IONIC EQUILIBRIUM

1. INTRODUCTION

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 :

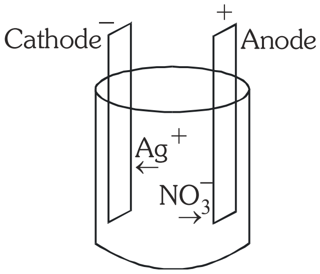
(a) Metallic or electronic conductors :

Those conductor which show conductivity due to motion of free electrons. Resistance increases with 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 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.

1.2 DEGREE OF DISSOCIATION / IONISATION

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

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

1.3 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	(b) Weak elecrolyte
$\alpha = 100\ \%$	$\alpha << 100\ \%$

(iv) Nature of solvent :

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

$H_2O \rightarrow \mu = 81$

$D_2O \rightarrow \mu = 79$

$C_6H_6 \rightarrow \mu = 2.5$

$CCl_4 \rightarrow \mu = 0$

Ex.1 Which one has greater α_1 or α_2 for the following equation :

(i) $NH_4OH + H_2O \rightarrow \alpha_1$

(ii) $NH_4OH + D_2O \rightarrow \alpha_2$

Sol. Dielectric constant of H_2O is more than that of D_2O, so $\alpha_1 > \alpha_2$

(v) Mixing of Ions :

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

1.4 OSTWALD'S DILUTION LAW (FOR WEAK ELECTROLYTE)

- For a weak electrolyte A^+B^- dissolved in water, if α is the degree of dissociation then

$$\begin{array}{llll} & AB & \rightleftharpoons & A^+ \quad + \quad B^- \\ \text{initial conc.} & C\,M & & 0 \qquad\quad 0 \\ \text{conc-at eq.} & C(1-\alpha)M & & C\alpha M \quad C\alpha M \end{array}$$

Then according to law of mass action,

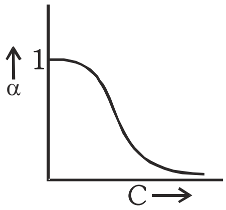
$$K_{diss} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha . C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = \text{dissociation constant of the weak electrolyte.}$$

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

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

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

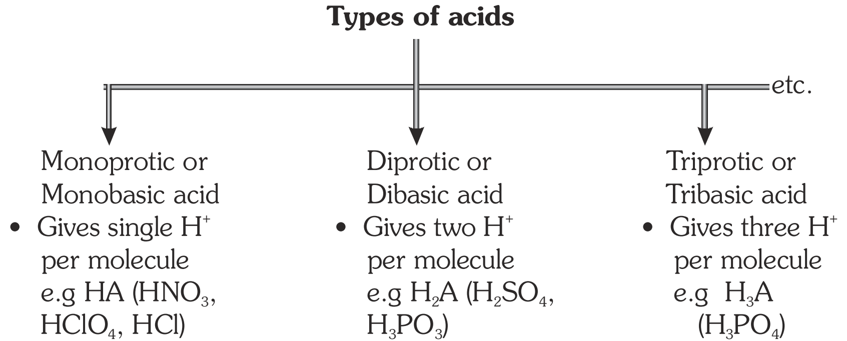
- As concentration increases $\Rightarrow$ α decreases
- At infinite dilution α reaches its maximum value, unity.



2. ACIDS BASES AND SALTS

2.1 Arrhenius concept :

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



Types of acids

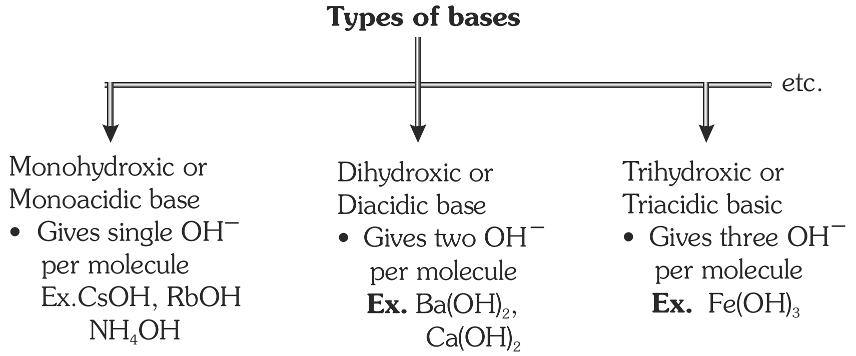
etc.

Monoprotic or Monobasic acid
- Gives single H^+ per molecule e.g HA (HNO_3, $HClO_4$, HCl)

Diprotic or Dibasic acid
- Gives two H^+ per molecule e.g H_2A (H_2SO_4, H_3PO_3)

Triprotic or Tribasic acid
- Gives three H^+ per molecule e.g H_3A (H_3PO_4)

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



Types of bases

etc.

Monohydroxic or Monoacidic base
- Gives single OH^- per molecule Ex.CsOH, RbOH NH_4OH

Dihydroxic or Diacidic base
- Gives two OH^- per molecule **Ex.** $Ba(OH)_2$, $Ca(OH)_2$

Trihydroxic or Triacidic basic
- Gives three OH^- 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) $HA \rightleftharpoons H^+ + A^-$;

$$K_a = \frac{[H^+][A^-]}{[HA]} = \text{dissocation or ionisation constant of acid.}$$

(c) Similarly

$BOH \rightleftharpoons B^+ + OH^-$;

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \text{dissocation or ionisation constant of base}$$

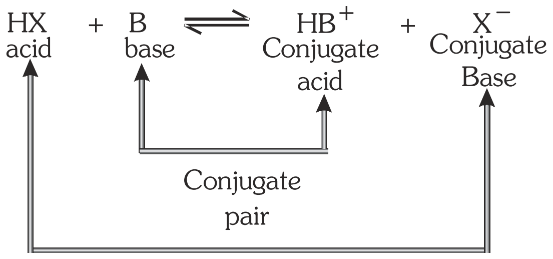
(d) Larger the value of K_a or K_b, stronger is the acid or base respectively.

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

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

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

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



- 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^+	+	$[Fe(H_2O)_5(OH)]^{2+}$

- 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^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	H_2O	H_3O^+
HSO_4^-	SO_4^{2-}	RNH_2	RNH_3^+
H_2O	OH^-		

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

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

base

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

acid

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

Bronsted - Lowery acids and bases can be

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

Table - 1

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^+, $N_2H_5^+$, PH_4^+, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$ etc.	$[Fe(H_2O)_5OH]^{2+}$ $[Al(H_2O)_5OH]^{2+}$ etc.
Anionic	HS^-, HSO_3^-, $H_2PO_4^-$,HSO_4^- HCO_3^-, HPO_4^{2-}, etc. all amphiprotic anions	Cl^-, Br^-, OH^-, HSO_4^-, CN^-, CO_3^{2-},SO_4^{2-},NH_2^-, CH_3COO^- ,etc. all amphiprotic anions

2.3 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^+, Fe^{2+}, Na^+, 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^-, H^-, NH_2^-, etc.

3. PROPERTIES OF WATER

(i) Molar concentration / Molarity of water :

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

(ii) Ionic product of water :

According to arrhenius concept, $H_2O \rightleftharpoons H^+ + OH^-$

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

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

(iii) Degree of dissociation of water :

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

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

(iv) Dissociation or ionisation constant of water :

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

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

Ex.2. 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.

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

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

Ex.3 Calculate ionic product of H_2O at 50°C.

Sol. $\Delta H = 13.7 \times 10^3$ *cal*

$$\log \frac{K_2}{10^{-14}} = \frac{13.7 \times 10^3}{2}\left(\frac{1}{298} - \frac{1}{323}\right)$$

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

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

Answer :(D)

Ex.5 ***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

Sol. (B)

4. Acidity and pH scale :

(i) Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water.

So greater then tendency to give H^+, more will be the acidic strength of the substance.

(ii) 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.

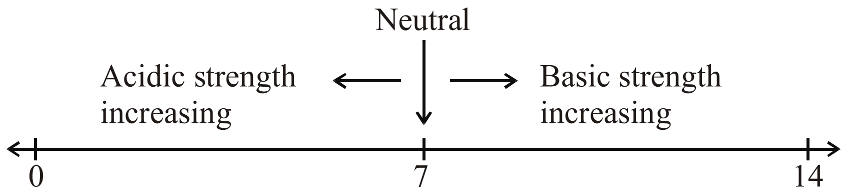
(iii) The concentration of H^+ ions is written in a simplified form introduced by **Sorenson** known as pH scale. pH is defined as negative logarithm of activity of H^+ ions.

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

(iv) Activity of H^+ ions is the molar concentration of free H^+ ions or H_3O^+ ions in a dilute solution, but unitless.

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

$$\left.\begin{array}{lcl} pH = 7 = pOH & \Rightarrow & \text{neutral} \\ pH < 7 \text{ or } pOH > 7 & \Rightarrow & \text{acidic} \\ pH > 7 \text{ or } pOH < 7 & \Rightarrow & \text{Basic} \end{array}\right\} \text{ at } 25\ ^\circ C$$



4.1 pH Calculation of different Types of solutions :

(a) Strong acid solution :

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

So $[H^+]$ = normality of strong acid solution

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

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Ex.6 Calculate pH of 10^{-8} M HCl solution.

Sol. $H_2O \rightleftharpoons H^+ + OH^-$

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

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

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

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

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

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

$$pH = -\log[H^+]$$

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

4.2 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 $[H^+]$

Ex.7 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)

$$\begin{array}{cccccc} H_2O & \rightleftharpoons & OH^- & + & H^+ \\ - & & (x + 10^{-7}) & & x \end{array}$$

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

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

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

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

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

$pH = 14 - 6.79 = 7.21$

4.3 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 $= N_1V_1$

Number of H^+ 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]

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \qquad \begin{bmatrix} \text{where} & N = M \times n \\ & n = \text{Basicity of acid} \end{bmatrix}$$

4.4 pH of mixture of two strong bases :

Similar to above calculation

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

$$\begin{bmatrix} \text{where} & N = M \times n \\ & n = \text{Acidity of base} \end{bmatrix}$$

Ex.8 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)

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

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

$pH = 3 - \log 8 = 2.1$

Ex.9 500 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.

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

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

$V_2 + V_1 = 1\ L$

$V_F = 100\ L$

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

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

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

$$H_2O \rightleftharpoons \underset{x}{H^+} + \underset{(x + 3 \times 10^{-7})}{OH^-}$$

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

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

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

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

4.5 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_1V_1

  Number of OH^- ions from II-solution = N_2V_2

If $N_1V_1 > N_2V_2$

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

Solution will be acidic in nature

If $N_2V_2 > N_1V_1$

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

Solution will be basic in nature

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

Ex.10 Calculate pH of mixture of (400 mL, $\frac{1}{200}$ M $Ba(OH)_2$) + (400 mL, $\frac{1}{50}$ M HCl)+(200 mL of water)

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

Ex.11 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) ?

Sol. 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

$\therefore$ $[OH^-]$ from NaOH $= \dfrac{2}{500} = 4 \times 10^{-3}$ M

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

$\therefore$ $pOH = 2.3979$

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

4.6 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^+	+	A^-
t = 0	C		0		0
t_{eq}	$C(1-\alpha)$		$C\alpha$		$C\alpha$

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

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 $\alpha < 0.1$ or 10%)

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

On increasing the dilution $\Rightarrow C\downarrow = \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

Ex.12 ***Calculate pH of : (a) 10^{-1} M CH_3COOH (b) 10^{-3} M CH_3COOH (c) 10^{-6} M CH_3COOH***
Take $K_a = 2 \times 10^{-5}$

Sol. **(a)** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$\begin{array}{ccc} C & 0 & 0 \\ C(1-\alpha) & C\alpha & C\alpha \end{array}$$

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

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

(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

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

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

(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, $2 \times 10^{-5} = 10^{-6}\frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$ or 95%

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

- 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 $\simeq$ pH of 10^{-6} M CH_3COOH $\simeq$ 6)

Ex.13 K_a for acid HA is 2.5×10^{-8} calculate for its decimolar solution at 25°C.
(i) % dissociation (ii) pH (iii) OH^- ion concentration

Sol. $HA \rightleftharpoons H^+ + A^-$

$$\begin{array}{ccc} C & 0 & 0 \\ C(1-\alpha) & C\alpha & C\alpha \end{array}$$

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

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

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

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

So $pH = 5 - \log 5 = 4.30$

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

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

Ex.14 ***Determine the degree of dissociation of 0.05 M NH_4OH at 25°C in a solution of pH = 10.***

Sol.

$NH_4OH \rightleftharpoons$	NH_4^+	+ OH^-
C	0	0

Given, pH = 10

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

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

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

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

Ex.15 ***The concentration of $[H^+]$ and $[OH^-]$ 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***

Sol. **(A)**

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

Ex.16 ***When a 0.1 N solution of an acid at 25°C has a degree of ionisation of 4%, the concentration of OH^- present is :***

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

Sol. **(C)**

$$[H^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3}\text{ M} \quad \text{or} \quad [OH^-] = \frac{10^{-14}}{[H^+]} = 2.5 \times 10^{-12}\text{ N}$$

Ex.17 ***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 :***

Sol.

	$CH_3COOH \rightleftharpoons$	CH_3COO^-	+ H^+
Initially	0.1	0	0
at equilibrium	0.1(1–0.0132)	0.1× 0.0132	0.1× 0.0132

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{0.1\times0.0132\times0.1\times0.0132}{0.1(1-0.0132)} = 1.76 \times 10^{-5}$$

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

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

- Weak acid and Strong acid both will contribute H^+ ion.
- For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To 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 $[H^+]$ from SA $= C_1$
  the weak acid will dissociate as follows.

$$\begin{array}{llll} HA & \rightleftharpoons \; H^+ & + & A^- \\ C_2 & \quad\; 0 & & 0 \\ C_2(1-\alpha) & \quad C_2\alpha + C_1 & & C_2\alpha \end{array} \qquad K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \qquad (\alpha <<< 1)$$

(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^+ ion concentration $= C_1 + C_2\alpha$

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

4.8 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

$$\begin{array}{lllll|llll} & HA_1 & \rightleftharpoons \; H^+ & + & A_1^- & HA_2 & \rightleftharpoons \; H^+ & + & A_2^- \\ t=0 & C_1 & \quad 0 & & 0 & C_2 & \quad 0 & & 0 \\ \text{At eq.} & C_1(1-\alpha_1) & C_1\alpha_1 + C_2\alpha_2 & & C_1\alpha_1 & C_2(1-\alpha_2) & C_2\alpha_2 + C_1\alpha_1 & & C_2\alpha_2 \end{array}$$

$$K_{a_1} = \frac{C_1\alpha_1(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \qquad\Bigg|\qquad K_{a_2} = \frac{(C_2\alpha_2 + C_1\alpha_1)C_2\alpha_2}{C_2(1-\alpha_2)}$$

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

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

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

$$= \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

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

Ex.18 ***Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH_3COOH solution given that K_{a_1} (HOCl) = 2×10^{-4} , K_{a_2} (CH_3COOH) = 2×10^{-5}***

Also calculate OH^-, OCl^-, CH_3COO^-

Sol. Final solution volume become double

$C_1 = 0.01, \quad C_2 = 0.1$

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

$$= \sqrt{2\times10^{-6} + 2\times10^{-6}} = 2 \times 10^{-3}$$

$$pH = 3 - \log 2 = 3 - 0.3010 = 2.69$$

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

$$HOCl \rightleftharpoons H^+ + OCl^-$$

$C_1(1-\alpha_1) \qquad C_1\alpha_1 + C_2\alpha_2 \qquad C_1\alpha_1$

$[OCl^-] = C_1\alpha_1$

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

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

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$C_2(1-\alpha_2) \qquad C_1\alpha_1 + C_2\alpha_2 \qquad C_2\alpha_2$

$[CH_3COO^-] = C_2\alpha_2$

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

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

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

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

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

4.9 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 equilbria exist.

If

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

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

I step

$$H_2A + H_2O \rightleftharpoons HA^- + H_3O^+$$

at eq. $c(1-\alpha_1) \qquad c\alpha_1(1-\alpha_2) \qquad (c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{eq})_1[H_2O] = \frac{[H_3O^+][HA^-]}{[H_2A]} = \mathbf{K_{a_1}}$$

II step

$$HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+$$

at eq. $c\alpha_1(1-\alpha_2) \qquad c\alpha_1\alpha_2 \qquad (c\alpha_1 + c\alpha_1\alpha_2)$

$$(K_{eq})_2[H_2O] = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = \mathbf{K_{a_2}}$$

$$\therefore \quad \mathbf{K}_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1-\alpha_2)]}{c(1-\alpha_1)} \qquad\qquad \mathbf{K}_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2)]}{c\alpha_1(1-\alpha_2)}$$

$$= \frac{[c\alpha_1(1+\alpha_2)][\alpha_1(1-\alpha_2)]}{1-\alpha_1} \quad \text{....... (i)} \qquad\qquad = \frac{[c\alpha_1(1+\alpha_2)]\alpha_2}{1-\alpha_2} \quad \text{...... (ii)}$$

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, $[H_3O^+]$ can be calculated as

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

Finally, for calculation of 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, $\mathbf{K}_{a_2} << \mathbf{K}_{a_1}$ 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 $\quad \mathbf{K}_{a_1} = \dfrac{C\alpha_1 \times \alpha_1}{1-\alpha_1}$

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

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

Ex.19 Calculate pH of $[HS^-]$, $[S^{2-}]$, $[Cl^-]$ 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.

Sol. HCl + H_2S

0.1   0.1

$C_1 = C_2 = 0.1$

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

$$H_2S \rightleftharpoons H^+ + HS^-$$

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

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

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

$$HS^- \rightleftharpoons S^{2-} + H^+$$

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

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

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

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

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

4.10 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 $[H^+]$ of both acids should be equal i.e.

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

4.11 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, $pK_b = -\log K_b$

5. 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.

5.1 Classification of salts :

The salts may be classified into following categories.

(a) Normal salt :

(i) The salt formed by the loss of all possible protons (replaceable H^+ 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, $Fe(OH)_2$ Cl, $Bi(OH)_2Cl$ etc.

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

5.2 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^+ and OH^- ions of water.

Salt hydrolysis is reverse process of neutralization.

$$\text{Water} + \text{Salt} \rightleftharpoons \text{Acid} + \text{Base}\ ; \qquad \Delta H = +ve$$

5.2.1 Hydrolysis of strong acid - weak base [SA - WB] type salt –

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

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

$$NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

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

(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 $[H^+]$ is increased.

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

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

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

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

For weak Base $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{....(ii)}$$

For water $H_2O \rightleftharpoons H^+ + OH^-$

$$K_w = [OH^-]\,[H^+] \qquad \text{.....(iii)}$$

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

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} = [H^+]\,[OH^-]$$

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

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

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

$$\begin{array}{llll} NH_4^+ + H_2O \rightleftharpoons & NH_4OH & + \ H^+ & \\ C & 0 & 0 & \text{(initial concentration at equilibrium)} \\ C - Ch & Ch & Ch & \end{array}$$

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

Since h <<<< 1

then $(1 - h) \approx 1$

$\therefore \quad K_h = Ch^2$

$$\Rightarrow \quad h = \sqrt{\frac{K_h}{C}}$$

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

(vi) pH of the solution :

$$pH = -\log [H^+]$$

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

On taking – log on both sides

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

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

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

Ex.20 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^+] and pH of solution?

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

Sol. (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) $[H^+] = Ch$

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

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

Ex.21 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}.

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

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

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

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

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

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

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

$$= 5.35\ gL^{-1}$$

5.2.2 Hydrolysis of [WA – SB] type salt :

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

$$NaCN + H_2O \rightleftharpoons NaOH + HCN$$

$$Na^+ + CN^- + H_2O \rightleftharpoons Na^+ + OH^- + HCN$$

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

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

(ii) Solution is basic in nature as $[OH^-]$ increases.

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

(iv) Relation between K_h, K_w, K_a

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

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

$$\frac{[HCN][OH^-]}{[CN^-]} \times \frac{[CN^-][H^+]}{[HCN]} = [H^+][OH^-]$$

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

(v) Degree of hydrolysis :

$$\begin{array}{llll} CN^- + H_2O \rightleftharpoons & HCN & + \ OH^- & \\ C & 0 & 0 & \text{Initial concentration at equlibrium} \\ C - Ch & Ch & Ch & \end{array}$$

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

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

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

$$\therefore \quad K_h = Ch^2$$

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

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

(vi) pH of the solution

$[OH^-] = Ch$

$$\left[OH^-\right] = \sqrt{\frac{K_w \times C}{K_a}}$$

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

On taking – log on both sides

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

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

Ex.22 Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN, K_a for HCN is 6.2× 10^{-12}.

Sol. NaCN is a salt of strong base NaOH and weak acid HCN. Na^+ does not react with water whereas CN^- reacts with water as here under

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

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

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

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

$[OH^-] = x$

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

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

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

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

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

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

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

Ex.23. Calculate for 0.01 N solution of sodium acetate -

(i) Hydrolysis constant

(ii) Degree of hydrolysis

(iii) pH

Given K_a of CH_3COOH = 1.9×10^{-5}.

Sol. For $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

	CH_3COONa	CH_3COOH	$NaOH$
Initial	C	0	0
After	C(1–h)	Ch	Ch

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

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

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

pOH = 5.64

$\therefore$ pH = 14 – 5.64 = 8.36

5.2.3 Hydrolysis of (WA - WB) type salt :

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

$$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$$

$$NH_4^+ + CN^- + H_2O \rightleftharpoons NH_4OH + HCN$$

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

$NH_4^+ + CN^- + H_2O \rightleftharpoons NH_4OH + HCN$

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \quad \text{..... (i)}$$

$$\frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]} \times \frac{[NH_4^+][OH^-]}{[NH_4OH]} \times \frac{[H^+][CN^-]}{[HCN]} = [H^+][OH^-]$$

$K_h \times K_b \times K_a = K_w$

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

(ii) Degree of Hydrolysis :

NH_4^+	+	CN^- + H_2O	$\rightleftharpoons$	NH_4OH	+	HCN	
C		C		0		0	Initial concentration
							at equilibrium
C – Ch		C – Ch		Ch		Ch	

$$K_h = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-]}$$

Since h <<<< 1
Then (1 – h) ≈ 1

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

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

(iii) pH of the solution

From eq. (iii)

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$[H^+] = \frac{K_a \times [HCN]}{[CN^-]}$$

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

Since h <<<< 1, (1 – h) ≈ 1

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

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

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

On taking – log on both sides

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

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

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

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

Ex.24 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 $K_b = 1.8 \times 10^{-5}$

Sol.	NH_4OH	+	CH_3COOH	→	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

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

Ex.25 In the following which one has highest / maximum degree of hydrolysis.

(1) 0.01 M – NH_4Cl	***(2) 0.1 M –NH_4Cl***
(3) 0.001 M –NH_4Cl	***(4) Same***

Sol. [3]

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

Ex.26 In the following which one has lowest value of degree of hydrolysis.

(1) 0.01 M – CH_3COONH_4	***(2) 0.1 M – CH_3COONH_4***
(3) 0.001 M – CH_3COONH_4	***(4) Same***

Sol. [4]

Ex.27 ***Find out the concentration of [H^+] in 0.1M CH_3COONa solution ($K_a = 10^{-5}$)***

Sol. *Salt is [WA – SB] type*

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

Ex.28 Calculate the degree of hydrolysis of a mixture containing 0.1N NH_4OH and 0.1N HCN

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

Sol. *Salt is [WA – WB]*

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

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

5.2.4 Hydrolysis of [SA – SB] type salt :

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

$$NaCl + H_2O \rightleftharpoons NaOH + HCl$$

$$Na^+ + Cl^- + H_2O \rightleftharpoons Na^+ + OH^- + H^+ + Cl^-$$

$H_2O \rightleftharpoons H^+ + OH^-$ (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

5.2.5 Hydrolysis of Amphiprotic Anion :

$NaHCO_3$, NaHS, etc., can undergo ionisation to from H^+ ion and can undergo hydrolysis to from OH^- (Na^+ ion is not hydrolysed)

(a) (i) $HCO_3^- + H_2O \xrightleftharpoons{\text{ionisation}} CO_3^{2-} + H_3O^+$ (acid)

(ii) $HCO_3^- + H_2O \xrightleftharpoons{\text{hydrolysis}} H_2CO_3 + OH^-$ (base)

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

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

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

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

$$HCO_3^- + H_2O \xrightleftharpoons{Kw/Ka_1} H_2CO_3 + OH^-$$

$$HCO_3^- + H_2O \xrightleftharpoons{Ka_2} CO_3^{-2} + H_3O^+$$

$\because$ H^+ and OH^- also react

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

$$\therefore [H_2CO_3] \approx [CO_3^{-2}] \quad .....(1)$$

$$\frac{Kw}{Ka_1} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} \Rightarrow \frac{1}{Ka_1} = \frac{[H_2CO_3]}{[H^+][HCO_3^-]} \quad ....(2)$$

$$\frac{[CO_3^{-2}][H^+]}{[HCO_3^-]} = Ka_2 \qquad \text{....(3)}$$

Divide (2) by (3)

$$[H^+] = \sqrt{Ka_1Ka_2} \Rightarrow pH = \frac{pKa_1 + pKa_2}{2}$$

Ex.29 Calculate the pH of 0.5 M Na_3PO_4 in aqueous solution ?

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

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

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

$$pK_a = -\log K_a = 12.38$$

$$\text{or} \quad pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\log C$$

$$pH = 13.04$$

DO YOUR SELF-1

Q.1 Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be - **[AIEEE-2005]**

(A) 3.88×10^{6} (B) 3.98×10^{8} (C) 3.98×10^{-6} (D) 3.68×10^{-6}

Q.2 In aqueous solution the ionization constants for carbonic acid are

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$ **[AIEEE–2010]**

Select the correct statement for a saturated 0.034 M solution of the carbonic acid :-

(A) The concentration of H^+ is double that of CO_3^{2-}

(B) The concentration of CO_3^{2-} is 0.034 M

(C) The concentration of CO_3^{2-} is greater than that of HCO_3^-

(D) The concentrations of H^+ and HCO_3^- are approximately equal

6 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.

6.1 Types of buffer solutions

(A) Simple buffer solution (B) Mixed buffer solution

6.2 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 dissociated completely.

$$CH_3COONH_4 \longrightarrow CH_3COO^- + NH_4^+$$

If a strong acid such as HCl is added then

$$HCl \longrightarrow H^+ + Cl^-$$

The H^+ ions from the added acid (HCl) combine with CH_3COO^- ions to form CH_3COOH, which is a weak acid so will not further ionized.

Thus there is no rise in H^+ ion concentration and the pH remains constant.

$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$ (Weak acid)

- If a strong base is added as NaOH

$NaOH \longrightarrow Na^+ + OH^-$

$NH_4^+ + OH^- \rightleftharpoons NH_4(OH)$ (Weak base)

Thus change in OH^- ion concentration is resisted by NH_4^+ 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 :-

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

6.3 MIXED BUFFER SOLUTIONS :

6.3.1 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

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (Weakly ionised)

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$ (Highly ionised)

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

$CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO^-$.

Thus there is no increase in OH^- ion concentration and hence the pH of the solution remains constant.

pH of a acidic buffer solution (Henderson equation) :

Consider a buffer mixture (acidic buffer)

HA + NaA ($CH_3COOH + CH_3COONa$)

where A = CH_3COO, $A^- = CH_3COO^-$

$HA \rightleftharpoons H^+ + A^-$

$NaA \longrightarrow Na^+ + A^-$

Applying law of mass action to dissociation equilibrium of HA

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

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

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

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

$[A^-]$ = 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.)

Note : A solution can act as buffer only if ratio of concentration of salt to acid is between 0.1 to 10.

CH_3COOH	: CH_3COONa	
1	10	$pH = pK_a + 1$
10	1	$pH = pK_a - 1$

Thus pH range of an acidic buffer solution is $(pK_a + 1)$ to $(pK_a - 1)$

pH range = $pK_a \pm 1$

Maximum buffer action will be only when ratio of concentration of acid and salt is 1. So for maximum buffer action, $pH = pK_a$

Ex.30 ***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)***

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

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

Moles of CH_3COONa in solution $\frac{100 \times 0.2}{1000} = 0.02$

Let, volume of 0.2 acetic acid added = V mL

$\therefore$ Moles of acetic acid $= \frac{V \times 0.2}{1000}$

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

$\therefore$ V = 5.49 mL

Ex.31 ***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)***

Sol. *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.*	

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

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

Ex.32 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}.

Sol. (a) *Initially [Acetic acid] =1 M*

[Acetate] = 1 M

Now 0.2 moles of HCl are added to it.

	HCl +	CH_3COO^- →	CH_3COOH +	Cl^-
Mole before reaction	0.2	1	1	0
Mole after reaction	0	0.8	1.2	0.2

$\therefore$ *New* $[CH_3COOH] = 1.2\ ;\ [CH_3COO^-] = 0.8$

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

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

(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^- →	CH_3COOH +	Cl^-
Mole before reaction	0.2	0.1	0.1	0
Mole after reaction	0.1	0	0.2	0.1

$\therefore\quad [H^+]$ *from free HCl = 0.1 M*

$\therefore\quad pH = 1$

Note: *CH_3COOH no doubt gives H^+ but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H^+ from CH_3COOH may be neglected.*

6.3.2 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.

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (Weakly ionised)

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ (Highly ionised)

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

$NH_4^+ + OH^- \rightleftharpoons NH_4OH$

If a few drops of a acid (HCl) are added the H^+ from acid combine with NH_4OH to form H_2O and NH_4^+ ions.

$NH_4OH + H^+ \rightleftharpoons NH_4^+ + H_2O$

Thus the addition of acid does not increase the H^+ ion concentration and hence pH remains unchanged.

- **pH of basic buffer solution :**

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]} = \frac{K_b[Base]}{[Salt]}$$

(NH_4^+ mainly comes from salt)

taking –log on both side

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

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

❖ **pOH range :**

A solution can act as buffer solution only if ratio of concentration of salt to base is from 0.1 to 10.

NH_4OH	:	NH_4Cl	
1		10	$pOH = pK_b + 1$
10		1	$pOH = pK_b - 1$

So pOH range is $pK_b \pm 1$

❖ **Condition for maximum buffer action :**

$[NH_4OH]$	:	$[NH_4Cl]$
1		1

$$pOH = pK_b + \log\frac{1}{1}$$

$pOH = pK_b$ and $pH = 14 - pK_b$

Maximum buffer action because pH remains constant.

***Ex.33* 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 ?**

Sol. $B + H_2O \rightleftharpoons BH^+ + OH^-$

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

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

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

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

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

Let, volume of HCl taken = xL

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

After the reaction, millimole of BH^+ formed = 0.01 × (x)

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

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

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

$\therefore$ Volume of base = 0.917 L

***Ex.34* 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***

Sol. **(B)** $pOH = pk_b + \log\frac{[salt]}{[base]}$ for NH_4Cl = 0.5 and NH_4OH = 0.1

pOH will be maximum and so pH will be minimum.

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Ex.35 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.

Sol. ***Case I :***

	BOH	+	HCl	$\longrightarrow$	BCl	+	H_2O
Millimole before reac.	a		$0.1\times 5=0.5$		0		0
Millimole after reac.	(a–0.5)		0		0.5		0.5

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

$$\because \quad pH = 10.04 \quad so \quad pOH = 3.96$$

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

Case II :

	BOH	+	HCl	$\longrightarrow$	BCl	+	H_2O
Millimole before reac.	a		$0.1\times 20 = 2$		0		0
Millimole after reac.	(a–2)		0		2		2

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

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

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

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

7. 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 change 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)

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

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

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

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

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

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

Indicator	**pH range**	**Colour change (acidic to basic medium)**	**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

Ex.36 The disso. const. of a basic indicator is 2×10^{-7}. Calculate its pH range.

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

Ex.37 The pH range of an acidic indicator HIn is 4.0 - 5.2 . Calculate dissociation constant. Also calculate $\frac{In^-}{HIn}$ for the appearence of solution in single colour.

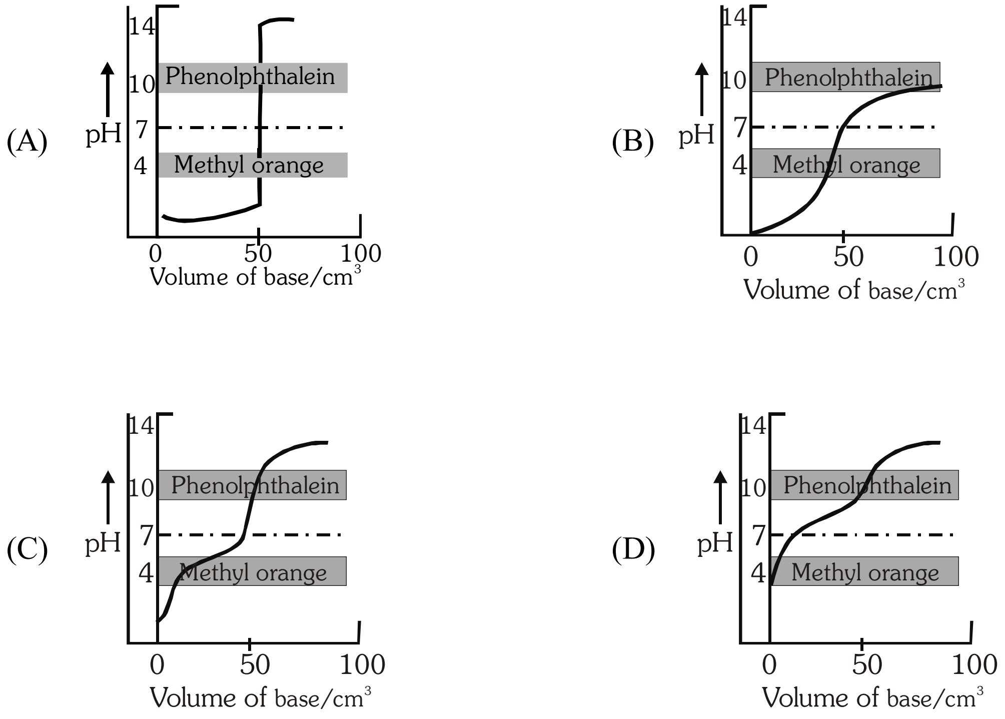
Sol. Diss. constant = 2.5×10^{-5} , 4

9.1 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.



Titration curves : (A) strong base with strong acid ; (B) weak base with strong acid ; (C) strong base with weak acid ; (D) weak base with weak acid.

7.2 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.

7.3 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.

7.4 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.

Ex.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.

Sol. $HBPh \rightleftharpoons H^+ + BPh^-$

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

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

$\therefore \quad pH = 5.165$

Also if pH = 5.84

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

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

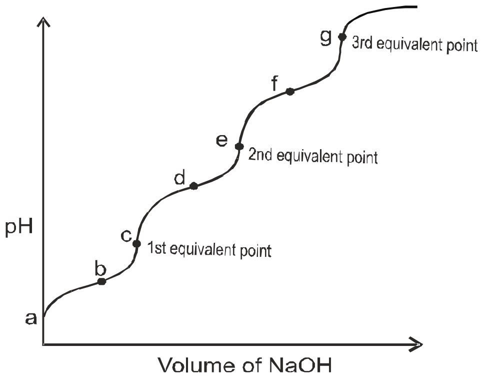
7.5 Titration of Poly protic acid v/s S.B. :

50 mL of 0.1 M H_3PO_4 agent 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

$pK_{a1} = 3 \qquad pK_{a2} = 7$, $pK_{a3} = 11$



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

(b) $H_3PO_4 \quad + \quad NaOH \quad \rightleftharpoons \quad NaH_2PO_4 + H_2O$

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 $H_2PO_4^-$ amphoteric species

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

(d)

$$\begin{array}{lcccc} & NaH_2PO_4 & + \ NaOH & \longrightarrow Na_2HPO_4 & + \ H_2O \\ t=0 & 5\text{ M mol} & 2.5\text{ M mol} & 0 & - \\ & 2.5\text{ M mol} & & 2.5\text{ M mol} & - \end{array}$$

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

(e) HPO_4^{2-} solution (amphoteric species)

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

(f)

$$\begin{array}{cccc} Na_2HPO_4 & + \ NaOH & \longrightarrow Na_3PO_4 & + \ H_2O \\ 5 & 2.5 & 0 & - \\ 2.5 & 0 & 2.5 & - \end{array}$$

$pH = pK_{a3} + \log 1/1 = 0$

(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

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

$pH = 12.3$

(i) 90 mL

$$\begin{array}{ccc} NaH_2PO_4 \ + & NaOH & \longrightarrow Na_2HPO_4 + H_2O \\ 5 & 4 & 0 \\ 1 & 0 & 4 \end{array}$$

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

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10. SOLUBILITY (s) & SOLUBILITY PRODUCT (K_{sp})

10.1 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

10.2 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 elecrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into Ag^+ and Cl^- ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions, Ag^+ and Cl^- ions.

$$AgCl_{(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} Ag^+_{(aq)} + Cl^-_{(aq)}$$

according to law of mass action

$$K = \frac{[Ag^+].[Cl^-]}{[AgCl]}$$

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

So, $\quad K.[AgCl] = [Ag^+].[Cl^-]$

$\therefore \quad K_{sp} = [Ag^+] . [Cl^-]$

- **K_{sp} for $CaCl_2$** $\quad CaCl_2(s) \rightleftharpoons Ca^{+2}(aq) + 2Cl^-(aq)$
  Solubility product in terms of concentration of ions $\quad K_{sp} = [Ca^{+2}]\ [Cl^-]^2$
- **K_{sp} for $AlCl_3$** $\quad AlCl_3(s) \rightleftharpoons Al^{+3}(aq) + 3Cl^-(aq)$
  Solubility product in terms of concentration of ions $K_{sp} = [Al^{+3}]\ [Cl^-]^3$
- **General form** $\quad A_xB_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$
  $K_{sp} = [A^{+y}]^x\ [B^{-x}]^y$

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.

10.3 APPLICATION OF SOLUBILITY PRODUCT (K_{sp}) :

10.3.1 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.

$$\begin{array}{lccc} AB(s) & \rightleftharpoons & A^+(aq) & + \ B^-(aq) \\ a & & 0 & 0 \\ (a-s) & & s & s \end{array}$$

$K_{sp} = [A^+]\ [B^-]$

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

(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.

$$\begin{array}{llll} AB_2(s) & \rightleftharpoons & A^{+2}(aq) + & 2B^{-}(aq) \\ a & & 0 & 0 \\ a-s & & s & 2s \end{array}$$

$K_{sp} = [A^{+2}]\,[B^-]^2$

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

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

(iii) General form :

$$\begin{array}{lllll} A_xB_y(aq) & \rightleftharpoons & xA^{+y}(aq) & + & yB^{-x}(aq) \\ a & & 0 & & 0 \\ a-s & & xs & & ys \end{array}$$

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

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

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

10.4 COMMON ION EFFECT ON SOLUBILITY :

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 reestablished so, the solubility of substances decreases.

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

$$\begin{array}{llllll} AgCl & \rightleftharpoons & Ag^+ & + & Cl^- & \quad CM.NaCl \\ & & SM & & SM & \quad \text{(Let solubility of AgCl is S mol L}^{-1}) \end{array}$$

$K_{sp} = [Ag^+]\,[Cl^-]$

$K_{sp} = S^2$

In NaCl solution

$$\begin{array}{lllll} NaCl & \longrightarrow & Na^+ & + & Cl^- \\ C & & C & & C \end{array}$$

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

$$\begin{array}{lllll} AgCl & \rightleftharpoons & Ag^+ & + & Cl^- \\ & & S' & & S'+C \end{array}$$

$K_{sp} = [Ag^+]'\,[Cl^-]'$

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

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

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

10.5 SIMULTANEOUS SOLUBILITY :

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

10.6 SOLUBILITY IN APPROPRIATE BUFFER SOLUTIONS :

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

10.7 EFFECT ON SOLUBILITY BECAUSE OF COMPLEX FORMATION :

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

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

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

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

10.8 CONDITION OF PRECIPITATION /IONIC PRODUCT (IP 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.

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

10.9 SELECTIVE PRECIPITATION :

When the k_{sp} values differ then one of the salt can be selectively precipitated.

Q.1 Solid $Ba(NO_3)_2$ is gradully dissolved in a 1.0×10^{-4} M Na_2CO_3 solution.At what concentration of Ba^{2+} will a precipitate begin to form?

(K_{SP} for Ba $CO_3 = 5.1 \times 10^{-9}$) **[AIEEE-2009]**

(A) 8.1×10^{-8} M (B) 8.1×10^{-7} M (C) 4.1×10^{-5} M (D) 5.1×10^{-5} M

DO YOUR SELF-2

Q.1 The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be **[AIEEE-2003]**

(A) 1×10^{-15} (B) 1×10^{-10} (C) 4×10^{-15} (D) 4×10^{-10}

Q.2 The solubility of $Mg(OH)_2$ is x mole/lit. then its solubility product is- **[AIEEE-2002]**

(A) x^3 (B) $5x^3$ (C) $4x^3$ (D) $2x^2$

Q.3 The molar solubility in mol L^{-1} of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{SP}. 's' is given in terms of K_{SP} by relation : **[AIEEE-2004]**

(A) $s = (K_{SP} / 128)^{1/4}$ (B) $s = (128K_{SP})^{1/4}$ (C) $s = (256K_{SP})^{1/5}$ (D) $s = (K_{SP}/256)^{1/5}$

Q.4 The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is - **[AIEEE-2005]**

(A) 1.0×10^{-4} M (B) 2.0×10^{-6} M (C) 4.0×10^{-10} M (D) 1.6×10^{-4} M

Q.5 In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is - **[AIEEE-2007]**

$$AgIO_3 \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution ?

(A) 28.3×10^{-2} g (B) 2.83×10^{-3} g (C) 1.0×10^{-7} g (D) 1.0×10^{-4} g

Q.6 The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt. BA, will be - **[AIEEE-2008]**

(A) 9.58 (B) 4.79 (C) 7.01 (D) 9.22

Q.7 Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is :- **[AIEEE–2010]**

(A) 5.0×10^{-8} g (B) 1.2×10^{-10} g (C) 1.2×10^{-9} g (D) 6.2×10^{-5} g

Q.8 At 25° C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ?**[AIEEE–2010]**

(A) 8 (B) 9 (C) 10 (D) 11

Ex. 39. (i) $Al_2(SO_4)_3(s) \rightleftharpoons 2Al^{+3}(aq) + 3SO_4^{-2}(aq)$

$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108\, S^5$$

(ii) $Na_2KPO_4(s) \rightleftharpoons 2Na^+(aq) + K^+(aq) + PO_4^{-3}(aq)$

$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$

(iii) $NaKRbPO_4(s) \rightleftharpoons Na^+(aq) + K^+(aq) + Rb^+(aq) + PO_4^{-3}(aq)$

$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 \times (S)^{1+1+1+1} = S^4$$

Ex. 40. If solubility product of the base $M(OH)_3$ is 2.7×10^{-11}, the concentration of OH^- will be

(1) 3×10^{-3} (2) 3×10^{-4} (3) 10^{-3} (4) 10^{-11}

Answer :(3)

Ex. 41. The solubility of $BaSO_4$ in water is 1.07×10^{-5} mol dm^{-3}. Estimate its solubility product.

Sol. *Solubility equilibrium for $BaSO_4$ is*

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

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

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

Ex. 42. 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})

Sol. *The solubility equilibrium of AgBr is*

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

The molar solubility S of AgBr is given by

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

The solubility in g dm^{-3} = *molar solubility* (*mol* dm^{-3}) × *molar mass* (*g* mol^{-1})

$$= 7.2 \times 10^{-7} \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3}$$

Ex. 43. What is the maximum volume of water required to dissolve 1 g of calcium sulphate at 25°C. For calcium sulphate, $K_{sp} = 9.0 \times 10^{-6}$.

Sol. $CaSO_4\,(aq) \rightleftharpoons Ca^{2+}\,(aq) + SO_4^{2-}\,(aq)$

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

$K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = S^2$

$$\therefore S = \sqrt{K_{sp}} = \sqrt{9.0 \times 10^{-6}}$$

$$= 3 \times 10^{-3} \text{ mol } L^{-1}$$

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

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

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

Ex. 44. Equal volumes of 0.04 M $CaCl_2$ and 0.0008 M Na_2SO_4 are mixed. Will a precipitate form? K_{sp} for $CaSO_4 = 2.4 \times 10^{-5}$

Sol.

$$\begin{array}{lccccccccc} & CaCl_2 & + & Na_2SO_4 & \rightarrow & CaSO_4 & + & 2NaCl \\ \text{Millimole added} & 0.04\,V & & 0.0008 \times V & & 0 & & 0 \end{array}$$

Suppose V mL of both are mixed

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

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

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

Thus, $[Ca^{2+}]\,[SO_4^{2-}]$ *in solution* $< K_{sp}$

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

$\therefore$ $CaSO_4$ *will not precipitate.*

Ex. 45. Calculate simultaneous solubility of silverthiocyanate and sliver bromide in water given that k_{sp} of silver thiocyanate = 10^{-12} and k_{sp} of silver bromide = 5×10^{-13} respectively.

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

$$AgSCN \rightleftharpoons \underset{x+y}{Ag^+} + \underset{x}{SCN^-} \qquad AgBr \rightleftharpoons \underset{x+y}{Ag^+} + \underset{y}{Br^-}$$

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

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

On solving we get, $x = 2y$

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

Ex. 46. What $[H^+]$ must be maintained in saturated $H_2S(0.1\ M)$ to precipitate CdS but not ZnS, if $[Cd^{2+}] = [Zn^{2+}] = 0.1$ initially ?

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

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

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

Sol. *In order to prevent precipitation of ZnS*

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

(ionic product)

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

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

This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x. Thus for $H_2S \rightleftharpoons 2H^+ + S^{2-}$

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

$$\text{or} \quad x = [H^+] = 0.1\ M$$

$\therefore$ *No ZnS will precipitate at a concentration of H^+ greater than 0.1 M*

Ex. 47. What must be the concentration of aq. NH_3(eq.) which must be added to a solution containing 4×10^{-3} M Ag^+ 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 $[Ag(NH_3)_2]^+$ is $K_{formation} = \frac{10^8}{6}$.

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

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

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

This quantity is so small that almost all the Ag^+ ion will be consumed.

$$\begin{array}{llll} Ag^+ \;+ & 2NH_3 \rightleftharpoons & [Ag(NH_3)_2]^+ & K = \dfrac{10^8}{6} \\ 4\times10^{-3} & b & 0 & \\ 1.8\times10^{-7} & (b-8\times10^{-3}) & 4\times10^{-3} & K = \dfrac{10^8}{6} = \dfrac{4\times10^{-3}}{1.8\times10^{-7}\times(b-8\times10^{-3})^2} \end{array}$$

$\Rightarrow \quad b = 0.0445$

Ex. 48. 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 ?

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

Sol.

$$\begin{array}{lll} Ag^+ \quad + & 2NH_3 \rightleftharpoons & [Ag(NH_3)_2^+] \\ 0.10\text{ M} & 2.00 & 0 \\ 0.10-0.10 & (2-0.20\text{ M}) & 0.10\text{ M} \\ = 0 & = 1.80\text{ M} & \end{array}$$

It is assumed that all Ag^+ ions have been complexed and only x amount is left

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

$\therefore \quad x = 1.93 \times 10^{-9}$ M = $[Ag^+]$ *undisolved*

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

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

Hence, AgCl (s) will not precipitate.

Ex. 49. What is the concentration of Ag^+ 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?

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

Sol. *Let us first assume that 0.01 M $AgNO_3$ shall combine with 0.02 NH_3 to form 0.01 M $Ag(NH_3)_2^+$ and the consider its dissociation.*

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

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$Ag(NH_3)_2^+$	Ag^+	$2NH_3$
$(0.01 - x)$ $= 0.01$ M	x	$(0.98 + 2x)$ ≈ 0.98 M
		....Equib. conc.

Since $x <<< 1$

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

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

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

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

ANSWERS

DO YOUR SELF-1

Q.1 Ans.(C)	Q.2 Ans.(D)	Q.3 Ans.(D)

DO YOUR SELF-2

Q.1 Ans.(C)	Q.2 Ans.(C)	Q.3 Ans.(D)
Q.4 Ans.(A)	Q.5 Ans.(B)	Q.6 Ans.(C)
Q.7 Ans.(C)	Q.8 Ans.(C)	

PREVIOUS YEARS MISCELLANEOUS QUESTION

Q.1 What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ? **[JEE '1998]**

Ans. pH = 11.3010

$[H^+]=10^{-2}$ 200 ml

$[OH^-] = 10^{-2}$ 300 ml

	H^+	+	OH^-	$\rightleftharpoons$	H_2O
t = 0 mm	2		3		–
t mm	–		1		–

$$\left[OH^-\right]=\frac{1}{500}$$

$$\left[OH^-\right]=2\times10^{-3}$$

pOH = 3 – log 2

pH = 11 + log 2

= 11.3010

Q.2 The pH of 0.1 M solution of the following salts increases in the order **[JEE 1999]**

(A) NaCl < NH_4Cl < NaCN < HCl
(B) HCl < NH_4Cl < NaCl < NaCN
(C) NaCN < NH_4Cl < NaCl < HCl
(D) HCl < NaCl < NaCN < NH_4Cl

Ans. (B)

Sol.

NaCl	pH = 7
NH_4Cl	pH < 7
NaCN	pH > 7
HCl	pH < 7

HCl < NH_4Cl< NaCl < NaCN

Q.3 A buffer solution can be prepared from a mixture of **[JEE 1999]**

(A) sodium acetate and acetic acid in water

(B) sodium acetate and hydrochloric acid in water

(C) ammonia and ammonium chloride in water

(D) ammonia and sodium hydroxide in water.

Ans. (A, B, C)

Sol. (A) True
(B) AcNa + HCl → HAc + NaCl True
(C) True
Ans. (A) (B) & (C)

Q.4 The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6}M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. **[JEE '1999]**

Ans. $s = 1.203 \times 10^{-3}$M

Q.5 The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **[JEE 2000]**

[Given : $10^{-1.92} = 1.2 \times 10^{-2}$, $\sqrt{5.5678} = 2.5627$, log (1.2213) = 0.0868]

Q.5 Ans. pH = 0.91325

Sol. $$\text{ppm} = 10 = \frac{p_{SO_2}}{P_{Total}} \times 10^6$$

$p_{SO_2=10^{-5}}$

$\left[H^+\right] = \left[H_2SO_3\right] = 1.3653 \times 10^{-5}$

pH = 4.86

Q.6 For sparingly soluble salt ApBq, the relationship of its solubility product (L_s) with its solubility (S) is - **[JEE 2001]**

(A) $L_s = S^{p+q}.\ p^p.\ q^q$ (B) $L_s = S^{p+q}.\ p^p.\ q^p$ (C) $L_s = S^{pq}.\ p^p.\ q^q$ (D) $L_s = S^{pq}.\ (p.q)^{p+q}$

Ans. (A)

$$ApBq \rightleftharpoons pA^{+q} + qB^{-p}$$

$L_s = (ps)^P\ (qs)^q$

$L_s = p^p\ q^q\ \ s^{p+q}$

Q.7 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is 1.75×10^{-5} M. **[JEE 2002]**

Ans. (a) 0.0175% , (b) 4.757

Sol. $$\underset{.1-x}{HAc} \rightleftharpoons \underset{x+.1}{H^+} + \underset{x}{Ac^-}$$

$$\underset{-}{HCl} \rightleftharpoons \underset{.x+.1}{H^+} + \underset{.1}{Cl^-}$$

$$1.75 \times 10^{-5} = \frac{(.1)(x)}{(.1)}$$

$x = 1.75 \times 10^{-5}$

$$\alpha_{HAc} = \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$$

$\%\alpha_{HAc} = .0175$

$[H^+] = .1$

pH = 1

(b) $HCl + NaOH \rightarrow NaCl + H_2O$

t = 0 100 $\frac{6}{40} \times 1000$

t = 0 100 150

$HAc + NaOH \rightarrow AcNa + H_2O$

t = 0 100 50 – –

t 50 – 50 –

[pH = pKa = 5 – log 1.75]

[pH = 4.75]

Q.8 A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16}M sulphide ion. If K_{sp}, MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first ? **[JEE 2003]**

(A) FeS (B) MnS (C) HgS (D) ZnS

Ans. (C)

Sol. $I.P = [M^{+2}]\,[S^{2-}] = (10^{-3})\,(10^{-16}) = 10^{-19}$

$I.P > K_{SP}$

HgS will ppt first

Q.9 Will the pH of water be same at 4°C and 25°C ? Explain. **[JEE 2003]**

Ans. No, it will be > 7 at 0°C.

Sol. $H_2O \rightleftharpoons H^+ + OH^-$ $\quad \Delta H = +Ve$

On increasing temp reaction will move in forward direction hence $[H^+]$ will increase and pH will decrease

Q.10 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given $Ka(HA) = 5 \times 10^{-6}$ and $\alpha << 1$. **[JEE 2004]**

Ans. pH = 9

Sol. $pH = \frac{1}{2}\left[p^{Kw} + p^{Ka} + \log C_0\right]$

$$= = \frac{1}{2}[14 + 6 - \log 5 + \log 0.1]$$

$$= = \frac{1}{2}[20 - 1 - 0.7]$$

$$= \frac{1}{2}[18.3]$$

pH = 9.15

Q.11 HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is

(A) 0.01% (B) 0.0001% (C) 0.1% (D) 0.5% **[JEE 2004]**

Ans. (A)

Sol. $K_h = \frac{K_w}{K_a} = 10^{-9}$

$$h = \sqrt{\frac{K_h}{C_0}} = \sqrt{10^{-8}} = 10^{-4}$$

$\%h = 10^{-2} = 0.01\%$

Q.12 CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is

(A) 1.6×10^{-11} (B) 8×10^{-11} (C) 5×10^{-5} (D) 2×10^{-2} **[JEE 2005]**

Ans. (B)

Sol.	CH_3NH_3OH	+	HCl	→	CH_3NH_3Cl	+	H_2O
t = 0 mole	0.1		0.08		–		–
t mole	.02		–		.08		–

$$pOH = pKb + \log 4$$

$$pOH = 4 - \log 5 + \log 4$$

$$-\log\left[OH^-\right] = -\log\left[\frac{5}{4}\times 10^{-4}\right]$$

$$\left[OH^-\right] = \frac{5}{4}\times 10^{-4}$$

$$\left[H^+\right] = \frac{10^{-14}}{\frac{5}{4}\times 10^{-4}} = \frac{4}{5}\times 10^{-10} = 8\times 10^{-11}$$ Ans. [B]

Q.13 If $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $K_1 = 1.6 \times 10^3$ and **[JEE 2006]**

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 = 6.8 \times 10^3$.

The formation constant of $[Ag(NH_3)_2]^+$ is :

(A) 6.08×10^{-6} (B) 6.8×10^{-6} (C) 1.6×10^3 (D) 1.088×10^7

Ans. **(D)**

Q.14 The species present in solution when CO_2 is dissolved in water :

(A) CO_2, H_2CO_3, HCO_3^-, CO_3^{2-} (B) H_2CO_3, CO_3^{2-} **[JEE 2006]**

(C) CO_3^{2-}, HCO_3^- (D) CO_2, H_2CO_3

Ans. **(A)**

Q.15 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is **[JEE 2008]**

($K_w = 1 \times 10^{-14}$ at 25°C)

(A) 3.7×10^{-13} M (B) 3.2×10^{-7} M (C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

Ans. **(D)**

Sol. No. of geq of BOH = no. of geq of HCℓ

$$2.5 \times \frac{2}{5} = \frac{2}{15} \times V$$

$v = 7.5$ ml

$$[\text{salt}] = \frac{1}{10} M$$

$$K_h = \frac{C_0 h^2}{1-h} \Rightarrow 10^{-2} = \left(\frac{1}{10}\right)\frac{h^2}{1-h}$$

$1 - h = 10h^2$

$10h^2 + h - 1 = 0$

$$h = \frac{-1+\sqrt{1+40}}{20}$$

$$h = \left(\frac{\sqrt{41}-1}{20}\right)$$

Q.16 Solubility product constants (K_{SP}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order :

(A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$ **[JEE 2008]**

(C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$

Ans. **(D)**

Sol. MX $S_1^2 = 4 \times 10^{-8}$ $S_1 = 2 \times 10^{-4}$ M

MX_2 $4S_2^3 = 3.2 \times 10^{-14}$ $S_2 = 8 \times 10^{-15}$ M

M_3X $27S_3^4 = 27 \times 10^{-16}$ $S_3 = 10^{-4}$ M

$S_1 > S_3 > S_2$

$MX > M_3X > MX_2$

Ans. (D)

Q.17 The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is **[JEE 2009]**

Ans. **(8)**

Sol. $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$

$$h = \sqrt{\frac{K_h}{C_o}} = \sqrt{\frac{10^{-10}}{10^{-2}}} = 10^{-4}$$

$$pH = \frac{1}{2}\,[pKw + pKa + \log Co]$$

$$pH = \frac{1}{2}\,[14 + 4 + \log 10^{-2}]$$

$$pH = \frac{1}{2}[16] = 8$$

Ans. 08

Q.18 Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) – **[JEE 2009]**

(A) HNO_3 and CH_3COOH (B) KOH and CH_3COONa

(C) HNO_3 and CH_3COONa (D) CH_3COOH and CH_3COONa

Ans. **(C), (D)**

EXERCISE-S-I

IONIZATION CONSTANTS AND pH

Q.1 Calculate the number of H^+ present in one ml of solution whose pH is 13. [$N_A = 6.022 \times 10^{23}$] **IE0001**

Q.2 (i) K_w for H_2O is 9×10^{-14} at 60°C. What is pH of water at 60°C. (log 3 = 0.47) **IE0002**

(ii) What is the nature of solution at 60°C whose **IE0003**

(a) pH = 6.7 (b) pH = 6.35

Q.3 The value of K_w at the physiological temperature (37°C) is 2.56×10^{-14}. What is the pH at the neutral point of water at this temperature? (log 2 = 0.3) **IE0004**

Q.4 Calculate pH of following solutions :

(a) 0.1 M HCl **IE0005**

(b) 0.1 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) ($\log\sqrt{1.8} = 0.13$) **IE0006**

(c) 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$) **IE0007**

(d) 10^{-8} M HCl [$\sqrt{401} = (20.02)$] [log 1.051 = 0.03] **IE0008**

(e) 10^{-10} M NaOH **IE0009**

(f) 10^{-6} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) **IE0010**

(g) 10^{-8} M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) [$\sqrt{401} = (20.02)$] [log 1.051 = 0.03] **IE0011**

(h) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times. (log2 = 0.3) **IE0012**

(i) 10^{-3} mole of KOH dissolved in 100 L of water. **IE0013**

(j) Equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution **IE0014**

Q.5 Calculate :

(a) K_a for a monobasic acid whose 0.10 M solution has pH of 4.50.

(b) K_b for a monoacidic base whose 0.10 M solution has a pH of 10.50. **IE0015**

Q.6 Calculate the ratio of degree of dissociation (α_2/α_1) when an acetic acid solution is diluted 100 times. Assume $\alpha << 1$, even on dilution. [Given $K_a = 10^{-5}$ M] **IE0016**

Q.7 Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids.[Given $K_{a(CH_3COOH)} = 1.8\times10^{-5}$; $K_{a(HCN)} = 6\times10^{-10}$, $\sqrt{3} = 1.732$] **IE0017**

Q.8 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 ? **IE0018**

Q.9 The pH of aqueous solution of ammonia is 10. Find molarity of solution. K_b (NH_4OH) = 10^{-5}. **IE0019**

Q.10 The solution of weak monoprotic acid which is 0.01 M, has pH = 3. Calculate K_a of weak acid. **IE0020**

Q.11 Boric acid is a weak monobasic acid. It ionizes in water as

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ : K_a = 8 \times 10^{-10}$$

Calculate pH of 0.5 M boric acid. **[log 2 = 0.3]** **IE0021**

MIXTURE OF TWO OR MORE ACIDS / BASES

Q.12 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :- [log 5.05 = 0.7] **IE0022**

Q.13 Calculate pH of following solutions : [log 0.3 = – 0.522]

(a) 0.1 M H_2SO_4 (50 ml) + 0.4 M HCl 50 (ml)

(b) 0.1 M HA + 0.1 M HB [K_a (HA) = 5×10^{-5} ; K_a (HB) = 4×10^{-5}] **IE0023**

Q.14 Calculate pH of a solution containing 0.1M HA (Ka = 10^{-5}) & 0.1 M HCl. **IE0024**

POLYPROTIC ACIDS & BASES

Q.15 What are the concentration of H^+, $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ in a 0.1 M solution of oxalic acid ?

[$K_1 = 10^{-2}$ M and $K_2 = 10^{-5}$ M] $\left[\sqrt{41} = 6.4\right]$ **IE0025**

Q.16 Calculate pH of 0.2 M – $B(OH)_2$ solution.

($K_{b_1} = 2 \times 10^{-5}$; $K_{b_2} = 4 \times 10^{-11}$, log2 = 0.3) **IE0026**

HYDROLYSIS

Q.17 What is the OH^- concentration of a 0.18 M solution of CH_3COONa. [$K_a(CH_3COOH) = 1.8 \times 10^{-5}$] **IE0027**

Q.18 Calculate the pH of a 2.0 M solution of NH_4Cl. [K_b (NH_3) = 2×10^{-5}] **IE0028**

Q.19 0.25 M solution of pyridinium chloride $C_5H_6N^+Cl^-$ was found to have a pH of 2.699. What is K_b for pyridine, C_5H_5N ? (log2 = 0.3010) **IE0029**

Q.20 Calculate the extent of hydrolysis & the pH of 0.02 M CH_3COONH_4.

[K_b (NH_3)= 1.8×10^{-5}, $K_a(CH_3COOH) = 1.8 \times 10^{-5}$] **IE0030**

Q.21 Calculate the percent hydrolysis in a 0.06 M solution of KCN. [K_a(HCN) = 6×10^{-10}] **IE0031**

Q.22 What is the pH of 0.1M $NaHCO_3$? $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$ for carbonic acids. [log5 = 0.7] **IE0032**

Q.23 The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}

(a) Calculate the pH of a 0.001 M solution of $ZnCl_2$

(b) What is the basic dissociation constant of $Zn(OH)^+$? **IE0033**

BUFFER SOLUTION

Q.24 Calculate the pH of solution containing 0.1M - HCN and 0.1M - NaCN. Ka of HCN = 10^{-9} **IE0034**

Q.25 Calculate the pH of solution containing 0.2 M - NH_4OH and 0.1 M – NH_4Cl. K_b of NH_4OH = 1.8×10^{-5}. (log2 = 0.3, log 1.8 = 0.26) **IE0035**

Q.26 0.4 mole CH_3COONa is added in 500 ml 0.4 M –CH_3COOH solutions. What is the pH of final solution ? K_a of CH_3COOH = 1.8×10^{-5}. (log2 = 0.3, log 1.8 = 0.26). **IE0036**

Q.27 A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x. **IE0037**

Q.28 Determine $[OH^-]$ of a 0.050 M solution of ammonia to which sufficient NH_4Cl has been added to make the total [NH_4^+] equal to 0.100.[$K_{b(NH_3)} = 1.8 \times 10^{-5}$] **IE0038**

Q.29 Calculate the pH of a solution containing 0.2 M HCO_3^- and 0.1 M CO_3^{2-}

[$K_1(H_2CO_3) = 4 \times 10^{-7}$; K_2 (HCO_3^-) = 4×10^{-11}] **IE0039**

Q.30 Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M $HC_2H_3O_2$ and 50.0 mL of 0.100 M NaOH.[$K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$, $pK_a = 4.74$] **IE0040**

Q.31 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, calculate pH. [log 2 = 0.3] **IE0041**

Q.32 Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3 . [K_b (NH_3) = 1.8×10^{-5}, $pK_b = 4.74$, log 3 = 0.477] **IE0042**

Q.33 In 100 ml buffer solution of 0.1M CH_3COOH & 0.1M CH_3COONa, how many millimoles of NaOH should be added to increase it's pH by 0.3. **IE0043**
Given (log 2 = 0.3)

ACID BASE REACTIONS & TITRATIONS

Q.34 Calculate OH^- concentration at the equivalent point when a solution of 0.2 M acetic acid is titrated with a solution of 0.2 M NaOH. K_a for the acid = 10^{-5}. **IE0044**

Q.35 Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid, CH_3COOH, with 22.0 mL of 0.10 M NaOH. [$K_a = 2 \times 10^{-5}$, log2 = 0.3] **IE0045**

Q.36 Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40M HCl.[$K_b = 2 \times 10^{-5}$] **IE0046**

Q.37 CH_3COOH (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml 20 ml, 25 ml, 40 ml, 50 ml of NaOH. K_a of CH_3COOH is 2×10^{-5}. **IE0047**
[log 2 = 0.3010, log3 = 0.4771]

INDICATORS

Q.38 For the acid indicator thymol blue, pH is 3 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with $[H^+] = 4 \times 10^{-3}$ M. **IE0048**

Q.39 Bromophenol blue is an acid indicator with a K_a value of 6×10^{-5} . What % of this indicator is in its basic form at a pH of 5 ? **IE0049**

Q.40 At what pH does an indicator change colour if the indicator is a weak acid with $K_{ind} = 4 \times 10^{-4}$. For which one(s) of the following neutralizations would the indicator be useful ? Explain.
(a) NaOH + CH_3COOH (b) HCl + NH_3 (c) HCl + NaOH **IE0050**

Q.41 An acid indicator has a K_a of 3×10^{-5}. The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75 % blue? [log 3 = 0.477] **IE0051**

SOLUBILITY & SOLUBILITY PRODUCT'S

Q.42 The values of K_{sp} for the slightly soluble salts MX and QX_2 are each equal to 4.0×10^{-18}. Which salt is more soluble? Explain your answer fully. **IE0052**

Q.43 The solubility of $PbSO_4$ in water is 0.0608 g/L. Calculate the solubility product constant of $PbSO_4$. Molar mass $PbSO_4$ = 304 g/mole **IE0053**

Q.44 How many mole CuI ($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ? **IE0054**

Q.45 A solution of saturated CaF_2 is found to contain 4×10^{-4} M fluoride ion. Calculate the K_{sp} of CaF_2. Neglect hydrolysis. **IE0055**

Q.46 The solubility of ML_2 (formula weight = 60 g/mol) in water is 2.4×10^{-5} g/100 mL solution. Calculate the solubility product constant for ML_2. **IE0056**

Q.47 Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3 , $K_{sp} = 1.08 \times 10^{-23}$ **IE0057**

Q.48 Determine the solubility of AgCl in 0.1 M $BaCl_2$. [K_{sp} for AgCl = 1×10^{-10}] **IE0058**

Q.49 Calculate solubility of $Ca_3(PO_4)_2$ ($K_{sp} = 10^{-15}$) in presence of 0.1 M $CaCl_2$ solution. **IE0059**

SIMULTANEOUS SOLUBILITY

Q.50 Calculate the Simultaneous solubility of AgSCN and AgBr. K_{sp} (AgSCN) = 3.2×10^{-12}, K_{sp}(AgBr) = 8×10^{-13}. **IE0060**

COMPLEX FORMATION

Q.51 Calculate the solubility of AgCl in 0.2 M - NH_3 solution.
Given : K_{sp} of AgCl = 2×10^{-10} , K_f of $Ag(NH_3)_2^+ = 8 \times 10^6$. **IE0061**

SOLUBILITY, CONSIDERING HYDROLYSIS

Q.52 Calculate the solubility of AgCN in a buffer solution at pH = 3.0. .
Given : K_{sp} of AgCN = 8×10^{-10} , K_a of HCN = 5×10^{-10}. **IE0062**

PRECIPITATION

Q.53 A solution has a Mg^{2+} concentration of 0.0010 mol/L. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is [K_{sp}= 1.2×10^{-11}]
(a) 10^{-5} mol/L (b) 10^{-3} mol/L ? **IE0063**

Q.54 200 ml of 2×10^{-4}M – $AgNO_3$ solution is mixed with 400 ml of 1.2×10^{-6} M – NaCl solution. Predict whether precipitation of AgCl will occur or not. Ksp of AgCl = 2×10^{-10}. **IE0064**

Q.55 Calculate the minimum mass of Na_2SO_4 needed to just start precipitation of $BaSO_4$ from 500 ml of 2×10^{-5}M - $BaCl_2$ solution. Ksp of $BaSO_4$ = 8×10^{-8}.
[Na = 23, S = 32, O = 16] **IE0065**

EXERCISE S-II

Q.1 What are the concentrations of H^+, HSO_4^-, SO_4^{2-} and H_2SO_4 in a 0.20 M solution of sulphuric acid?

Given: $H_2SO_4 \longrightarrow H^+ + HSO_4^-$; strong [$\sqrt{521} = 22.83$]

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$; $K_2 = 10^{-2}$ M **IE0066**

Q.2 Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms and both can react with water to give a basic solution [log 2 = 0.3]

$Nic (aq) + H_2O (l) \rightleftharpoons NicH^+ (aq) + OH^- (aq)$

$NicH^+ (aq) + H_2O (l) \rightleftharpoons NicH_2^{2+} (aq) + OH^- (aq)$

K_{b_1} is 8×10^{-7} and K_{b_2} is 10^{-10}. Calculate the approximate pH of a 0.20 M solution. **IE0067**

Q.3 An aqueous solution contains 0.01 M RNH_2 ($K_b = 2 \times 10^{-6}$) & 10^{-4} M NaOH. The concentration of OH^- is nearly : **IE0068**

Q.4 Calculate the pH of 1.0×10^{-3} M sodium phenoxide, $NaOC_6H_5$. K_a for HOC_6H_5 is 0.6×10^{-10}. [log3 = 0.48] **IE0069**

Q.5 Calculate the pH of 0.1 M solution of (i) $NaHCO_3$, (ii) Na_2HPO_4 and (iii) NaH_2PO_4. Given that:

$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.2 \times 10^{-7}$ M

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 4.8 \times 10^{-11}$ M

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = 7.5 \times 10^{-3}$ M

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = 6.2 \times 10^{-8}$ M

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = 1.0 \times 10^{-12}$ M

(log 4.2 = 0.62, log 4.8 = 6.8, log 6.2 = 0.80, log 7.5 = 0.88) **IE0070**

Q.6 An ammonia-ammonium chloride buffer has a pH value of 9 with $[NH_3] = 0.25$. What will be the new pH if 500 ml 0.1 M KOH is added to 200 ml buffer solution ($K_b = 2 \times 10^{-5}$) [log 2 = 0.3] **IE0071**

Q.7 10 ml of 0.1M weak acid HA($k_a = 10^{-5}$) is mixed with 10 ml 0.2M HCl and 10 ml 0.1M NaOH. Find the value of $[A^-]$ in the resulting solution. **IE0072**

Q.8 150 ml of 0.5 M HCN (Ka = 3.75×10^{-9}) was reacted with 1.5 M KOH for complete neutralisation. What will be molarity of HCN at equilibrium. **IE0073**

Q.9 How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $Ag(NH_3)_2^+$ is the only complex formed. [$K_f(Ag(NH_3)_2^+) = 1 \times 10^8$; K_{sp} (AgBr) = 5×10^{-13}]

$[\sqrt{50} \simeq 7]$ **IE0074**

Q.10 Calculate solubility of PbI_2 ($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°, which is 90% dissociated.

$$\left(\frac{14}{(0.81)(3.6)}\right)^{1/3} = 1.7$$

IE0075

EXERCISE O-I

Single correct

Q.1 The conjugate acid of NH_2^- is

(A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4 **IE0076**

Q.2 Which of the following is not a Bronsted acid:-

(A) $CH_3NH_4^+$ (B) CH_3COO^- (C) H_2O (D) HSO_4^- **IE0077**

Q.3 In the reaction

$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$, the conjugate base of HNO_3 is :-

(A) H_2O (B) H_3O^+ (C) NO_3^- (D) H_3O^+ and NO_3^- **IE0078**

Q.4 Out of the following, amphiprotic species in aqueous medium are

I: HPO_3^{2-} II OH^- III $H_2PO_4^-$ IV HCO_3^-

(A) I, III, IV (B) I and III (C) III and IV (D) All **IE0079**

Q.5 When ammonia is added to water, it decreases the concentration of which of the following ion

(A) OH^- (B) H_3O^+ (C) NH_4^+ (D) NH_4^+ & OH^- **IE0080**

Q.6 Which of the following pair is Lewis acid & Lewis base & Product of these is also Lewis base

(A) BF_3 , NH_3 (B) $SiCl_4$, $2Cl^-$ (C) $\overset{\oplus}{CH_3}$, $^{\ominus}OC_2H_5$ (D) All of these **IE0081**

Q.7 Ionic product of water will increase, if :-

(A) Pressure is decreased (B) H^+ is added

(C) OH^- is increased (D) Temperature is increased **IE0082**

Q.8 At 60°C, pure water has $[H_3O^+]=10^{-6.7}$mol/lit. what is the value of K_W at 60°C :-

(A) 10^{-6} (B) 10^{-12} (C) 10^{-67} (D) $10^{-13.4}$ **IE0083**

Q.9 Liquid NH_3 ionises to a slight extent. At a certain temperature its self ionization constant $K_{SIC(NH_3)} = 10^{-30}$. The number of NH_4^+ ions present per 100 cm^3 of pure liquid are

(A) 10^{-15} (B) 6.022×10^8 (C) 6.022×10^7 (D) None **IE0084**

Q.10 The pH of solution is increased from 3 to 6. Its H^+ ion conc. will be :-

(A) Reduced to half (B) Doubled

(C) Reduced by 1000 times (D) Increased by 1000 times **IE0085**

Q.11. pOH of [**1/200**] mol/m^3 H_2SO_4 (aq.) solution at 25°C is-

(A) 2 (B) 5 (C) 9 (D) 12 **IE0086**

Q.12 Degree of dissociation of 0.1 N CH_3COOH is :- (Dissociation constant = 1×10^{-5})

(A) 10^{-5} (B) 10^{-4} (C) 10^{-3} (D) 10^{-2} **IE0087**

Q.13 The pH of a 0.02 M ammonia solution which is 5% ionised will be :-

(A) 2 (B) 11 (C) 5 (D) 7 **IE0088**

Q.14 The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is

(A) 1 (B) 2 (C) 3 (D) 11 **IE0089**

Q.15 The concentration of $[H^+]$ and concentration of $[OH]^-$ of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water $=1 \times 10^{-14}$]

(A) 0.02×10^{-3} M and 5×10^{-11} M (B) 1×10^{-3} M and 3×10^{-11} M

(C) 2×10^{-3} M and 5×10^{-12} M (D) 3×10^{-2} M and 4×10^{-13} M **IE0090**

Q.16 What is the quantity of NaOH present in 250 cc of the solution, so that it gives a pH = 13 :-

(A) 10^{-13} g (B) 10^{-1} g (C) 1.0 g (D) 4.0 g **IE0091**

Q.17 An aqueous solution of HCl is 10^{-9} M HCl. The pH of the solution should be:-

(A) 9 (B) Between 6 and 7 (C) 7 (D) Unpredictable **IE0092**

Q.18. The moles of H^+ from H_2O in a 1*l*, $\sqrt{5} \times 10^{-7}$ M HCl solution at 25°C, is

$(\sqrt{5} = 2.23)$

(A) 10^{-7} (B) 6.85×10^{-8} (C) 3.85×10^{-8} (D) 10^{-8} **IE0093**

Q.19 Which one of the following has highest pH:-

(A) Distilled water (B) 1 M NH_3

(C) 1 M NaOH (D) Water saturated with chlorine **IE0094**

Q.20 8 gm NaOH and 4.9 gm H_2SO_4 are present in one litre of the solution. What is its pH

(A) 1 (B) 13 (C) 12 (D) 2 **IE0095**

Q.21 10 ml of $\frac{M}{200}$ H_2SO_4 is mixed with 40 ml of $\frac{M}{200}$ H_2SO_4. The pH of the resulting solution is

(A) 1 (B) 2 (C) 2.3 (D) none of these **IE0096**

Q.22 Which of the following solution will have pH close to 1.0?

(A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH

(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH

(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH

(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH **IE0097**

Q.23 A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:

(A) 3 (B) 4 (C) 3000 (D) 10000 **IE0098**

Q.24 The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be :

(A) 5.0×10^{-5} (B) 5.0×10^{15} (C) 5.0×10^{-15} (D) 0.2×10^{5} **IE0099**

Q.25 If pK_b for fluoride ion at 25° C is 10.4, the ionisation constant of hydrofluoric acid in water at this temperature is : (log2 = 0.3)

(A) 4×10^{-11} (B) 3×10^{-3} (C) 2.5×10^{-4} (D) 2×10^{-2} **IE0100**

Q.26 pH of an aqueous solution of NaCl at 85°C should be

(A) 7 (B) > 7 (C) < 7 (D) 0 **IE0101**

Q.27 1 cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be

(A) 7 (B) 3 (C) 4 (D) 1 **IE0102**

Q.28 The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 0.5. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be

(A) 100% (B) 50% (C) 25% (D) none of these **IE0103**

Q.29 What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 2×10^{-9} and $K_w = 1.0 \times 10^{-14}$

(A) 2 (B) 5.26 (C) 8.2 (D) 9.6 **IE0104**

Q.30 The compound whose 0.1 M solution is basic is

(A) Ammonium acetate (B) Ammonium chloride

(C) Ammonium sulphate (D) Sodium acetate **IE0105**

Q.31 If equilibrium constant of

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

is 1.8×10^{-5}, equilibrium constant for

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$ is

(A) 1.8×10^{-9} (B) 1.8×10^{9} (C) 5.55×10^{-9} (D) 5.55×10^{10} **IE0106**

Q.32 The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be :

(A) 8.58 (B) 4.79 (C) 7.01 (D) 9.22 **IE0107**

Q.33 The highest pH value is of :-

(A) 0.1 M NaCl (B) 0.1 M NH_4Cl

(C) 0.1 M CH_3COONa (D) 0.1 M CH_3COONH_4 **IE0108**

Q.34 pH of K_2S solution is:-

(A) 7 (B) Less than 7 (C) More than 7 (D) 0 **IE0109**

Q.35 Degree of Hydrolysis of $\frac{N}{100}$ solution of KCN is (Given Ka = 1.6×10^{-9})

(A) 2.5×10^{-3} (B) 2.5×10^{-2} (C) 2.5×10^{-4} (D) 2.5×10^{-5} **IE0110**

Q.36 A solution of $FeCl_3$ in water acts as acidic due to :-

(A) Acidic impurities (B) Ionisation (C) Hydrolysis of Fe^{3+}(D) Dissociation **IE0111**

Q.37 If 40 ml of 0.2 M KOH is added to 160 ml of 0.1 M HCOOH [$K_a = 2\times10^{-4}$], the pOH of the resulting solution is [log 2 = 0.3]

(A) 3.4 (B) 3.7 (C) 7 (D) 10.3 **IE0112**

Q.38 1 M NaCl and 1M HCl are present in an aqueous solution. The solution is

(A) not a buffer solution and with pH < 7 (B) not a buffer solution with pH > 7

(C) a buffer solution with pH < 7 (D) a buffer solution with pH > 7 **IE0113**

Q.39 The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is :

(A) 4.5 (B) 2.5 (C) 9.5 (D) 7.0 **IE0114**

Q.40 To a 50 ml. of 0.05M formic acid, how much volume of 0.10M sodium formate must be added to get a buffer solution of pH = 4.0 ?

(pK_a of the acid is 3.7) (log2 = 0.3)

(A) 40 ml. (B) 4 ml. (C) 50 ml. (D) 100 ml. **IE0115**

Q.41 Which can act as buffer :-

(A) NH_4OH + NaOH

(B) HCOOH + HCl

(C) 40 ml. of 0.1 M NaCN + 20 ml. of 0.1 M HCl

(D) All of them **IE0116**

Q.42 If equal volume of 0.05 M ammonium hydroxide solution is dissolved in 0.001 M ammonium chloride solution. What will be the OH^- ion concentration of this solution : $\sqrt{32.8} = 5.73$

$K_b(NH_4OH) = 1.8 \times 10^{-5}$

(A) 3.0×10^{-3} (B) 4.66×10^{-4} (C) 9.0×10^{-3} (D) 9.0×10^{-4} **IE0117**

Q.43 Calculate the pH of a buffer prepared by mixing 600 cc of 0.6 M NH_3 and 400 cc of 0.5 M NH_4Cl. K_b for $NH_3 = 1.8 \times 10^{-5}$, (log 1.8 = 0.26)

(A) 11.3 (B) 9.0 (C) 9.52 (D) 5 **IE0118**

Q.44 pK_b for NH_4OH at certain temperature is 4.74. The pH of basic buffer containing equimolar concentration of NH_4OH and NH_4Cl will be:-

(A) 7.74 (B) 4.74 (C) 2.37 (D) 9.26 **IE0119**

Q.45 On addition of NaOH to CH_3COOH solution, 60% of the acid is neutralised. If pK_a of CH_3COOH is 4.7 then the pH of the resulting solution is :-

(A) More than 4.7 but less than 5.0 (B) Less than 4.7 but more than 4.0

(C) More than 5.0 (D) Remains unchanged **IE0120**

Q.46 Henderson equation $pH - pK_a = 5$ will be applicable to an acidic buffer when :-

(A) [Acid] = [Conjugate base] (B) [Acid] × 10^5 = [Conjugate base]

(C) [Acid] = [Conjugate base] × 10^5 (D) [acid] = 2 [conjugate base] **IE0121**

Q.47 What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ($K_a = 3 \times 10^{-5}$ at 25°C) to obtain a buffer solution of pH 4.7

[log2 = 0.3]

(A) 4.52×10^{-2} mol (B) 3.52×10^{-2} mol (C) 2.52×10^{-2} mol (D) 3×10^{-2} mol **IE0122**

Q.48 In a buffer solution the ratio of concentration of NH_4Cl and NH_4OH is 1 : 1. When it changes in 2 : 1, what will be the value of pH of buffer ?

(A) Increase (B) Decrease (C) No effect (D) None **IE0123**

Q.49 The buffer solution play an important role in :-

(A) Increasing the pH value (B) Decreasing the pH value

(C) Keeping the pH constant (D) Solution will be neutral **IE0124**

Q.50 The total number of different kind of acidic buffers obtained during the titration of H_3PO_4 with NaOH are :

(A) 3 (B) 1 (C) 2 (D) 0 **IE0125**

Q.51 Which of the following solutions does not act as buffer :

(A) $H_3PO_4 + NaH_2PO_4$ (B) $NaHCO_3 + H_2CO_3$

(C) $NH_4Cl + HCl$ (D) $CH_3COOH + CH_3COONa$ **IE0126**

Q.52 Half of the formic acid solution is neutralised on addition of a KOH solution to it. If K_a (HCOOH) = 2×10^{-4} then pH of the solution is : - (log 2 = 0.3010)

(A) 3.6990 (B) 10.3010 (C) 3.85 (D) 4.3010 **IE0127**

Q.53 When 0.02 moles of NaOH are added to a litre of buffer solution, its pH changes from 5.75 to 5.80. What is its buffer capacity :-

(A) 0.4 (B) 0.05 (C) – 0.05 (D) 2.5 **IE0128**

Q.54 Calculate pH when 100 ml of 0.2M NaOH is reacted with 100 ml of 0.2 M CH_3COOH ($K_a = 10^{-5}$)

(A) 9 (B) 7 (C) 5 (D) 2 **IE0129**

Q.55 At 90°C , pure water has $[H^+] = 10^{-6}$ M, if 100 ml of 0.2 M HNO_3 is added to 20 ml of 1 M NaOH at 90°C then pH of the resulting solution will be

(A) 5 (B) 6 (C) 7 (D) None of these **IE0130**

Q.56 When 20 ml of $\frac{M}{20}$ NaOH are added to 10 ml of $\frac{M}{10}$ HCl, the resulting solution will:-

(A) Turn blue litmus red (B) Turn phenolphthalein solution pink colour

(C) Turn methyl orange red (D) Will have no effect on either red or blue litmus

IE0131

Q.57 The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression :-

(A) $\log \frac{[HIn]}{[In^-]} = pK_{In} - pH$ (B) $\log \frac{[HIn]}{[In^-]} = pH - pK_{In}$

(C) $\log \frac{[In^-]}{[HIn]} = pH + pK_{In}$ (D) $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$ **IE0132**

Q.58 Calculate the pH range in which an acid indicator with K_{acid} (indicator) = 1.0×10^{-5} changes colour when the concentration of the indicator is 1×10^{-3}M.

(A) 5 ± 1 (B) 11 ± 1 (C) 3 ± 1 (D) 8 ± 1 **IE0133**

Q.59 In what pH range will a 1×10^{-4} M solution of an indicator will K_b (indicator) = 1×10^{-11} change colour?

(A) 7.0 ± 1 (B) 3.0 ± 1 (C) 5.5 ± 1 (D) 11.0 ± 1 **IE0134**

Q.60 Indicator which is used in the titration of CH_3COOH & NaOH :–

(A) Methyl orange (B) Methyl red (C) Phenolphthalein (D) Litmus **IE0135**

Q.61 Phenolphthalein is a :-

(A) Strong acid (B) Strong base (C) Weak base (D) Weak acid **IE0136**

Q.62 pH–range of Methyl red indicator is :–

(A) 4·4–6·5 (B) 6·8–10·8 (C) 8 – 9·6 (D) 6·8 – 8·2 **IE0137**

Q.63 In the volumetric estimation of HCl, if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration :-

(A) NaOH (B) RbOH (C) KOH (D) NH_4OH **IE0138**

Q.64 Phenolphthalein does not act as an indicator for the titration between :-

(A) KOH and H_2SO_4 (B) NaOH and CH_3COOH

(C) Oxalic acid and $KMnO_4$ (D) $Ba(OH)_2$ and HCl **IE0139**

Q.65 For weak acid and strong base titration, the indicator used is :-

(A) Potassium di-chromate (B) Methyl orange

(C) Litmus (D) Phenolphthalein **IE0140**

Q.66 The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is

(A) 6 y^2 (B) 64 y^4 (C) 36 y^5 (D) 108 y^5 **IE0141**

Q.67 If K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of this substance in mole per m^3 is

(A) 8×10^{-3} (B) 6.4×10^{-5} (C) 8×10^{-6} (D) 8 **IE0142**

Q.68 If the solubility of AgCl (formula mass=143) in water at 25°C is 1.43×10^{-4} gm/100 ml of solution then the value of K_{sp} will be :–

(A) 1×10^{-5} (B) 2×10^{-5} (C) 1×10^{-10} (D) 2×10^{-10} **IE0143**

Q.69 One litre of saturated solution of $CaCO_3$ is evaporated to dryness, 7.0 g of residue is left. The solubility product for $CaCO_3$ is:-

(A) 4.9×10^{-3} (B) 4.9×10^{-5} (C) 4.9×10^{-9} (D) 4.9×10^{-7} **IE0144**

Q.70 A_3B_2 is a sparingly soluble salt of molar mass M (g mol^{-1}) and solubility x g lit^{-1}. The ratio of the molar concentration of B^{3-} to the solubility product of the salt is

(A) $108\,\frac{x^5}{M^5}$ (B) $\frac{1}{108}\frac{M^4}{x^4}$ (C) $\frac{1}{54}\frac{M^4}{x^4}$ (D) None **IE0145**

Q.71. Solubility of Ag_2CrO_4 ($K_{sp} = 4 \times 10^{-13}$) in 0.1 M K_2CrO_4 solution will be :–

(A) 10^{-3} M (B) 10^{-6} M (C) 4×10^{-6} M (D) 5×10^{-7} M **IE0146**

Q.72. How many times solubility of CaF_2 is decreased in 4×10^{-3} M KF (aq.) solution as compare to pure water at 25°C. Given K_{sp} (CaF_2) = 3.2×10^{-11}

(A) 50 (B) 100 (C) 500 (D) 1000 **IE0147**

Q.73 At 30^0C, In which of the one litre solution, the solubility of Ag_2CO_3 (solubility product = 8×10^{-12}) will be maximum :-

(A) 0.05 M Na_2CO_3 (B) Pure water (C) 0.05 M $AgNO_3$ (D) 0.05 M NH_3 **IE0148**

Q.74 What will happen if the pH of the solution of 0.001 M $Mg(NO_3)_2$ solution is adjusted to pH = 9 (K_{sp} of $Mg(OH)_2$ = 8.9×10^{-12})

(A) ppt will take place (B) ppt will not take place

(C) Solution will be saturated (D) None of these **IE0149**

Q.75 Na_3PO_4 which should be added in 10 L of 1.0×10^{-5} M - $BaCl_2$ solution without any precipitation of $Ba_3(PO_4)_2$ is [Ksp of $Ba_3(PO_4)_2$] = 4×10^{-23}

(A) 2×10^{-4} gm (B) 0.328 gm (C) 0.164 gm (D) 0.82 gm **IE0150**

EXERCISE O-II

Single correct :

Q.1 The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :- [log 5.05 = 0.7]

(A) 3.3 (B) 3.5 (C) 4.5 (D) 4.0 **IE0151**

Q.2 How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 :-

(A) 1 (B) 0.02 (C) 0.009 (D) 0.01 **IE0152**

Q.3 Which of the following is most soluble in water?

(A) MnS ($K_{sp}= 8\times10^{-37}$) (B) ZnS ($K_{sp}= 7\times10^{-16}$)

(C) Bi_2S_3 ($K_{sp}= 1\times10^{-72}$) (D) $Ag_3(PO_4)$ ($K_{sp}= 1.8\times10^{-18}$) **IE0153**

Q.4 Solubility of AgBr will be minimum in :-

(A) Pure water (B) 0.1 M $CaBr_2$ (C) 0.1 M NaBr (D) 0.1 M $AgNO_3$ **IE0154**

Q.5 pH of solution at first 1/4th equivalence point of Na_2CO_3 when titrated with HCl will be (for H_2CO_3 $K_{a_1} = 10^{-7}$; $K_{a_2} = 10^{-11}$)

(A) 7 + log 3 (B) 7 – log3 (C) 11 + log3 (D) 11 – log3 **IE0155**

Q.6 An acid-base indicator has a $K_a = 1.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. Calculate the pH change required to change the colour of the indicator from 80% red to 80% blue. [log 2 = 0.3]

(A) 1.20 (B) 0.80 (C) 0.20 (D) 1.40 **IE0156**

Assertion /Reason :

Q.7 **Statement-1** pH of 10^{-7} M NaOH solution is exist between 7 to 7.3 at 25°C.

Statement-2 Due to common ion effect ionization of water is reduced.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true. **IE0157**

Q.8 **Statement-1** : On dilution of a concentrated solution of CH_3COOH , the concentration of $[H^+]$ decreases.

Statement-2 : Increase in volume is more than the increase in degree of ionisation.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true. **IE0158**

Multiple correct :

Q.9 Which of the following is correct for 0.1 M BOH solution ($K_b = 10^{-5}$)

(A) pH of solution is 11

(B) OH^- concentration is 10^{-3} mol/L

(C) it's salt with HCl (i.e. BCl) form the acidic solution in water

(D) Phenolphthalein indicator can be used during the titration of BOH with HCl **IE0159**

Q.10 For weak monobasic acid, HA, the dissociation constant is 2×10^{-6}, at 25ºC. Which of the following is/are correct regarding this acid? [log2= 0.3]

(A) $A^- + H_2O \rightleftharpoons HA + OH^-$; $K_{eq} = 5 \times 10^{-9}$

(B) The equilibrium constant for the reaction of HA with aq. NaOH is 2×10^8

(C) The pH of 0.1 M, HA solution is 3.35

(D) solution of A^- is basic **IE0160**

Q.11 If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 >> K_2$ which is/are incorrect.

(A) $[H^+] = [H_2PO_4^-]$ (B) $[H^+] = \sqrt{K_1[H_3PO_4]}$

(C) $K_2 = [HPO_4^{--}]$ (D) $[H^+] = 3[PO_4^{3-}]$ **IE0161**

Q.12 10 ml. of a solution contains 0.1 M NH_4Cl + 0.01M NH_4OH. Which addition would not change the pH of solution :–

(A) Adding 1 ml. water (B) Adding 5 ml. of 0.1 M NH_4Cl

(C) Adding 5 ml. of 0.1 M NH_4OH (D) Adding 10 ml. of 0.1 M NH_4Cl **IE0162**

Q.13 When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

(A) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-) (B) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(C) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-) (D) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-) **IE0163**

Paragraph for Q.14 to Q.16

8 gm weak acid HX (molecular mass = 80) is dissolved is 100 ml water. ($K_a = 10^{-4}$)

Q.14 Find pH of solution-

(A) 3.3 (B) 2 (C) 2.3 (D) 3 **IE0164**

Q.15 If it is titrated with 0.25 M NaOH find pH at equivalence point (log5 = 0.7)

(A) 9.15 (B) 8.65 (C) 4.65 (D) 4.85 **IE0165**

Q.16 Find $[H^+]$ if 10^{-3} mol HCl is added to 100 ml original solution $\left(\sqrt{41} = 6.4 \ ; \ \sqrt{5} = 2.24\right)$

(A) 0.62×10^{-2} (B) 1.62×10^{-2} (C) 2.7×10^{-2} (D) 0.27×10^{-2} **IE0166**

MATCH THE COLUMN :

Q.17 Match the effect of addition of 1 M NaOH to 100 mL 1 M CH_3COOH (in Column I) with pH (in Column II) :

Column-I	Column-II
(A) 25 mL of NaOH	(P) pK_a
(B) 50 mL of NaOH	(Q) $pK_a + \log 3$
(C) 75 mL of NaOH	(R) $pK_a - \log 3$
(D) 100 mL of NaOH	(S) $\frac{1}{2}[pK_w + pK_a - \log 2]$

IE0167

TABLE TYPE QUESTION :

Column-I (solution)	Column-II (pH of solution)	Column-III (Introduction about solution)
(A) CH_3COOH(0.2M, 1L) + NaOH (0.1M, 1 L)	(P) 1.3	(1) pH is determined by strong acid
(B) CH_3COOH(0.1M ,1 L) + HCl (0.1 M, 1 L)	(Q) 7	(2) Buffer solution at its maximum buffer capacity
(C) CH_3COOH(0.1M, 1 L) + NH_4OH (0.1M, 1 L)	(R) 9	(3) pH is determined by salt hydrolysis.
(D) NH_4Cl (200 ml, 0.1M) + NaOH (100 ml, 0.1M)	(S) 5	(4) pH is determined by buffer solution

(Given : $(K_a)_{CH_3COOH} = 10^{-5}$, $(K_b)_{NH_4OH} = 10^{-5}$, log 2 = 0.3

Q.18 Which of the following is incorrectly matched

(A) A - S - 4 (B) B - P - 1 (C) D - R - 2 (D) C - Q - 1 **IE0168**

Q.19 If 0.15 mole NaOH is added in solution (B) of column-I then which of the following is correct

(A) S - 3 (B) S - 4 (C) R - 1 (D) P - 3 **IE0169**

Q.20 If 0.1mole HCl is added in solution (A) of column-I then pH of the resulting solution will be

(A) 7 (B) 13 (C) 3.0 (D) 1 **IE0170**

J-MAIN

Q.1 The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is :-

[AIEEE–2011]

(1) $\sqrt[2]{1.6\times10^{-30}}$ (2) $\sqrt[4]{1.6\times10^{-30}}$ (3) $\sqrt[4]{1.6\times10^{-30}/27}$ (4) $1.6 \times 10^{-30}/27$ **IE0171**

Q.2 An acid HA ionises as

$HA \rightleftharpoons H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be :- **[AIEEE–2011]**

(1) 1×10^{-10} (2) 5 (3) 5×10^{-8} (4) 1×10^{-5} **IE0172**

Q.3 If K_{sp} of CaF_2 at 25°C is 1.7×10^{-10}, the combination amongst the following which gives a precipitate of CaF_2 is :- **[JEE-MAIN(online)–2012]**

(1) 1×10^{-2} M Ca^{2+} and 1×10^{-5} M F^- (2) 1×10^{-4} M Ca^{2+} and 1×10^{-4} M F^-

(3) 1×10^{-3} M Ca^{2+} and 1×10^{-5} M F^- (4) 1×10^{-2} M Ca^{2+} and 1×10^{-3} M F^- **IE0173**

Q.4 The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, Ka of this acid is :- **[AIEEE–2012]**

(1) 1×10^{-7} (2) 3×10^{-7} (3) 1×10^{-3} (4) 1×10^{-5} **IE0174**

Q.5 How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[AIEEE–2013]**

(1) 0.1 L (2) 0.9 L (3) 2.0 L (4) 9.0 L **IE0175**

Q.6 Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At which concentration of Ba^{2+}, precipitate of $BaCO_3$ begins to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)

(1) 5.1×10^{-5} M (2) 8.1×10^{-7}M **[JEE-MAIN(Online)–2013]**

(3) 4.1×10^{-5} M (4) 7.1×10^{-8}M **IE0176**

Q.7 NaOH is a strong base. What will be pH of 5.0×10^{-2}M NaOH solution ? (log2 = 0.3)

[JEE-MAIN(Online)–2013]

(1) 13.70 (2) 13.00 (3) 14.00 (4) 12.70 **IE0177**

Q.8 Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts Hg_2Cl_2, $Cr_2(SO_4)_3$, $BaSO_4$ and $CrCl_3$ respectively ? **[JEE-MAIN(Online)–2013]**

(1) $\left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}, \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}, (K_{sp})^{\frac{1}{2}}, \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$ (2) $(K_{sp})^{\frac{1}{2}}, \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}, \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}, \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

(3) $(K_{sp})^{\frac{1}{2}}, \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}, \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}, \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$ (4) $\left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}, \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}, (K_{sp})^{\frac{1}{2}}, \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$ **IE0178**

Q.9 What would be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL? **[JEE-MAIN(Online)–2013]**

(Ka = 1.75×10^{-5}, pKa = 4.76)

(1) $4.76 < pH < 5.0$

(2) $pH < 4.70$

(3) pH of solution will be equal to pH of acetic acid

(4) pH = 4.70

IE0179

Q.10 In some solutions, the concentration of H_3O^+ remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as :-**[JEE-MAIN(Online)–2014]**

(1) Colloidal solutions (2) True solutions

(3) Ideal solutions (4) Buffer solutions **IE0180**

Q.11 Zirconium phosphate $[Zr_3(PO_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ?

(1) $S = \{K_{sp}/144\}^{1/7}$ (2) $S = \{K_{sp}/(6912)^{1/7}\}$ **[JEE-MAIN(Online)–2014]**

(3) $S = (K_{sp}/6912)^{1/7}$ (4) $S = \{K_{sp}/6912\}^{7}$ **IE0181**

Q.12 pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is **[JEE-MAIN(Offine)–2017]**

(1) 7.2 (2) 6.9 (3) 7.0 (4) 1.0 **IE0182**

Q.13 Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is 10^{-5}, the ratio of salt to acid concentration in the buffer solution will be :

[JEE-MAIN(Online)–2017]

(1) 4 : 5 (2) 1 : 10 (3) 10 : 1 (4) 5 : 4 **IE0183**

Q.14 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If pK_b of ammonia solution is 4.75, the pH of the mixture will be:- **[JEE-MAIN(Online)–2017]**

(1) 8.25 (2) 4.75 (3) 9.25 (4) 3.75 **IE0184**

Q.15 Which of the following salts is the most basic in aqueous solution ? **[JEE-MAIN(Offine)–2018]**

(1) CH_3COOK (2) $FeCl_3$ (3) $Pb(CH_3COO)_2$ (4) $Al(CN)_3$ **IE0185**

Q.16 An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination ? **[JEE-MAIN(Offine)–2018]**

	Base	**Acid**	**End point**
(1)	Strong	Strong	Pinkish red to yellow
(2)	Weak	Strong	Yellow to pinkish red
(3)	Strong	Strong	Pink to colourless
(4)	Weak	Strong	Colourless to pink

IE0186

Q.17 An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is : **[JEE-MAIN(Offine)–2018]**

(1) 3×10^{-20} (2) 6×10^{-21} (3) 5×10^{-19} (4) 5×10^{-8} **IE0187**

Q.18 A aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+} ? **[JEE-MAIN(Offine)–2018]**

(1) 2×10^{-9} M (2) 1.1×10^{-9} M (3) 1.0×10^{-10} M (4) 5×10^{-9} M **IE0188**

Q.19 Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1 ? **[JEE-MAIN(Online)–2018]**

(1) $75\text{mL}\frac{M}{5}\text{HCl}+25\text{mL}\frac{M}{5}\text{NaOH}$

(2) $100\text{mL}\frac{M}{10}\text{HCl}+100\text{mL}\frac{M}{10}\text{NaOH}$

(3) $55\text{mL}\frac{M}{10}\text{HCl}+45\text{mL}\frac{M}{10}\text{NaOH}$

(4) $60\text{mL}\frac{M}{10}\text{HCl}+40\text{mL}\frac{M}{10}\text{NaOH}$ **IE0189**

Q.20 The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$; atomic mass of Pb = 207 u) is : **[JEE-MAIN(Online)–2018]**

(1) 0.36 L (2) 0.18 L (3) 17.98 L (4)1.798 L **IE0190**

21. A soft drink was bottled with a partial pressure of CO_2 of 3 bar over the liquid at room temperature. The partial pressure of CO_2 over the solution approaches a value of 30 bar when 44 g of CO_2 is dissolved in 1 kg of water at room temperature. The approximate pH of the soft drink is __________ $\times 10^{-1}$. **IE0191**

[JEE-MAIN(Online)–2020]

(First dissociation constant of $H_2CO_3 = 4.0 \times 10^{-7}$; log 2 = 0.3; density of the soft drink = 1 g mL^{-1})

22. If the solubility product of AB_2 is 3.20×10^{-11} M^3, then the solubility of AB_2 in pure water is_ _ _ _ _ $\times 10^{-4}$ mol L^{-1}. [Assuming that neither kind of ion reacts with water] **IE0192**

[JEE-MAIN(Online)–2020]

23. Arrange the following solutions is the decreasing order of pOH : **[JEE-MAIN(Online)–2020]**

(A) 0.01 M HCl (B) 0.01 M NaOH

(C) 0.01 M CH_3COONa (D) 0.01 M NaCl

(1) (B) > (C) > (D) > (A) (2) (A) > (C) > (D) > (B)

(3) (B) > (D) > (C) > (A) (4) (A) > (D) > (Q > (B) **IE0193**

24. For the following Assertion and Reason, the correct option is **[JEE-MAIN(Online)–2020]**

Assertion (A) : When Cu (II) and sulphide ions are mixed, they react together extremely quickly to give a solid.

Reason (R) : The equilibrium constant of $Cu^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CuS(s)$ is high because the solubility product is low.

(1) Both (A) and (R) are true and (R) is the explanation for (A)

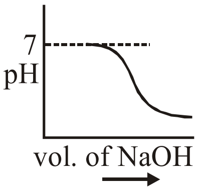
(2) Both (A) and (R) are false

(3) (A) is false and (R) is true

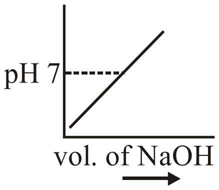
(4) Both (A) and (R) are true but (R) is not the explanation for (A) **IE0194**

25. 100 mL of 0.1 M HCl is taken in a beaker and to it 100 mL of 0.1 M NaOH is added in steps of 2 mL and the pH is continuously measured. Which of the following graphs correctly depicts the change in pH? **[JEE-MAIN(Online)–2020]**

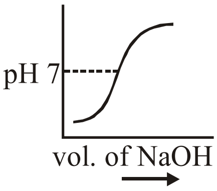
(1)



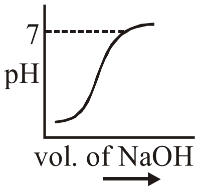
(2)



(3)



(4)



IE0195

J-ADVANCE

Q.1 In 1 L saturated solution of AgCl [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of 'x' is. **[JEE -2011]**

IE0196

Q.2 The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25ºC. The K_a of HA is **[JEE 2013]**

(A) 1×10^{-4} (B) 1×10^{-5} (C) 1×10^{-6} (D) 1×10^{-3} **IE0197**

Q.3 The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is **[JEE 2013]**

(A) 1.1×10^{-11} (B) 1.1×10^{-10} (C) 1.1×10^{-12} (D) 1.1×10^{-9} **IE0198**

Paragraph For Questions 4 and 5

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 ºC was measured for the beaker and its contents. **(Expt-1).** Because the enthalpy of neutralisation of a strong acid with a strong base is a constant ($-57.0\ kJmol^{-1}$), this experiment could be used to measure the calorimeter constant. In a second experiment **(Expt-2)**, 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0M NaOH (under identical conditions to **(Expt-1)**) where a temperature rise of 5.6 ºC was measured.

(Consider heat capacity of all solutions as $4.2\ Jg^{-1}K^{-1}$ and density of all solutions as $1.0\ g\ mL^{-1}$)

Q.4 Enthalpy of dissociation (in $kJ\ mol^{-1}$) of acetic acid obtained from the **Expt-2** is **[JEE 2015]**

(A) 1.0 (B) 10.0 (C) 24.5 (D) 51.4 **IE0199**

Q.5 The pH of the solution after **Expt-2**

(A) 2.8 (B) 4.7 (C) 5.0 (D) 7.0 **IE0200**

Q.6 The solubility of a salt of weak acid(AB) at pH 3 is $Y \times 10^{-3}\ mol\ L^{-1}$. The value of Y is___.

(Given that the value of solubility product of AB (K_{sp}) = 2×10^{-10} and the value of ionization constant of HB(K_a) = 1×10^{-8}) $\sqrt{20} = 4.47$ **[JEE 2018]**

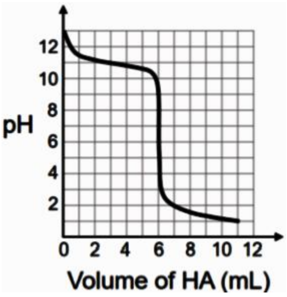
IE0201

Q.7 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink color is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution ? **[JEE 2020]**

Exp. No.	Vol. of NaOH (mL)
1	12.5
2	10.5
3	9.0
4	9.0
5	9.0

IE0202

Q.8 A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base? The neutralization reaction is given by $B + HA \rightarrow BH^+ + A^-$.



[JEE 2020]

IE0203

Q.9 An acidified solution of 0.05 M Zn^{2+} is saturated with 0.1 M H_2S. What is the minimum molar concentration (M) of H+ required to prevent the precipitation of ZnS ?

Use K_{sp} (ZnS) = 1.25×10^{-22} and **[JEE 2020]**

Overall dissociation constant of H_2S , $K_{NET} = K_1K_2 = 1 \times 10^{-21}$

IE0204

ANSWER KEY

EXERCISE-S-I

Q.1 Ans.6.022×10^{7}

Q.2 Ans.(i) 6.53 ; (ii) (a) Basic , (b) Acidic

Q.3 Ans.6.8

Q.4 Ans.(a) 1, (b) 2.87, (c) 11.13 (d) 6.97, (e) 7, (f) 6 , (g) 6.97, (h) 11.30 (i) 9 , (j) 3

Q.5 Ans.(a) $K_a = 10^{-8}$, (b) $K_b = 10^{-6}$

Q.6 Ans.10

Q.7 Ans.173.2 : 1

Q.8 Ans.0.009

Q.9 Ans.1.1×10^{-3} M

Q.10 Ans.1.11×10^{-4}

Q.11 Ans.4.7

Q.12 Ans.3.3

Q.13 Ans.(a) 0.522 , (b) 2.522

Q.14 Ans. (1)

Q.15 Ans. 0.027 M, 0.073 M, 0.027 M, 10^{-5} M

Q.16 Ans. 11.3

Q.17 Ans.10^{-5}M

Q.18 Ans.pH = 4.5

Q.19 Ans.$K_b = 6.25\times10^{-10}$

Q.20 Ans.0.56%, pH = 7

Q.21 Ans.1.667%

Q.22 Ans.8.3

Q.23 Ans.(a) 6, (b) 1×10^{-5}

Q.24 Ans. 9.0

Q.25 Ans. 9.56

Q.26 5.04

Q.27 Ans. 0.05 mol

Q.28 Ans. $[OH^-] = 9.0\times10^{-6}$M

Q.29 Ans.(10.1)

Q.30 Ans.4.74

Q.31 Ans.9.56

Q.32 Ans.8.783

Q.33 Ans.(3.33)

Q.34 Ans. 10^{-5} M

Q.35 Ans. 8.7 , $[H_3O^+] = 2\times10^{-9}$M

Q.36 Ans. 5 , 10^{-5} M

Q.37 **Ans. (i) 2.85, (ii) 4.0969, (iii) 4.5229, (iv) 4.699, (v) 5.301, (vi) 8.699**

Q.38 **Ans. $[HI_n] = 80$ %**

Q.39 **Ans. 85.71%**

Q.40 **Ans. (b), (c)**

Q.41 **Ans.ΔpH = 0.954**

Q.42 **Ans. QX_2 is more soluble**

Q.43 **Ans. 4×10^{-8}**

Q.44 **Ans. 5×10^{-11}**

Q.45 **Ans. 3.2×10^{-11}**

Q.46 **Ans. 2.56×10^{-16}**

Q.47 **Ans. 1.0×10^{-5} mol/lit**

Q.48 **Ans. 5×10^{-10} M**

Q.49 **Ans.5×10^{-7}**

Q.50 **Ans. 4×10^{-7} mol/L AgBr, 1.6×10^{-6} mol/L AgSCN**

Q.51 **Ans. 8×10^{-3} M**

Q.52 **Ans. 4×10^{-2}M**

Q.53 **Ans.(a) no precipitation will occur, (b) a precipitate will form**

Q.54 **Ans.No.**

Q.55 **Ans.0.284 gm**

EXERCISE S-II

Q.1 **Ans. 0.209 M, 0.191 M, 9.15×10^{-3} M, 0**

Q.2 **Ans. 10.6**

Q.3 **Ans. $(2 \times 10^{-4}$M)**

Q.4 **Ans. pH = 10.52**

Q.5 **Ans. 8.35, 9.60, 4.66**

Q.6 **Ans.(9.6)**

Q.7 **Ans.(10^{-5}M)**

Q.8. **Ans (10^{-3}M)**

Q.9 **Ans. 2.8×10^{-3} mole**

Q.10 **Ans. 1.6×10^{-3}**

EXERCISE O-I

Q.1 Ans.(A)
Q.2 Ans.(B)
Q.3 Ans.(C)
Q.4 Ans.(C)
Q.5 Ans.(B)
Q.6 Ans.(C)
Q.7 Ans.(D)
Q.8 Ans.(D)
Q.9 Ans.(C)
Q.10 Ans.(C)
Q.11. Ans (C)
Q.12 Ans.(D)
Q.13 Ans.(B)
Q.14 Ans.(B)
Q.15 Ans.(C)
Q.16 Ans.(C)
Q.17 Ans.(B)
Q.18. Ans.(C)
Q.19 Ans.(C)
Q.20 Ans.(B)
Q.21 Ans.(B)
Q.22 Ans.(D)
Q.23 Ans.(D)
Q.24 Ans.(C)
Q.25 Ans.(C)
Q.26 Ans.(C)
Q.27 Ans.(B)
Q.28 Ans.(B)
Q.29 Ans.(A)
Q.30 Ans.(D)
Q.31 Ans.(B)
Q.32 Ans.(C)
Q.33 Ans.(C)
Q.34 Ans.(C)
Q.35 Ans.(B)
Q.36 Ans.(C)
Q.37 Ans.(D)
Q.38 Ans.(A)
Q.39 Ans.(C)

Q.40 Ans.(C)	Q.41 Ans.(C)	Q.42 Ans.(B)
Q.43 Ans.(C)	Q.44 Ans.(D)	Q.45 Ans.(A)
Q.46 Ans.(B)	Q.47 Ans.(D)	Q.48 Ans.(B)
Q.49 Ans.(C)	Q.50 Ans.(A)	Q.51 Ans.(C)
Q.52 Ans.(A)	Q.53 Ans.(A)	Q.54. Ans.(A)
Q.55. Ans.(B)	Q.56 Ans.(D)	Q.57 Ans.(A)
Q.58 Ans.(A)	Q.59 Ans.(B)	Q.60 Ans.(C)
Q.61 Ans.(D)	Q.62 Ans.(A)	Q.63 Ans.(D)
Q.64 Ans.(C)	Q.65 Ans.(D)	Q.66 Ans.(D)
Q.67 Ans.(D)	Q.68 Ans.(C)	Q.69 Ans.(A)
Q.70. Sol.(C)	Q.71. Ans.(B)	Q.72. Ans.(B)
Q.73 Ans.(D)	Q.74 Ans.(B)	Q.75 Ans.(B)

EXERCISE O-II

Q.1 Ans.(A)	Q.2 Ans.(C)	Q.3 Ans.(D)
Q.4 Ans.(B)	Q.5 Ans (C)	Q.6 Ans.(A)
Q.7 Ans.(A)	Q.8 Ans.(A)	Q.9 Ans. (A,B,C)
Q.10 Ans.(A,B,C,D)	Q.11 Ans.(D)	Q.12 Ans.(A)
Q.13 Ans.(A)	Q.14 Ans(B)	Q.15 Ans(B)
Q.16 Ans (B)	Q.17 Ans. A - (R), B - (P), C - (Q), D - (S)	
Q.18 Ans.(D)	Q.19 Ans.(B)	Q.20 Ans.(C)

J-MAIN

Q.1 Ans.(3)	Q.2 Ans.(1)	Q.3 Ans.(4)
Q.4 Ans.(4)	Q.5 Ans.(4)	Q.6 Ans.(1)
Q.7 Ans.(4)	Q.8 Ans.(1)	Q.9 Ans.(1)
Q.10 Ans.(4)	Q.11 Ans.(3)	Q.12 Ans.(2)
Q.13 Ans.(3)	Q.14 Ans.(3)	Q.15 Ans.(1)
Q.16 Ans.(2)	Q.17 Ans.(1)	Q.18 Ans.(2)
Q.19 Ans.(1)	Q.20 Ans.(2)	Q.21. Ans.(37)
Q.22. Ans2.00	Q.23. Ans.(4)	Q.24. Ans.(4)
Q.25. Ans.(3)		

J-ADVANCE

Q.1 Ans.(7)	Q.2 Ans.(A)	Q.3 Ans.(B)
Q.4 Ans.(A)	Q.5 Ans.(B)	Q.6 Ans.(4.47)
Q.7 Ans. (0.11)	Q.8 Ans. 2.30 to 3.00	Q.9 Ans.0.20