 14.$$

### Degree of dissociation ( $\alpha$ )

- When an electrolyte is dissolved in a solvent (H<sub>2</sub>O), it spontaneously dissociates into ions.  
 ○ It may dissociate partially ( $\alpha < 1$ ) or sometimes completely ( $\alpha \approx 1$ )



**D10 :** The degree of dissociation of an electrolyte ( $\alpha$ ) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\mathbf{F4 :} \quad \alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

The value of  $\alpha$  depends on :

- Nature of electrolyte:** Strong electrolytes dissociate completely ( $\alpha = 1$ ) whereas weak electrolytes dissociate partially. ( $\alpha < 1$ )
- Nature of solvent:** A solvent having high value of dielectric constant will favour dissociation. (Generally polar solvents)
- Dilution:** For weak electrolytes, degree of dissociation will increase with dilution (**Ostwald's dilution law**)
- Temperature:** On increasing temperature, generally degree of dissociation increases. (For endothermic dissociations)





- (e) **Presence of other solute:** When a substance is present in a solution, it may effect the dissociation of another substance. Generally, presence of common ion suppresses degree of dissociation of weak electrolyte. (**Common ion effect**)

**(D) pH Calculation : Strong acid SolutionS, strong base solutions, solutions containing mixture of two or more strong acids, solutions containing mixture of two or more strong bases, solutions containing mixture of strong acid and strong base**

**(a) Strong acid solution :**

- (i) If  $[H^+]_{\text{from strong acid}}$  is greater than  $10^{-6}$  M

In this case,  $H^+$  ions coming from water can be neglected.

**F5 :** So,  $[H^+] = \text{Molarity of strong acid solution} \times \text{number of } H^+ \text{ ions per acid molecule.}$

- (ii) If  $[H^+]_{\text{from strong acid}}$  is less than  $10^{-6}$  M

In this case,  $H^+$  ions coming from water cannot be neglected.

**F6 :** So,  $[H^+] = [H^+]_{\text{from strong acid}} + [H^+]_{\text{coming from water in presence of this strong acid.}}$

### Solved Examples

**Ex-7.** Find the pH of :

(a)  $10^{-3}$  M  $HNO_3$  solution

(b)  $10^{-4}$  M  $H_2SO_4$  solution (Take  $\log 2 = 0.3$ )

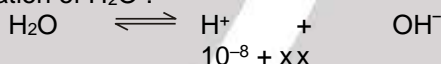
**Sol.** (a)  $pH = -\log[H^+]_{HNO_3} = -\log(10^{-3}) = 3$

(b)  $pH = -\log[H^+]_{H_2SO_4} = -\log(2 \times 10^{-4}) = 4 - \log 2 = 3.7$

In both solutions,  $[H^+]_{\text{from strong acid}} > 10^{-6}$  M. So  $H^+$  from water has not been considered.

**Ex-8.** Calculate pH of  $10^{-8}$  M  $HCl$  solution at  $25^\circ C$ . (Take  $\log 1.05 = 0.02$ )

**Sol.** Here,  $[H^+]_{HCl} = 10^{-8}$  M ( $< 10^{-6}$  M). So  $[H^+]_{\text{from water}}$  has to be considered. But,  $[H^+]_{\text{from } H_2O} \neq 10^{-7}$  M because of common ion effect exerted on it by  $H^+$  ions of  $HCl$ . So, considering dissociation of  $H_2O$  :



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

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

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

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

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

$$pH = 7 - \log 1.05 \approx 6.98$$

**Note :** For  $10^{-9}$  M  $HCl$   $pH \approx 7$ , For  $10^{-12}$  M  $HCl$   $pH \approx 7$

**(b) Strong base solution :**

- (i) If  $[OH^-]_{\text{from strong base}}$  is greater than  $10^{-6}$  M

In this case,  $OH^-$  ions coming from water can be neglected.

**F7 :** So,  $[OH^-] = \text{Molarity of strong base solution} \times \text{number of } OH^- \text{ ions per base molecule.}$

- (ii) If  $[OH^-]_{\text{from strong base}}$  is less than  $10^{-6}$  M

In this case  $OH^-$  ions coming from water cannot be neglected.

**F8 :** So,  $[OH^-] = [OH^-]_{\text{from strong base}} + [OH^-]_{\text{coming from water in presence of this strong base.}}$

### Solved Examples

**Example-9.** What will be the pH of  $5 \times 10^{-6}$  M  $Ba(OH)_2$  solution at  $25^\circ C$  ?

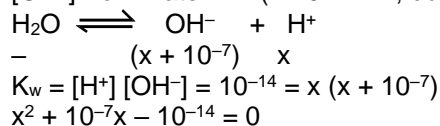
**Solution.**  $[OH^-]_{\text{from strong base}} = 2(5 \times 10^{-6}) = 10^{-5}$  M

$$\therefore pH = 14 - p(OH) = 14 - (-\log [OH^-]) = 14 - (-\log 10^{-5}) = 14 - 5 = 9$$



**Example-10.** Calculate pH of  $10^{-7}$  M of NaOH solution at  $25^{\circ}\text{C}$ . (Take  $\log 0.618 = 0.21$ )

**Solution.**  $[\text{OH}^-]$  from NaOH =  $10^{-7}$  M ( $< 10^{-6}$  M)  
 $[\text{OH}^-]$  from water =  $x$  ( $< 10^{-7}$  M ; due to common ion effect)



$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \text{ M} = [\text{H}^+] \quad (\sqrt{5} = 2.236)$$

$$\therefore \text{pH} = 7.21$$

### pH OF ACIDS/BASES MIXTURES :

#### (A) Mixture of two strong acids :

If  $V_1$  volume of a strong acid solution with  $\text{H}^+$  concentration  $[\text{H}^+]_1$  is mixed with  $V_2$  volume of another strong acid solution with  $\text{H}^+$  concentration  $[\text{H}^+]_2$ , then

moles of  $\text{H}^+$  ions from I-solution =  $M_1 V_1$

moles of  $\text{H}^+$  ions from II-solution =  $M_2 V_2$

If final  $\text{H}^+$  ion concentration is  $[\text{H}^+]_f$  and final volume is  $V_f (= V_1 + V_2)$ , then :

$$[\text{H}^+]_f V_f = [\text{H}^+]_1 V_1 + [\text{H}^+]_2 V_2$$

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

$$\text{F9 : } \therefore [\text{H}^+]_f = \frac{[\text{H}^+]_1 V_1 + [\text{H}^+]_2 V_2}{V_1 + V_2}$$

#### (B) Mixture of two strong bases :

Similar to above calculation,

$$\text{F10 : } [\text{OH}^-]_f = \frac{[\text{OH}^-]_1 V_1 + [\text{OH}^-]_2 V_2}{V_1 + V_2} \quad \& \quad [\text{H}^+]_f = \frac{10^{-14}}{[\text{OH}^-]_f}$$

### Solved Examples

**Ex-11.** Calculate pH of mixture of (400 mL,  $\frac{1}{200}$  M  $\text{H}_2\text{SO}_4$ ) + (400 mL,  $\frac{1}{100}$  M  $\text{HCl}$ ) + (200 mL of water).

Take  $\log 2 = 0.3$

**Sol.**  $[\text{H}^+]_1 V_1 = \frac{1}{100} \times \frac{400}{1000} = \frac{4}{1000}$ ,  $[\text{H}^+]_2 V_2 = \frac{4}{1000}$ ,  $\text{H}^+$  ions from water can be neglected

$$[\text{H}^+]_1 V_1 + [\text{H}^+]_2 V_2 = 8 \times 10^{-3} \text{ and } V_f = 0.4 + 0.4 + 0.2 = 1 \text{ L}$$

$$\Rightarrow [\text{H}^+]_f = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3} \text{ M} \quad \therefore \text{pH} = 3 - \log 8 = 2.1.$$

**Ex-12.** 500 mL of  $10^{-5}$  M NaOH is mixed with 500 mL of  $2.5 \times 10^{-5}$  M of  $\text{Ba}(\text{OH})_2$ . To the resulting solution, 99 L water is added. Calculate pH of final solution. Take  $\log 0.303 = -0.52$ .

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

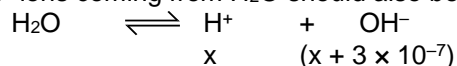
$$V_i = 1 \text{ L} \quad \& \quad V_f = 100 \text{ L}$$

no. of moles of  $[\text{OH}^-]$  in resulting solution = no. of moles of  $[\text{OH}^-]$  in final

$$3 \times 10^{-5} = [\text{OH}^-]_f \times 100$$

$$\therefore [\text{OH}^-]_f = 3 \times 10^{-7} \text{ M} (< 10^{-6} \text{ M})$$

So,  $\text{OH}^-$  ions coming from  $\text{H}_2\text{O}$  should also be considered.



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

$$\therefore x = \left( \frac{\sqrt{13}-3}{2} \right) \times 10^{-7} \text{ M} = [\text{H}^+]$$

$$\text{So, } \text{pH} = 7 - \log 0.303 = 7.52.$$



**(C) Mixture of a strong acid and a strong base :**

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic, depending on which component has been taken in excess.

**Der5:** If  $V_1$  volume of a strong acid solution with  $H^+$  concentration  $[H^+]$  is mixed with  $V_2$  volume of a strong base solution with  $OH^-$  concentration  $[OH^-]$ , then

Number of moles  $H^+$  ions from I-solution =  $[H^+]_1 V_1$

Number of moles  $OH^-$  ions from II-solution =  $[OH^-]_2 V_2$

**F11 :**

If  $[H^+]V_1 > [OH^-]V_2$

$$[H^+] = \frac{[H^+]V_1 - [OH^-]V_2}{V_1 + V_2}$$

final solution will be acidic in nature

If  $[OH^-]V_2 > [H^+]V_1$

$$[OH^-] = \frac{[OH^-]V_2 - [H^+]V_1}{V_1 + V_2}$$

final solution will be basic in nature

$$\text{Further, } [H^+]_f = \frac{10^{-14}}{[OH^-]_f} \text{ (at } 25^\circ\text{C)}$$

## Solved Examples

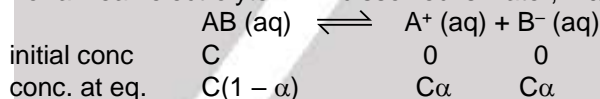
**Ex-13.** Calculate pH of mixture of (400 mL,  $\frac{1}{200}$  M  $Ba(OH)_2$ ) + (400 mL,  $\frac{1}{50}$  M  $HCl$ ) + (200 mL of Water)

**Sol.**  $[H^+]_f = \frac{\left(0.4 \times \frac{1}{50}\right) - \left(0.4 \times \frac{1}{200} \times 2\right)}{0.4 + 0.4 + 0.2} = 4 \times 10^{-3} \text{ M.}$  So,  $pH = 3 - 2\log 2 = 2.4.$

## (E) Ostwald's Dilution Law, pH calculation: Solutions of weak monoprotic acid, solutions of weak monoacidic base

### Ostwald's Dilution Law

**Der6 :** For a weak electrolyte  $A^+B^-$  dissolved in water, if  $\alpha$  is the degree of dissociation then :



Then,

**F12 :**  $K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$  = dissociation constant of the weak electrolyte

( $K_{eq} = K_a$  for weak acid;  $K_b$  for weak base)

**F13 :** If  $\alpha$  is negligible in comparison to unity, then  $1 - \alpha \approx 1$ . So  $K_{eq} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{eq}}{C}}$

$$\alpha \propto \frac{1}{\sqrt{\text{concentration}}}$$

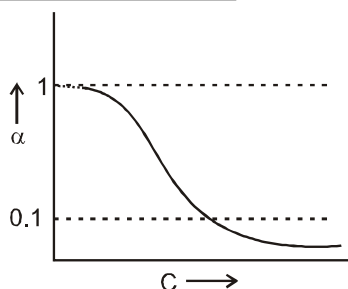
- As concentration increases  $\Rightarrow \alpha$  decreases

**F14 :**  $[A^+] = [B^-] = C\alpha = \sqrt{CK_{eq}}$ . Upon dilution,  $C \downarrow$  &  $K_{eq}$  remains same, so  $[ions] \downarrow$  and moles of ions  $\uparrow$

- At infinite dilution  $\alpha$  reaches its maximum value, unity (1). Here, weak electrolyte also starts behaving like a strong electrolyte.



Figure-2

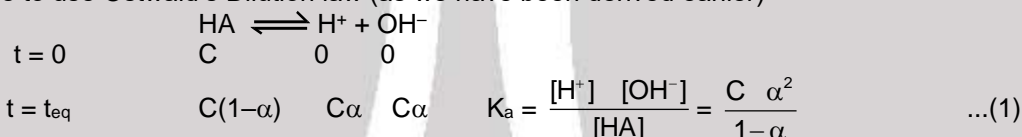


### pH calculation : Solutions of weak monoprotic acid, solutions of weak monoacidic base

#### Weak Acid (monoprotic) solution :

- Weak acid does not dissociate 100% therefore we have to calculate the percentage dissociation using  $K_a$  (dissociation constant of the acid).

**Der7 :** We have to use Ostwald's Dilution law (as we have been derived earlier)



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

**F15 :**  $[\text{H}^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \Rightarrow \text{So, pH} = \frac{1}{2}(\text{p}K_a - \log C)$  (valid if  $\alpha < 0.1$  or 10%)  
 on dilution  $\Rightarrow C \downarrow \Rightarrow \alpha \uparrow$  and  $[\text{H}^+] \downarrow \Rightarrow \text{pH} \uparrow$

**Note :** If  $\alpha$  obtained from  $\sqrt{\frac{K_a}{C}}$  is greater than 0.1, solve quadratic equation (1) and get accurate  $\alpha$ .  
 Then,  $[\text{H}^+] = C\alpha$  & now pH calculation can be done.

### Solved Examples

**Ex-14.** 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  $K_a = 2 \times 10^{-5}$ , at  $25^\circ\text{C}$ .

**Sol.** (a)  $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}}$  ( $\alpha \ll 0.1$ )

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

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

So, we have to do the exact calculations

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

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

(c) If approximation is used, then  $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20}$  ( $> 1$ ; not possible)

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

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

- At very low concentration (at infinite dilution), weak electrolyte will be almost 100% dissociated, so it will behave as strong electrolyte

pH of  $10^{-6}$  M HCl  $\approx$  pH of  $10^{-6}$  M  $\text{CH}_3\text{COOH} \approx 6$

**Weak base (monoacidic) solution :**

Proceed similarly as done for weak monoprotic acid.

$$\text{F16 : } \therefore \text{pOH} = \frac{1}{2} (\text{pK}_b - \log C) \quad (\text{if } \alpha < 0.1 \text{ or } 10\%)$$

& then  $\text{pH} = 14 - \text{pOH}$ .

**Isohydric solutions:**

**D11 :** If the concentration of the common ions in the solution of two electrolytes, for example  $\text{H}^+$  ion concentration in two acid solutions  $\text{HA}_1$  and  $\text{HA}_2$  or  $\text{OH}^-$  ion concentration in two base solutions  $\text{B}_1\text{OH}$  and  $\text{B}_2\text{OH}$  is same, then on mixing them, there is no change in the degree of dissociation of either of the electrolytes (common ion effect is not exerted by one on other). Such solutions are called isohydric solutions.

Consider two isohydric solutions of weak acids  $\text{HA}_1$  and  $\text{HA}_2$ . Let  $C_1$  and  $C_2$  be their concentration and  $\alpha_1$  and  $\alpha_2$  be their degree of dissociation. Then,

$$\text{F17 : } C_1\alpha_1 = C_2\alpha_2 \text{ (on equating the } \text{H}^+ \text{ concentrations from both acids).}$$

**Relative strength of acids and bases :**

In practice,  $K_a$  is used to define the strength only of those acids that are weaker than  $\text{H}_3\text{O}^+$  and  $K_b$  is used to define the strength of only those bases that are weaker than  $\text{OH}^-$ . For two weak acids  $\text{HA}_1$  and  $\text{HA}_2$  of ionisation constant  $K_{a1}$  and  $K_{a2}$  respectively at the same concentration  $C$ , we have :

$$\text{F18 : } \frac{\text{Acid strength of } \text{HA}_1}{\text{Acid strength of } \text{HA}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

Similarly, relative strengths of any two weak bases at the same concentration are given by the ratio of the square-roots of their dissociation constants i.e.,

$$\text{F19 : } \frac{\text{Basic strength of } \text{BOH}_1}{\text{Basic strength of } \text{BOH}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

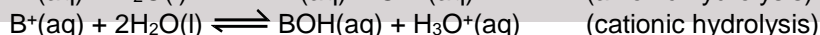
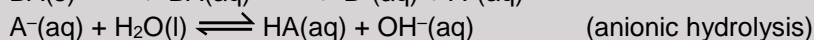
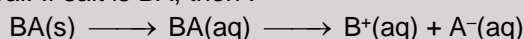
**(F) Salt Hydrolysis, pH calculation : solutions of salt of monoprotic acid and monoacidic base****Salt Hydrolysis**

**D12 : Hydrolysis :** The reaction of an ion with water in which either  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  is produced, by dissociation of water molecule.

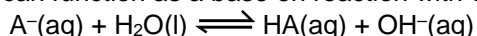


When acids and bases are mixed so that none of the two is left, then we will have salt solution in water and we have to calculate pH of salt solution.

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 on reaction with water will 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  $\text{BA}$ , then :

**ANIONIC HYDROLYSIS**

Anions can function as a base on reaction with water and hydrolyse 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 have conjugate acids weaker than  $\text{H}_2\text{O}$ , will show complete hydrolysis in aqueous medium.



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

The anions, which are weaker base than  $\text{OH}^-$  and have conjugate acids stronger 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 :  $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$

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

**(c) No hydrolysis**

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

For example :  $\text{Cl}^- + \text{H}_2\text{O} \nrightarrow \text{HCl} + \text{OH}^-$

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

**CATIONIC HYDROLYSIS**

Cations can function as acid on reaction with water and hydrolyse as follows :



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

**(a) Complete hydrolysis**

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

For example :  $\text{PH}_4^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{PH}_3$

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

The cations, which 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 :  $\text{NH}_4^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}_3\text{O}^+$

Other examples 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. Examples are alkali and alkaline earth metal ions.

For example :  $\text{Na}^+ + 2\text{H}_2\text{O} \nrightarrow \text{NaOH} + \text{H}_3\text{O}^+$

**pH calculation : Solutions of salt of monoprotic acid and monoacidic base.**

There are four types of salts :

(A) Salt of strong acid and strong base

(B) Salt of strong acid and weak base

(C) Salt of weak acid and strong base

(D) Salt of weak acid and weak base

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

Currently considering only monoprotic acids & monoacidic bases,

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

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



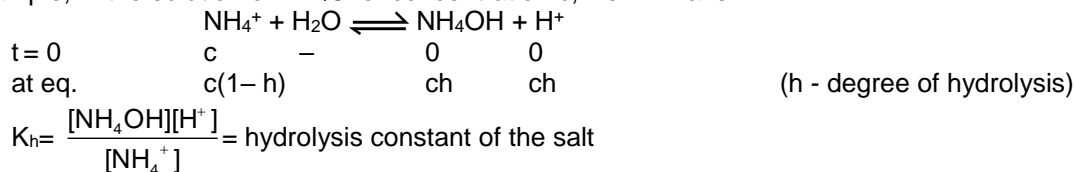
Thus, the pH of solution will be 7 (neutral solution at  $25^\circ\text{C}$ ).

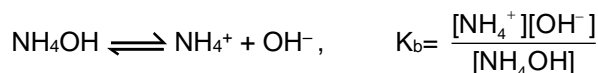
**(B) Salt of strong acid and weak base**

Examples can be  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$

Only the cation will undergo hydrolysis and the solution will be acidic in nature. Cation is considered responsible for the acidic nature of solution.

**Der8 :** For example, in the solution of  $\text{NH}_4\text{Cl}$  of concentration  $c$ , we will have :





From above equations, we can get :

$$K_h \times K_b = K_w$$

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)} \quad \dots(2)$$

**F20 :** Generally,  $h \ll 1 \therefore 1-h \approx 1$ . So we get  $\Rightarrow h = \sqrt{\frac{K_h}{c}}$

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

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

**F21 :**  $\Rightarrow \text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$  (valid if  $h < 0.1$  or 10%)

**Note :** (1)  $c$  is the concentration of ion undergoing hydrolysis, not the concentration of salt.

(2) If  $h$  obtained from  $\sqrt{\frac{K_h}{c}}$  is greater than 0.1, solve quadratic equation (2) and get accurate  $h$ . Then,  $[\text{H}^+] = ch$  & now pH calculation can be done.

## Solved Examples

**Ex-15.** Calculate degree of hydrolysis,  $K_h$  and pH of 1 M urea hydrochloride solution in water,  $K_b$  (Urea) =  $1.5 \times 10^{-14}$  at  $25^\circ\text{C}$ . Consider urea as a monoacidic base. Take  $\log 0.55 = -0.26$ .

**Sol.**  $\text{NH}_2\text{CONH}_3\text{Cl}$  is a salt of SA + WB

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.5 \times 10^{-14}} = 6.667 \times 10^{-1}$$

$$\text{Now } h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{1.5 \times 10^{-14} \times 1}}$$

or  $h = 0.816 (> 0.1)$  So we use actual relation

$$K_h = \frac{Ch^2}{1-h} = \frac{1}{1.5}$$

$$1.5h^2 + h - 1 = 0 \quad \Rightarrow \quad h = 0.55$$

$$[\text{H}^+] = ch = 0.55 \text{ M}$$

$$\therefore \text{pH} = 0.26.$$

**Ex-16.** Equal volume of 0.2 M  $\text{NH}_4\text{OH}$  (or ammonia) and 0.1 M  $\text{H}_2\text{SO}_4$  are mixed. Calculate pH of final solution. Given :  $K_b$  of  $\text{NH}_3 = 1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ .

**Sol.**  $C = [\text{NH}_4^+] = 0.1 \text{ M}$  ( $\because$  volume got doubled, so concentration must have been halved)

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.1}} \quad (< 0.1)$$

$$\therefore \text{pH} = \frac{1}{2} \{14 - 4.74 + 1\} = \frac{10.26}{2} = 5.13$$

### (C) Salt of weak acid and strong base

The examples can be  $\text{CH}_3\text{COONa}$ ,  $\text{KCN}$  etc.

**Der9 :** Proceeding similar to above analysis of salt of weak base & strong acid, we will get :

$$K_h \times K_a = K_w \quad \& \quad K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)}$$



**F22 :** So,  $h = \sqrt{\frac{K_h}{c}}$

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

$$\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \sqrt{\frac{K_w \times K_a}{c}}$$

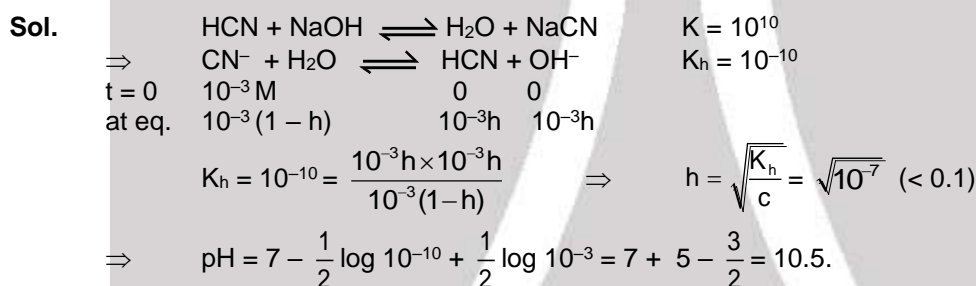
$$\text{pH} = -\log [\text{H}^+] = -\frac{1}{2} [\log K_w + \log K_a - \log c]$$

**F23 :**  $\therefore \text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$  (valid if  $h < 0.1$  or 10%)

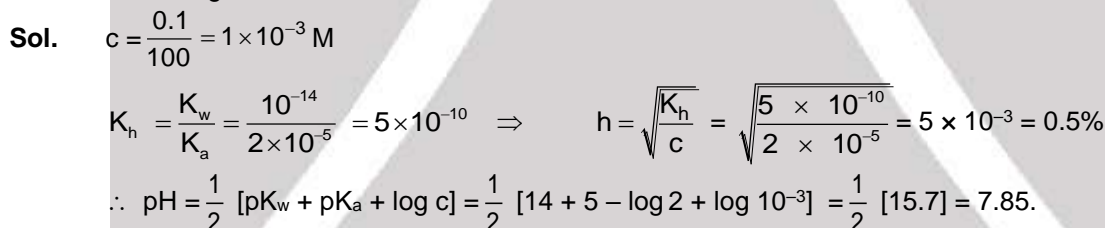
○ Solution will be basic in nature due to hydrolysis of anion.

### Solved Examples

**Ex-17.** If the equilibrium constant for reaction of HCN with NaOH is  $10^{10}$ , then calculate pH of  $10^{-3}$  M NaCN solution at  $25^\circ\text{C}$ .

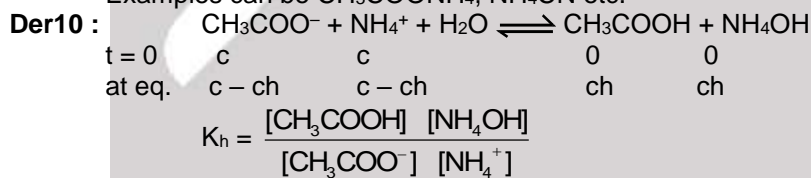


**Ex-18.** Calculate degree of hydrolysis( $h$ ) and pH of solution obtained by dissolving 0.1 mole of  $\text{CH}_3\text{COONa}$  in water to get 100 L of solution. Take  $K_a$  of acetic acid =  $2 \times 10^{-5}$  at  $25^\circ\text{C}$ .



#### (D) Salt of weak acid and weak base

Examples can be  $\text{CH}_3\text{COONH}_4$ ,  $\text{NH}_4\text{CN}$  etc.



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

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





F24 :  $\Rightarrow \left( \frac{h}{1-h} \right) = \sqrt{K_h}$

From (ii) equation,

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

F25 :  $pH = -\log [H^+] = \frac{1}{2} [pK_w + pK_a - pK_b]$

- This formula is always valid for any  $K_a$  and  $K_b$  at any temperature, for any  $h$ .
- pH is independent of concentration of salt solution.
- Even if  $K_a$  of weak acid  $\neq K_b$  of weak base, degree of hydrolysis of cations & anions are very close to each other when they are getting hydrolysed in presence of each other. So, for numerical analysis, they are taken same.

### Solved Examples

**Ex-19.** Calculate pH and degree of hydrolysis of  $10^{-2}$  M  $NH_4CN$  solution.

Given that  $K_a$  of  $HCN = 5 \times 10^{-10}$  and  $K_b$  of  $(aq.NH_3) = 2 \times 10^{-5}$  at  $25^\circ C$ .

**Sol.**  $pH = \frac{1}{2} [14 + pK_a - pK_b] = \frac{1}{2} [14 + 10 - \log 5 - 5 + \log 2] = \frac{1}{2} [18.6] = 9.3$

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

$\Rightarrow 2h = 1$

$\Rightarrow h = \frac{1}{2} = 0.5$

Table-5

Types of salt	Expression for $K_h$	Expression for $h$	Expression for pH
(i) Salt of weak acid and strong base	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\left( \frac{K_h}{C} \right)}$ ( $h < 0.1$ )	$pH = \frac{1}{2} [pK_w + pK_a + \log C]$
(ii) Salt of strong acid and weak base	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\left( \frac{K_h}{C} \right)}$ ( $h < 0.1$ )	$pH = \frac{1}{2} [pK_w - pK_b - \log C]$
(iii) Salt of weak acid and weak base	$K_h = \frac{K_w}{K_a K_b}$	$\frac{h}{1-h} = \sqrt{K_h}$	$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$

## Ionic Equilibrium-II

### (A) Buffer Solution: Definition and identification

**D13 :** Buffer solutions are those solutions which resist a change in pH upon addition of small amount of small amount of acid or base.

This does not mean that the pH will not change, all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.

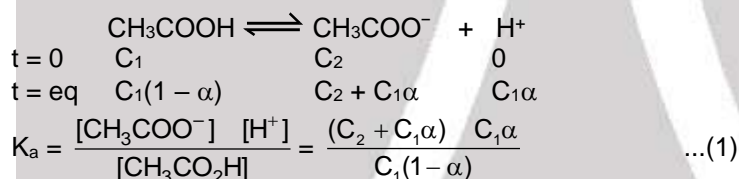


There are various types of buffers :

- (i) **Buffer of a weak acid and its salt with a strong base** : Can be prepared by  
 (a) Mixing weak acid solution and solution of its salt with a strong base.  
 (b) Mixing weak acid solution and lesser amount of strong base solution than that required for neutralization.  
 (c) Mixing salt solution of a weak acid and strong base with lesser amount of strong acid solution than that required for complete reaction.  
 Eg. A solution containing  $\text{CH}_3\text{COOH}$  &  $\text{CH}_3\text{COONa}$ .
- (ii) **Buffer of a weak base and its salt with a strong acid** : Can be prepared by  
 (a) Mixing weak base solution and solution of its salt with a strong acid.  
 (b) Mixing weak base solution and lesser amount of strong acid solution than that required for neutralization.  
 (c) Mixing salt solution of a weak base and strong acid with lesser amount of strong base solution than that required for complete reaction.  
 Eg. A solution containing  $\text{NH}_4\text{OH}$  &  $\text{NH}_4\text{Cl}$ .
- (iii) **Solution of salt of a weak acid and a weak base** :  
 Eg. A solution of  $\text{CH}_3\text{COONH}_4$ .

## (B) pH calculation: Buffer solutions generated from monobasic acid / monoacidic base

**Der11:** To calculate the pH of a buffer solution consisting of a weak acid ( $\text{CH}_3\text{COOH}$ ;  $C_1$  concentration) and its salt with a strong base ( $\text{CH}_3\text{COONa}$ ;  $C_2$  concentration of anion), we have :



Expecting  $\alpha \ll 1$  (due to common ion effect exerted by  $\text{CH}_3\text{COO}^-$  on dissociation of  $\text{CH}_3\text{COOH}$ ),

$$\alpha = \frac{K_a}{C_2} \quad \dots(2)$$

$$\therefore [\text{H}^+] = C_1\alpha = K_a \times \frac{C_1}{C_2}$$

$$\text{Taking log of both sides,} \quad \log [\text{H}^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Anion of Salt}]}$$

$$\text{F26 : } \therefore \text{pH} = \text{pK}_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$$

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

**NOTE :** If  $\alpha$  from (2) comes greater than 0.1, calculate exact  $\alpha$  by solving quadratic (1) & then  $[\text{H}^+] = C_1\alpha$ .

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

$$\text{F27 : } \text{pOH} = \text{pK}_b + \log \frac{[\text{Cation of Salt}]}{[\text{Base}]}$$

## Solved Examples

**Ex-20.** Calculate the amount of  $(\text{NH}_4)_2\text{SO}_4$  in grams which must be added to 500 ml of 0.2 M  $\text{NH}_3$  to give a solution of pH = 9.3. Given  $\text{pK}_b$  for  $\text{NH}_3 = 4.7$

**Sol.** This is a buffer solution made up of weak base and its salt with a strong acid. On checking  $\alpha$  (refer derivation), it comes less than 0.1 (can be considered negligible).

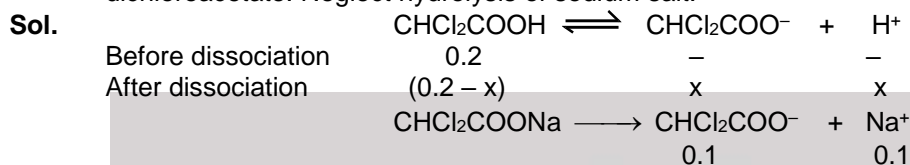
$$\therefore \text{pOH} = \text{pK}_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]} \quad (\text{Cation of salt here is same as conjugate acid})$$



$$4.7 = 4.7 + \log \frac{x}{0.2} \Rightarrow x = [\text{NH}_4^+] = 0.2, \text{ so concentration of } (\text{NH}_4)_2\text{SO}_4 \text{ required} = 0.1 \text{ M}$$

- $\therefore$  moles of  $(\text{NH}_4)_2\text{SO}_4$  needed =  $0.1 \times 0.5 = 0.05$   
 $\therefore$  weight of  $(\text{NH}_4)_2\text{SO}_4$  needed =  $132 \times 0.05 = 6.6 \text{ g}$

**Ex-21.** Calculate  $[\text{H}^+]$  in a 0.20 M solution of dichloroacetic acid ( $K_a = 5 \times 10^{-2}$ ) that also contains 0.1 M sodium dichloroacetate. Neglect hydrolysis of sodium salt.



For the dissociation of acid

$$K_a = 5 \times 10^{-2} = \frac{[\text{CHCl}_2\text{COO}^-][\text{H}^+]}{[\text{CHCl}_2\text{COOH}]} \quad \text{or} \quad 0.05 = \frac{[0.1 + x][x]}{[0.2 - x]}$$

$$x = 0.05 \quad \text{or} \quad [\text{H}^+] = 0.05 \text{ M.}$$

## Ionic Equilibrium-III

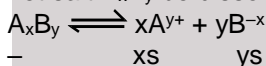
### (A) Solubility, Solubility Product and simple solubility calculations

**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.

#### Simple solubility

Let salt  $A_xB_y$  be dissolved in water. Let its solubility in  $\text{H}_2\text{O} = 's' \text{ M}$ . Then :



**F28 :**  $\therefore K_{sp} = (xs)^x (ys)^y = x^x \cdot y^y \cdot (s)^{x+y}$

### Solved Examples

**Ex-22.** Calculate  $K_{sp}$  of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  at a particular temperature, where solubility in water =  $s \text{ mol/L}$

**Sol.**  $K_{sp} = 4^4 \cdot 3^3 \cdot (s)^{3+4} = 6912 s^7$

### (B) Condition of precipitation, common ion effect on solubility

#### Condition of precipitation

- Consider ionic product ( $K_{IP}$ ) similar to reaction quotient  $Q$  in chemical equilibrium.
- For precipitation, ionic product ( $K_{IP}$ ) should be greater than solubility product  $K_{sp}$ . This will make the equilibrium of undissolved salt and dissolved salt shift in backward direction leading to precipitation.
- After precipitation, solution will become saturated and  $K_{IP} = K_{sp}$ .
- Remember to modify the concentration of the precipitating ions because of volume change occurring upon mixing both solutions.

### Solved Examples

**Ex-23.** You are given  $10^{-5} \text{ M}$   $\text{NaCl}$  solution and  $10^{-8} \text{ M}$   $\text{AgNO}_3$  solution. They are mixed in 1:1 volume ratio. Predict whether  $\text{AgCl}$  will be precipitated or not, if solubility product ( $K_{sp}$ ) of  $\text{AgCl} = 10^{-10}$ .

**Sol.** Upon mixing equal volumes, volume of solution will get doubled. So concentration of each ion will get halved from original value.

$$\text{Ionic product } K_{IP} = ([\text{Ag}^+][\text{Cl}^-])_{\text{upon mixing}} = \frac{10^{-5}}{2} \times \frac{10^{-8}}{2} = 25 \times 10^{-15} (< K_{sp})$$

Hence, no precipitation will take place.



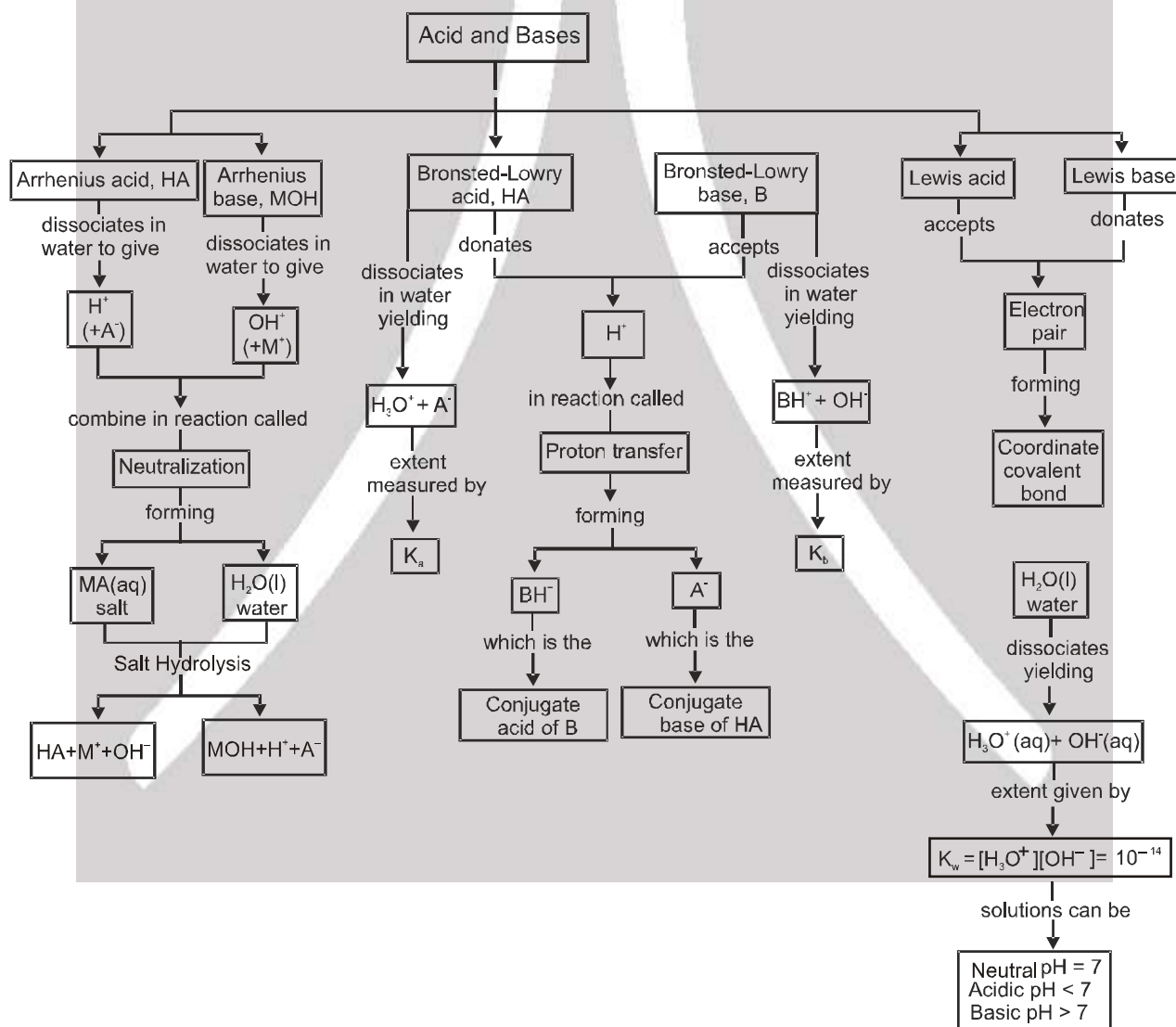
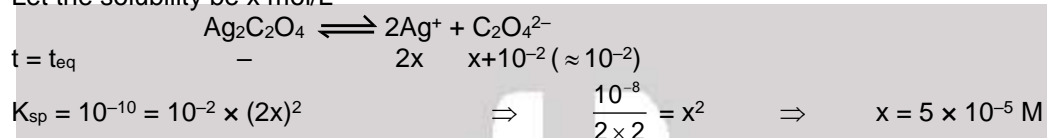
### Common Ion effect on solubility

- Because of the presence of common ion in solution, the solubility of the sparingly soluble salt generally decreases.
- Neglect the concentration of common ion coming from sparingly soluble salt with respect to that coming from completely soluble salt.

### Solved Examples

**Ex-24.** Calculate solubility of silver oxalate in  $10^{-2}$  M potassium oxalate solution. Given that  $K_{sp}$  of silver oxalate  $= 10^{-10}$ .

**Sol.** Let the solubility be  $x$  mol/L





## Check List

Definitions (D)			
D1	Arrhenius Acid	F14	Concentrations of ions produced by weak electrolyte (with $\alpha < 0.1$ )
D2	Arrhenius Base	F15	$[H^+]$ & pH of a weak monoprotic acid solution
D3	Brønsted–Lowry Acid	F16	pOH of a weak monoacidic base solution
D4	Brønsted–Lowry Base	F17	Condition for two solution to be isohydric
D5	Amphiprotic species	F18	Relative strength of two weak acids
D6	Lewis Acid	F19	Relative strength of two weak bases
D7	Lewis Base	F20	Degree of hydrolysis (h) of a salt of WB & SA ( $< 0.1$ )
D8	pH & pOH scale	F21	pH of a solution of a salt of WB & SA ( $h < 0.1$ )
D9	Autoprotolysis	F22	Degree of hydrolysis (h) of a salt of WA & SB ( $< 0.1$ )
D10	Degree of dissociation ( $\alpha$ )	F23	pH of a solution of a salt of WA & SB ( $h < 0.1$ )
D11	Isohydric Solutions	F24	Degree of hydrolysis (h) of a salt of WA & WB
D12	Hydrolysis	F25	pH of a solution of a salt of WA & WB
D13	Buffer solution	F26	pH of a buffer solution of WA & its conjugate base
Formulae (F)		F27	pH of a buffer solution of WB & its conjugate acid
F1	Ionic Product of Water ( $K_w$ )	F28	Relation between solubility(s) & solubility product ( $K_{sp}$ ) for sparingly soluble salts
F2	pH	Derivation (Der)	
F3	pOH	Der1	Absolute dissociation constant of water ( $K_a$ or $K_b$ )
F4	$\alpha$	Der2	Relation between pH & pOH for an aqueous solution
F5	$[H^+]$ in strong acid solution ( $H^+$ from $H_2O$ negligible)	Der3	Relation between $pK_a$ & $pK_b$ for a conjugate acid base pair
F6	$[H^+]$ in strong acid solution ( $H^+$ from $H_2O$ significant)	Der4	$[H^+]/[OH^-]$ in a solution containing mixture of SA & SB
F7	$[OH^-]$ in strong base solution ( $OH^-$ from $H_2O$ negligible)	Der5	Ostwald's Dilution Law
F8	$[OH^-]$ in strong base solution ( $OH^-$ from $H_2O$ significant)	Der6	Equilibrium of a weak monoprotic acid
F9	$[H^+]$ in a solution containing mixture of two strong acids	Der7	Hydrolysis of cation in a salt solution of WB & SA
F10	$[OH^-]$ in a solution containing mixture of two strong bases	Der8	Hydrolysis of anion in a salt solution of WA & SB
F11	$[H^+]/[OH^-]$ in a solution containing mixture of a strong acid & a strong base	Der9	Hydrolysis of cation & anion in a salt solution of WA & WB
F12	$K_{eq}$ for a weak electrolyte (in terms of C & $\alpha$ )	Der10	pH calculation of a buffer solution consisting of a weak acid & its salt with SB
F13	$\alpha$ for weak electrolyte (if $< 0.1$ )	Der11	

### MISCELLANEOUS SOLVED PROBLEMS (MSPs)

- Which of the following is the strongest base?  
(A)  $C_2H_5^-$  (B)  $C_2H_5COO^-$  (C)  $C_2H_5O^-$  (D)  $OH^-$   
**Ans.** (A)  
**Sol.** Acidic strength,  $C_2H_6 < C_2H_5OH < H_2O < C_2H_5COOH$   
Weakest acid will have strongest conjugate base.
- A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be pH of resulting solution.  
**Sol.**  $[HCl]_i = 10^{-5} \text{ M}$  since pH = 5  
Since volume of original solution has been made 1000 times, so concentration of solution will decrease by 1000 times.  
 $\therefore [HCl]_f = 10^{-8} \text{ M}$ . So  $H^+$  from water should also be considered (as done in solved example-8)  
Then, pH of resulting solution = **6.96**
- Calculate the pH of 0.001 M HOCl having 25% dissociation. Also calculate dissociation constant of the acid. Take  $\log 2 = 0.3$   
**Sol.**  $HOCl \rightleftharpoons H^+ + OCl^-$   

t=0	a	0	0
t=eq	$a - a\alpha$	$a\alpha$	$a\alpha$

So,  $[H^+] = a\alpha = 10^{-3} \times \frac{25}{100} = 2.5 \times 10^{-4}$   
So, pH = **3.6**  
Now,  $K_a = \frac{(a\alpha)(a\alpha)}{a(1-\alpha)} = \frac{a\alpha^2}{1-\alpha} = \frac{1}{12} \times 10^{-3}$
- The solubility product of  $SrF_2$  in water is  $8 \times 10^{-10}$ . Calculate its solubility in 0.1 M NaF aqueous solution.  
**Sol.**  $K_{sp} = [Sr^{2+}][F^-]^2$   
 $8 \times 10^{-10} = s[2s + 0.1]^2 = s[0.1]^2$  (neglecting the  $F^-$  coming from sparingly soluble salt  $SrF_2$ )  
 $\therefore s = \frac{8 \times 10^{-10}}{(0.1)^2} = 8 \times 10^{-8} \text{ M}$