

# CHEMISTRY

# IONIC EQUILIBRIUM

## Contents

Topic	Page No.
Theory	01 – 21
Exercise - 1	22 – 33
Exercise - 2	33 – 37
Part - I : Objective Questions	
Part - II : Assertion/Reasoning	
Exercise - 3	37 – 40
Part - I : JEE (Main) /AIEEE Questions	
Part - II : JEE (Adv.)/ IIT-JEE Questions	
Answer Key	41 – 42
JEE(Main) Practice Test Paper	43 – 46
JEE(Main) Test Paper Answers	47
JEE(Main) Test Paper Solutions	47 – 49

### JEE(MAIN) SYLLABUS

Ionic equilibrium: Weak and strong electrolytes, ionization of electrolytes, various concepts of acids and bases (Arrhenius, Bronsted – Lowry and Lewis) and their ionization, acid – base equilibria (including multistage ionization) and ionization constants, ionization of water, pH scale, common ion effect, hydrolysis of salts and pH of their solutions, solubility of sparingly soluble salts and solubility products, buffer solutions.

### JEE(ADVANCED) SYLLABUS

Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts.

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# Ionic Equilibrium

## Introduction

### Degree of dissociation

- When an electrolyte is dissolved in a solvent (H<sub>2</sub>O), it spontaneously dissociates into ions. It may dissociate partially ( $\alpha \ll 1$ ) or sometimes completely ( $\alpha \approx 1$ )
- Eg.  $\text{NaCl} + \text{aq} \rightleftharpoons \text{Na}^+ (\text{aq}) + \text{Cl}^- (\text{aq})$  ( $\alpha \approx 1$ )
- $\text{CH}_3\text{COOH} + \text{aq} \rightleftharpoons \text{CH}_3\text{COO}^- (\text{aq}) + \text{H}^+ (\text{aq})$  ( $\alpha \ll 1$ )
- The degree of dissociation of an electrolyte ( $\alpha$ ) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

The value of  $\alpha$  depends

- (a) **Nature of electrolyte** : Strong electrolyte dissociate completely where as weak electrolytes dissociate partially.
- (b) **Nature of solvent** : A solvent having high value of **dielectric constant** and high **solvation** (in water hydration) will favour dissociation.
- (c) **Dilution** : For some electrolytes degree of dissociation will increase by dilution (**Ostwald's dilution law**)
- (d) **Temperature** : On increasing temperature generally degree of dissociation increases.
- (e) **Presence of other solute** :  
When a substance is present it may affect the solubility of the another solute. Generally common ion present in both the substance affects most.

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

- For a weak electrolyte  $\text{A}^+\text{B}^-$  dissolved in water, if  $\alpha$  is the degree of dissociation then

	$\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$
initial conc	C      0      0
conc-at eq.	$C(1-\alpha)$ $C\alpha$ $C\alpha$

Then according to law of mass action,

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

= dissociation constant of the weak electrolyte

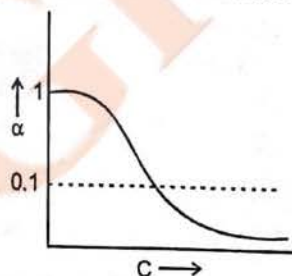
$[C = \frac{1}{V}]$ , then  $V = 1/C$  (volume of Solution in which 1 mole is present) is called **dilution**, so  $k_{\text{eq}} = \frac{\alpha^2}{(1-\alpha)V}$

If  $\alpha$  is negligible in comparison to unity then,  $1 - \alpha \approx 1$ . So  $k_{\text{eq}} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{k_{\text{eq}}}{C}} = \sqrt{k_{\text{eq}} \cdot V}$ .

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

{ Thumb rule }

- as concentration increases  $\Rightarrow \alpha$  decreases
- at infinite dilution  $\alpha$  reaches its maximum value, unity.



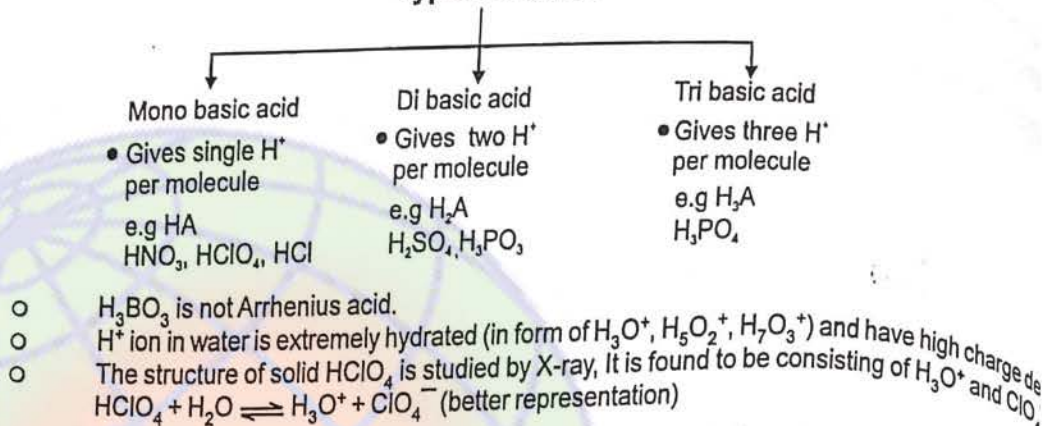
*Ionic Equilibrium*

**ACIDS BASES AND SALTS :**

● **Arrhenius concept :**

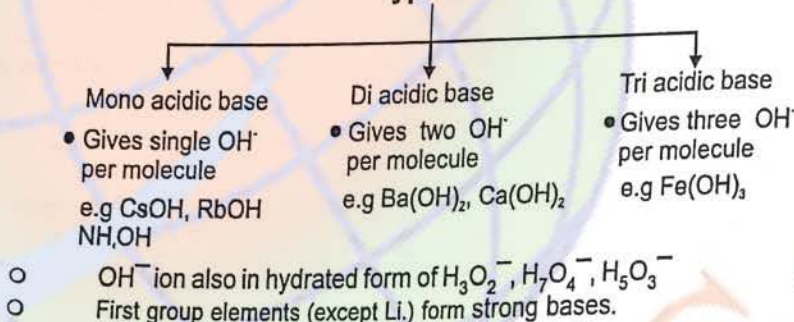
**Arrhenius Acid :** Substance which gives  $H^+$  ion on dissolving in water ( $H^+$  donor)  
eg.  $HNO_3$ ,  $HClO_4$ ,  $HCl$ ,  $HI$ ,  $HBr$ ,  $H_2SO_4$ ,  $H_3PO_4$  etc.

**Types of acids**



**Arrhenius base :** Any substance which releases  $OH^-$  (hydroxyl) ion in water ( $OH^-$  ion donor)

**Types of base**



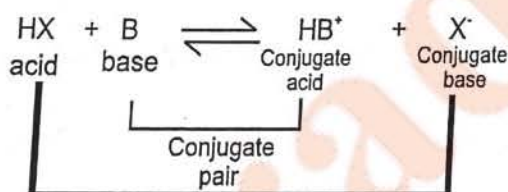
**Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)**

**Acid :** substances which donate  $H^+$  are Bronsted Lowry acids ( $H^+$  donor)

**Base :** substances which accept  $H^+$  are Bronsted Lowry bases ( $H^+$  acceptor)

**Conjugate acid - base pairs**

In a typical acid base reaction



- Forward reaction – Here  $HX$  being a proton donor is an acid  
 $B$  being a proton acceptor is a base.
- Backward reaction – Here  $HB^+$  being a proton donor is an acid  
 $X^-$  being a proton acceptor is a base.

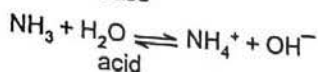
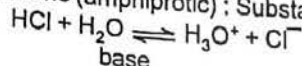
Acid	Base	Conjugate Acid	Conjugate Base
○ $HCl$	+ $H_2O$	$\rightleftharpoons$ $H_3O^+$	+ $Cl^-$
○ $HSO_4^-$	+ $NH_3$	$\rightleftharpoons$ $NH_4^+$	+ $SO_4^{2-}$
○ $[Fe(H_2O)_6]^{3+}$	+ $H_2O$	$\rightleftharpoons$ $H_3O^+$	+ $[Fe(H_2O)_5(OH)]^{2+}$



**Ionic Equilibrium**

- Conjugate acid - base pair differ by only one proton
- Strong acid will have weak conjugate base and vice versa
- Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

Amphoteric (amphiprotic) : Substances which can act as acid as well as base are known as amphoteric



**Solved Examples**

Ex.1. Write the conjugate bases of HCl, H<sub>2</sub>SO<sub>4</sub>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>O and conjugate acids of NH<sub>3</sub>, H<sub>2</sub>O and RNH<sub>2</sub>.

Sol. Acid	Conjugate base	Base	Conjugate acid
HCl	Cl <sup>-</sup>	NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	RNH <sub>2</sub>	RNH <sub>3</sub> <sup>+</sup>
H <sub>2</sub> O	OH <sup>-</sup>		

**Lewis concept (electronic concept) :**

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

Acid → e<sup>-</sup> pair acceptor  
 e.g. Electron deficient molecules : BF<sub>3</sub>, AlCl<sub>3</sub>  
 Cations : H<sup>+</sup>, Fe<sup>2+</sup>, Na<sup>+</sup>  
 Molecules with vacant orbitals : SF<sub>4</sub>, PF<sub>3</sub>

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

Base → (One electron pair donate)  
 e.g. Molecules with lone pairs : NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH

**Solved Examples**

Ex.2. In which of the following reactions does NH<sub>3</sub> act as an acid ?

- (1) NH<sub>3</sub> + H<sup>+</sup> → NH<sub>4</sub><sup>+</sup>                      (2) NH<sub>3</sub> + Na → NaNH<sub>2</sub> +  $\frac{1}{2}$  H<sub>2</sub>  
 (3) NH<sub>3</sub> + HCl → NH<sub>4</sub>Cl                      (4) None of these

Sol. (B) In the following reaction, NH<sub>3</sub> changes to NaNH<sub>2</sub> which contains NH<sub>2</sub><sup>-</sup> ion. This means that NH<sub>3</sub> has donated a proton to Na and hence acts as an acid.

Ex.3. Sulphanilic acid is a / an

- (1) Arrhenius acid                                      (2) Lewis base  
 (3) Neither (1) or (2)                              (4) Both (1) and (2)



is capable of donating H<sup>+</sup> and hence it acts as arrhenius acid while nitrogen in the NH<sub>2</sub> group contains lone pair of electrons and hence can act as lewis base by donating it.

Ex.4. Ammonium ion is

- (1) A Lewis acid                      (2) Lewis base                      (3) Bronsted acid                      (4) Bronsted base

Sol. Correct answer is (3).

*Ionic Equilibrium*

**PROPERTIES OF WATER :**

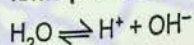
● **Amphoteric (amphiprotic) Acid/base nature:**  
 Water - an acid as well as base according to Arrhenius and Bronsted-Lowry theory but according to Lewis concept it can only be taken as base.

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

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

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

● **Ionic product of water :** According to Arrhenius concept



so, ionic product of water,  $K_w = [H^+][OH^-] = 10^{-14}$  at 25° (exp.)  
 dissociation of water, is endothermic, so on increasing temperature  $K_{eq}$  increases  
 $K_w$  increases with increase in temperature.

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

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

○ 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.

● **Degree of dissociation of water :**

$H_2O \rightleftharpoons H^+ + OH^- \Rightarrow \alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18 \times 10^{-10}$  or  $1.8 \times 10^{-7}\%$

● **Absolute dissociation constant of water :**

$H_2O \rightleftharpoons H^+ + OH^- \quad K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$

So,  $pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$

**Acidity and pH scale :**

- Acidic strength means the tendency of an acid to give  $H_3O^+$  or  $H^+$  ions in water.  
 So greater the tendency to give  $H^+$ , more will be the acidic strength of the substance.
- Basic strength means the tendency of a base to give  $OH^-$  ions in water.  
 So greater the tendency to give  $OH^-$  ions, more will be basic strength of the substance.
- The concentration of  $H^+$  ions is written in a simplified form introduced by Sorenson known as pH scale.  
 pH is defined as negative logarithm of activity of  $H^+$  ions.

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

- Activity of  $H^+$  ions is the concentration of free  $H^+$  ions or  $H_3O^+$  ions in a Solution.
- For dilute Solutions  $[H^+] \leq 1M$  concentration can be taken as activity of  $H^+$  ions while for higher concentrations the activity would be much less than the concentration itself, so it is calculated experimentally.
- The pH scale was marked from 0 to 14 with central point at 7 at 25°C taking water as solvent.
- If the temperature is 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 > 14



### Solved Examples

- Ex.5. For which temperature the  $pK_w$  of pure water can be greater than 14.  
 (1) 20 °C (2) 30 °C (3) 40 °C (4) 50 °C **Ans. (1)**
- Ex.6. For pure water at 10 °C and 60 °C, the correct statement is  
 (1)  $pOH_{10°C} = pOH_{60°C}$  (2)  $pOH_{10°C} > pOH_{60°C}$  (3)  $pOH_{60°C} > pOH_{10°C}$  (4) Can't say **Ans. (2)**
- Ex.7. For pure water at 25 °C and 50 °C the correct statement is  
 (1)  $pH_{25°C} = pH_{50°C}$  (2)  $pH_{25°C} > pH_{50°C}$  (3)  $pH_{50°C} > pH_{25°C}$  (4) Can't say **Ans. (2)**

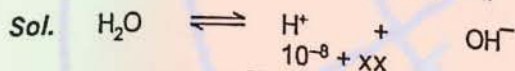
### pH Calculations of Different Types of Solutions :

(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  $[H^+] =$  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,  
 So  $[H^+] =$  normality of strong acid +  $H^+$  ions coming from water in presence of this strong acid

### Solved Examples

Ex.8. Calculate pH of  $10^{-8}$  M HCl Solution.



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

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

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

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

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

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

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

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

(b) Strong base Solution :

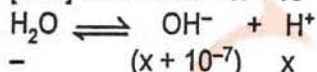
Calculate the  $[OH^-]$  which will be equal to normality of the strong base solution and then use  $K_w = [H^+] \times [OH^-] = 10^{-14}$ , to calculate  $[H^+]$ .

### Solved Examples

Ex.9. 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)



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

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

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

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

$$pOH = 7 - \log (1.618) = 6.79$$

$$pH = 14 - 6.79 = 7.21$$

**Ionic Equilibrium**

**(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

$$[OH^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad [H^+] = \frac{10^{-14}}{[OH^-]}$$

**Solved Examples**

**Ex.10.** Calculate pH of mixture of (400ml,  $\frac{1}{200}$  M  $H_2SO_4$ ) + (400ml,  $\frac{1}{100}$  M HCl) + (200 ml of water)

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

$$N_1 V_1 + N_2 V_2 = 8 \times 10^{-3} \quad [H^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$$

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

**(e) pH of 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.
- 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  $H^+$  ions from I-solution =  $N_1 V_1$   
 Number of  $OH^-$  ions from II-solution =  $N_2 V_2$

If  $N_1 V_1 > N_2 V_2$

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

solution will be acidic in nature

If  $N_2 V_2 > N_1 V_1$

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

solution will be basic in nature

$$[H^+] = \frac{10^{-14}}{[OH^-]}$$

**Solved Examples**

**Ex.11.** Calculate pH of mixture of (400ml,  $\frac{1}{200}$  M  $Ba(OH)_2$ ) + (400ml,  $\frac{1}{50}$  M HCl) + (200ml of Water)

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

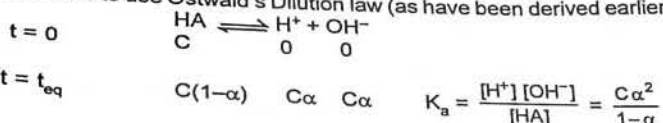
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Ionic Equilibrium

- (f) **pH of a 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.
- We have to use Ostwald's Dilution law (as have been derived earlier)



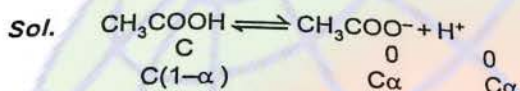
If  $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx \text{C}\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{\text{C}}}$  (is valid if  $\alpha < 0.1$  or 10%)

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

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

Solved Examples

Ex.12. Calculate pH of  $10^{-1}$  M  $\text{CH}_3\text{COOH}$   
Take  $K_a = 2 \times 10^{-5}$ .

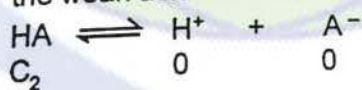


$$K_a = \frac{\text{C}\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{\text{C}}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

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

- At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociated, so behave as strong electrolyte  
(pH) of  $10^{-6}$  M HCl  $\approx$  pH of  $10^{-6}$  M  $\text{CH}_3\text{COOH} \approx 6$

- (g) **pH of a mixture of weak acid(monoprotic) and a strong acid Solution :**
- Weak acid and Strong acid both will contribute  $\text{H}^+$  ion.
- For the first approximation we can neglect the  $\text{H}^+$  ions coming from the weak acid Solution and calculate the pH of the Solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- If  $[\text{SA}] = \text{C}_1$  and  $[\text{WA}] = \text{C}_2$ , then  $[\text{H}^+]$  from SA =  $\text{C}_1$   
the weak acid will dissociate as follows.



$$K_a = \frac{(\text{C}_2\alpha + \text{C}_1)\text{C}_2\alpha}{\text{C}_2(1-\alpha)} \quad (\alpha \ll 1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$$K_a = (\text{C}_2\alpha + \text{C}_1)\alpha$$

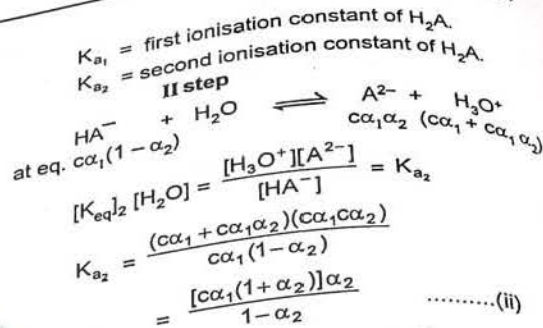
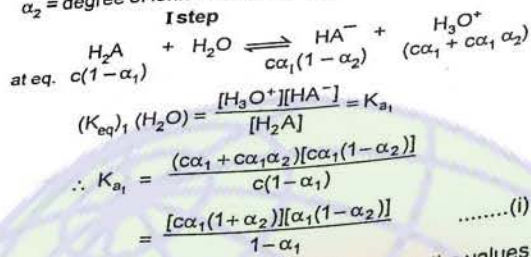
$$\text{Total } \text{H}^+ \text{ ion concentration} = \text{C}_1 + \text{C}_2\alpha$$

- If the total  $[\text{H}^+]$  from the acid is less than  $10^{-6}$  M, then contribution from the water can be neglected at  $25^\circ\text{C}$  temp., if not then we have to take  $[\text{H}^+]$  from the water also.

- (h) **pH of a Solution of a polyprotic weak acid :**
- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water.
- Let us take a weak diprotic acid ( $\text{H}_2\text{A}$ ) in water whose concentration is  $\text{cM}$ .
- In an aqueous Solution, following equilibria exist.

Ionic Equilibrium

If  $\alpha_1$  = degree of ionization of  $H_2A$  in presence of  $HA^-$   
 $\alpha_2$  = degree of ionisation of  $HA^-$  in presence of  $H_2A$ .



Knowing the values of  $K_{a1}$ ,  $K_{a2}$  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  $\alpha_2$   $[H_3O^+]$  can be calculated as.

- $[H_3O^+]_T = \alpha_1 + \alpha_1\alpha_2$   
 Finally, for calculating pH  
 • If the total  $[H_3O^+] < 10^{-6}$  M, the contribution of  $H_3O^+$  from water should be added  
 • If the total  $[H_3O^+] > 10^{-6}$  M, then  $[H_3O^+]$  contribution from water can be ignored.  
 Using this  $[H_3O^+]$ , pH of the Solution can be calculated.

**Approximation**

For diprotic acids,  $K_{a2} \ll K_{a1}$  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

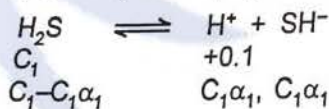
$$K_{a1} = \frac{c\alpha_1 \times \alpha_1}{1 - \alpha_1}$$

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

**Solved Examples**

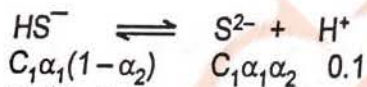
**Ex.13.** Calculate pH,  $[HS^-]$ ,  $S^{2-}$ ,  $[Cl^-]$  in a Solution which is 0.1 M HCl & 0.1 M  $H_2S$  given that  $K_{a1}(H_2S) = 10^{-7}$ ,  $K_{a2}(H_2S) = 10^{-14}$  also calculate  $\alpha_1$  &  $\alpha_2$

**Sol.**  $HCl + H_2S$   
 0.1       $C = 0.1$   
 $\therefore pH = 1$  (most of  $[H^+]$  comes from HCl)



$$K_{a1} = \frac{C_1\alpha_1 \times 10^{-1}}{C_1(1-\alpha_1)}$$

$$\alpha_1 = \frac{10^{-7}}{10^{-1}} = 10^{-6}$$



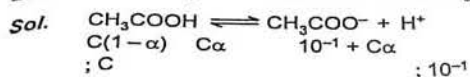
$$10^{-14} = 0.1 \times \alpha_2$$

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

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

**Ionic Equilibrium**

**Ex.14.** Calculate pH  $10^{-1}$  M HCl in  $10^{-3}$  M  $\text{CH}_3\text{COOH}$  [ $K_a = 2 \times 10^{-5}$ ]



$\text{H}^+$  ion can be treated completely from HCl due to less dissociation of  $\text{CH}_3\text{COOH}$  and its low conc.

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

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

$$[\text{H}^+]_{\text{CH}_3\text{COOH}} = C\alpha = 2 \times 10^{-7}$$

All these steps can be followed for the calculation of pOH for weak base and their mixtures (we just have to replace  $K_a$  with  $K_b$ ).

(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)

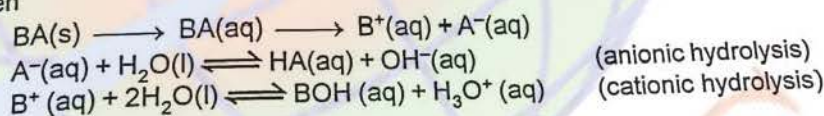
First case will lead to phenomenon of SALT HYDROLYSIS and second case will lead to formation of BUFFER SOLUTIONS.

**Salt Hydrolysis (Reverse of neutralisation)**



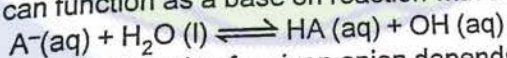
When acids and bases are mixed in equal amounts(equivalents), then we will be having salt Solutions only in the water and we have to calculate pH of salt Solutions.

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**

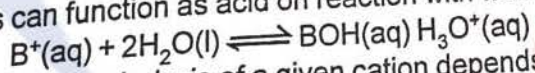
Anions can function as a base on reaction with water and hydrolyse as follows :



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

**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.

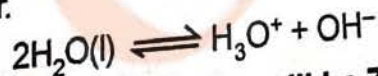
**There are four types of salt.**

- (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 :**

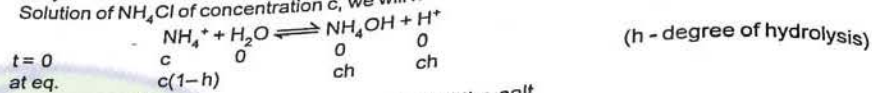
Neither of the ions will undergo hydrolysis so the Solution contain only the equilibrium of ionization of water.



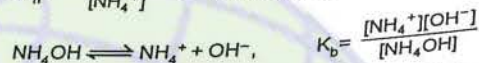
Thus, the pH of Solution will be 7(neutral Solution).

**Ionic Equilibrium**

(ii) **Salt of strong acid and weak base :**  
 The Examples can be  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{AlCl}_3$  Solution will be acidic in nature. for Example in the  
 Only the cation will undergo hydrolysis and 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

$$K_h \times K_b = K_w$$

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

(generally  $1-h \approx 1$ ) so we get,  $\Rightarrow h = \sqrt{\frac{K_h}{c}}$

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

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

**Solved Examples**

**Ex.15.** Calculate degree of hydrolysis,  $K_h$ ,  $h$  and  $\text{pH}$  of 1M urea hydrochloride Solution in water,  $K_b(\text{Urea}) = 1.5 \times 10^{-14}$ .

**Sol.**  $\text{NH}_2\text{CONHCl}$  is a salt of (SA + WB)

$$\text{So } h = \sqrt{\frac{K_w}{K_b \cdot C}} = \sqrt{\frac{10^{-14}}{1.5 \times 10^{-14} \times 1}} \quad \text{or} \quad h = 81.65\%$$

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

$$\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C = 7 - \frac{1}{2} (13.82) - \frac{1}{2} \log (1) \quad \text{or} \quad \text{pH} = 0.09 \text{ Ans.}$$

**Ex.16.** Equal vol. of 0.2 M  $\text{NH}_4\text{OH}$  (or ammonia) of 0.1 M  $\text{H}_2\text{SO}_4$  are mixed calculate  $\text{pH}$  of final Solution (given that)

**Sol.**  $K_b$  of  $\text{NH}_3 = 1.8 \times 10^{-5}$

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

(iii) **Salt of weak acid and strong base :**

The Examples can be  $\text{CH}_3\text{COONa}$ ,  $\text{KCN}$ ,  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{K}_3\text{PO}_4$

Similar to above analysis we will get

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

(generally  $1-h \approx 1$ ) so we get,  $\Rightarrow h = \sqrt{\frac{k_h}{c}}$

$$k_h \times k_a = k_w$$

$$[\text{OH}^-] = ch = \sqrt{k_h \times c} = \sqrt{\frac{k_w \times c}{k_a}}$$

$$\text{pH} = -\log [\text{H}^+] = -\frac{1}{2} [\log k_w + \log k_a - \log c] = \frac{1}{2} [\text{p}k_w + \text{p}k_a + \log c]$$

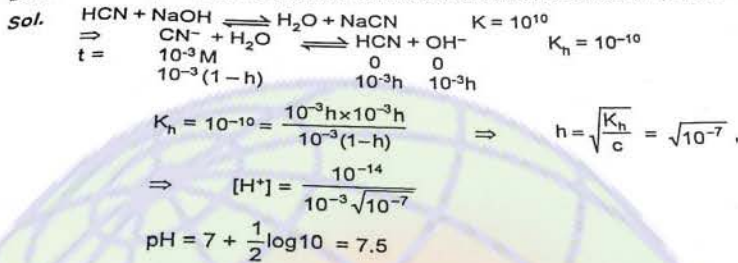


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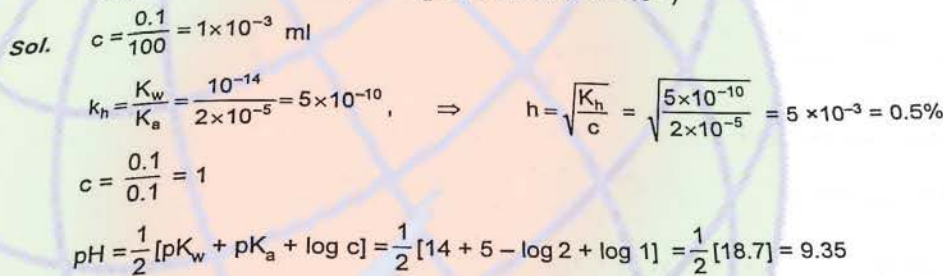
Ionic Equilibrium

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.

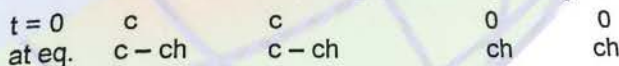
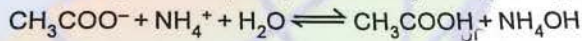


Ex.18. Calculate degree of hydrolysis(h) and pH of Solution obtained by dissolving 0.1 mole of  $\text{CH}_3\text{COONa}$  in water to get 100ml of Solution (take  $K_a$  of acetic acid =  $2 \times 10^{-5}$ )

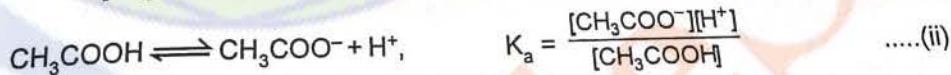


(iv) Salt of weak acid and weak base :

Examples can include  $\text{CH}_3\text{COONH}_4$ ,  $\text{NH}_4\text{CN}$ ,  $\text{Ca}(\text{CH}_3\text{COO})_2$ ,  $\text{MgC}_2\text{O}_4$



$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \dots(i)$



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

$[\text{H}^+] = k_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = K_a \frac{ch}{c(1-h)} = K_a \times \frac{h}{1-h} = K_a \times \sqrt{K_h} = K_a \times \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}}$

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

Ionic Equilibrium

Solved Examples

Ex.19. Calculate pH of  $10^{-2}$  M  $\text{NH}_4\text{CN}$  Solution given that  $K_a$  of  $\text{HCN} = 5 \times 10^{-10}$  and  $K_b$  of  $(\text{aq. NH}_3) = 2 \times 10^{-5}$ .

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

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

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

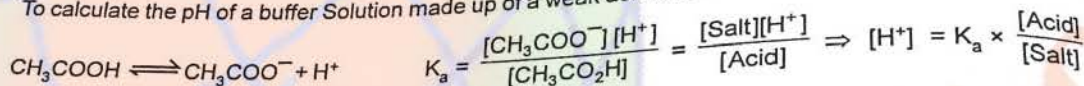
**BUFFER SOLUTION** (If the acids and bases are mixed in different amounts (equivalents))

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.

There are various types of buffers :

- (i) Buffer of weak acid and its salt with a strong base ;
- (ii) Buffer of a weak base and its salt with a strong acid.
- (iii) The Solution of the salt of a weak acid and a weak base.

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.  $\log [\text{H}^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]}$

$\therefore \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

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 :

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

**Buffer Capacity** : It is defined as the mole of a strong acid or strong base required to change the pH of a buffer by one unit, for 1 L Buffer solution.

**Maximum buffer capacity** : It can be proved that the maximum buffer capacity is achieved when the salt and acid or base concentration is equal.

Solved Examples

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

Sol.  $\text{pOH} = \text{p}K_b + \log \frac{[\text{Cojugate acid / salt}]}{[\text{Base}]}$

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

$\therefore$  moles of  $\text{SO}_4^{2-}$  needed = 0.05

mol weight of  $(\text{NH}_4)_2\text{SO}_4 = 132$  gm/mole

$\therefore$  weight of  $(\text{NH}_4)_2\text{SO}_4$  needed =  $132 \times 0.05 = 6.6$  gm

**Ionic Equilibrium**

**Ex.21.** 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 10ml 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.**  $pH = pK_a + \log \frac{\text{salt}}{\text{acid}}$

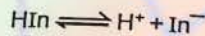
$$\Rightarrow 7.4 = 6.7 + \log \frac{\text{salt}}{\text{acid}} \Rightarrow \frac{\text{salt}}{\text{acid}} = 5$$

$$\Rightarrow 5 \times 2.5 \times 10 = 5 \times V \Rightarrow \text{required volume} = 25 \text{ ml}$$

**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 ionised form while its unionised form is colourless)

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



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

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

Taking negative logarithm of both sides

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

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

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  $In^-$ , then it is seen that the Solution acquires a distinct colour of  $In^-$  only when the concentration of  $In^-$  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  $In^-$  the minimum ratio of  $\frac{[In^-]}{[HIn]}$  should be 10.

$$\therefore pH = pK_{HIn} + \log (10) = pK_{HIn} + 1$$

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

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

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

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