03 Ionic Equilibrium

Introduction : Ionic Equilibrium

Ionic equilibrium deals with the equilibrium of any substance with its ions in solution. The substance producing ions are called electrolytes.

According to conductivity, substances are of two types :

(i) Non-Conductor : Those substances which do not show the flow of current or electricity.

Ex. Non - metals, plastic rubber, wood, etc.

Exception – Graphite is a non-metal but shows conductivity due to motion of free electrons.

(ii) Conductors : Those substances which show conductivity or flow of current are called conductors.

These are of 2 types :

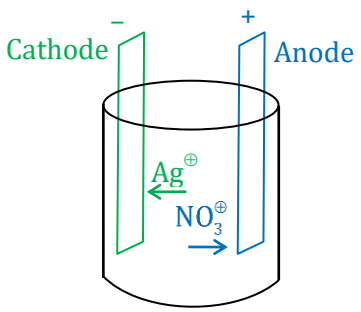
(a) Metallic or Electronic conductors :

Those conductors which show conductivity due to motion of free electrons. Resistance increases with increases in temperature.

Ex. All metals, Graphite

(b) Ionic or Electrolytic conductors :

Those conductors which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode).



The current flows through the solution due to the movement of the ions. Resistance decrease with increases in temperature.

According to strength, ionic conductors are of two types :

(i) Strong electrolyte : Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

For strong electrolyte the value of degree of dissociation is 100%.

i.e. : $\alpha = 1$

Ex. (a) Strong acid → H_2SO_4, HCl, HNO_3 $HClO_4$, H_2SO_5, HBr, HI, $HBrO_4$, HIO_4, RSO_3H

(b) Strong base → KOH, NaOH, $Ba(OH)_2$ CsOH, RbOH

(c) All soluble salts → NaCl, KCl, $CuSO_4$.....

(ii) Weak electrolytes : Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.

Ex. (a) Weak acid : HCN, CH_3COOH, HCOOH, H_2CO_3, H_3PO_3, H_3PO_2, etc.

(b) Weak base : NH_4OH, $Cu(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, etc.

Degree of dissociation (α):

- When an electrolyte is dissolved in a solvent (H_2O), it spontaneously dissociates into ions.
- It may dissociate partially ($\alpha < 1$) or sometimes completely ($\alpha = 1$)
- The degree of dissociation (α) of an electrolyte is the fraction of mole of the electrolyte that has dissociated under the given conditions.

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

Factors affecting the value of degree of dissociation :

(i) Dilution : $\alpha \propto \sqrt{V}$. So on dilution, α increases

(ii) Temperature : On increasing temperature, ionization increases so, α increases

(iii) Nature of electrolyte :

(a) Strong electrolyte $\alpha = 100\ \%$ (b) Weak electrolyte $\alpha << 100\ \%$

(iv) Nature of solvent :

If dielectric constant, μ , of solvent increases, then the value of α increases.

$H_2O \rightarrow \mu = 81$

$D_2O \rightarrow \mu = 79$

$C_6H_6 \rightarrow \mu = 2.5$

$CCl_4 \rightarrow \mu = 0$

MIXING OF IONS :

Common ion Effect	Odd ion Effect
$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$ On mixing NH_4Cl $NH_4Cl \rightarrow NH_4^{\oplus} + Cl^{\ominus}$ Due to mixing of common ion, concentration of ammonium ion will increase therefore equilibrium will shift in backward direction means α decreases.	$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$ On mixing HCl $HCl \rightarrow H^{\oplus} + Cl^{\ominus}$ Due to reaction of $OH^{\ominus}$ ions with $H^{\oplus}$ ion, concentration of $OH^{\ominus}$ will decrease $\therefore$ Equilibrium will shift in forward direction means α increases.

Ostwald's Dilution Law (For weak electrolyte) :

- For a weak electrolyte $A^{\oplus}B^{\ominus}$ dissolved in water, if α is the degree of dissociation then

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

Then according to law of mass action,

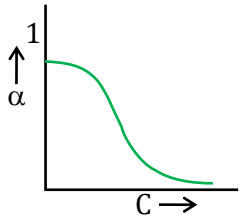
$$K_{diss} = \frac{[A^{\oplus}][B^{\ominus}]}{[AB]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$ = dissociation constant of the weak electrolyte.

$C = \frac{1}{V}$, then V = 1/C (volume of solution in which 1 mole is present) is called dilution, so $K_{diss} = \frac{\alpha^2}{(1-\alpha)V}$

If α is negligible in comparison to unity, $1 - \alpha = 1$. so $K_{diss} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{diss}}{C}} = \sqrt{K_{diss} V}$

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

- As concentration increases $\Rightarrow$ α decreases
- At infinite dilution α reaches its maximum value, unity.



Classification of Acids & Bases

Arrhenius concept :

(i) Arrhenius Acid : Substance which gives $H^{\oplus}$ ion on dissolving in water ($H^{\oplus}$ donor)

Ex. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

Types of acids

Monoprotic or Monobasic acid	Diprotic or Dibasic acid	Triprotic or Tribasic acid
• Gives single $H^{\oplus}$ per molecule e.g. HA (HNO_3, HCl)	• Gives two $H^{\oplus}$ per molecule e.g. H_2A (H_2SO_4, H_3PO_3)	• Gives three $H^{\oplus}$ per molecule e.g. H_3A (H_3PO_4)

(ii) Arrhenius base : Any substance which releases $OH^{\ominus}$ (hydroxyl) ion in water ($OH^{\ominus}$ ion donor)

Types of bases

Monohydroxic or Monoacidic base	Dihydroxic or Diacidic base	Trihydroxic or Triacidic basic
• Gives single $OH^{\ominus}$ per molecule Ex. CsOH, RbOH, NH_4OH	• Gives two $OH^{\ominus}$ per molecule Ex. $Ba(OH)_2$, $Ca(OH)_2$	• Gives three $OH^{\ominus}$ per molecule EX. $Fe(OH)_3$

(iii) Strength of Acid or Base :

(a) Strength of acids or bases depends on the extent of its ionisation. Hence equilibrium constant K_a or K_b respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

(b) $HA \rightleftharpoons H^{\oplus} + A^{\ominus}$;

$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$ = dissociation or ionisation constant of acid.

(c) Similarly,

$BOH \rightleftharpoons B^{\oplus} + OH^{\ominus}$;

$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$ = dissociation or ionisation constant of base

(d) Larger the value of K_a or K_b, stronger is the acid or base respectively.

Relative strength of weak acids and bases :

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Similarly, for bases, $\frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$

The modern method is to convert K_a as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit pK_a. Thus, if K_a for acid is equal to 10^{-4}, $pK_a = 4$. So higher pK_a value means lower acid strength, that is, $pK_a = -\log K_a$

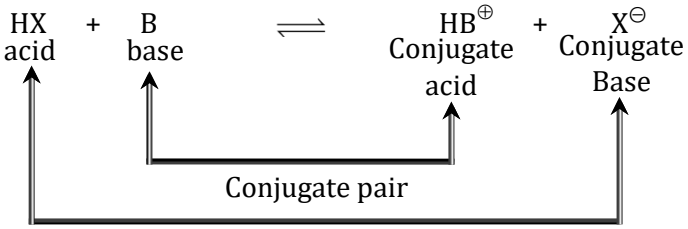
Also, $pK_b = -\log K_b$

Bronsted - Lowry concept: (Conjugate acid - Base concept) :

(i) Acid : substances which donate $H^{\oplus}$ are Bronsted Lowry acids ($H^{\oplus}$ donor)

(ii) Base : substances which accept $H^{\oplus}$ are Bronsted Lowry bases ($H^{\oplus}$ acceptor)

(iii) Conjugate acid - base pairs : In a typical acid base reaction, $HX + B \rightleftharpoons X^{\ominus} + HB^{\oplus}$



- Forward reaction - Here HX being a proton donor is an acid
  B being a proton acceptor is a base.
- Backward reaction - Here $HB^{\oplus}$ being a proton donor is an acid
  $X^{\ominus}$ being a proton acceptor is a base.

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

- Conjugate acid - base pair differ by only one proton.
- Strong acid will have weak conjugate base and vice versa.

Acid	Conjugate base	Base	Conjugate acid
HCl	$Cl^{\ominus}$	NH_3	$NH_4^{\oplus}$
H_2SO_4	$HSO_4^{\ominus}$	H_2O	$H_3O^{\oplus}$
$HSO_4^{\ominus}$	$SO_4^{2\ominus}$	RNH_2	$RNH_3^{\oplus}$
H_2O	$OH^{\ominus}$		

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

$HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$

base

$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$

Acid

(v) Classification of Bronsted - Lowery Acids and Bases :

Bronsted - Lowery acids and bases can be

(i) Molecular (ii) Cationic and (iii) Anionic

Type	Acid	Base
Molecular	HCl, HNO_3, $HClO_4$, H_2SO_4, H_3PO_4, H_2O etc.	NH_3, N_2H_4, Amines, H_2O, Alcohol, Ethers, etc.
Cationic	$NH_4^{\oplus}$, $N_2H_5^{\oplus}$, $PH_4^{\oplus}$, $[Fe(H_2O)_6]^{3\oplus}$, $[Al(H_2O)_6]^{3\oplus}$ etc.	$[Fe(H_2O)_5OH]^{2\oplus}$ $[Al(H_2O)_5OH]^{2\oplus}$ etc.
Anionic	$HS^{\ominus}$, $HSO_3^{\ominus}$, $H_2PO_4^{\ominus}$, $HSO_4^{\ominus}$, $HCO_3^{\ominus}$, $HPO_4^{2\ominus}$, etc. all amphiprotic anions	$Cl^{\ominus}$, $Br^{\ominus}$, $OH^{\ominus}$, $HSO_4^{\ominus}$, $CN^{\ominus}$, $CO_3^{2\ominus}$, $SO_4^{2\ominus}$, $NH_2^{\ominus}$, $CH_3COO^{\ominus}$, etc. all amphiprotic anions

Lewis concept (Electronic Concept) :

(i) Acid : An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Ex. Electron deficient molecules : BF_3, $AlCl_3$, etc.

Cations : $H^{\oplus}$, $Fe^{2\oplus}$, $Na^{\oplus}$, etc.

Molecules with vacant orbitals : SF_4, PF_3

(ii) Base : A base is any molecule/ion which has a pair of electrons which can be donated.

Ex. Molecules with lone pairs : NH_3, PH_3, H_2O, CH_3OH

Anions : $OH^{\ominus}$, $H^{\ominus}$, $NH_2^{\ominus}$, etc.

Properties of water :

(i) Molar concentration / Molarity of water :

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

(ii) Ionic product of water :

According to Arrhenius concept, $H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

So, ionic product of water, $K_w = [H^{\oplus}][OH^{\ominus}] = 10^{-14}$ at 25° (experimental)

Dissociation of water is endothermic, so on increasing temperature K_w increases.

(iii) Degree of dissociation of water :

$$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus} \Rightarrow \alpha = \frac{\text{decrease in concentration}}{\text{initially concentration}}$$

$$= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\% \text{ [at 25°C]}$$

(iv) Dissociation or ionisation constant of water :

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

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

Illustration 1:

At dissociation constant of heavy water is 4×10^{-15} at 35°C. If its density is 1.04 g/mL. Calculate its ionic product & degree of dissociation.

Solution :

$$K_w = K_d[D_2O] = \left(4 \times 10^{-15} \times \frac{1040}{20}\right) = 2.08 \times 10^{-13}$$

$$d = \sqrt{\frac{K_w}{C}} = \sqrt{\frac{2.08 \times 10^{-13}}{52}} = 12.64 \times 10^{-8}$$

Illustration 2:

Calculate ionic product of H_2O at 50°C.

Solution :

$\Delta H = 13.7 \times 10^3$ cal

$$\log \frac{K_2}{10^{-14}} = \frac{13.7 \times 10^3}{2.3032}\left(\frac{1}{298} - \frac{1}{323}\right)$$

Illustration 3:

The hydronium ion conc. in an aq. H_2CO_3 solution is 4×10^{-4} M at 25°C $OH^{\ominus}$ ion conc. in the solution is :

(A) 0 (B) 2.5×10^{-10} (C) 2.5×10^3 (D) 2.5×10^{-11} M

Ans. (D)

Solution :

$K_w = [OH^{\ominus}]\,[H^{\oplus}]$

$10^{-14} = [OH^{\ominus}]\,[4 \times 10^{-4}]$

$[OH^{\ominus}] = 2.5 \times 10^{-11}$ M

Illustration 4:

Select the correct option from the following ?

(A) pK_W increases with increase of temperature

(B) pK_W decreases with increase of temperature

(C) $pK_W = 14$ at all temperatures

(D) $pK_W = pH$ at all temperatures

Ans. (B)

Acidity and pH scale :

(i) Acidic strength means the tendency of an acid to give $H_3O^{\oplus}$ or $H^{\oplus}$ ions in water.

So greater then tendency to give $H^{\oplus}$, more will be the acidic strength of the substance.

(ii) Basic strength means the tendency of a base to give $OH^{\ominus}$ ions in water.

So greater the tendency to give $OH^{\ominus}$ ions, more will be basic strength of the substance.

(iii) The concentration of $H^{\oplus}$ ions is written in a simplified form introduced by Sorenson known as pH scale.

pH is defined as negative logarithm of activity of $H^{\oplus}$ ions.

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

(iv) Activity of $H^{\oplus}$ ions is the molar concentration of free $H^{\oplus}$ ions or $H_3O^{\oplus}$ ions in a dilute solution, but unitless.

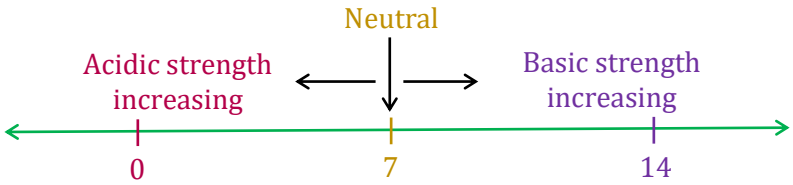
(v) Now $pH = -\log[H^{\oplus}] = 7$ and $pOH = -\log[OH^{\ominus}] = 7$ for water at 25°C (experimental)

$pH = 7 = pOH \Rightarrow$ neutral

$pH < 7$ or $pOH > 7 \Rightarrow$ acidic

$pH > 7$ or $pOH < 7 \Rightarrow$ Basic

} at 25 °C



Calculation of pH for different types of solutions :

(a) Strong acid solution :

(i) If concentration of $H^{\oplus}$ ions is greater than 10^{-6} M, $H^{\oplus}$ ions coming from water can be neglected,

So $[H^{\oplus}]$ = normality of strong acid solution

(ii) If concentration is less than 10^{-6} M, $H^{\oplus}$ ions coming from water cannot be neglected.

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

(b) Strong base solution :

Calculate the $[OH^{\ominus}]$ which will be equal to normality of the strong base solution and then use

$K_w = [H^{\oplus}] \times [OH^{\ominus}] = 10^{-14}$, to calculate $[H^{\oplus}]$

Illustration 5:

Calculate pH of 10^{-8} M HCl solution.

Solution :

$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

$10^{-8}+x \quad x$

$k_w = [H^{\oplus}][OH^{\ominus}]$

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

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

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

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

$pH = -\log [H^{\oplus}]$

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

Illustration 6:

Calculate pH of 10^{-7} M of NaOH solution

Solution :

$[OH^{\ominus}]$ from NaOH = 10^{-7}

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

$H_2O \rightleftharpoons OH^{\ominus} + H^{\oplus}$

$- \quad (x + 10^{-7}) \quad x$

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

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

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

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

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

$pH = 14 - 6.79 = 7.21$

(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 $H^{\oplus}$ ions from I-solution = N_1V_1

Number of $H^{\oplus}$ ions from II-solution = N_2V_2

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

$NV = N_1V_1 + N_2V_2$

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

$$[H^{\oplus}] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \qquad \left[\begin{array}{l}\text{where} \quad N = M \times n \\ \qquad\quad n = \text{Basicity of acid}\end{array}\right]$$

(d) pH of mixture of two strong bases :

Similar to above calculation

$[OH^{\ominus}] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$ $[H^{\oplus}] = \frac{10^{-14}}{[OH^{\ominus}]}$

Illustration 7:

Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M H_2SO_4) + (400 mL, $\frac{1}{100}$ M HCl) + (200 mL of water)

Solution :

$N_1V_1 = \frac{1}{200} \times \frac{400}{1000} \times 2 = \frac{4}{1000}$, $N_2V_2 = \frac{4}{1000}$, $H^{\oplus}$ ions from water will be neglected

$N_1V_1 + N_2V_2 = 8 \times 10^{-3}$ $[H^{\oplus}] = \frac{8\times10^{-3}}{1} = 8 \times 10^{-3}$

$pH = 3 - \log 8 = 2.1$

Illustration 8:

500 mL of 10^{-5} M NaOH is mixed with 500 mL of 2.5×10^{-5} M of $Ba(OH)_2$. To the resulting solution 99 L water is added. Calculate pH.

Solution :

$[OH^{\ominus}] = \frac{500\times10^{-5} + 500\times2\times2.5\times10^{-5}}{1000} = 3 \times 10^{-5}$ M

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

$V_2 + V_1 = 1$ L

$V_F = 100$ L

no. of moles of $[OH^{\ominus}]$ initially = no. of moles of $[OH^{\ominus}]$

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

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

$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

$x \quad (x + 3 \times 10^{-7})$

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

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

$x = 0.302 \times 10^{-7}$

$[OH^{\ominus}]_{Net} = 3.302 \times 10^{-7}$

$[H^{\oplus}] = \frac{10^{-14}}{3.302\times10^{-7}} = 3.03\times10^{-8}$

$pH = 7.52$

(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 $H^{\oplus}$ ions from I-solution = N_1V_1

  Number of $OH^{\ominus}$ ions from II-solution = N_2V_2

  If $N_1V_1 > N_2V_2$

  $[H^{\oplus}] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$

  Solution will be acidic in nature

  If $N_2V_2 > N_1V_1$

  $[OH^{\ominus}] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$

  Solution will be basic in nature

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

Illustration 9:

Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M $Ba(OH)_2$) + (400 mL, M HCl)+(200 mL of water)

Solution :

$$N = \frac{400}{1000} \times \frac{1}{2} \times 2 - \frac{400}{1000} \times \frac{1}{2} \times 1$$

$[OH^{\ominus}] = 0.2$

pOH = 1 – 0.3 = 0.7

pH = 14 – 0.7 = 13.3

Illustration 10:

What will be the resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0) ?

Solution :

pH of HCl = 2

$\therefore$ $[HCl] = 10^{-2}$ M

pH of NaOH = 12, pOH = 2 $\therefore$ $[NaOH] = 10^{-2}$ M

	HCl	+	NaOH	$\longrightarrow$	NaCl	+	H_2O
Meq. Initial	150×10^{-2} = 1.5		350×10^{-2} = 3.5		0		0
Meq. final	0		2		1.5		1.5

$\therefore$ $[OH^{\ominus}]$ from NaOH = 4×10^{-3} M

pOH = $-\log[OH^{\ominus}] = -\log(4 \times 10^{-3})$

$\therefore$ pOH = 2.3979

$\therefore$ pH = 14 – pOH = 14 – 2.3979 = 11.6021

(f) pH of a weak acid or weak base (monoprotic) solution :

- Weak acid does not dissociated 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)

	HA	$\rightleftharpoons$	$H^{\oplus}$	+	$A^{\ominus}$
t = 0	C		0		0
t_{eq}	C(1 – α)		Cα		Cα

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

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

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

On increasing the dilution $\Rightarrow$ C↓ = α↑ and $[H^{\oplus}]\downarrow \Rightarrow$ pH↑

Illustration 11:

Calculate pH of following Solution

(a) 10^{-1} M CH_3COOH

(b) 10^{-3} M CH_3COOH

(c) 10^{-6} M CH_3COOH

Given ; $K_a = 2 \times 10^{-5}$

Solution :

(a)

CH_3COOH	$\rightleftharpoons$	$CH_3COO^{\ominus}$	+	$H^{\oplus}$
C		0		0
C(1 – α)		Cα		Cα

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2\times10^{-5}}{10^{-1}}} = \sqrt{2\times10^{-4}} \quad (\alpha << 0.1)$$

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

(b) $\alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2\times10^{-5}}{10^{-3}}} = \sqrt{2\times10^{-2}} \quad (\alpha > 0.1)$

So we have to do the exact calculations

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2\times10^{-5} = \frac{10^{-3}\times\alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\ \%$$

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

(c) If approximation is used the, $\alpha = \sqrt{\frac{2\times10^{-5}}{10^{-6}}} = \sqrt{20} > 1$,

So we have to do the exact calculation, $2\times10^{-5} = 10^{-6}\frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$ or 95%

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

- At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte.
  (pH) of 10^{-6} M HCl ≃ pH of 10^{-6} M CH_3COOH ≃ 6)

Illustration 12:

K_a for acid HA is 2.5×10^{-8} calculate for its decimolar solution at 25°C.
(a) % dissociation
(b) pH
(c) $OH^{\ominus}$ ion concentration

Solution :

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

C	0	0
C(1–α)	Cα	Cα

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \Rightarrow K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

(i) $\therefore \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5\times10^{-8}}{1/10}}$ (C = 1/10 M)

$= 5 \times 10^{-4} = 0.05\%$

(ii) $[H^{\oplus}] = C\alpha = \frac{1}{10}\times5\times10^{-4} = 5 \times 10^{-5}$ mol/L

So, pH = 5 – log 5 = 4.30

(iii) $[H^{\oplus}]\,[OH^{\ominus}] = 1 \times 10^{-14}$

$\therefore \quad [OH^{\ominus}] = \frac{10^{-14}}{5\times10^{-5}} = 2 \times 10^{-10}$ mol/L

Illustration 13:

Determine the degree of dissociation of 0.05 M NH_4OH at 25°C in a solution of pH = 10.

Solution :

$$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$

C	0	0

Given, pH = 10

$[H^{\oplus}] = 10^{-10}$

$[H^{\oplus}]\,[OH^{\ominus}] = 1 \times 10^{-14}$

$\therefore \quad [OH^{\ominus}] = \frac{1\times10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$

$\therefore \quad \alpha = \frac{[OH^{\ominus}]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3}$ or 0.2 %

Illustration 14:

The concentration of $[H^{\oplus}]$ and $[OH^{\ominus}]$ of the 10^{-1} M aqueous solution of 2% ionised weak acid is :
(A) 2×10^{-3} M and 5×10^{-12} M (B) 1×10^{-3} M and 3×10^{-11} M
(C) 2×10^{-4} M and 5×10^{-11} M (D) 3×10^{-2} M and 4×10^{-13} M

Ans. (A)

Solution :

$[H^{\oplus}] = C\alpha = 2 \times 10^{-3}$ M or $[OH^{\ominus}] = \dfrac{10^{-14}}{[H^{\oplus}]} = 5 \times 10^{-12}$ M

Illustration 15:

When a 0.1 N solution of an acid at 25°C has a degree of ionisation of 4%, the concentration of $OH^{\ominus}$ present is :

(A) 2.5×10^{-3} (B) 2.5×10^{-11} (C) 2.5×10^{-12} (D) 2.5×10^{-13}

Ans. (C)

Solution :

$[H^{\oplus}] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3}$ M or $[OH^{\ominus}] = \dfrac{10^{-14}}{[H^{\oplus}]} = 2.5 \times 10^{-12}$ N

Illustration 16:

The degree of dissociation of acetic acid in a 0.1 M solution is 1.32×10^{-2}. Calculate dissociation constant of acid and its pK_a value :

Solution:

	CH_3COOH	$\rightleftharpoons$	$CH_3COO^{\ominus}$	+	$H^{\oplus}$
Initially	0.1		0		0
at equilibrium	0.1(1–0.0132)		0.1× 0.0132		0.1× 0.0132

$K_a = \dfrac{[CH_3COO^{\ominus}][H^{\oplus}]}{[CH_3COOH]} = \dfrac{0.1 \times 0.0132 \times 0.1 \times 0.0132}{0.1(1-0.0132)} = 1.76 \times 10^{-5}$

$pK_a = -\log K_a = -\log (1.76 \times 10^{-5}) = 4.75$

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

- Weak acid and Strong acid both will contribute $H^{\oplus}$ ion.
- For the first approximation we can neglect the $H^{\oplus}$ 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 [SA] = C_1 and [WA] = C_2, then $[H^{\oplus}]$ from SA = C_1
  the weak acid will dissociate as follows.

HA	$\rightleftharpoons$	$H^{\oplus}$	+	$A^{\ominus}$
C_2		0		0
$C_2(1-\alpha)$		$C_2\alpha + C_1$		$C_2\alpha$

$K_a = \dfrac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)}$ $(\alpha <<< 1)$

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

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

Total $H^{\oplus}$ ion concentration = $C_1 + C_2\alpha$

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

Illustration 17:

Calculate pH, $[HS^{\ominus}]$, $[S^{2\ominus}]$, $[Cl^{\ominus}]$ in a solution which is 0.1 M HCl & 0.1 M H_2S given that K_{a_1} $(H_2S) = 10^{-7}$, $Ka_2(H_2S) = 10^{-14}$ also calculate α_1 & α_2.

Solution :

HCl + H_2S

0.1 0.1

$C_1 = C_2 = 0.1$

$\therefore$ pH = 1 (most of $[H^{\oplus}]$ comes from HCl]

$H_2S \rightleftharpoons H^{\oplus} + HS^{\ominus}$

$0.1(1-\alpha_1)$ 10^{-1} $C\alpha_1 = 0.1\,\alpha_1$

$$Ka_1 = \frac{C\alpha_1 \times 10^{-1}}{C(1-\alpha_1)} = \frac{10^{-7}}{10^{-1}} = \alpha_1 \quad (\because 1-\alpha_1 = 1)$$

$\Rightarrow \alpha_1 = 10^{-6}$

$HS^{\ominus} \rightleftharpoons S^{2\ominus} + H^{\oplus}$

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

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

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

$[S^{2\ominus}] = C\alpha_1\alpha_2$

$= 10^{-6} \times 10^{-1} \times 10^{-13} = 10^{-20}$ M

$[Cl^{\ominus}] = 0.1$ M

$[HS^{\ominus}] = C\alpha_1(1-\alpha_2)$

$= C\alpha_1$

$= 10^{-1} \times 10^{-6} = 10^{-7}$

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

- Both acids will dissociate partially.
- Let the acid are HA_1 & HA_2 and their final concentrations are C_1 & C_2 respectively, then

	$HA_1 \rightleftharpoons$	$H^{\oplus}$	+	$A_1^{\ominus}$
t = 0	C_1	0		0
At eq.	$C_1(1-\alpha_1)$	$C_1\alpha_1 + C_2\alpha_2$		$C_1\alpha_1$

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)}$$

	$HA_2 \rightleftharpoons$	$H^{\oplus}$	+	$A_2^{\ominus}$
t = 0	C_2	0		0
At eq.	$C_2(1-\alpha_2)$	$C_2\alpha_2 + C_1\alpha_1$		$C_2\alpha_2$

$$K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

(Since α_1, α_2 both are small in comparison to unity)

$$K_{a_1} = (C_1\alpha_1 + C_2\alpha_2)\alpha_1 \; ; \; K_{a_2} = (C_1\alpha_1 + C_2\alpha_2)\alpha_2 \quad \Rightarrow \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^{\oplus}] = C_1\alpha_1 + C_2\alpha_2 = \frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} + \frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1} + C_2K_{a_2}}} \Rightarrow [H^{\oplus}] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

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

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

Illustration 18:

Calculate pH of solution obtained by mixing equal vol. of 0.01 M HOCl & 0.1 M CH_3COOH solution given that K_{a_1} (HOCl) = 2×10^{-4} , K_{a_2} (CH_3COOH) = 2×10^{-5}

Also calculate $OH^{\ominus}$, $OCl^{\ominus}$, $CH_3COO^{\ominus}$

Solution:

Final solution volume become double

$C_1 = 0.01$, $C_2 = 0.1$

$[H^{\oplus}] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2} = \sqrt{2\times10^{-4}\times0.01 + 2\times10^{-5}\times0.1} = \sqrt{2\times10^{-6} + 2\times10^{-6}} = 2 \times 10^{-3}$

pH = 3 – log2 = 3 – 0.3010 = 2.69

$\alpha_1 = \frac{2\times10^{-4}}{2\times10^{-3}} = 10^{-1}$ $\alpha_2 = \frac{2\times10^{-5}}{2\times10^{-3}} = 10^{-2}$

$HOCl \rightleftharpoons$	$H^{\oplus}$ +	$OCl^{\ominus}$
$C_1(1-\alpha_1)$	$C_1\alpha_1 + C_2\alpha_2$	$C_1\alpha_1$

$[OCl^{\ominus}] = C_1\alpha_1$

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

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

$CH_3COOH \rightleftharpoons$	$H^{\oplus}$ +	$CH_3COO^{\ominus}$
$C_2(1-\alpha_2)$	$C_1\alpha_1 + C_2\alpha_2$	$C_2\alpha_2$

$[CH_3COO^{\ominus}] = C_2\alpha_2$

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

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

$[OH^{\ominus}] = \frac{K_w}{[H^{\oplus}]} = \frac{10^{-14}}{2\times10^{-3}} = 0.5 \times 10^{-11} = 5 \times 10^{-12}$ M

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

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

(i) 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 (H_2A) in water whose concentration is c M. In an aqueous solution, following equilibria exist.

If

α_1 = degree of ionization of H_2A in presence of $HA^{\ominus}$ K_{a_1} = first ionisation constant of H_2A

α_2 = degree of ionisation of $HA^{\ominus}$ in presence of H_2A K_{a_2} = second ionisation constant of H_2A

Step-I	Step-II
$H_2A + H_2O \rightleftharpoons HA^{\ominus} + H_3O^{\oplus}$	$HA^{\ominus} + H_2O \rightleftharpoons A^{2\ominus} + H_3O^{\oplus}$
at eq. $c(1-\alpha_1)$ $c\alpha_1(1-\alpha_2)$ $(c\alpha_1 + c\alpha_1\alpha_2)$	at eq. $c\alpha_1(1-\alpha_2)$ $c\alpha_1\alpha_2$ $(c\alpha_1 + c\alpha_1\alpha_2)$
$(K_{eq})_1[H_2O] = \frac{[H_3O^{\oplus}][HA^{\ominus}]}{[H_2A]} = K_{a_1}$	$(K_{eq})_2[H_2O] = \frac{[H_3O^{\oplus}][A^{2\ominus}]}{[HA^{\ominus}]} = K_{a_2}$
$\therefore K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)}$	$K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2)]}{c\alpha_1(1-\alpha_2)}$
$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1}$ ...(i)	$= \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2}$ ...(ii)

Knowing the values of K_{a_1}, K_{a_2} and c, the values of α_1 and α_2 can be calculated using equations (i) and (ii) After getting the values of α_1 and α_2, $[H_3O^{\oplus}]$ can be calculated as

$[H_3O^{\oplus}]_T = c\alpha_1 + c\alpha_1\alpha_2$

Finally, for calculation of pH

- If the total $[H_3O^{\oplus}] < 10^{-6}$ M, the contribution of $H_3O^{\oplus}$ from water should be added.
- If the total $[H_3O^{\oplus}] > 10^{-6}$ M, then $[H_3O^{\oplus}]$ contribution from water can be ignored.

Using this $[H_3O^{\oplus}]$, pH of the solution can be calculated.

Approximation :

For diprotic acids, $K_{a_2} << K_{a_1}$ and α_2 would be even smaller than α_1

$\therefore \quad 1 - \alpha_2 \approx 1$ and $1 + \alpha_2 \approx 1$

Thus, equation (i) can be reduced to $K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1-\alpha_1}$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the $[H_3O^{\oplus}]$ can be calculated from its first equilibrium constant expression alone provided $K_{a_2} << K_{a_1}$.

Isohydric solutions :

(i) Solutions of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of dissociation of either of the electrolyte.

(ii) Let the isohydric solution is made by HA_1 and HA_2 acids, then $[H^{\oplus}]$ of both acids should be equal i.e.

$$\sqrt{K_{a_1}C_1} = \sqrt{K_{a_2}C_2} \text{ or } \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

Salts :

(i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.

(ii) Salts may taste salty, bitter or sweet or tasteless.

(iii) Solution of salts may be acidic, basic or neutral.

(iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis.

(v) The salts are generally crystalline solids.

Classification of salts :

The salts may be classified into four categories.

(a) Normal salt :

(i) The salt formed by the loss of all possible protons (replaceable $H^{\oplus}$ ions)

Ex. NaCl, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_3BO_3, Na_2HPO_3, NaH_2PO_2 etc.

(b) Acid salts :

(i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.

Ex. $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4 etc.

(ii) Above salts when neutralized by base form normal salts.

(c) Basic salts :

(i) Salts formed by in complete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.
Ex. $Zn(OH)Cl$, $Mg(OH)Cl$, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$ etc.

(ii) Above salts when neutralised by acids form normal salts.

Hydrolysis of salts :

Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of $H^{\oplus}$ and $OH^{\ominus}$ ions of water.

Salt hydrolysis is reverse process of neutralization.

Water + Salt $\rightleftharpoons$ Acid + Base ; ΔH = +ve

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 H_3O^+ ions and the anions on reaction with water will produce OH^- ions. Depending on the extent of hydrolysis and on the amounts of H_3O^+ and OH^- ions, the solution can be acidic, basic or neutral. If salt is BA, then :

$BA(s) \longrightarrow BA(aq) \longrightarrow B^+(aq) + A^-(aq)$

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$ (anionic hydrolysis)

$B^+(aq) + 2H_2O(l) \rightleftharpoons BOH(aq) + H_3O^+(aq)$ (cationic hydrolysis)

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

$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$

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

(a) Complete hydrolysis : The anions, which are stronger base than OH^- and have conjugate acids weaker than H_2O, will show complete hydrolysis in aqueous medium.

For example : $H^- + H_2O \longrightarrow H_2 + OH^-$; $NH_2^- + H_2O \longrightarrow NH_3 + OH^-$

(b) Hydrolysis to a limited extent : The anions, which are weaker base than OH^- and have conjugate acids stronger than H_2O but weaker acid than H_3O^+, will hydrolyse to a limited extent in aqueous medium.

For example : $CN^- + H_2O \rightleftharpoons HCN + OH^-$

Other examples are CH_3COO^-, NO_2^-, S^{2-} etc.

(c) No hydrolysis : The anions, which are weaker base than OH^- and have conjugate acids stronger than both H_2O and H_3O^+, do not hydrolyse at all.

For example : $Cl^- + H_2O \not\longrightarrow HCl + OH^-$

Other examples include HSO_4^-, NO_3^-, ClO_4^- etc.

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

$B^+(aq) + 2H_2O(l) \rightleftharpoons BOH(aq) + H_3O^+(aq)$

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

(a) Complete hydrolysis : The cations, which are stronger acids than H_3O^+ and their conjugate bases are very much weaker than H_2O will show complete hydrolysis.

For example : $PH_4^+ + H_2O \longrightarrow H_3O^+ + PH_3$

(b) Hydrolysis to a limited extent : The cations, which weaker acid than H_3O^+ ion and their conjugate bases are stonger than H_2O but weaker than OH^-, show hydrolysis to a limited extent.

For example : $NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$

Other examples are $C_6H_5NH_3^+$, $CH_3NH_3^+$ etc.

(c) No hydrolysis : The cations, which are weaker acid than H_3O^+ and their conjugate bases are stronger than both H_2O and OH^-, do not hydrolyze at all. Examples are alkali and alkaline earth metal ions.

For example : $Na^+ + 2H_2O \not\rightarrow NaOH + H_3O^+$

Hydrolysis of Strong Acid – Strong Base [S.A – S.B] Type salt :

Ex. NaCl, $BaCl_2$, Na_2SO_4, $KClO_4$ etc.

$NaCl + H_2O \rightleftharpoons NaOH + HCl$

$Na^{\oplus} + Cl^{\ominus} + H_2O \rightleftharpoons Na^{\oplus} + OH^{\ominus} + H^{\oplus} + Cl^{\ominus}$

$H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$ (It is not salt hydrolysis)

(1) Hydrolysis of salt of [SA – SB] is not possible

(2) Solution is neutral in nature (pH = pOH = 7)

(3) pH of the solution is 7

Hydrolysis of Strong acid - Weak base [S.A – W.B] Type Salt:

Ex. $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $ZnCl_2$, $CuCl_2$, $CaCl_2$

$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

$NH_4^{\oplus} + Cl^{\ominus} + H_2O \rightleftharpoons NH_4OH + H^{\oplus} + Cl^{\ominus}$

Net reaction : $NH_4^{\oplus} + H_2O \rightleftharpoons NH_4OH + H^{\oplus}$

(i) In this type of salt hydrolysis, cation reacts with H_2O, therefore called as **cationic hydrolysis.**

(ii) Solution is acidic in nature (SAWB) as $[H^{\oplus}]$ is increased.

(iii) pH of the solution is less than 7.

(iv) **Relation between K_h, K_W & K_b**

$NH_4^{\oplus} + H_2O \rightleftharpoons NH_4OH + H^{\oplus}$

Hydrolysis constant $K_h = \dfrac{[NH_4OH][H^{\oplus}]}{[NH_4^{\oplus}]}$ ...(i)

For weak Base $NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$

$K_b = \dfrac{[NH_4^{\oplus}][OH^{\ominus}]}{[NH_4OH]}$ ...(ii)

For water $H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

$K_w = [OH^{\ominus}]\,[H^{\oplus}]$ ...(iii)

Now multiplying Eq. (1) & (2) = Eq. (3)

$$\frac{[NH_4OH][H^{\oplus}]}{[NH_4^{\oplus}]} \times \frac{[NH_4^{\oplus}][OH^{\ominus}]}{[NH_4OH]} = [H^{\oplus}]\,[OH^{\ominus}]$$

i.e. $K_h \times K_b = K_w$

$$\boxed{K_h = \frac{K_w}{K_b}}$$

(v) Degree of hydrolysis – (Represented by h)

$NH_4^{\oplus} + H_2O \rightleftharpoons NH_4OH + H^{\oplus}$

C	0	0	(initial concentration at equilibrium)
C – Ch	Ch	Ch	

$$K_h = \frac{[NH_4OH][H^{\oplus}]}{[NH_4^{\oplus}]} = \frac{Ch^2}{(1-h)}$$

Since h <<<< 1

then $(1 - h) \approx 1$

$$\therefore \quad K_h = Ch^2 \quad \Rightarrow \quad h = \sqrt{\frac{K_h}{C}}$$

$$\therefore \Rightarrow \quad h = \sqrt{\frac{\frac{K_w}{K_b}}{C}} \quad \Rightarrow \quad \boxed{h = \sqrt{\frac{K_w}{K_b \times C}}}$$

(vi) pH of the solution :

$pH = -\log [H^{\oplus}]$

$$\Rightarrow [H^{\oplus}] = \sqrt{\frac{K_w \times C}{K_b}}$$

On taking – log on both sides

$$pH = -\log\left(\frac{K_w \times C}{K_b}\right)^{1/2}$$

$$pH = -\frac{1}{2}\log K_b - \frac{1}{2}\log C - \frac{1}{2}(-\log K_b)$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

Illustration 19:

Find out the K_h of centi normal [10^{-2} N] solution of NH_4Cl (SA - WB) if dissociation constant of NH_4OH is 10^{-6} and $K_w = 10^{-14}$. Find out degree of hydrolysis and also find $[H^{\oplus}]$ and pH of solution?

(Given : $K_w = 10^{-14}$; $K_b = 10^{-6}$)

Solution:

(1) $$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(3) $[H^{\oplus}] = Ch$

$= 10^{-2} \times 10^{-3} = 10^{-5}$

(4) $pH = -\log [H^{\oplus}] = -\log [10^{-5}] = +5 \log 10 = +5 \times 1 = 5$

Illustration 20:

How many grams of NH_4Cl should be dissolved per litre of solution to have a pH of 5.13 ?

K_b for NH_3 is 1.8×10^{-5}.

Solution :

NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

$pH = \frac{1}{2}[pK_W - \log C - pK_b]$

$\Rightarrow 10.26 = 14 - \log C - 4.74$

$\Rightarrow \log C = 9.26 - 10.26 = -1.0$

$\therefore C = 10^{-1}$ M

$[NH_4Cl] = 10^{-1}$ M

$W_{NH_4NO_3} = 10^{-1} \times 53.5\ gL^{-1}$

$= 5.35\ gL^{-1}$

Hydrolysis of Weak Acid-Strong Base [W.A – S.B] Type salt :

Ex. KCN, NaCN, K_2CO_3, $BaCO_3$, K_3PO_4

$NaCN + H_2O \rightleftharpoons NaOH + HCN$

$Na^{\oplus} + CN^{\ominus} + H_2O \rightleftharpoons Na^{\oplus} + OH^{\ominus} + HCN$

$CN^{\ominus} + H_2O \rightleftharpoons HCN + OH^{\ominus}$

(i) In this type of salt hydrolysis anion reacts with water therefore called as anionic hydrolysis.

(ii) Solution is basic in nature as $[OH^{\ominus}]$ increases.

(iii) pH of the solution is greater than 7.

(iv) Relation between K_h, K_w, K_a

$CN^{\ominus} + H_2O \rightarrow HCN + OH^{\ominus}$

$K_h = \frac{[HCN][OH^{\ominus}]}{[CN^{\ominus}]}$ ...(i)

For weak acid

$HCN \rightleftharpoons CN^{\ominus} + H^{\oplus}$

$K_a = \frac{[CN^{\ominus}][H^{\oplus}]}{[HCN]}$ ...(ii)

For water $H_2O \rightleftharpoons H^{\oplus} + OH^{\ominus}$

$K_w = [OH^{\ominus}][H^{\oplus}]$ ...(iii)

Now multiply equation (i) & (ii) = equation (iii)

$$\frac{[HCN][OH^{\ominus}]}{[CN^{\ominus}]} \times \frac{[CN^{\ominus}][H^{\oplus}]}{[HCN]} = [H^{\oplus}][OH^{\ominus}]$$

$K_h \times K_a = K_w$

$$\boxed{K_h = \frac{K_w}{K_a}}$$

(v) Degree of hydrolysis :

$CN^{\ominus} + H_2O \rightleftharpoons HCN + OH^{\ominus}$

C	0	0	Initial concentration at equilibrium
C – Ch	Ch	Ch	

$$K_h = \frac{[HCN][OH^{\ominus}]}{[CN^{\ominus}]}$$

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

Since h <<<< 1, therefore $(1 - h) \approx 1$

$\therefore \quad K_h = Ch^2$

$$h^2 = \frac{K_h}{C} \Rightarrow \boxed{h = \sqrt{\frac{K_h}{C}}}$$

$$\boxed{h = \sqrt{\frac{K_w}{K_a \times C}}}$$

(vi) pH of the solution

$[OH^{\ominus}] = Ch$

$$[OH^{\ominus}] = \sqrt{\frac{K_w \times C}{K_a}}$$

$$[H^{\oplus}] = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} \Rightarrow \boxed{[H^{\oplus}] = \sqrt{\frac{K_w \times K_a}{C}}}$$

On taking – log on both sides

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

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

Illustration 21:

Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN, K_a for HCN is 6.2×10^{-12}.

Solution:

NaCN is a salt of strong base NaOH and weak acid HCN. $Na^{\oplus}$ does not react with water whereas $CN^{\ominus}$ reacts with water as here under

$CN^{\ominus} + H_2O \rightleftharpoons HCN + OH^{\ominus}$

$K_h = -\frac{[HCN][OH^{\ominus}]}{[CN^{\ominus}]} = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2\times10^{-12}} = 1.6 \times 10^{-3}$

Let, x moles of salt undergo hydrolysis then concentrations of various species would be

$[CN^{\ominus}] = (0.01 - x) \approx 0.01$, $[HCN] = x$

$[OH^{\ominus}] = x$

$\therefore \quad K_h = \frac{x.x}{0.01} = 1.6 \times 10^{-3}$

$\therefore \quad x^2 = 1.6 \times 10^{-5}$

$\therefore \quad x = 4 \times 10^{-3}$

$[OH^{\ominus}] = x = 4 \times 10^{-3}$ M

$[H_3O^{\oplus}] = \frac{K_W}{[OH^{\ominus}]} = \frac{10^{-14}}{4\times10^{-3}} = 0.25 \times 10^{-11}$

$pH = -\log(0.25 \times 10^{-11}) = 11.6020$

Degree of hydrolysis $= \frac{x}{0.01} = \frac{4\times10^{-3}}{0.01} = 4 \times 10^{-1}$

Illustration 22:

Calculate for 0.01 N solution of sodium acetate -

(i) Hydrolysis constant (ii) Degree of hydrolysis (iii) pH

Given K_a of $CH_3COOH = 1.9 \times 10^{-5}$.

Solution:

For	CH_3COONa +	H_2O $\rightleftharpoons$	CH_3COOH +	NaOH
Initial	C	0	0	
After	C(1–h)	Ch	Ch	

(i) $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9\times10^{-5}} = 5.26 \times 10^{-10}$

(ii) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26\times10^{-10}}{0.01}} = 2.29 \times 10^{-4}$ M

(iii) $[OH^{\ominus}]$ from NaOH, a strong base = $Ch = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6}$ M

$pOH = 5.64$

$\therefore \quad pH = 14 - 5.64 = 8.36$

Hydrolysis of Weak Acid-Weak Base (W.A – W.B) Type salt :

Ex. NH_4CN, $CaCO_3$, $(NH_4)_2CO_3$, $ZnHPO_3$

$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$

$NH_4^{\oplus} + CN^{\ominus} + H_2O \rightleftharpoons NH_4OH + HCN$

Solution is almost neutral but it may be acidic or basic depending upon the nature of acid & base & pH of the solution is near to 7.

For WA - WB types of salt :

		$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1.	Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2.	Nature	Acidic	Basic	Neutral
3.	pH	pH < 7	pH > 7	pH = 7

(i) Relation between K_h, K_w, K_a & K_b

$NH_4^{\oplus} + CN^{\ominus} + H_2O \rightleftharpoons NH_4OH + HCN$

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^{\oplus}][CN^{\ominus}]} \qquad ...(i)$$

$$\frac{[NH_4OH][HCN]}{[NH_4^{\oplus}][CN^{\ominus}]} \times \frac{[NH_4^{\oplus}][OH^{\ominus}]}{[NH_4OH]} \times \frac{[H^{\oplus}][CN^{\ominus}]}{[HCN]} = [H^{\oplus}]\,[OH^{\ominus}]$$

$K_h \times K_b \times K_a = K_w$

$$\boxed{K_h = \frac{K_w}{K_a \times K_b}}$$

(ii) Degree of Hydrolysis :

$NH_4^{\oplus}$	+ $CN^{\ominus}$	+ H_2O $\rightleftharpoons$	NH_4OH	+ HCN	
C	C		0	0	Initial concentration at equilibrium
C – Ch	C – Ch		Ch	Ch	

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^{\oplus}][CN^{\ominus}]}$$

Since h <<<< 1

Then (1 – h) ≈ 1

$$\therefore \quad \boxed{K_h = h^2} \text{ or } h^2 = \frac{K_W}{K_a \times K_b}$$

$$h = \sqrt{\frac{K_W}{K_a \times K_b}} \qquad ...(v)$$

(iii) pH of the solution

From eq. (iii)

$$K_a = \frac{[H^{\oplus}][CN^{\ominus}]}{[HCN]}$$

$$[H^{\oplus}] = \frac{K_a \times [HCN]}{[CN^{\ominus}]}$$

$$[H^{\oplus}] = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since, h <<<< 1, (1 – h) ≈ 1

$[H^{\oplus}] = K_a \times h$ [Now put the value of h from eq. (5)]

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[H^{\oplus}] = \sqrt{\frac{K_w \times K_a}{K_b}}}$$

On taking – log on both sides

$$-\log [H^{\oplus}] = -\log \left(\frac{K_w \times K_a}{K_b} \right)^{1/2}$$

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

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

NOTE :

Degree of hydrolysis of [WA – WB] type salt does not depend on the concentration of salt.

Illustration 23:

Salt of weak acid and weak base

(i) Calculate pH of the mixture (25 mL of 0.1 M NH_4OH + 25 mL of 0.1 M CH_3COOH).

Given that K_a : 1.8×10^{-5}, and $K_b = 1.8 \times 10^{-5}$

Solution:

	NH_4OH	+	CH_3COOH	$\rightarrow$	CH_3COONH_4	+	H_2O
Initial milli moles	25×0.1		25×0.1		0		0
	$= 2.5$		$= 2.5$		–		
Final milli moles	0		0		2.5		2.5

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$pH = \frac{pK_w + pK_a - pK_b}{2} = \frac{1}{2} (-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

Illustration 24:

In the following which one has highest / maximum degree of hydrolysis.

(A) 0.01 M – NH_4Cl (B) 0.1 M –NH_4Cl (C) 0.001 M –NH_4Cl (D) Same

Ans. (C)

Solution:

$$\left(h = \sqrt{\frac{K_h}{C}} \quad \text{if C decreases, h increases} \right)$$

Illustration 25:

In the following which one has lowest value of degree of hydrolysis.

(A) 0.01 M – CH_3COONH_4 (B) 0.1 M – CH_3COONH_4

(C) 0.001 M – CH_3COONH_4 (D) Same

Ans. (D)

Illustration 26:

Find out the concentration of $[H^{\oplus}]$ in 0.1M CH_3COONa solution ($K_a = 10^{-5}$)

Solution:

Salt is [WA – SB] type

$$\therefore \quad [H^{\oplus}] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{10^{-14} \times 10^{-5}}{10^{-1}}} = \sqrt{10^{-19} \times 10^{+1}} = \sqrt{10^{-18}} = 10^{-9}$$

Illustration 27:

Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN

$K_a = 10^{-5}$ & $K_b = 10^{-5}$

Solution:

Salt is [WA – WB]

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

$$= \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

Hydrolysis of amphiprotic anion :

$NaHCO_3$, NaHS, etc., can undergo ionisation to from $H^{\oplus}$ ion and can undergo hydrolysis to from $OH^{\ominus}$ ($Na^{\oplus}$ ion is not hydrolysed)

(a) (i) $HCO_3^{\ominus} + H_2O \underset{}{\overset{\text{ionisation}}{\rightleftharpoons}} CO_3^{2\ominus} + H_3O^{\oplus}$ (acid)

(ii) $HCO_3^{\ominus} + H_2O \underset{}{\overset{\text{hydrolysis}}{\rightleftharpoons}} H_2CO_3 + OH^{\ominus}$ (base)

$$pH(HCO_3^{\ominus}) = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right)$$

(b) Similarly, for $H_2PO_4^{\ominus}$ and $HPO_4^{2\ominus}$ amphiprotic anions.

$$pH_{(H_2PO_4^{\ominus})} = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right) \text{ and } pH_{(HPO_4^{2\ominus})} = \left(\frac{pK_{a_2} + pK_{a_3}}{2}\right)$$

$$\underset{CM}{NaHCO_3} \longrightarrow \underset{C}{Na^{\oplus}} + \underset{C}{HCO_3^{\ominus}}$$

$$HCO_3^{\ominus} + H_2O \overset{Ka/Ka_1}{\rightleftharpoons} H_2CO_3 + OH^{\ominus}$$

$$HCO_3^{\ominus} + H_2O \overset{Ka_2}{\rightleftharpoons} CO_3^{2\ominus} + H_3O^{\oplus}$$

$\because$ $H^{\oplus}$ and $OH^{\ominus}$ also react

$\therefore$ We can safely assume that both reactions have nearly same degree of dissociation

$$\therefore \quad [H_2CO_3] \approx [CO_3^{2\ominus}] \qquad \ldots(1)$$

$$\frac{Kw}{Ka_1} = \frac{[H_2CO_3][OH^{\ominus}]}{[HCO_3^{\ominus}]} \Rightarrow \frac{1}{Ka_1} = \frac{[H_2CO_3]}{[H^{\oplus}][HCO_3^{\ominus}]} \qquad \ldots(2)$$

$$\frac{[CO_3^{2\ominus}][H^{\oplus}]}{[HCO_3^{\ominus}]} = Ka_2 \qquad \ldots(3)$$

Divide (2) by (3)

$$[H^{\oplus}] = \sqrt{Ka_1 Ka_2} \Rightarrow pH = \frac{pKa_1 + pKa_2}{2}$$

Illustration 28:

Calculate the pH of 0.5 M Na_3PO_4 in aqueous solution ?

$PO_4^{3\ominus} + H_2O \rightleftharpoons HPO_4^{2\ominus} + OH^{\ominus}$; $K_b\,(PO_4^{3\ominus}) = 2.4 \times 10^{-2}$

Solution:

$HPO_4^{2\ominus}$ and $PO_4^{3\ominus}$ are conjugate acid and base so $K_a \times K_b = 10^{-14}$

$K_a(HPO_4^{2\ominus}) = \dfrac{10^{-14}}{2.4\times10^{-2}} = 4.17 \times 10^{-13}$

$pK_a = -\log K_a = 12.38$

or $pH = 7 + \dfrac{1}{2}pK_a + \dfrac{1}{2}\log C$

$pH = 13.04$

Buffer Solutions : A solution that resists change in pH value upon addition of small amount of strong acid or base or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

Types of buffer solutions

(a) Simple buffer solution (b) Mixed buffer solution

(a) Simple buffer solution :

A salt of weak acid and weak base in water e.g. CH_3COONH_4, $HCOONH_4$, AgCN, NH_4CN.

Buffer action of simple buffer solution

Consider a simple buffer solution of CH_3COONH_4, since it is a salt will be dissociated completely.

$CH_3COONH_4 \longrightarrow CH_3COO^{\ominus} + NH_4^{\oplus}$

If a strong acid such as HCl is added then

$HCl \longrightarrow H^{\oplus} + Cl^{\ominus}$

The $H^{\oplus}$ ions from the added acid (HCl) combine with $CH_3COO^{\ominus}$ ions to form CH_3COOH, which is a weak acid so will not further ionized.

Thus, there is no rise in $H^{\oplus}$ ion concentration and the pH remain constant.

$CH_3COO^{\ominus} + H^{\oplus} \rightleftharpoons CH_3COOH$ (Weak acid)

If a strong base is added as NaOH

$NaOH \longrightarrow Na^{\oplus} + OH^{\ominus}$

$NH_4^{\oplus} + OH^{\ominus} \rightleftharpoons NH_4(OH)$ (Weak base)

Thus, change in $OH^{\ominus}$ ion concentration is resisted by $NH_4^{\oplus}$ ions by forming NH_4OH which is a weak base. So, it will not further ionized and pH remains constant. pH of a simple buffer solution :-

$$\boxed{pH = 7 + \frac{1}{2}pk_a - \frac{1}{2}pk_b}$$

(b) Mixed buffer solutions : Acidic buffer solution

An acidic buffer solution consists of solution of a weak acid and its salt with strong base. The best known example is a mixture of solution of acetic acid and its salt with strong base (CH_3COONa). Other example : HCN + KCN, ($H_2CO_3 + NaHCO_3$) $\longrightarrow$ blood

$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$ (Weakly ionised)

$CH_3COONa \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$ (Highly ionised)

When a few drops of an acid (HCl) are added to it, the $H^{\oplus}$ ions from the added acid (HCl) combine with the $CH_3COO^{\ominus}$ ions to form CH_3COOH. Thus, there is no rise in $H^{\oplus}$ ion concentration and the pH of solution remains constant. On the other hand, when a few drops of base(NaOH) are added, the $OH^{\ominus}$ of the added base reacts with acetic acid to form unionise water and acetate ions.

$CH_3COOH + OH^{\ominus} \rightleftharpoons H_2O + CH_3COO^{\ominus}$.

Thus there is no increase in $OH^{\ominus}$ ion concentration and hence the pH of the solution remains constant.

pH of an acidic buffer solution (Henderson equation) :

Consider a buffer mixture (acidic buffer)

HA + NaA ($CH_3COOH + CH_3COONa$)

where A = CH_3COO, $A^{\ominus} = CH_3COO^{\ominus}$

$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$

$NaA \longrightarrow Na^{\oplus} + A^{\ominus}$

Applying law of mass action to dissociation equilibrium of HA

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}; \text{ so } [H^{\oplus}] = \frac{K_a[HA]}{[A^{\ominus}]}$$

$$\text{taking log, } \log [H^{\oplus}] = \log K_a + \log \frac{[HA]}{[A^{\ominus}]}$$

$$-\log [H^{\oplus}] = -\log K_a - \log \frac{[HA]}{[A^{\ominus}]}$$

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

$[A^{\ominus}]$ = Initial concentration of salt as it is mainly comes from salt.

[HA] = Initial concentration of the acid.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$ (it is known as Henderson-Hasselbalch equation.)

Illustration 29:

How much volume of 0.2 M solution of acetic acid should be added to 100 mL of 0.2 M solution of sodium acetate to prepare a buffer solution of pH = 6.00 ? (pK_a for acetic acid is 4.74)

Solution:

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

$\log\frac{[Salt]}{[Acid]} = pH - pK_a = 6.00 - 4.74 = 1.26 \quad \therefore \quad \frac{[Salt]}{[Acid]} = 18.2$

Moles of CH_3COONa in solution $\frac{100\times0.2}{1000} = 0.02$

Let, volume of 0.2 acetic acid added = V mL

$\therefore$ Moles of acetic acid = $\frac{V\times0.2}{1000}$

$\therefore \quad \frac{0.02}{V\times\frac{0.2}{1000}} = 18.2$

$\therefore$ V = 5.49 mL

Illustration 30:

Calculate the pH after the addition of 80 mL and 100 mL respectively of 0.1 N NaOH to 100 mL, 0.1 N CH_3COOH. (Given pK_a for CH_3COOH = 4.74)

Solution:

If 80 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH_3COOH, acidic buffer will form as

	H_3CCOOH	+ NaOH	$\longrightarrow$ $H_3CCOONa$	+ H_2O
Initial	0.01 eq.	0.008 eq.	0	0
Final	0.002 eq.	0	0.008 eq.	

$pH = pK_a + \log\frac{[CH_3COO^{\ominus}]}{[CH_3COOH]} = 4.74 + \log\frac{0.008}{0.002} = 5.342$

If 100 mL of 0.1 N NaOH is added is added to 100 mL of 0.1 N CH_3COOH, complete neutralization takes place and the concentration of $H_3CCOONa$ = $\frac{0.1}{2}$M = 0.05 M

Now, $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 8.72$

Illustration 31:

Calculate the pH of a solution when 0.20 moles of HCl is added to one litre solution containing -

(a) 1 M each of acetic acid and acetate ion ?

(b) 0.1 M each of acetic acid and acetate ion ?

Given K_a for acetic acid is 1.8×10^{-5}.

Solution:

(a) Initially [Acetic acid] =1 M

[Acetate] = 1 M

Now 0.2 moles of HCl are added to it.

	HCl	+ $CH_3COO^{\ominus}$	$\rightarrow$ CH_3COOH	+ $Cl^{\ominus}$
Mole before reaction	0.2	1	1	0
Mole after reaction	0	0.8	1.2	0.2

$\therefore$ New $[CH_3COOH] = 1.2$; $[CH_3COO^{\ominus}] = 0.8$

$\therefore \quad pH = pk_a + \log\frac{[conjugate]}{[acid]}$

$\therefore \quad pH = -\log 1.8 \times 10^{-5} + \log\frac{0.8}{1.2} = 4.5686$

(b) In II case initially [Acetic acid] = 0.1 M

[Acetate] = 0.1 M

Now 0.2 mole of HCl are added to it

	HCl	+	$CH_3COO^{\ominus}$	$\rightarrow$	CH_3COOH	+	$Cl^{\ominus}$
Mole before reaction	0.2		0.1		0.1		0
Mole after reaction	0.1		0		0.2		0.1

$\therefore$ $[H^{\oplus}]$ from free HCl = 0.1 M

$\therefore$ pH = 1

NOTE :

CH_3COOH no doubt gives $H^{\oplus}$ but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, $H^{\oplus}$ from CH_3COOH may be neglected.

Mixed buffer solutions : Basic buffer solution

A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of NH_4OH and NH_4Cl.

$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$ (Weakly ionised)

$NH_4Cl \longrightarrow NH_4^{\oplus} + Cl^{\ominus}$ (Highly ionised)

When a few drops of a base (NaOH) are added, the $OH^{\ominus}$ ions from NaOH combine with $NH_4^{\oplus}$ ions to form feebly ionised NH_4OH thus there is no rise in the concentration of $OH^{\ominus}$ ions and hence the pH value remains constant.

$NH_4^{\oplus} + OH^{\ominus} \rightleftharpoons NH_4OH$

If a few drops of an acid (HCl) are added the $H^{\oplus}$ from acid combine with NH_4OH to form H_2O and $NH_4^{\oplus}$ ions.

$NH_4OH + H^{\oplus} \rightleftharpoons NH_4^{\oplus} + H_2O$

Thus the addition of acid does not increase the $H^{\oplus}$ ion concentration and hence pH remains unchanged.

pH of basic buffer solution :

$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$

$NH_4Cl \rightarrow NH_4^{\oplus} + Cl^{\ominus}$

$$K_b = \frac{[NH_4^{\oplus}][OH^{\ominus}]}{[NH_4OH]}$$

$$[OH^{\ominus}] = \frac{K_b[NH_4OH]}{[NH_4^{\oplus}]} = \frac{K_b[Base]}{[Salt]}$$

(mainly comes from salt)

taking –log on both side

$$-\log OH^{\ominus} = -\log \frac{K_b[Base]}{[Salt]} \Rightarrow pOH = -\log K_b - \log \frac{[Base]}{[Salt]}$$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \Rightarrow pH = 14 - pOH$$

Illustration 32:

An organic base B has K_b value equal to 1×10^{-8}. In what amounts should 0.01 M HCl and 0.01 M solution of B be mixed to prepare 1 L of a buffer solution having pH = 7.0 ?

Solution:

$B + H_2O \rightleftharpoons BH^{\oplus} + OH^{\ominus}$

$K_b = \frac{[BH^{\oplus}][OH^{\ominus}]}{[B]} = 1 \times 10^{-8}$

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

$\Rightarrow \; 7 = -\log(10^{-8}) + \log \frac{[BH^{\oplus}]}{[B]} \Rightarrow 7 = 8 + \log \frac{[BH^{\oplus}]}{[B]}$

$\log \frac{[BH^{\oplus}]}{[B]} = -1$

$\therefore \quad \frac{[BH^{\oplus}]}{[B]} = 10^{-1} = 0.1$

Let, volume of HCl taken = xL

$\therefore$ Volume of base taken = (1 – x) L

After the reaction, millimole of $BH^{\oplus}$ formed = 0.01 × (x)

Millimoles of base left = 0.01 (1 – 2x)

$\therefore \quad \frac{[BH^{\oplus}]}{[B]} = \frac{x}{[1-2x]} = 0.1$

$\therefore$ x = 0.083 L = Volume of HCl

$\therefore$ Volume of base = 0.917 L

Illustration 33:

Which of the following buffers containing NH_4OH and NH_4Cl show the lowest pH value?

	conc. of NH_4OH (mol L^{-1})	conc. of NH_4Cl (mol L^{-1})
(A)	0.50	0.50
(B)	0.10	0.50
(C)	0.50	1.50
(D)	0.50	0.10

Ans. (B)

Solution:

$pOH = pK_b + \log \frac{[salt]}{[base]}$ for $NH_4Cl = 0.5$ and $NH_4OH = 0.1$

pOH will be maximum and so pH will be minimum.

Illustration 34:

A solution of weak base BOH was titrated with 0.1 N HCl. The pH of the solution was found to be 10.04 and 9.14 after the addition of 5 mL and 20 mL of the acid respectively. Find the dissociation constant of the base.

Solution:

Case I :

	BOH	+ HCl	⟶	BCl	+ H_2O
Millimole before reaction	a	0.1× 5=0.5		0	0
Millimole after reaction	(a–0.5)	0		0.5	0.5

$\therefore$ $pOH = -\log K_b + \log \frac{[BCl]}{[BOH]}$ ...(i)

$\because$ pH = 10.04 so pOH = 3.96

$\therefore$ $3.96 = -\log K_b + \log \frac{0.5}{(a-0.5)}$ ...(ii)

Case II :

	BOH	+ HCl	⟶	BCl	+ H_2O
Millimole before reaction	a	0.1× 20=2		0	0
Millimole after reaction	(a–2)	0		2	2

$\therefore$ $pOH = -\log K_b + \log \frac{[BCl]}{[BOH]}$ ...(iii)

$\because$ pH = 9.14 $\therefore$ pOH = 4.86

$\therefore$ $4.86 = -\log K_b + \log \frac{2}{(a-2)}$ ...(iv)

Solving Eqs. (ii) and (iv), $K_b = 1.81 \times 10^{-5}$

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

Let there be a buffer solution of volume 1 L with 'b' mole of anion (coming from salt) and 'a' mole of weak acid. The pH of the buffer would be given by :

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

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

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

Differentiating with respect to x we get

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

Taking the inverse

$\frac{dx}{d\Delta pH} = 2.303\frac{(a+x)(b-x)}{a+b} \approx 2.303\frac{ab}{a+b}$. This is defined as buffer capacity. It is the ratio of the small amount of acid or base added to the change in pH caused in the buffer.

Maximum buffer capacity : Differentiating buffer capacity with respect to 'b', the amount of salt present in the solution and equating it to zero, we get

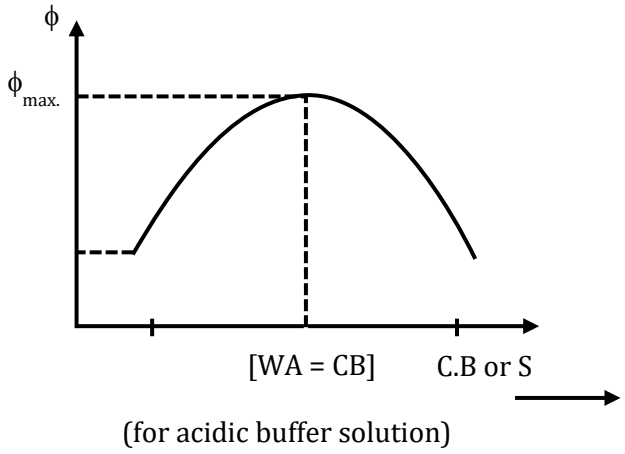
$$\frac{d}{db}\left(\frac{dx}{d\Delta pH}\right) = 2.303\frac{[-1\times(b-x)]+[1\times(a-b+x)]}{a} = 0$$

a – b + 2x = 0 ; Since x is very small we ignore 2x and we get

a – b = 0

$\therefore$ b = a $\Rightarrow$ [Acid] = [Anion of salt]

The buffer shows maximum buffer capacity when the amounts of acid (or base) and the anion (or cation) from salt are same.



(for acidic buffer solution)

Illustration 35:

Calculate the buffer capacity of 1 L solution of :
(i) 0.1M CH_3COOH and 0.1M CH_3COONa
(ii) 0.2M CH_3COOH and 0.2M CH_3COONa
Given : pK_a (CH_3COOH) = 4.74
Which will be a better buffer ?

Solution:

Buffer capacity = $\frac{2.303(a+x)(b-x)}{a+b} \approx \frac{2.303\,ab}{a+b}$ x << a, b

(i) Buffer capacity = $\frac{0.1\times0.1\times2.303}{0.1+0.1} = 0.11515$

(ii) Buffer capacity = $\frac{0.2\times0.2\times2.303}{0.2+0.2} = 0.2303$

Second buffer solution (having greater buffer capacity) can be called better buffer.

Indicators :

The stage of titration when complete reaction occur between the solution is called **equivalent point.** The stage of titration when sudden change in colour of solution is observed is called **end point.** A perfect indicator response sudden colour changes exactly on completion of reaction. An **indicator** is a substance which response sudden change in colour of solution at the end point or neutral point of the acid-base titration. **At end point** $N_1V_1 = N_2V_2$

(i) The indicators in acid-base titration changes colour on changing the pH of solution.

(ii) All the acid-base indicators are either weak organic acid or base and having different colour for unionized and ionised form.

(iii) A mixture of two colour is recognized in a single colour if the conc. of one is 10 times or more than that of others. (This 10 time is flexible)

$$\underset{\text{colour X}}{HA} \rightleftharpoons \underset{\text{colour Y}}{A^{\ominus}} + H^{\oplus}$$

Diss. const. or (Ionisation const.) = $K_a = K_{in} = \frac{[H^{\oplus}][A]}{[HA]}$

$$pH = pK_{in} + \log\frac{[A^{\ominus}]}{[HA]}$$

(a) The solution will appear only of colour Y, if $\frac{[A^{\ominus}]}{[HA]} \geq 10 \Rightarrow pH \geq (pK_{in} + 1)$

(b) The solution will appear only of colour X, if $\frac{[A^{\ominus}]}{[HA]} \leq \frac{1}{10} \Rightarrow pH \leq (pK_{in} - 1)$

pH of solution below and above which solution appears in a single colour is called pH range of indicator.

Indicator	pH range	Colour change	pK_a
Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolpthalein	8.3 – 10.5	Colourless to pink	9.6

Illustration 36:

The disso. const. of a basic indicator is 2×10^{-7}. Calculate its pH range.

Solution:

5.7 – 7.7 = pOH $\quad\quad$ $\therefore$ pH = 6.3 – 8.3

Illustration 37:

The pH range of an acidic indicator HIn is 4.0 - 5.2. Calculate dissociation constant. Also calculate $\frac{In^{\ominus}}{HIn}$ for the appearance of solution in single colour.

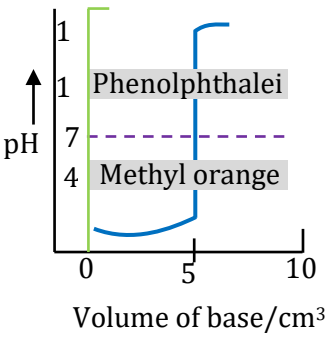
Solution:

Diss. constant = 2.5×10^{-5}, 4

(A) Titration of strong acid against strong alkali :

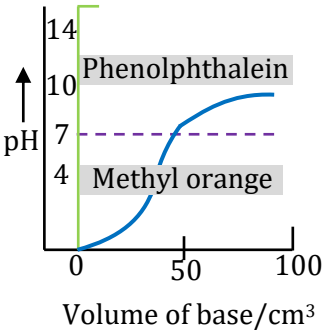
The graph (A) shows how pH changes during the titration of 50 cm^3 of 0.1 M HCl with 0.1 M NaOH.

$NaOH\ (aq) + HCl\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (\ell)$



The pH of 0.1 M solution of HCl in the beginning would be 1. As alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple calculations that pH of the solution is 3.7 when 49.8 cm^3 of 0.1 M NaOH solution have been added. The pH suddenly changes to 10 after addition of 50.1 cm^3 of the NaOH solution. Thus, any indicator having pH range between 3.5 to 10 will identify the equivalence point. This means that any one of phenolphthalein, methyl orange or bromothymol blue could be used as an indicator.

(B) Titration of strong acid against weak alkali :

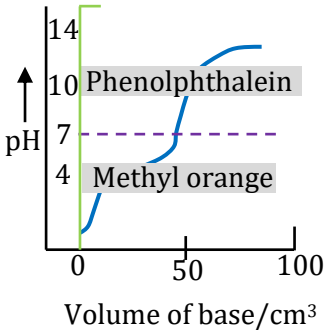


The graph (B) shows how pH changes during titration of 50 cm^3 of 0.1 M HCl with 0.1 M NH_3.

$HCl\ (aq) + NH_4OH\ (aq) \longrightarrow NH_4Cl\ (aq) + H_2O\ (\ell)$

In this case, the pH changes rapidly from 3.5 to 7.0 at the equivalence point. Methyl orange, methyl red and bromocresol green are suitable indicators for this type of titration. Phenolphthalein is unsuitable because its pH range lies outside the vertical portion of the curve.

(C) Titration of weak acid against strong base :

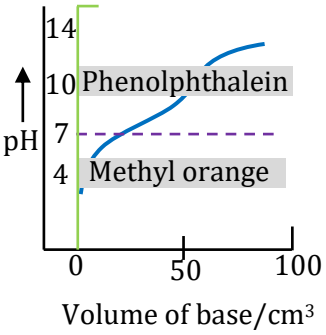


The graph (C) shows how pH changes during titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NaOH.

$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (\ell)$

The vertical portion of this titration curve lies between pH range 7 to 10.6. Phenolphthalein is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

(D) Titration of weak acid against weak base :



The graph (D) represents the titration curve obtained for titration of 50 cm^3 of 0.1 M CH_3COOH with 0.1 M NH_3.

$CH_3COOH\ (aq) + NH_4OH\ (aq) \longrightarrow CH_3COONH_4\ (aq) + H_2O\ (\ell)$

For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

Illustration 38:

Bromophenol blue is an indicator with a value of $K_a = 6.84 \times 10^{-6}$. At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 5.84.

Solution:

$HBPh \rightleftharpoons H^{\oplus} + BPh^{\ominus}$

$K_a = \dfrac{[H^{\oplus}][BPh^{\ominus}]}{[HBPh]}$, when $BPh^{\ominus} = HBPh$, indicator will work. Thus

$[H^{\oplus}] = 6.84 \times 10^{-6}$

$\therefore$ pH = 5.165

Also if pH = 5.84

or $[H^{\oplus}] = 1.44 \times 10^{-6}$, then

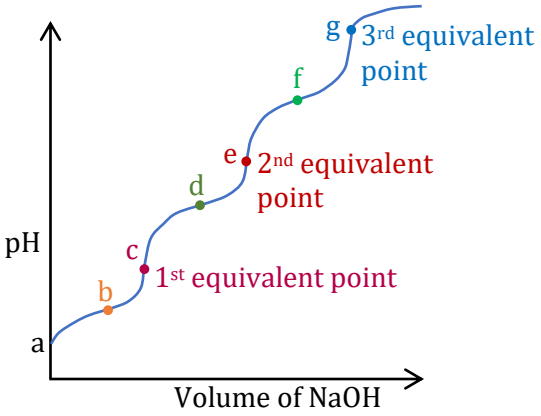
$K_a = \dfrac{[H^{\oplus}][BPh^{\ominus}]}{[HBPh]}$ or $6.84 \times 10^{-6} = \dfrac{1.44\times10^{-6}.C\alpha}{C(1-\alpha)}$ or $\alpha = 0.83$ or 83 %

Titration of poly protic acid v/s Strong Base :

50 mL of 0.1 M H_3PO_4 against 0.1 M NaOH. Calculate pH when vol. of NaOH added is

(a) 0 mL (b) 25 mL (c) 50 mL (d) 75 mL (e) 100 mL

(f) 125 mL (g) 150 mL (h) 200 mL (i) 90 mL



Given : $pK_{a1} = 3$, $pK_{a2} = 7$, $pK_{a3} = 11$

(a) $pH = 1/2\ (pK_{a1} - \log C) = 1/2\ (3 + 1) = 2$

(b)

	H_3PO_4	+ NaOH	$\rightleftharpoons$	NaH_2PO_4	+ H_2O
t = 0	5 Mmol	2.5 Mmol		0	–
	2.5 M mol	0		2.5 M mol	

$pH = pK_{a1} + \log 1/1 = pK_{a1} = 3$

(c) Solution of $H_2PO_4^{\ominus}$ amphoteric species

$$pH = \frac{pK_{a1} + pK_{a2}}{2} = \frac{3+7}{2} = 5$$

(d)

	NaH_2PO_4	+ NaOH	$\longrightarrow$	Na_2HPO_4	+ H_2O
t = 0	5 M mol	2.5 M mol		0	–
	2.5 M mol			2.5 M mol	–

$pH = \log 1/1 + pK_{a2} = 7$

(e) $H_2PO_4^{2\ominus}$ solution (amphoteric species)

$$pH = \frac{pK_{a2} + pK_{a3}}{2} = 9$$

(f)

Na_2HPO_4	+ NaOH	$\longrightarrow$	Na_3PO_4	+ H_2O
5	2.5		0	–
2.5	0		2.5	–

$pH = pK_{a3} + \log 1/1 = 11$

(g) 3rd eq. pt Na_3PO_4 solution

$[Na_3PO_4] = 5/200 = 1/40$

$pH = 1/2\{pK_w + pK_{a3} + \log C\} = 1/2\ (14 + 11 - 2 + 0.4) = 11.7$

(h) 200 mL

hydrolysis of Na_3PO_4 can be neglected in presence of NaOH

$[NaOH] = 5/250 = 1/50$ $pOH = 1.7$

$pH = 12.3$

(i) 90 mL

NaH_2PO_4	+ NaOH	$\longrightarrow$	Na_2HPO_4 + H_2O
5	4		0
1	0		4

$pH = pK_{a2} + \log 4 = 7.6$

Solubility (s) & solubility product (K_{sp}) :

Solubility :

At constant temperature, the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of saturated solution is called solubility.

Solubility depends on the following –

(i) Temperature

(ii) Presence of common ion

(iii) Nature of solvent

Solubility product (K_{sp}) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- A solution which remains in contact with undissolved solute is said to be saturated.
- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into $Ag^{\oplus}$ and $Cl^{\ominus}$ ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, $Ag^{\oplus}$ and $Cl^{\ominus}$ ions.

  according to law of mass action

$$K = \frac{\left[Ag^{\oplus}\right].\left[Cl^{\ominus}\right]}{\left[AgCl\right]}$$

  Since, the concentration of undissolved solid AgCl is constant. Thus, the product K.[AgCl] gives another constant which is designated as K_{sp}

  So, $K.[AgCl] = [Ag^{\oplus}].[Cl^{\ominus}]$

  $\therefore$ $K_{sp} = [Ag^{\oplus}] . [Cl^{\ominus}]$

- **K_{sp} for $CaCl_2$** $CaCl_2(s) \rightleftharpoons Ca^{2\oplus}(aq) + 2Cl^{\ominus}(aq)$

  Solubility product in terms of concentration of ions $K_{sp} = [Ca^{2\oplus}] [Cl^{\ominus}]^2$

- **K_{sp} for $AlCl_3$** $AlCl_3(s) \rightleftharpoons Al^{3\oplus}(aq) + 3Cl^{\ominus}(aq)$

  Solubility product in terms of concentration of ions $K_{sp} = [Al^{\oplus 3}] [Cl^{\ominus}]^3$

- **General form** $A_xB_y(s) \rightleftharpoons xA^{-y}(aq) + yB^{-x}(aq)$ $K_{sp} = [A^{-y}]^x [B^{-x}]^y$

Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of ions given by the dissociation of electrolyte at a given temperature when the solution is saturated.

Application of solubility product (K_{sp}) :

To find out the solubility (S) :

(i) K_{sp} of AB (mono-mono, di-di, tri-tri valency) type salt)–

Ex. NaCl, $BaSO_4$, CH_3COONa, $CaCO_3$, NaCN, KCN, NH_4CN, NH_4Cl etc.

$AB(s)$	$\rightleftharpoons$	$A^{\oplus}(aq)$	+	$B^{\ominus}(aq)$
a		0		0
(a–s)		s		s

$K_{sp} = [A^{\oplus}] [B^{\ominus}]$

$K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

(ii) K_{sp} of AB_2 or A_2B (mono-di or di-mono valency) type salt –

Ex. $CaCl_2$, $CaBr_2$, K_2S, $(NH_4)_2SO_4$, K_2SO_4, K_2CO_3 etc.

$$AB_2(s) \rightleftharpoons A^{2\oplus}(aq) + 2B^{\ominus}(aq)$$

a	0	0
a – s	s	2s

$K_{sp} = [A^{2\oplus}]\,[B^{\ominus}]^2$

$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$

$$s = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

(iii) General form :

$$A_xB_y(aq) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$$

a	0	0
a–s	xs	ys

$K_{sp} = [A^{-y}]^x \,.\, [B^{-x}]^y$

$K_{sp} = (xs)^x .\, (ys)^y$

$$\boxed{K_{sp} = x^x . y^y . s^{(x+y)}}$$

Factors Affecting Solubility : Common Ion Effect

Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle, on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is re-established so, the solubility of substances decreases.

Ex. Find out the solubility of AgCl in water and in the presence of CM – NaCl solution?

$$AgCl \rightleftharpoons Ag^{\oplus} + Cl^{\ominus}$$

s M	SM		(Let solubility of AgCl is S mol L^{-1})

$K_{sp} = [Ag^{\oplus}]\,[Cl^{\ominus}]$

$K_{sp} = S^2$

In NaCl solution

$$NaCl \longrightarrow Na^{\oplus} + Cl^{\ominus}$$

C	C	C

Let solubility of AgCl in the presence of NaCl solution is S' mol L^{-1}

$$AgCl \rightleftharpoons Ag^{\oplus} + Cl^{\ominus}$$

S'	S'	+	C

$K_{sp} = [Ag^{\oplus}]'\,[Cl^{\ominus}]'$

$K_{sp} = S'\,(S' + C) = S'^2 + S'C$ (Neglecting the higher power terms of S')

$K_{sp} = S'\,C$

$$\boxed{S' = \frac{K_{sp}}{C}}$$

Factors Affecting Solubility : Complex formation

Solubility of AgCl in aqueous NH_3 is roughly 10,000 times as its solubility in water, due to complex formation.

$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$

$Ag^{\oplus}(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{\oplus}(aq)$; $K_{eq} = K_{stability} = K_{formation}$

and $\frac{1}{K_{stability}} = K_{dissociation} = K_{instability}$

Illustration 39:

What must be the concentration of aq. NH_3(eq.) which must be added to a solution containing 4×10^{-3} M $Ag^{\oplus}$ and 0.001 M NaCl, to prevent the precipitation of AgCl.

Given that $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ and the formation constant of $[Ag(NH_3)_2]^{\oplus}$ is $K_{formation} = \frac{10^8}{6}$.

Solution:

Calculate silver ion concentration which can be allowed to remain in the solution,

$1.8 \times 10^{-10} = [Ag^{\oplus}][Cl^{\ominus}]$

$[Ag^{\oplus}] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7}$ M,

This quantity is so small that almost all the $Ag^{\oplus}$ ion will be consumed.

$Ag^{\oplus}$	+	$2NH_3$	$\rightleftharpoons$	$[Ag(NH_3)_2]^{\oplus}$	$K = \frac{10^8}{6}$
4×10^{-3}		b		0	
1.8×10^{-7}		$(b - 8 \times 10^{-3})$		4×10^{-3}	$K = \frac{10^8}{6} = \frac{4 \times 10^{-3}}{1.8 \times 10^{-7} \times (b - 8 \times 10^{-3})^2}$

$\Rightarrow$ b= 0.0445

Simultaneous solubility :

When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the solution.

Illustration 40:

Calculate simultaneous solubility of silver thiocyanate and sliver bromide in water given that k_{sp} of silver thiocyanate = 10^{-12} and k_{sp} of silver bromide = 5×10^{-13} respectively.

Solution:

Let the solubility of AgSCN be x and that of AgBr is y, then

$AgSCN \rightleftharpoons$	$Ag^{\oplus}$	+	$SCN^{\ominus}$	$AgBr \rightleftharpoons$	$Ag^{\oplus}$	+	$Br^{\ominus}$
	x + y		x		x + y		y

$10^{-12} = x\,(x + y)$ ...(i)

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

On solving we get, $x = 2y$

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

Solubility in appropriate buffer solutions :

Appropriate buffer means that the components of buffer should not interfere with the salt or only $H^{\oplus}$ or $OH^{\ominus}$ ions should be interacting with the ions of the salt.

Condition of precipitation /ionic product (I.P or Q_{sp}) :

Ionic product (IP) of an electrolyte is defined in the same way as K_{sp}. The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K_{sp} contains only equilibrium concentration. Thus, for AgCl.

$IP = [Ag^{\oplus}]_i\,[Cl^{\ominus}]_i$ and $K_{sp} = [Ag^{\oplus}]_{eq}.[Cl^{\ominus}]_{eq}$

- Ionic product changes with concentration but K_{sp} does not.
- To decide whether an ionic compound will precipitate, its K_{sp} is compared with the value of ionic product. The following three cases arise :
  (i) $IP < K_{sp}$: The solution is unsaturated and precipitation will not occur.
  (ii) $IP = K_{sp}$: The solution is saturated and solubility equilibrium exists.
  (iii) $IP > K_{sp}$: The solution is supersaturated and hence precipitation of the compound will occur.
  Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

Selective Precipitation :

The scheme of Qualitative Analysis is based on the Principle of Selective Precipitation. Let us consider a mixture containing Ag^{+}, Cu^{2+} and Fe^{3+}.

Step 1 : Add dil HCl to the solution of the mixture. Ag^{+} will precipitate as AgCl. It is removed by filtration.

Step 2 : Pass H_2S through the filtrate. Cu^{2+} is precipitated as CuS and removed by filtration.

Step 3 : Add NH_4OH or NaOH solution to filtrate. Fe^{3+} is precipitated as $Fe(OH)_3$.

In this way ions are precipitated from solution one by one. **The precipitation of cations from solution one at a time is called Selective precipitation.**

Illustration 41:

If solubility product of the base $M(OH)_3$ is 2.7×10^{-11}, the concentration of $OH^{\ominus}$ will be

(A) 3×10^{-3} (B) 3×10^{-4} (C) 10^{-3} (D) 10^{-11}

Ans. (C)

Illustration 42:

The solubility of $BaSO_4$ in water is 1.07×10^{-5} mol dm^{-3}. Estimate its solubility product.

Solution:

Solubility equilibrium for $BaSO_4$ is

$$BaSO_{4(s)} \rightleftharpoons Ba^{2\oplus}_{(aq)} + SO^{2\ominus}_{4(aq)}$$

Now, $S = 1.07 \times 10^{-5}$ M

Hence, $K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$

Illustration 43:

The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol dm^{-3} and g dm^{-3}.
(Molar mass of AgBr. = 187.8 g mol^{-1})

Solution:

The solubility equilibrium of AgBr is

$$AgBr_{(s)} \rightleftharpoons Ag^{\oplus}_{(aq)} + Br^{\oplus}_{(aq)}$$

The molar solubility S of AgBr is given by

$$S = \sqrt{K_{sp}} = \sqrt{5.2\times10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The solubility in g dm^{-3} = molar solubility (mol dm^{-3}) × molar mass (g mol^{-1})
$= 7.2 \times 10^{-7} \times 187.8 = 1.35 \times 10^{-4}$ g dm^{-3}

Illustration 44:

What is the maximum volume of water required to dissolve 1 g of calcium sulphate at 25°C. For calcium sulphate, $K_{sp} = 9.0 \times 10^{-6}$.

Solution:

$CaSO_4$ (aq) $AgBr_{(s)} \rightleftharpoons Ag^{\oplus}_{(aq)} + Br^{\ominus}_{(aq)}$ $Ca^{2\oplus}$ (aq) + $SO_4^{2\ominus}$ (aq)

If S is the solubility of $CaSO_4$ in moles L^{-1}

$K_{sp} = [Ca^{2\oplus}] \times [SO_4^{2\ominus}] = S^2$

$\therefore S = \sqrt{K_{sp}} = \sqrt{9.0\times10^{-6}}$

$= 3 \times 10^{-3}$ mol $L^{-1} = 3 \times 10^{-3} \times 136$ g $L^{-1} = 0.408$ gL^{-1}

For dissolving 0.408 g of $CaSO_4$ water required = 1 L

$\therefore$ For dissolving 1g $CaSO_4$ water required $= \frac{1}{0.408}$ L $= 2.45$ L

Illustration 45:

Equal volumes of 0.04 M $CaCl_2$ and 0.0008 M Na_2SO_4 are mixed. Will a precipitate form? K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$

Solution:

	$CaCl_2$	+ Na_2SO_4	→ $CaSO_4$	+ 2NaCl
Millimole added	0.04 V	0.0008× V	0	0

Suppose V mL of both are mixed

$\therefore [Ca^{2\oplus}] = \frac{0.04V}{2V}$

$[SO_4^{2\ominus}] = \frac{0.0008V}{2V}$

$\therefore [Ca^{2\oplus}][SO_4^{2\ominus}] = \frac{0.04V}{2V} \times \frac{0.0008V}{2V} = 8 \times 10^{-6}$

Thus, $[Ca^{2\oplus}][SO_4^{2\ominus}]$ in solution < K_{sp}

$8 \times 10^{-6} < 2.4 \times 10^{-5}$

$\therefore$ $CaSO_4$ will not precipitate.

Illustration 46:

What $[H^{\oplus}]$ must be maintained in saturated H_2S(0.1 M) to precipitate CdS but not ZnS, if $[Cd^{2\oplus}] = [Zn^{2\oplus}] = 0.1$ initially ?

$K_{sp} = (CdS) = 8 \times 10^{-27}$

$K_{sp} = (ZnS) = 1 \times 10^{-21}$

$K_a = (H_2S) = 1.1 \times 10^{-21}$

Solution:

In order to prevent precipitation of ZnS

$[Zn^{2\oplus}]\,[S^{2\ominus}] < K_{sp}(ZnS) = 1 \times 10^{-21}$

(ionic product)

or $(0.1)\,[S^{2\ominus}] < 1 \times 10^{-21}$

or $[S^{2\ominus}] < 1 \times 10^{-20}$

This is the maximum value of $[S^{2\ominus}]$ before ZnS will precipitate. Let $[H^{\oplus}]$ to maintain this $[S^{2\ominus}]$ be x. Thus for

$H_2S \rightleftharpoons 2H^{\oplus} + S^{2\ominus}$

$$K_a = \frac{[H^{\oplus}]^2[S^{2\ominus}]}{[H_2S]} = \frac{x^2(1\times10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

or $x = [H^{\oplus}] = 0.1$ M

$\therefore$ No ZnS will precipitate at a concentration of $H^{\oplus}$ greater than 0.1 M

Illustration 47:

0.10 mol sample of $AgNO_3$ is dissolved in one litre of 2.00 M NH_3. Is it possible to form AgCl(s) in the solution by adding 0.010 mol of NaCl ?

($K_{sp(AgCl)} = 1.8 \times 10^{-10}$, $K_{f[Ag(NH_3)_2^{\oplus}]} = 1.6 \times 10^{7}$)

Solution:

$Ag^{\oplus}$	+	$2NH_3$	$\rightleftharpoons$	$[Ag(NH_3)_2^{\oplus}]$
0.10 M		2.00		0
0.10–0.10 = 0		(2–0.20 M) = 1.80 M		0.10 M

It is assumed that all $Ag^{\oplus}$ ions have been complexed and only x amount is left

$$K_f = \frac{[Ag(NH_3)_2^{\oplus}]}{[Ag^{\oplus}]\,[NH_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(1.80)^2}$$

$\therefore$ $x = 1.93 \times 10^{-9}$ M = $[Ag^{\oplus}]$ undissolved

$[Cl^{\ominus}] = 1.0 \times 10^{-2}$ M

$\therefore$ $[Ag^{\oplus}]\,[Cl^{\ominus}] = 1.93 \times 10^{-9} \times 1.0 \times 10^{-2} = 1.93 \times 10^{-11} < 1.8 \times 10^{-10}\,[K_{sp(AgCl)}]$

Hence, AgCl (s) will not precipitate.

Illustration 48:

What is the concentration of $Ag^{\oplus}$ ions in 0.01 M $AgNO_3$ that is also 1.0 M NH_3 ? Will AgCl precipitate from a solution that is 0.01 M $AgNO_3$, 0.01 M NaCl and 1 M NH_3?

$K_d[Ag(NH_3)_2^{\oplus}] = 5.88 \times 10^{-8}$; $K_{sp}(AgCl) = 1.8 \times 10^{-10}$.

Solution :

Let us first assume that 0.01 M $AgNO_3$ shall combine with 0.02 NH_3 to form 0.01 M $Ag(NH_3)_2^{\oplus}$ and the consider its dissociation.

$AgNO_3$	+	$2NH_3$	$\longrightarrow$	$Ag(NH_3)_2^{\oplus}$	... Initial conc.
0.01 M		1 M		0	
0		(1–0.02)=0.98M		0.01 M	... at eq. conc.

$$Ag(NH_3)_2^{\oplus} \rightleftharpoons Ag^{\oplus} + 2NH_3$$

(0.01 – x)	x	(0.98 + 2x)	
= 0.01 M		≈ 0.98 M	... Equib. conc.

Since x <<< 1

$$K_d = \frac{[Ag^{\oplus}][NH_3]^2}{[Ag(NH_3)_2^{\oplus}]} = 5.88 \times 10^{-8}$$

$$\therefore \quad [Ag^{\oplus}] = \frac{5.88 \times 10^{-8} \times 0.01}{(0.98)^2} = 6.12 \times 10^{-10}\ M$$

Further, ionic product of AgCl = $[Ag^{\oplus}]\ [Cl^{\ominus}] = (6.12 \times 10^{-10})\ (0.01) = 6.12 \times 10^{-12}$

Because the ionic product is smaller than $K_{sp} = 1.8 \times 10^{-10}$, no precipitate should form.

SOLVED EXAMPLE

1. Simultaneous solubility of two sparingly soluble salts A & B having some common ion :
(A) is greater than their respective solubilities in separate solutions.
(B) lies in between their solubilities in separate solutions.
(C) is less than its solubility in separate solutions for more soluble salt, but is greater than its solubility in separate solution for less soluble salt.
(D) is less than their respective solubilities in separate solutions.

Ans. **(D)**

Sol. Ion produced from one salt will exert common ion effect on the solubility of other salt. As a result, solubility of both salts will decrease.

2. Upon mixing equal volumes of 0.02 M $AgNO_3$ & 0.16 M KCN solutions :
(Assume no hydrolysis of any ion).

Given : $Ag^+(aq.) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-(aq)$; $K_C = 10^{18}$

(A) $[NO_3^-] = 0.01$ M ; $[K^+] = 0.08$ M (B) $[CN^-] = 0.06$ M

(C) $[Ag(CN)_2^-] = 0.01$ M (D) All of these

Ans. **(D)**

Sol.

	$Ag^+(aq.)$	+ $2CN^-(aq)$	$\rightleftharpoons$	$[Ag(CN)_2]^-(aq)$; $K_C = 10^{18}$
t = 0	0.01	0.08		0
t = eq (≈ 0)				x ≈ 0.06

(Upon mixing equal volumes, volume gets doubled. So initial concentrations get halved).

3. In the above question $[Ag^+]$ is about :
(A) 2.78×10^{-18} M
(B) 1.67×10^{-19} M
(C) No free Ag^+ ions will be left in the solution
(D) Cannot be determined

Ans. **(A)**

Sol. $10^{18} = \dfrac{0.01}{(0.06)^2(x)} \Rightarrow x = 2.78 \times 10^{-18}$ M.

4. In a solution containing equal concentrations of X^-, Y^- & Z^-, MCl(s) (a readily soluble salt) is gradually added. If K_{sp} (MX) > K_{sp} (MY) > K_{sp} (MZ), then : (Assume no hydrolysis of any ion).
(A) MX will precipitate first.
(B) MY will precipitate first.
(C) MZ will precipitate first.
(D) Nothing can be said about which salt will precipitate first, as numerical data is not given.

Ans. **(C)**

Sol. The salt with least K_{sp} is precipitated first (in this case).

5. In above question, If $[X^-]_i : [Y^-]_i : [Z^-]_i = 100 : 10 : 1$ & $K_{sp}[MX] : K_{sp}[MY] : K_{sp}[MZ] = 10 : 0.1 : 1$, order of precipitation will be :

(A) MZ, then MX & MY at last (B) MY, then MX & MZ at last

(C) MX, then MY & MZ at last (D) MY, then MZ & MX at last

Ans. **(B)**

Sol. Calculation of concentration of M^+ required for precipitation (K_{sp}(salt) = [Anion] $[M^+]_{\text{min. req. for salt's pptn.}}$)

$MX : [M^+]_{MX} = \frac{10}{100} = 0.1\ M$

$MY : [M^+]_{MY} = \frac{0.1}{10} = 0.01\ M$

$MZ : [M^+]_{MZ} = \frac{1}{1} = 1\ M$

Order for precipitation is increasing order of $[M^+]_{salt}$, so, first MY, then MX and then MZ.

6. A solution which is 0.1 M in NaI and also 0.1 M in Na_2SO_4 is treated with solid $Pb(NO_3)_2$. Which compound, PbI_2 or $PbSO_4$, will precipitate first ? What is the concentration of anion of the least soluble compound when the more soluble one starts precipitating ? $K_{sp}(PbI_2) = 9 \times 10^{-9}$, $K_{sp}(PbSO_4) = 1.8 \times 10^{-8}$. Assume no hydrolysis of Pb^{2+} ion.

Ans. **($PbSO_4$, 0.02 M)**

Sol. (1) [NaI] = 0.1 M

$NaI \longrightarrow Na^+ + I^-$

0.1 M 0.1 M 0.1 M

(2) $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{-2}$

0.1 M 0.2 M 0.1 M

For precipitation of PbI_2,

$K_{sp}(PbI_2) = [Pb^{+2}][I^-]^2 = 9 \times 10^{-9}$

$\Rightarrow [Pb^{+2}] \times (0.1)^2 = 9 \times 10^{-9}$

$\Rightarrow [Pb^{+2}]_{req} = 9 \times 10^{-7}\ M$

For precipitation of $PbSO_4$,

$K_{sp}(PbSO_4) = [Pb^{+2}][SO_4^{-2}] = 1.8 \times 10^{-8}$

$\Rightarrow [Pb^{+2}] \times 0.1 = 1.8 \times 10^{-8}$

$\Rightarrow [Pb^{+2}]_{req} = 1.8 \times 10^{-7}\ M$

For precipitation of $PbSO_4$, required conc. of Pb^{+2} is less.

So, $PbSO_4$ precipitates first.

When PbI_2 (more soluble compound) starts precipitating, $[Pb^{2+}] = 9 \times 10^{-7}$ M.

Then, conc. of anion of less soluble salt can be obtained as follows :

$K_{sp}(PbSO_4) = [Pb^{+2}][SO_4^{-2}] = 1.8 \times 10^{-8} \Rightarrow (9 \times 10^{-7})[SO_4^{-2}] = 1.8 \times 10^{-8}$

$[SO_4^{-2}] = 0.02\ M$

7. 0.1 mole AgCl(s) is added to 1 litre H_2O. Next, crystals of NaBr are added until 75% of the AgCl is converted to AgBr(s), the less soluble silver halide. What is $[Br^-]$ in the resulting solution ? K_{sp} of AgCl is 1.75×10^{-10} and K_{sp} of AgBr is 5.25×10^{-13}. Assume no hydrolysis of Ag^+ ion.

Ans. **$(2.25 \times 10^{-4}$ M)**

Sol. $[Ag^+]\,[Cl^-] = 1.75 \times 10^{-10}$

$[Ag^+]\,[Br^-] = 5.25 \times 10^{-13}$

$$\Rightarrow [Br^-] = \frac{5.25\times10^{-13}}{1.75\times10^{-10}} \times [Cl^-] = \frac{5.25\times10^{-13}}{1.75\times10^{-10}} \times (0.075) = 2.25 \times 10^{-4}\ \text{M}.$$