IONIC EQUILIBRIUM

Preface

Ionic Equilibrium is the equilibrium between the weak electrolyte and its ions.
This chapter deals with the study of electrolytes and their types, ionization principle of Arrhenius, Ostwalds dilution law, Ionization constants and their co-rrelations, ionic product of water, pH and pOH scales, types of salts & their hydrolysis, buffer solutions and solubility and solubility product for sparingly soluble salts

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total number of Questions in **Ionic Equilibrium** are :

In Chapter Examples 29

Solved Examples 40

Total no. of questions 69

1. ELECTRIC CONDUCTIVITY

Those substance which allow the electric current to pass through them are called electric conductors and property is called electric conductivity.

On the basis of Electric conductivity, substances are of two types -

1.1 Nonconductors :

Those substance which do not allow the electric current to pass through them are called nonconductors. eg. All covalent compounds & nonmetals.

1.2 Conductors :

Those substance which allow the electric current to pass through them are called conductors. eg. all metals, alloys, all acid and bases, salt and graphite etc.

On the basis of conducting units conductors are of two types -

1.2.1 Metallic or Electric Conductors :

Electricity conduct them due to the presence of free and mobile electron which act as electricity conducting unit called metallic or electric conductors. eg. Metals, Alloys, Graphite, Gas, Carbon etc.

1.2.2 Ionic Conductors or Electrolytes :

Conductors in which the current is passes through them due to the presence of free ions are called **Ionic Conductors or Electrolyte or Electrolytic conductors**.

Ionic conductors are further divided into two types on the basis of their strengths -

(a) **Strong electrolytes :**

(i) Those substance which are almost completely ionize into ions in their aqueous solution are called strong electrolytes.

(ii) Degree of ionization for this type of electrolyte is one i.e. $\alpha \cong 1$. eg. HCl, H_2SO_4, NaCl.HNO_3, KOH, NaOH, HNO_3, $AgNO_3$, $CuSO_4$, etc. Means all strong acids and bases and all types of salts.

(b) **Weak electrolytes :**

(i) Those substance which are ionize to a small extent in their aqueous solution are known weak electrolytes.eg. H_2O, CH_3COOH, NH_4OH, HCN, HCOOH, Liq. SO_2 etc. Means all weak acids and bases.

(ii) Degree of ionization for this types of electrolytes in α <<< 1.

2. IONIZATION OF WEAK ELECTROLYTES

2.1 Ionisation :

The process in which molecules of acids bases and salts when melted or dissolve in water dissociate into ions is called ionization.

2.1.1 Ionic Equilibrium :

Weak electrolytes are partially ionised in aqueous solution and an equilibrium is situated between the ionized and unionised electrolyte. This type of equilibrium is known as ionic equilibrium.

Let us consider an acid HA which when dissolved in water, an equilibrium will setup between ionized and unionized acid molecule as below -

$$HA + H_2O \rightleftharpoons H^+ + A^-$$

On applying the law of mass action, the equilibrium constant K is written as -

$$K = \frac{[H^+][A^-]}{[HA][H_2O]}$$

Since in an aqueous solution, the molar concentration of water is constant i.e. $[H_2O]$ = constant. Therefore K $[H_2O]$ replaced by a new constant K_a which is known as ionization acid constant or dissociation constant of acid. Thus,

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

'K_a' is the characteristic of the individual acid. From the above equation K_a is directly proportional to $[H^+]$ concentration hence, greater the K_a of an acid, more will be acidity.

Assume that the initial concentration of C is moles/lit. and α is the degree of ionization then

	HA + H_2O $\rightleftharpoons$	H^+	+ A^-
Initial concentration	C	0	0
Equilibrium concentration	$(1-\alpha)C$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{\alpha^2 C}{(1-\alpha)}$$

The degree of ionisation α is very small as compared to 1 means α <<< 1. So, $1 - \alpha = 1$

Thus, $K_a = \alpha^2 c$; $\alpha^2 = \frac{K_a}{C}$

or $\alpha = \sqrt{\frac{K_a}{C}}$ $\because$ $\frac{1}{C} = V$

So, $\boxed{\alpha = \sqrt{K_a \times V}}$

This equation is known as ostwald dilution law equation.

Similarly, for a weak base we have

$$\alpha = \sqrt{\frac{K_b}{C}} \qquad \because \qquad \frac{1}{C} = V$$

So, $\boxed{\alpha = \sqrt{K_b \times V}}$

Where,

K_b is the dissociation constant of weak base.

C is the initial concentration

α is the degree of dissociation of weak base.

Hence, according to **Ostwald** dilution law, the degree of ionization of weak electrolyte is directly proportional to the square root of volume containing one mole of electrolyte or Inversely proportional to the square root of its molar concentration.

Examples based on Ionisation of weak electrolyte

Ex.1 The degree of dissociation of 0.02 M CH_3COOH solution (K_a: 1.8×10^{-5}) is

(A) 3% (B) 0.03%

(C) 2% (D) 0.02%

(Ans. A)

Sol. $\alpha = \sqrt{\frac{K_a}{c}}$

$= \sqrt{\frac{1.8 \times 10^{-5}}{0.02}}$

$= 0.03$

Ex.2 The dissociation constant of CH_3COOH is 1.8×10^{-5}. Determine the H^+ ion concentration of 0.01 M solution of acetic acid at 25ºC –

(A) 5.5×10^{-5} (B) 1.8×10^{-5}

(C) 4.24×10^{-4} (D) 1.01×10^{-4}

(Ans. C)

Sol. We know

$$H^+ = \alpha C \quad \text{and} \quad \alpha = \sqrt{\frac{K_a}{C}}$$

$$H^+ = \sqrt{\frac{K_a}{C}} \times C = \sqrt{K_a \times C}$$

Given C = 0.01 M and $K_a = 1.8 \times 10^{-5}$

$$H^+ = \sqrt{1.8 \times 10^{-5} \times 10^{-2}}$$

$$= \sqrt{18 \times 10^{-8}}$$

$= \mathbf{4.24 \times 10^{-4}}$ **Ans.**

3. ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION OR IONIZATION

(a) When an electrolyte dissociates into water, it gives two types of charged particles called ions.

(b) Ions which carry (+) ve charge and move towards cathode are called as '**Cations**' while ions carrying (–) ve charge and moving towards anode called as '**anion**'.

(c) Every electrolytic solution is always neutral in nature.

(d) Quantity or part of electrolyte which is ionized or decomposed or dissociate called as **"Degree of Ionisation"**.

(e) Electrolyte which gives H^+ ions after dissociation in the aqueous solution is called as acid while that which gives OH^- after dissociation in the aqueous solution is called as base.

(f) Acidic strength of acids is directly proportional to the dissociation constant k_a.

$$k_a = -\log k_a = pk_a$$

Thus, Acidic strength $\propto k_a$

$$\propto \frac{1}{pk_a}$$

$$\propto pk_b$$

$$\propto \frac{1}{k_b}$$

(g) Similarly basic strength of bases is directly proportional to K_b.

$$k_b = -\log k_b = pk_b$$

Basic strength of base $\propto k_b$

$$\propto \frac{1}{pk_b}$$

$$\propto pk_a$$

$$\propto \frac{1}{k_a}$$

(h) Conductivity of solution depends upon the number of ions produced by the electrolyte, such as -

Conduction of solution $\propto$ number of ions produced by the electrolyte

(i) Solution of strong electrolyte has more electric conductivity property as compared to weak electrolyte.

(j) Only weak electrolyte followed the law of mass action and **Ostwalds dilution law**.

(k) When electricity passed through in the electrolytic solution, it gives only direction to movement of ions towards the electrodes.

(l) Movement of ions is inversely proportional to the molecular mass or atomic mass of ions.

Examples based on Arrhenius theory

Ex.3 The degree of ionization of a compound depends on

(A) size of solute

(B) nature of solute

(C) nature of vessel

(D) quantity of electricity passed

(Ans. B)

Sol. For strong electrolyte $\alpha \approx 100\%$, for weak electrolyte $\alpha \approx 1 - 10\%$, at the same concentration

Ex.4 $BaCl_2$ solution is always neutral in nature. Because -

(A) Number of barium ion = number of chloride ion

(B) Number of barium ion is just double than chloride ions

(C) Number of chloride ions are just half than Ba^{+2} ions.

(D) Number of Ba^{+2} ions is just half that of Cl^- ions

(Ans. D)

Sol. Magnitude of charge are equal in solution that's why solution is neutral in nature.

$$BaCl_2 \qquad Ba^{+2} + 2Cl^-$$

Ex.5 The acid with maximum strength has pK_a value equal to

(A) 30 (B) 4.5

(C) 1.0 (D) 2.0

(Ans. C)

Sol. Acidic strength $\propto K_a \propto \dfrac{1}{pK_a}$

3.1 Limitations of Arrhenius Concept : –

(a) H^+ and OH^- ions exist as hydrated ions.

(b) He was unable to explain the acidic nature of CO_2, SO_2 etc. and basic nature of NH_3, CaO, Na_2CO_3 etc.

(c) He could not explain the acid base reaction in the absence of water.

$$SO_3(g) + CaO(s) \rightarrow CaSO_4(g)$$

3.2 Factors affecting the degree of ionization : –

(a) **Temperature** – With the rise in temperature, the degree of dissociation of an electrolyte in solution increased. Thus,

Degree of dissociation $\propto$ Temperature

(b) **Dilution : –** On the increasing of dilution, the degree of dissociation increases. But at infinite dilution, their is no effect on the degree of dissociation.

(c) **Concentration of the solution : –**

Degree of dissociation

$$\propto \frac{1}{\text{Concentration of solution}}$$

$$\propto \frac{1}{\text{Amount of solute in given volume or wt. of solution}}$$

$\propto$ Amount of solvent

(d) **Nature of Solvent :–** Higher the dielectric constant of a solvent, more is its dissociation power or ionising power. Thus

Degree of ionization or dissociation of an electrolyte $\propto$ dielectric constant of solvent.

Dielectric constant :– The dielectric constant of solvent is a measure of its tendency to weaken the forces of attraction between oppositely charged ions of the given electrolyte or the force of attraction applied by solvent molecules or solute molecule is defined as Dielectric constant of solvent.

Note : – Water is the most powerful ionizing solvent as its dielectric constant is highest.

(e) **Presence of Common Ion :–** In the presence of a strong electrolyte having common ion, the degree of dissociation of an electrolyte decreases. eg. Ionisation of CH_3COOH is suppressed in the presence of HCl due to common H^+ ions.

(f) **Nature of Electrolyte :–** At constant temperature, electrolytes ionize to a different extent in their solutions of same concentration.

4. BRONSTED AND LOWRY CONCEPT OF ACIDS & BASES

4.1 Postulates :-

(1) Acid - Proton (H^+) donor

(2) Base - Proton (H^+) acceptor

e.g.

$HCl(aq) + H_2O(\ell) \rightleftharpoons H_2O^+(aq) + Cl^-(aq)$

Acid Base

$HCl(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$

Acid Base

$HCl(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COOH_2^+(aq) + Cl^-(aq)$

Acid Base

Note :- Here CH_3COOH has a less tendency to donate H^+ than HCl, therefore CH_3COOH acts as a weak base.

4.2 Conjugate Acid-Base Pair(CABP) :-

In an acid-base reaction

Acid $\longrightarrow$ H^+ + conjugate base

Base + H^+ $\longrightarrow$ conjugate acid.

e.g.

$HCl(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$

$Acid_1$ $Base_2$ $Acid_2$ $Base_1$

CABP

CABP

Note:- A CABP is different from each other only by single proton.

e.g.

HSO_4^- is the conjugate base of H_2SO_4 but SO_4^{2-} is not.

4.3 Relative strength of Acids/Bases :-

Any Species and its conjugate species are opposite of each other in terms of strength. e.g.

Acid (or Base)	*Conjugate Base (or Acid)*
(i) Weak	Strong
(ii) Strong	Weak

e.g.

Strength order of acids.

$HClO_4 > H_2SO_4 > HCl > CH_3COOH$

strength order of conjugate bases

$ClO_4^- < HSO_4^- < Cl^- < CH_3COO^-$

Examples based on Bronsted and Lowry concept of Acids and Bases

Ex.6 The conjugate base of HCO_3^- is -

(A) H_2CO_3 (B) CO_2

(C) H_2O (D) CO_3^-

(Ans. D)

Sol. $HCO_3^- \longrightarrow H^+ + CO_3^{2-}$

Acid Conjugate base

Ex.7 The conjugate acid of HSO_3^- is -

(A) SO_3^{2-} (B) SO_4^{2-}

(C) H_2SO_4 (D) H_2SO_3

(Ans. D)

Sol. $HSO_3^- + H^+ \longrightarrow H_2SO_3$

Base Conjugate acid

Ex.8 The conjugate base of H_2SO_4 in the following reaction is -

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

(A) H_2O (B) H_3O^+

(C) HSO_4^- (D) SO_4^{2-}

(Ans. C)

Ex.9 Which one of the following can act as Bronsted acid as well as Bronsted base ?

(A) CH_3COO^- (B) CO_3^{2-}

(C) HPO_4^{2-} (D) H_3PO_4

(Ans. C)

Sol. $PO_4^{3-} \xleftarrow{-H^+} HPO_4^{2-} \xrightarrow{+H^+} H_2PO_4^-$

5. IONIC PRODUCT OF WATER

Pure water is a very weak electrolyte -

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

on applying the law of mass action at equilibrium,

Then $K = \frac{[H^+][OH^-]}{[H_2O]}$

or $[H^+][OH^-] = K[H_2O]$

Since, ionization takes places to a very small extent, so the concentration of unionized water molecule is regarded as constant. Thus the product of $K[H_2O]$ gives another constant K_w.

So, $[H^+][OH^-] = K_W$

The product of concentration of H^+ and OH^- ion in water at a particular temperature is known as ionic product of water.

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

$K_W = 10^{-14}$

Note : – The value of K_W is increases with the increase in temperature i.e. the ionisation of water increases with increase in temperature and finally the concentration of H^+ and OH^- ion increases.

(a) Values of K_W at various temperature :–

	Temperature (ºC)	Value of K_W
(1)	0	0.11×10^{-14}
(2)	10	0.31×10^{-14}
(3)	20-35 or 25º (Room temp.)	1×10^{-14}
(4)	60	2.9×10^{-14}
(5)	80	5.6×10^{-14}
(6)	90	1×10^{-12}

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

$$-\log K_W = -\log [H^+] + (-) \log [OH^-]$$

$$pK_W = pH + pOH$$

$$\boxed{14 = pH + pOH}$$

The acidity and basicity depend upon the concentration of H^+ and OH^- ions.

If, $[H^+] > [OH^-]$ = Acidic solution

$[OH^-] > [H^+]$ = Basic solution

$[OH^-] = [H^+]$ = Neutral solution

Some Important Points to Remember : –

(a) Mass of 1 litre of water = 997 gm.

(b) Molar concentration of water = 55.5 gm-mole / litre.

(c) Number of water molecule in 1 litre of water = $55.5\times6.023\times10^{23} = 3.34\times10^{25}$.

(d) Concentration of H^+ ion in litre of neutral water = 10^{-7} moles / litre.

(e) Concentration of OH^- ion in litre of neutral water = 10^{-7} moles / litre.

(f) Number of H^+ ion in one litre of neutral water = 6.023×10^{16} .

(g) Number of OH^- ion in one litre of neutral water = 6.023×10^{16}.

(h) Hydrolysis constant of water -

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

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$= \frac{10^{-7}\times10^{-7}}{55.5} = 1.8 \times 10^{-16} \text{ Ans.}$$

Examples based on Ionic product of water

Ex.10 What will be the hydrogen ion concentration in a 0.175 M solution of HCl –

(A) 5.7×10^{-14} M (B) 6.75×10^{-12} M

(C) 5.75×10^{-10} M (D) 6.75×10^{-14} M

(Ans. A)

Sol. $K_W = [H^+][OH^-]$. $[H^+] = 0.175$ (Since HCl is a strong acid)

$\therefore [OH^-] = \frac{1\times10^{-14}}{0.175}$ = $\mathbf{5.7 \times 10^{-14}}$ **M**

Ex.11 What will be the hydrogen ion concentration of a 0.01 M solution of $Ca(OH)_2$ –

(A) 5×10^{-13} M (B) $5\ 5 \times 10^{-16}$

(C) 5×10^{-10} (D) None

(Ans. A)

Sol. $K_W = [H^+][OH^-]$

$[OH^-]$ = 0.02 M [Since there are 2 moles of OH^- per mode of $Ca(OH)_2$.]

$\therefore [H^+] = \frac{1\times10^{-14}}{0.02}$ = $\mathbf{5 \times 10^{-13}}$ **M**

Ex.12 The ionization constant for water is $1\times10^{-13.6}$ at 37ºC. What will be H_3O^+ and OH^- concentration at that temperature –

(A) 3.75×10^{-8} (B) 1.75×10^{-8}

(C) 1.58×10^{-7} (D) 1.85×10^{-8}

(Ans. C)

Sol. $K_W = [H^+][OH^-] = 1 \times 10^{-13.6}$

$[H^+][OH^-] = \sqrt{1\times10^{-13.6}}$ = $\mathbf{1.58 \times 10^{-7}}$

6. NEUTRALISATION

A reaction between acid and base to form salt and water molecule is known as neutralisation. In this type of reaction acid gives H^+ ion and base gives OH^- ion.

6.1 Salts :

(a) Species formed by the reaction of neutralization of acid and base is called as salt.

(b) salt formation is the exothermic process and released energy by this reaction is called as the heat of neutralization for 1 eq. monoacidic base and 1 eq. monobasic acid.

(c) The value of heat of neutralization is equal to 13.6 kcal.

(d) Salts are generally crystalline solid.

(e) Salts are classified into following four types.

6.1.1 Simple Salts :

These salts formed by the neutralisation process, which are of three types.

(a) Normal Salt : These salts are formed by the neutralization reaction of simple acid and simple base, like - NaCl, NH_4Cl, CH_3COONa, KNO_3 etc.

(b) Acid Salt : It is formed by the incomplete neutralization reaction of acid with the base is called the acidic salt and gives proton in aqueous solution. Like - $NaHCO_3$, $NaHSO_4$, Na_2HPO_4.

eg. $\underset{\text{(Dibasic)}}{H_2SO_4} + \underset{\text{1 mole}}{NaOH} \longrightarrow \underset{H^{\oplus}}{\overset{NaHSO_4}{\downarrow}}$

(c) Basic salt : Salt which is formed by the incomplete neutralization reaction of base with acid called the basic salt and gives OH^- ion in aqueous solution. Like - Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$ etc.

eg. $Ca(OH)_2 + \underset{\text{1mol}}{HCl} \longrightarrow \underset{\text{Basic salt}}{Ca(OH)Cl} + OH^-$

eg. $Mg(OH)_2 + \underset{\text{1mol}}{HNO_3} \longrightarrow \underset{\text{Basic salt}}{Mg(OH)NO_3}$

eg. $Al(OH)_3 + \underset{\text{1mol}}{HCl} \longrightarrow Al(OH)_2Cl \rightarrow \underset{\text{Basic salt}}{Al(OH)Cl_2}$

6.1.2 Mixed Salts :

Salt which are formed by the neutralization reaction of more than two different acids and bases are called mixed salt. Or Salts which furnish more than one cation or more than one anion when dissolved in water are also as mixed salt. **Like Rochelle salt**,

$Ca\begin{matrix} OCl \\ Cl \end{matrix}$ and $\begin{matrix} Na \\ K \end{matrix} SO_4$ etc.

eg. $\begin{matrix} HO-CH-COOH \\ | \\ HO-CH-COOH \end{matrix} + \begin{matrix} NaOH \\ KOH \end{matrix}$

(Two bases)

$\longrightarrow \begin{matrix} OH-CH-COONa \\ | \\ OH-CH-COOK \end{matrix}$

eg. $Ca(OH)_2 + \underset{\text{Two acids}}{HOCl / HCl} \longrightarrow CaOCl_2$

6.1.3 Double salts :

Salts which are formed by the addition of two or more simple salts are called as double salt.

eg. $K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow$ Potash alum

eg. $FeSO_4.(NH_4)_2SO_4.6H_2O \rightarrow$ Mohr's salt etc.

6.1.4 Complex salts : –

(a) Salt which are formed by the donation of electron pair by the legand molecule with the metal ion are called as complex salts. Or salts which are formed by the combination of simple salts or molecular compounds.

(b) Complex salts are stable in solid state.

(c) On dissolving the water, complex salts. Give minimum one complex ion -

eg. $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$

or all coordination compound

$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^4$

7. pH SCALE

(i) H^+ concentration in any solution can vary within a wide range from 1 mol dm^{-3} to 10^{-14} mol dm^{-3}. So a logarithmic notation has been devised by **Sorensen in 1909** to simplify the expression of these quantities.

(ii) The above notation is termed is p^H scale. According to the scale the hydrogen ion concentrations $[H^+]$ are expressed in terms of the numerical value of negative power to which 10 must be raised. i.e.

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

$$\text{or} \quad pH = -\log [H^+] = \log\left(\frac{1}{[H^+]}\right)$$

Note :

(i) $[H^+]$ should be taken always in mol dm^{-3} or mol L^{-1}.

(ii) Similarly $[OH^-]$ is also expressed i.e.
$pOH = -\log[OH^-]$
since we know $[H^+][OH^-] = K_w = 10^{-14}$
or **pH + pOH = 14 at 25ºC**

(iii)

$[H^+]$	$[OH^-]$	pH	pOH	Nature of solution
$10^o=1$	10^{-14}	0	14	Strongly Acidic
10^{-2}	10^{-12}	2	12	Acidic
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
10^{-9}	10^{-5}	9	5	Weakly basic
10^{-11}	10^{-3}	11	3	Basic
10^{-14}	$10^o=1$	14	0	Strongly basic

(iv) pH values of the solutions do not give immediate idea of the relative strength of the solution. e.g.

(a) For a solution of pH = 1 has a $[H^+]$ 100 times that of a solution of pH = 3. (not three times)

(b) A 4×10^{-5} N HCl is twice concentrated as a 2×10^{-5} N HCl solution but their pH values will be 4.4 and 4.7. (not double)

(v) A solution of an acid having very low concentration, say 10^{-8} N HCl, can not have pH = 8 as shown by definition but the pH will be less than 7.

7.1 Applications of pH

(a) pH of strong acid or strong base.

(i) pH of a strong acid or strong base can be calculated directly by its normality, since they are completely ionised.

e.g.

(a) For 10^{-2}M HCl $\equiv 10^{-2}$ N HCl

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

or $pH = -\log(10^{-2}) = 2$

(b) For 10^{-3} M NaOH $\equiv 10^{-3}$ N NaoH

$$[H^+] = \frac{10^{-14}}{[OH^-]} = 10^{-11}$$

or $pH = -\log(10^{-11}) = 11$

(c) For 10^{-2}M $H_2SO_4 \equiv 2\times10^{-2}$ N H_2SO_4

$[H^+] = 2\times10^{-2}$M

or $pH = -\log(2 \times 10^{-2}) = 1.699$

(d) For 10^{-3}M $Mg(OH)_2 \equiv 2 \times 10^{-3}$ N $Mg(OH)_2$

$$[H^+] = \frac{10^{-4}}{2 \times 10^{-3}} = 5 \times 10^{-12} \text{ M}$$

or $pH = -\log(5 \times 10^{-12}) = 11.3$

Note: Normality = Acidity or Basicity × Molarity

(b) pH of weak acid or weak base

(i) For weak acid or base $[H^+]$ can not be calculated by its concentration only since they are partially ionised.

(ii) For $[H^+]$ calculation either K_a (or K_b) or degree of dissociation will be required in addition to its concentrations (C).

(iii) As we know for weak acids

$[H^+] = \sqrt{K_a . C}$ or $[H^+] = C\alpha$

so $$\mathbf{pH = \frac{1}{2}(pK_a - \log C)}$$

(iv) For weak bases, $[OH^-] = \sqrt{K_b . C}$

or $[OH^-] = C\alpha$

so $$\mathbf{pOH = \frac{1}{2}(pk_b - \log C)}$$

8. HYDROLYSIS

It is defined as a process involving the reaction of water on a salt to form mixture of acid and base.

(a) It is the just reverse process of neutralization

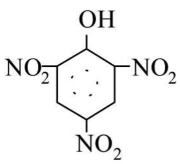
$$\text{Salt + water} \rightleftharpoons \text{Acid + Base}$$

(b) In this reaction the solution is always neutral when both acid and base are strong.

(c) If acid is stronger than base, the solution is acidic and if base is stronger than acid, the solution is basic.

(d) Depending upon the nature of an acid or a base, there can be four types of salt -

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

Strong acids	Weak acids	Strong bases	Weak bases
HCl	CH_3COOH	NaOH	NH_4OH
H_2SO_4	HCN	KOH	LiOH
HNO_3	H_2CO_3	RbOH	$Ca(OH)_2$
$HClO_4$	H_3PO_4	CsOH	$Be(OH)_2$
HI	H_3PO_3	$Ba(OH)_2$	$Zn(OH)_2$
H_2SO_3	HOCl		$Al(OH)_3$
	COOH | COOH		$Fe(OH)_3$ RNH_2 NH_3

8.1 Hydrolysis of Salt of Strong acid and Strong base :

$$\underset{\text{strong acid}}{HCl} + \underset{\text{strong base}}{NaOH} \longrightarrow \underset{\text{salt}}{NaCl} + H_2O$$

on Hydrolysis,

$$NaCl + H_2O \longrightarrow NaOH + HCl$$

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

Result:

$$H_2O \longrightarrow H^+ + OH^-$$

Thus, hydrolysis does not occur. So, the solution is neutral in nature i.e. salt of strong acid and strong base does not hydrolysed.

Note : No hydrolysis reaction takes place due to conjugate acid and base of this type of salt, which are weak.

8.2 Hydrolysis of Salt of Strong acid and Weak base :

$$\underset{\text{strong acid}}{HCl} + \underset{\text{strong base}}{NH_4OH} \longrightarrow \underset{\text{salt}}{NH_4Cl} + H_2O$$

on hydrolysis,

$$\underset{\text{Salt}}{NH_4Cl} + H_2O \longrightarrow \underset{\text{weak base}}{NH_4OH} + \underset{\text{strong acid}}{HCl}$$

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

Final equation

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

‘

A. Relation between hydrolysis constant of water (K_h), weak base dissociation constant (K_b) and ionic product of water (K_w) :

Let us consider a salt – BA

$$H_2O + \underset{\text{Salt}}{BA} \rightleftharpoons \underset{\text{weak base}}{BOH} + \underset{\text{strong acid}}{HA}$$

$$B^+ + A^- \rightleftharpoons BOH + H^+ + A^-$$

Resultant eq. $B^+ + H_2O \rightleftharpoons BOH + H^+$

on applying the law of mass action

$$K = \frac{[BOH][H^+]}{[B^+][H_2O]}$$

concentration of $[H_2O]$ remains almost constant means only one H_2O molecule is ionized out of 55 crore molecule of H_2O.

So, $$K[H_2O] = \frac{[BOH][H^+]}{[B^+]}$$

$$K_h = \frac{[BOH][H^+]}{[B^+]} \quad \text{----(1)}$$

Some part of H_2O would be ionized otherwise reaction will not be reversible.

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

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K[H_2O] = [H^+][OH^-]$$

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

$$[H^+] = \frac{K_W}{[OH^-]} \quad \text{----(2)}$$

Similarly some part of BOH will be also ionized -

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

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$[B^+] = \frac{K_b \times [BOH]}{[OH^-]} \quad \text{----(3)}$$

On putting the value of $[H^+]$ and $[B^+]$ on the equation (1) by the equation (2) and (3), we get -

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

B. Calculation of degree of hydrolysis : –

Assume the original concentration of the salt in the solution is C moles / lit. and h is its degree of hydrolysis at this concentration. Then we have -

	B^+ + H_2O	$\rightleftharpoons$ BOH	+ H^+
Initial molar	C	0	0

concentration

Molar concentration at equilibrium $(1-h)C$ hC hC

$\therefore$ $\frac{1-h}{V}$ $\frac{h}{V}$ $\frac{h}{V}$

$$K = \frac{[BOH][H^+]}{[B^+][H_2O]}$$

$$K[H_2O] = \frac{[BOH][H^+]}{[B^+]}$$

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

Since, h << 1, therefore $1 - h = 1$,

$$K_h = \frac{h^2}{V}$$

$$h^2 = K_h \times V$$

$$h = \sqrt{K_h V}$$

$\therefore$ K_h = Hydrolysis constant

Then, $h \propto \sqrt{V}$

Hence, the degree of hydrolysis is directly proportional to the square root of volume, inversely proportional to the square root of C.

$\therefore$ $h^2 = K_h \times V$ $\because$ $V = 1/C$

$$h^2 = \frac{K_h}{C}$$

$$\boxed{h = \sqrt{\frac{K_h}{C}}}$$

on putting the value of K_h in the above equation -

$$\boxed{h = \sqrt{\frac{K_W}{K_b \times C}}}$$

C. Calculation of hydrogen ion concentration or calculation of pH : –

Since, $[H^+] = \frac{K_W}{[OH^-]}$ and $[OH^-] = hC$

$$\therefore \quad [H^+] = \frac{K_W}{hC}$$

But $h = \sqrt{\frac{K_W}{K_b . C}}$

$$[H^+] = C\sqrt{\frac{K_W}{K_b . C}} = \sqrt{\frac{K_W C}{K_b}} = \left(\frac{K_W C}{K_b}\right)^{1/2}$$

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

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

$$pH = -\frac{1}{2}\log K_W + \frac{1}{2}\log K_b - \frac{1}{2}\log C$$

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

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

Here, on the study of above equation, we can say that the pH of the strong acid weak base is less than 7.

8.3 Hydrolysis of salt of Weak acid and Strong base :

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

on hydrolysis

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

Salt   Weak acid   strong base

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

Result : –

(i) Hydrolysis of salt of weak acid and strong base is called anionic hydrolysis.

(ii) Solution of this type of salt is basic in nature as forming of OH^- ion in resultant reaction.

(iii) This type of solution turns red litmus to blue.

(iv) As solution is basic, the pH will be greater than 7.

A. Relation between K_h, K_W and K_a :

Let us consider a salt - BA

$$H_2O + BA \rightleftharpoons BOH + HA$$

Salt   Strong base   Weak acid

$$B^+ + A^- \rightleftharpoons B^+ + OH^- + HA$$

Resultant equation :– $A^- + H_2O \rightleftharpoons OH^- + HA$

on applying the law of mass action,

$$K = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

Concentration of $[H_2O]$ remains almost constant means only one H_2O molecule is ionized out of 55 crore molecule of H_2O.

So, $$K[H_2O] = \frac{[HA][OH^-]}{[A^-]}$$

$$K_h = \frac{[HA][OH^-]}{[A^-]} \quad \text{---(1)}$$

Some part of H_2O would be ionized otherwise reaction will not be reversible -

$$\therefore \quad H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$K[H_2O] = [H^+] [OH^-]$

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

$$[OH^-] = \frac{K_W}{[H^+]} \quad \text{---(2)}$$

Similarly some part of HA will be also ionized.

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

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

$$[A^-] = \frac{K_a \times [HA]}{[H^+]} \quad \text{---(3)}$$

on putting the value of OH^- and A^- on the equation (1) by the equation (2) and (3), we get -

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

B. Calculation of degree of hydrolysis :

Assume the original concentration of salt in the solution is C moles / lit. and h is its degree of hydrolysis at this concentration. Then we have

	A^- + H_2O $\rightleftharpoons$	OH^-	+ HA
Initial molar concentration	C	0	0
Molar concentration at equilibrium	(1 – h)C	hC	hC

$$\therefore \quad K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{hC \times hC}{(1-h)C}$$

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

It h is very small as compared to one. Then (1 – h) can be equal to 1. Hence, the above equation becomes

$K_h = h^2C$

$$h = \sqrt{\frac{K_h}{C}} \qquad \because C = \frac{1}{V}$$

$$\therefore \quad h = \sqrt{K_h \times V}$$

Thus, the degree of hydrolysis of a salt of weak acid and strong base is inversely proportional to the square root of the molar concentration and directly proportional to the square root of the volume of the solution.

on putting the value of K_h, $h = \sqrt{\frac{K_W}{K_a C}}$

C. Calculation of hydrogen ion concentration or calculation of pH :

Since, $[H^+] = \frac{K_W}{[OH^-]}$ and $[OH^-] = hC$

$$\therefore \quad [H^+] = \frac{K_W}{hC}$$

but $$h = \sqrt{\frac{K_W}{K_a C}}$$

$$\therefore \quad [H^+] = \frac{K_W}{C} \times \sqrt{\frac{K_a C}{K_W}} = \sqrt{\frac{K_W K_a}{C}}$$

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

$$= -\log \sqrt{\frac{K_W . K_a}{C}}$$

$$= -\log \left(\frac{K_W . K_a}{C}\right)^{1/2}$$

$$= -\frac{1}{2}\log K_W - \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

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

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

Here, on the study of above equation, we can say that the pH of strong base weak acid salt is greater than 7 and therefore solution of salt of strong base weak acid be always alkaline.

8.4 Hydrolysis of salt of weak acid and weak base :

$$CH_3COOH + NH_4OH \rightleftharpoons CH_3COONH_4 + H_2O$$

on hydrolysis

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Salt Weak acid Weak base

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

Result : –

(i) $CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$
This type of salt hydrolysis is called isoionic salt hydrolysis.

Conditions :

(a) If $pK_a = pK_b$, the pH = 7 and solution is neutral.

(b) If $pK_a > pK_b$, the pH > 7 and solution is alkaline because here the acid is relatively weaker than base.

(c) If $pK_a < pK_b$, the pH < 7 and solution is acidic because here the base is relatively weaker than acid.

A. Relation between K_h, K_w, K_a and K_b :

Let us consider a salt - BA

$$BA + H_2O \rightleftharpoons HA + BOH$$

Weak acid Weak base

$$B^+ + A^- + H_2O \rightleftharpoons HA + BOH$$

Note : – Here is this solution the HA and BOH are weak acid and bases. So, They remain almost undissociated.

on applying the law os mass action,

$$K = \frac{[HA]\,[BOH]}{[B^+]\,[A^-]\,[H_2O]}$$

Concentration of $[H_2O]$ remains almost constant.

$$\text{So, } K[H_2O] = \frac{[HA]\,[BOH]}{[B^+]\,[A^-]}$$

$$K_h = \frac{[HA]\,[BOH]}{[B^+]\,[A^-]} \quad \text{---(1)}$$

Now, let us consider the dissociation of weak species HA and BOH -

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

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

$$\therefore \quad K_a = \frac{[H^+]\,[A^-]}{[HA]} \quad \text{---(2)}$$

$$\text{and} \quad K_b = \frac{[B^+]\,[OH^-]}{[BOH]} \quad \text{---(3)}$$

We know that,

$$K_W = [H^+]\,[OH^-] \quad \text{---(4)}$$

Dividing (4) by (2) and (3) -

$$\frac{K_W}{K_a \times K_b} = \frac{[H^+]\,[OH^-]\,[HA]\,[BOH]}{[H^+]\,[A^-]\,[B^+]\,[OH^-]}$$

$$= \frac{[HA]\,[BOH]}{[B^+]\,[A^-]} \quad \text{---(5)}$$

from equation (1) and (5) -

$$K_h = \frac{K_W}{K_a \times K_b} \quad \text{---(6)}$$

B. Calculation of degree of hydrolysis :

Assume again, the original concentration of salt in the solution is C moles / litre and h is its degree of hydrolysis at this concentration. Then we have

	B^+ +	A^- + $H_2O \rightleftharpoons$	HA +	BOH
Initial molar concentration	C	C	0	0
Molar concentration at equilibrium	(1 – h)C	(1 – h)C	hC	hC

$$\therefore \quad K_h = \frac{[HA]\,[BOH]}{[B^+]\,[A^-]}$$

$$= \frac{hC \times hC}{(1-h)C \times (1-h)C}$$

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

If h is very small as compared to 1 then (1 – h) is equal to 1. Hence the above equation becomes,

$$K_h = h^2$$

$$\text{or} \quad h = \sqrt{K_h}$$

Thus, the degree of hydrolysis in this case is independent of concentration or dilution of the salt.

on putting the value of K_h from equation (6)

$$h = \sqrt{\frac{K_W}{K_a \times K_b}}$$

C. Calculation of hydrogen ion concentration or calculation of pH :

In this type of cases, the hydrogen ion concentration may be calculated from the following equation of weak acid HA.

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

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

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

$$[H^+] = K_a\frac{hC}{(1-h)C} = K_a\frac{h}{(1-h)}$$

Since, h << 1 then (1 – h) = 1

$[H^+] = K_a \times h$

on putting the value of h

$$[H^+] = K_a\sqrt{\frac{K_W}{K_a.K_b}} = \sqrt{\frac{K_W.K_a}{K_b}}$$

We know that

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

$$= -\log\sqrt{\frac{K_W.K_a}{K_b}}$$

$$= -\log\left(\frac{K_W.K_a}{K_b}\right)^{1/2}$$

$$= -\frac{1}{2}\log K_W - \frac{1}{2}\log K_a + \frac{1}{2}pK_B$$

$$= \frac{1}{2}pK_w + \frac{1}{2}pK_A - \frac{1}{2}pK_b$$

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

Examples based on hydrolysis of different types of salts

Ex.13 A 0.01 M solution of HCN is 0.01% ionised. The ionisation constant of the acid is -

(A) 10^{-4} (B) 10^{-6}
(C) 10^{-10} (D) 10^{-8}

(Ans. C)

Sol. According to Ostwald's dilution Law

$$K_a = \frac{\alpha^2}{1-\alpha}.C = \alpha^2 C$$

K_a = Ionisation constant

α = Degree of dissociation

C = Molar concentration

For HCN, C = 0.01 M

$\alpha = 10^{-4}$

$\therefore$ $K_a = (10^{-4})^2 . (0.01) = 10^{-10}$

Ex.14 Freshly prepared Al $(OH)_3$ and Mg $(OH)_2$ are stirred vigorously in a buffer solution containing 0.25 M NH_4Cl and 0.05 M NH_4OH. What is the concentration of Al^{+3} ions in solution –

(A) 0.986×10^{-15} M (B) 1.286×10^{-15} M
(C) 2.286×10^{-15} M (D) 3.286×10^{-15} M

(Ans B)

Given-

[K_b $NH_4OH = 1.8 \times 10^{-5}$

K_{SP} $Al(OH)_3 = 6 \times 10^{-32}$]

Sol. $p(OH) = pK_b + \log\frac{[Salt]}{[Base]} = 4.74 + \log\frac{0.25}{0.05}$

$= 5.44$

$\therefore$ $[OH^-] = 3.6 \times 10^{-6}$ M

K_{SP} $Al(OH)_3 = 6 \times 10^{-32} = [Al^{+3}][OH^-]^3$

$\therefore$ $[Al^{+3}] = \frac{6 \times 10^{-32}}{(3600 \times 10^{-6})^3}$

$= 1.29 \times 10^{-15}$ M

Ex.15 What is the pH of solution having H^+ ion concentration of 0.052 mole/litre -

(A) 2.28 (B) 3.28
(C) 1.28 (D) 4.28

(Ans. C)

Sol. $[H^+]$ ion concentration = 0.052 mole/litre

$\therefore$ pH = – log $[H^+]$

= – log 0.052 = – log 5.2×10^{-2}

= – (–2 +0.716)

= 1.284

$\cong$ 1.28

Ex.16 What will be the pH of an aqueous solution 1.0 M ammonium formate assuming complete dissociation. (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)

(A) 8.5 (B) 6.5

(C) 9.5 (D) 5.5

(Ans. B)

Sol. The pH of salt $HCOONH_4$ (a salt of weak acid + weak base) is given by -

$HCOONH_4 + H_2O \quad HCOOH + NH_4OH$

pH = 1/2 [log K_b – log K_a – logK_W]

$\therefore$ pH = 1/2 [pK_a + pK_W – pK_b]

pH = 1/2 [3.8 + 14 – 4.8] **= 6.5**

Ex.17 What is the pH of 0.10 M CH_3COONa solution. Hydrolysis constant of sodium acetate is 5.6×10^{-10}–

(A) 8.874 (B) 88.74

(C) 887.4 (D) 0.88

(Ans. A)

Sol. Hydrolysis of the salt may be represented as

$CH_3COO^- + Na^+ + H_2O$

$CH_3COOH + Na^+ + OH^-$

or $CH_3COO^- + H_2O \quad CH_3COOH + OH^-$

At t=0	C	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_h = \frac{C^2\alpha^2}{C(1-\alpha)} = C\alpha^2 \quad \text{when } \alpha < 1$$

$$\alpha = \sqrt{\left(\frac{K_h}{C}\right)} = \sqrt{\left(\frac{5.6 \times 10^{-10}}{0.10}\right)}$$

$= 7.5 \times 10^{-5}$

$[OH^-]$ = $C\alpha$ = $0.10 \times 7.5 \times 10^{-5}$

pOH = – log (7.5×10^{-6}) = 5.126

pH = 14 – pOH = 14 – 5.126

= 8.874

Ex.18 What will be the pH value of a 0.1 M aqueous solution of NH_4Cl ?

(Given pK_{NH_4OH} = 4.73)

(A) 37.8 (B) 378

(C) 3.78 (D) None

(Ans. C)

Sol. NH_4CN is salt of weak acid and weak base; its pH may be determined using following formula

$$pH = \frac{1}{2}[pK_W + pK_a - pK_b]$$

$$= \frac{1}{2}[14 + 9.04 - 4.73]$$

= 9.155

Ex.19 The pH of 0.1 M NH_4Cl solution is 5.13. What will be the dissociation constant of NH_4OH –

(A) 1.8×10^{-7} (B) 1.8×10^{-9}

(C) 1.8×10^{-5} (D) None

(Ans. C)

Sol. NH_4Cl is salt of weak base and strong acid, formula for pH of its hydrolysis may be calculated as,

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

where pH = 5.13

pK_W = – log K_W

= – log 10^{-14} = 14

log C = log 0.1 = – 1

Substituting the values in equation (1) we get –

$$5.13 = \frac{1}{2}[14 - pK_b + 1]$$

10.26 = 15 – pK_b

pK_a = 4.74

$\therefore$ – log K_b = pK_b = 4.74

K_b = antilog (–4.74)

K_b = **1.8×10^{-5}**

Ex.20 A certain weak acid has a dissociation constant of 1×10^{-4} the equilibrium constant for its reaction with strong bases is -

(A) 10^{-1} (B) 10^{-10}

(C) 10^{10} (D) 10^{14}

(Ans. C)

Sol. Weak acid + Strong base $\xrightleftharpoons{\text{Neutralization}}$ Salt + Water ----(1)

Salt + Water $\xrightleftharpoons{\text{Hydrolysis}}$ Weak acid + Strong base ---- (2)

Hydrolysis may be considered as reverse process of neutralization.

Thus, equilibrium constant for neutralization (1) will be equal to $1/K_h$. Where K_h is hydrolysis constant for equation (2)

$$K_{eq} = \frac{1}{K_h} = \frac{1}{K_w / K_a}$$

$$= \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = \mathbf{10^{10}}$$

9. BUFFER SOLUTIONS

(i) In certain applications of chemistry and biochemistry we require solutions of constant pH. Such solution are called buffer solution.

(ii) A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called buffer solution.

(iii) Buffer solutions are also called solutions of reverse acidity or alkalinity.

(iv) Following are the characteristics of buffer solutions

(a) It must have constant pH.

(b) Its pH should not be changed on long standing

(c) Its pH should not be changed on dilution.

(d) It pH should not be changed to any great extent on addition of small quantity of acid or base.

(v) Buffer solutions can be classified as follows.

(A) Simple buffer (B) Mixed buffer

9.1 Simple buffer

(i) It is a solution of one compound i.e. salts of WA + WB (Refer salt hydrolysis.)

(ii) Buffer action of such solution can be explained as follows,

In the salt solution of CH_3COONH_4 following equilibria will be there,

(a) $CH_3COO^+(aq.) + NH_4^+(aq.) + H_2O \rightleftharpoons CH_3COOH(aq.) + NH_4OH(aq.)$

(Salt hydrolysis)

(b) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (weak base)

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

(d) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ (feebly ionised)

on addition of small amount of acid the $[H^+]$ in solution will increase and

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

(from acid) (very less ionised)

equilibria will shift in forward direction. Similarly on addition of small amount of base, the $[OH^-]$ in solution will increase

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

(from base) (very less ionised)

equilibria will shift in forward direction Hence one can conclude that there will be no change (almost) in the pH of the solution.

(iii) Simple buffer solutions have very little significance since $pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$ so solution of desired pH can not be prepared.

9.2 Mixed buffer

Mixed buffers are solutions of more than one compounds.They can be further classified as

(a) Acidic buffer

(b) Basic buffer

(c) A mixture of an polyprotic acid and its acidic salt

(d) Solution of ampholyte or amphoteric electrolyte viz. Proteins and Amino acids.

Note :

(i) Ampholyte or amphoteric electrolytes are those which can show properties of both acid and base.

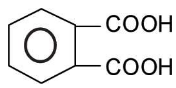
9.2.1 Acidic buffer

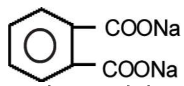
(i) These are the mixture of a weak acid and its salt with strong base.

e.g.

(a) $CH_3COOH + CH_3COONa$

(b) Boric acid (H_3BO_3) + Borax ($Na_2\ B_4O_7$)

(c) Phthalic acid  +

Sodium phthalate 

(ii) Buffer action of acidic buffer can be explained with following equilibria,

(a) $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ (Feebly ionised.)

(b) $CH_3COONa \longrightarrow Na^+ + CH_3COO^-$ (completely ionised.)

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

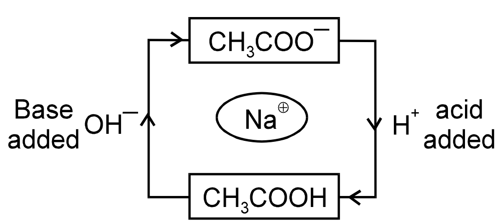
When a strong acid is added in the solution $[H^+]$ increases, which will combine with CH_3COO^- to form feebly ionised CH_3COOH, which is also suppressed by common ion effect,

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

Again when strong base is added in the solution it will attack on unionised acid CH_3COOH to form feebly ionised H_2O molecules

CH_3COOH + OH^- (from base) $\rightleftharpoons$ $CH_3COO^- + H_2O$

(iii) One can remember the buffer action of acidic buffer with the help of following figure -



(iv) pH of such acidic buffer can be calculated as follows.

(a) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (Ka)

(b) $CH_3COONa \xrightarrow{H_2O} CH_3COO^-(aq.) + Na^+ (aq.)$

CH_3COOH is feebly ionised and its ionisation is also suppressed by presence of common ion (CH_3COO^-). So one can fairly assume $[CH_3COO^-]$=[salt] and $[CH_3COOH]$=[Acid] taken initially in buffer solution.

so $$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

or $$[H^+] = \frac{Ka[CH_3COOH]}{[CH_3COO^-]}$$

$\log[H^+] = \log K_a + \log[CH_3COOH] - \log[CH_3COO^-]$

$-\log[H^+] =$

$-\log K_a - \log[CH_3COOH] + \log[CH_3COO^-]$

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

$$pH = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

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

Above equation called Henderson's equation.

* If we increase the concentration of given salt in acidic buffer, pH will also increases.
* If we increase the concentration of acid in acidic buffer, pH will decreases.
* If conc. and volume are given for salt and acid then the pH is given by the following formula-

$$pH = pK_a + \log\frac{[N_2V_2]}{[N_1V_1]}$$

Where N_2V_2 = conc. & volume of salt

N_1V_1 = conc. & volume of acid

Note : Mixture of weak acid and strong base solution can also act as an acidic buffer, if value of N_1V_1 of weak acid is greater than the value of N_2V_2 of strong base.

9.2.2 Basic Buffer

(i) These are the mixture of a weak base and its salt with strong acid.

e.g.

(a) $NH_4OH + NH_4Cl$

(b) Glycine (NH_2CH_2COOH) + Glycine hydrochloride ($Cl\overset{+}{N}H_3CH_2COOH$)

(ii) Buffer action of basic buffer can be explained with the help of following equilibria

(a) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (K_b)

(b) $NH_4Cl \longrightarrow NH_4^+ + Cl^-$

(c) $H_2O \rightleftharpoons H^+ + OH^-$ (Kw)

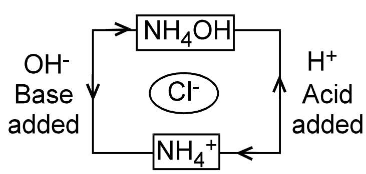
When a strong base is added in the solution $[OH^-]$ increases, which will combine with NH_4^+ to form feebly ionised NH_4OH, which is also suppressed by common ion effect.

$NH_4^+ + OH^-$(From base) $\rightleftharpoons NH_4OH$(Weak base)

Again when strong acid is added in the solution it will attack on unionised base NH_4OH to form feebly ionised H_2O molecules.

$NH_4OH + H^+$ (From acid) $\rightleftharpoons NH_4^+ + H_2O$

(iii) One can remember the buffer action of basic buffer with the help of following figure -



(iv) p^H of such basic buffer can be calculated from Henderson - Hasselbalch equation as follows.

(a) $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (K_b)

(b) $NH_4Cl \xrightarrow{H_2O} NH_4^+$ (aq.) + Cl^- (aq.)

NH_4OH is feebly ionised and its ionisation is also suppressed by presence of common ion (NH_4^+). So one can fairly assume $[NH_4^+]$ = [Salt] and $[NH_4OH]$ = [Base] taken initially in buffer solution.

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

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

$= \dfrac{K_a[\text{Base}]}{[\text{Salt}]}$

or $\mathbf{pOH = pK_b + \log\dfrac{[Salt]}{[Base]}}$

or $pH = 14 - pOH$

9.3 Buffer Capacity

(i) The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.

(ii) Buffer capacity is number moles of acid or base added in one litre of solution as to change the pH by unity, i.e.

Buffer capacity (ϕ)

$$= \frac{\text{Number of moles acid or base added to 1l sol.}}{\text{Change in pH}}$$

or $\phi = \dfrac{\partial b}{\partial(pH)}$

where ∂b is number of moles of acid or base added and $\partial(pH)$ is change in pH.

9.4 Applications of Buffer solutions in analytical chemistry.

(i) For the removal of PO_4^{3-} ion after second group using $CH_3COOH + CH_3COONa$ buffer.

(ii) For the precipitation of lead chromate quantitatively in gravimetric analysis using $CH_3COOH + CH_3COONa$ buffer.

(iii) For the precipitation of hydroxides of IIIrd group using $NH_4Cl + NH_4OH$ buffer.

(iv) A buffer solution of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ is used for precipitation of carbonates of Vth group.

Examples based on buffer solution

Ex.21 What will be the pH of the buffer solution containing 0.15 moles of NH_4OH and 0.25 moles of NH_4Cl. K_b for NH_4OH is 1.8×10^{-5} –

(A) 9.08 (B) 10.03
(C) 9.05 (D) 9.03

Sol. Since it is a basic buffer so,

pOH = pK_b+log[Salt]/[Base]

pOH = – log K_b+log[Salt/Base]

= $-\log(1.8\times10^{-5})+\log(0.25/0.15)$

= 4.74 + 0.22 = 4.96

or pOH = 4.97

pH = 14–pOH

= 14 – 4.97

= 9.03

Ans. (D)

Ex.22 Calculate the pH of a buffer prepared by mixing 300 cc of 0.3 M NH_3 and 500 cc of 0.5 M NH_4Cl.

Kb for NH_3 = 1.8 x 10^{-5}–

(A) 8.11 (B) 9.81

(C) 8.82 (D) None of these

Sol. Total volume of the buffer solution

= 300 cc + 500 cc = 800 cc

Number of milli moles of NH_3=300x0.3=90

Molarity of NH_3 (Base) in the buffer=90/800 M

NumberofmillimolesofNH_4Cl=500x0.5=250.0

Molarity of [salt] in the buffer = 250/800 M

Henderson's equation for basic buffer is:

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

$$= -\log 1.8 \times 10^{-5} + \log \frac{250/800}{90/800}$$

= 4.74 + log 250/90

= 4.74 + 0.44

= 5.18

pH = 14 – pOH = 14– 5.18 = 8.82

Ans. (C)

Ex.23 Calculate pH of the buffer solution containing 0.15 moles of NH_4OH and 0.25 moles of NH_4Cl. K_b for NH_4OH is 1.98 x 10^{-5}.

(A) 7.034 (B) 9.04

(C) 8.043 (D) None of these

Sol. Applying the equation,

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

$$= \log \frac{0.25}{0.15} - \log 1.8 \times 10^{-5}$$

= log 5 – log 3 – log 1.8 x 10^{-5}

= 4.96

pH = (14– 4.96) = 9.04

Ans.(B)

Ex.24 0.15 mole of pyridium chloride has been added into 500 cm^3 of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentrations the resulting solution assuming no change in volume.

(K_b for pyridine = 1.5 x 10^{-9} M)

(A) 4 (B) 9

(C) 5 (D) 8

Sol. Concentration of pyridium chloride

= 0.15 x 2 = 0.3 M.

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

$$= \log \frac{0.3}{0.2} - \log 1.5 \times 10^{-9} = 9$$

$[OH^-] = 10^{-pOH} = 10^{-9}$

pH = (14–pOH) = (14–9) = 5

Ans. (C)

10. SOLUBILITY (s)

At a constant temperature, the mass of a solute or electrolyte dissolved in the 100 gm of solvent in its saturated solution is called as solubility. Or number of gm mole of a solute dissolved in one litre of water at constant temperature is called as solubility of that solute.

Solubility of a solute in moles / litre

$$= \frac{\text{Solubility of solute in gm / litre}}{\text{molecular weight of the solute}}$$

10.1 Solubility product (K_{SP}) :

It is the product of the ionic concentration of the ions of binary solid electrolyte in saturated state at constant temperature.

(a) Let solubility of a compound $A_x B_y$ be s moles L^{-1} it means that if more than s moles are dissolved in solvent (one litre) only s moles will be soluble, rest will be insoluble, following equilibrium is established,

$$\underset{\text{Insoluble Solute}}{AB} \rightleftharpoons \underset{\text{Unionised}}{AB} \rightleftharpoons \underset{\text{Ions}}{A^+ + B^-}$$

(Saturated solution)

Note : – In the solubility s moles L^{-1}, moles of only unionised are counted moles of ions and insoluble solute do not have anything to do.

(b) According to law of mass action -

$$K_1 = \frac{[A^+][B^-]}{[AB]}$$

or $K_1 [AB] = [A^+] [B^-] = K_{SP}$

This K_{SP} is called **solubility product**.

(c) At a certain temperature solubility product of a compound is constant, it means that ions are formed in the manner that product of their concentration is always a constant. However, it becomes clear that if one of ions (A^+ or B^-) is added from outside, it would tend to increase K_{SP} because $[A^+]$ or $[B^-]$ has get increased, so that extra ions will react with other ions to convert in insoluble part and this will get precipitated.

(d) K_{SP} increases with increase in temperature.

(e) In a saturated solution.

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

(f) In an unsaturated solution of AB

$$K_{SP} > [A^+] [B^-]$$

i.e. more solute can be dissolved.

(g) In a supersaturated solution

$$K_{SP} < [A^+] [B^-]$$

i.e. precipitation will start to occur.

10.2 Relationship between Solubility and Solubility Product :

The equilibrium for a saturated solution of a salt $A_x B_y$ may be expressed as,

$$A_x B_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Thus, solubility product $K_{SP} = [A^{y+}]^x [B^{x-}]^y$

Let the solubility of the salt $A_x B_y$ in water at a particular temperature be 's' moles per litre then

$$A_x B_y \rightleftharpoons \underset{xs}{xA^{y+}} + \underset{ys}{yB^{x-}}$$

So, $K_{SP} = [xs]^x [ys]^y$

$K_{SP} = x^x . y^y (s)^{x+y}$

(a) **1 : 1 types salts or AB type of salts :**

eg. AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

$$AB \rightleftharpoons A^+ + B^-$$

let the solubility of AB is s moles per litre.

So, $K_{SP} = [A^+] [B^-] = s \times s = s^2$

$$s = \sqrt{K_{SP}}$$

(b) **1 : 2 or 2 : 1 type of salts or AB_2 or A_2B type of salts :**

eg. Ag_2CrO_4, PbI_2, Ag_2CO_3, CaF_2, $CaCl_2$ etc.

(i) $AB_2 \rightleftharpoons \underset{s}{A^{2+}} + \underset{2s}{2B^-}$

let the solubility of AB_2 is 's' moles per litre

So, $K_{SP} = [A^{2+}][B^-]^2 = s \times (2s)^2 = 4s^3$

$$s = \sqrt[3]{\frac{K_{SP}}{4}}$$

(ii) $A_2B \rightleftharpoons 2A^+ + B^{2-}$

let s the solubility of A_2B

So, $A_2B \rightleftharpoons \underset{2s}{2A^+} + \underset{s}{B^{2-}}$

$K_{SP} = [A^+]^2 [B^{-2}]$

$= (2s)^2 (s) = 4s^3$

$$s = \sqrt[3]{\frac{K_{SP}}{4}}$$

(c) **1 : 3 type of salts or salts of AB_3 or A_3B type of salt -**

AB_3 = Valency of A = 3 × Valency of B

eg. $FeCl_3$, $AlCl_3$, PCl_3, $Al(OH)_3$, $Fe(OH)_3$ etc.

A_3B = 3 × Valency of A = Valency of B

eg. Na_3BO_3, Na_3PO_4, H_3PO_4 etc.

(i) $AB_3 \rightleftharpoons A^{3+} + 3B^-$

let the solubility of A_3B is 's' mole / litre.

$AB_3 \rightleftharpoons \underset{s}{A^{3+}} + \underset{3s}{3B^-}$

$K_{SP} = [A^{3+}] [B^-]^3 = s \times (3s)^3 = 27s^4$

$$s = \sqrt[4]{\frac{K_{SP}}{27}}$$

(ii) $A_3B \rightleftharpoons 3A^+ + B^{-3}$

let the solubility of A_3B is 's' moles/litre.

$$A_3B \rightleftharpoons \underset{3s}{3A^+} + \underset{s}{B^{-3}}$$

$$K_{SP} = [A^+]^3 \; [B^{-3}]$$
$$= (3s)^3 \times s = 27s^4$$

$$s = \sqrt[4]{\frac{K_{SP}}{27}}$$

(d) **2 : 3 or A_2B_3 type of salts :**

eg. $Al_2(SO_4)_3$

$$A_2B_2 \rightleftharpoons 2A^{+3} + 3B^{-2}$$

let the solubility of salt A_2B_3 is 's' -

So, $A_2B_3 \rightleftharpoons \underset{2s}{2A^{+3}} + \underset{3s}{3B^{-2}}$

$$K_{SP} = [A^{+3}]^2 \; [B^{-2}]^3$$
$$= (2s)^2 \times (3s)^3$$
$$= 4s^2 \times 27 s^3$$
$$K_{SP} = 108 s^5$$
$$s = \sqrt[5]{\frac{K_{SP}}{108}}$$

Examples based on solubility and solubility product

Ex.25 The solubility of CaF_2 in water at 20ºC is 15.6 mg per dm^3 solution. What will be the solubility product of CaF_2 –

(A) 4.0×10^{-4} (B) 8.0×10^{-8}

(C) 32.0×10^{-12} (D) None

(Ans. C)

Sol. Solubility in moles per dm^3

$$= \frac{15.6 \times 10^{-3}}{78\,g/mole} = 2.0 \times 10^{-4}$$

$\because$ $CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$

$\therefore$ $[Ca^{+2}] = 2.0 \times 10^{-4}$

and $[F^-] = 2 \times 2.0 \times 10^{-4}$

Hence, solubility product K_{SP}

$= [Ca^{+2}]\,[F^-]^2 = [2.0 \times 10^{-4}]\,[4.0 \times 10^{-4}]$

$= 32 \times 10^{-12}$

Ex.26 Given the solubility product of F_3B_2 is 2×10^{-30}. What will be the solubility in moles/litre.

(A) $(1.85 \times 10^{-32})^{1/5}$ (B) $\left(\frac{2 \times 10^{-3}}{108}\right)^{1/5}$

(C) $\left(\frac{10-28}{5400}\right)^{1/5}$ (D) All

(Ans. B)

Sol. K_{SP} of $A_3B_2 = 2 \times 10^{-30}$.

$$A_3B_2 \rightleftharpoons 3A^{+2} + 2B^{-3}$$

Assume s is the solubility of A_3B_2

then $K_{SP} = (3s)^3 \; (2s)^2 = 108 s^5$

$$s = \sqrt[5]{\frac{K_{SP}}{108}}$$

$$s = \left(\frac{2 \times 10^{-30}}{108}\right)^{1/5}$$

Ex.27 How many milligrams of AgBr will dissolve in water to give litres of aqueous solution. Given K_{SP} for AgBr (Mol. wt. 188) $= 5.0 \times 10^{-13}$ M^2–

(A) 7.071×10^{-7} moles per litre

(B) 70.71×10^{-7} moles per litre

(C) 707.1×10^{-7} moles per litre

(D) None of these

(Ans. A)

Sol. $AgBr \rightleftharpoons Ag^+ + Br^-$ moles per litre

$K_{SP} = [Ag^+]\,[Br^-] = 5.0 \times 10^{-13}$

$= s \times s = s^2$

$s^2 = 50 \times 10^{-14}$

or s **$= 7.071 \times 10^{-7}$ moles per litre**

Ex.28 The solubility of AgCl is 0.0014 g per litre at 18ºC. What will be its solubility product at 18ºC. Molecular weight of AgCl = 143.5 –

(A) 3.952×10^{-10} (B) 0.0952×10^{-10}

(C) 1.952×10^{-10} (D) 0.952×10^{-10}

(Ans. D)

Sol. Solubility in moles $= \frac{0.0014}{143.5} = 0.9757 \times 10^{-5}$

Solubility product $K_{SP} = [Ag^+]\,[Cl^-]$

$= s \times s = s^2 = (0.9757 \times 10^{-5})^2$

$= 0.952 \times 10^{-10}$

Ex.29 What concentration of Ag^+ ions will be in equilibrium with a saturated solution containing a precipitate of Ag_2CrO_4 and CrO_4^- ion concentration of 0.40 moles per litre . Given K_{SP} of $Ag_2CrO_4 = 1.1 \times 10^{-11}$

(A) 5.2×10^{-6} moles per litre

(B) 2.5×10^{-6} moles per litre

(C) 7.5×10^{-6} moles per litre

(D) 5.9×10^{-6} moles per litre

(Ans. A)

Sol. K_{SP} $[Ag^+]^2$ $[CrO_4^{2-}]$ = 1.1×10^{-11}
= $[Ag^+]^2$ $[CrO_4^{2-}]$ = $[Ag^+]^2$ [0.40]

or $[Ag^+]^2 = \frac{1.1 \times 10^{-11}}{0.40} = 27.5 \times 10^{-12}$

or $[Ag^+]$ **= 5.2×10^{-6} moles per litre**

10.3 Applications of K_{SP} :

A. In purification of common salt : In a saturated solution of NaCl & impurities, by passing HCl gas through it, increase the Cl^- ion concentration which shifts the equilibrium $NaCl \rightleftharpoons Na^+ + Cl^-$ to left & causes the precipitation of NaCl.

B. In preparation of $NaHCO_3$ by solvay method : Precipitation of $NaHCO_3$ from its saturated solution is done by addition of NH_4HCO_3, HCO_3^- as common ion.

C. Predicting precipitation in Ionic reactions : Precipitation in an ionic reactions could be predicted by comparing K_{SP} to the ionic concentration product of ions.

D. Salting out action of Soap : When NaCl is added to saturated solution of soap (RCOONa) concentration of Na^+ increases & causes to precipitation of soap, it is due to $[Na^+]$ $[RCOO^-] > K_{SP}$.

E. In qualitative analysis : Qualitative analysis of mixtures is based on the principle of solubility product. Some important applications are as follows -

(a) **Precipitation of I group radicals :** Group reagent is dilute HCl. In the presence of dilute HCl, the ionic product of I group radicals as there chlorides becomes more than the solubility product. Thus I group radicals get precipitated as their chlorides.

(b) **Precipitation of II group radicals :** Group reagent is H_2S. In presence of dilute HCl, the dissociation of H_2S is suppressed due to common ion (H^+) and only ionic product of the sulphides of II group radicals exceeds their solubility product and get precipitated.

(c) **Precipitation of III group radicals :** Group reagent is NH_4OH in presence of NH_4Cl. The presence of NH_4Cl suppresses the ionisation of NH_4OH, NH^+_4 as common ion. Thus, the ionic product of hydroxides of III group radicals exceeds corresponding solubility products and get precipitated.

(d) **Precipitation of IV group radicals :** Group reagent is H_2S in presence of NH_4OH. In the presence of NH_4OH enhances the dissociation of H_2S. Thus, due to high ionisation of H_2S the concentration of S^{-2} ions increases and ionic product of sulphides of IV group radicals exceeds corresponding solubility product and get precipitated.

(e) **Precipitation of V group radicals :** Group reagent is ammonium carbonate in presence of NH_4Cl. Common ion NH_4^+ suppresses ionisation of $(NH_4)_2CO_3$ thus only V group carbonates having low solubility product get precipitated.

11. COMMON ION EFFECT

(a) If we consider ionisation of a weak electrolyte say CH_3COOH, it ionises as,

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

(b) What do we mean by this equilibrium and this equilibrium constant ? A stage will come such that concentration of CH_3COOH, CH_3COO^- and H^+ will not get changed further, their concentration on a definite mathematical calculation will give a constant called equilibrium constant which will remain constant at same temperature. It does not mean that reaction has stopped only concentration will remain same, ions will continue to change in molecule and molecule will continue to get ionised this is said to be **Dynamic Equilibrium**.

(c) Now suppose some how CH_3COO^- ions are added to the solution to increase CH_3COO^- ions concentration since mathematical calculation will tend to change itself to change that equilibrium constant, electrolyte (CH_3COOH) will do same thing in order to keep K_a constant because it has to be a constant, it will reduce its ionisation. Thus $[CH_3COOH]$ will increase, $[H^+]$ will decreases and K_a will remain constant.

(d) This is called **Common ion Effect** that if in a solution of weak electrolyte solution of strong electrolyte with one of its common ion is added ionisation of weak electrolyte is suppressed.

11.1 Effect of Common ion on Solubility :

As we saw that for a saturated solution product of concentration of ions should not exceed a constant called solubility product. Now suppose, we some how added extra common ions to increase concentration of ions it will tend product to exceed the constant but it cannot so ions will react to give molecule and get precipitated e.g. let solubility of AB in water be s moles L^{-1}. It is dissolved in solution CB having a common ion B^- let concentration of CB be C.

$$AB \rightleftharpoons A^+ + B^-$$
$$s \qquad\qquad s \qquad s$$

$K_{SP} = s^2 = [A^+][B^-]$ -----(1)

(Product should not exceed s^2 otherwise precipitation will start) Now. Let solubility of AB in CB be S_1.

$$CB \rightleftharpoons C^+ + B^-$$
$$C \qquad\qquad C \qquad C$$

$$AB \rightleftharpoons A^+ + B^-$$
$$s_1 \qquad\qquad s_1 \qquad s_1$$

$[A^+] = s_1$

$[B^-] = s_1 + C$

$K_{SP} = (s_1)(s_1 + C)$

If $s_1 <<< C$

$K_{SP} = s_1C = s^2$, from equation (1)

or $s_1 = \dfrac{s^2}{C}$

So, solubility gets reduced.

SOLVED EXAMPLES

Ex.1 How many hydrogen ions are present in 1 ml of a solution of pH =13 –

(A) 6.02×10^{13}

(B) 6.02×10^{12}

(C) 6.02×10^{7}

(D) 6.02×10^{5} **(Ans. C)**

Sol. pH = 13

$-\log [H^+] = 13$

or $[H^+] = 10^{-13}$ mole/litre

$[H^+]$ in 1 ml $= 10^{-16}$ moles

1 mole H^+ contains 6.023×10^{23} H^+ ions

$\therefore$ No. of H^+ ions in 10^{-16} moles

$= 6.023 \times 10^{23} \times 10^{-16}$ **= 6.023×10^{7}**

Ex.2 The pH of a 0.05 M solution of H_2SO_4 in water is nearly –

(A) 0.05 (B)1

(C) –1 (D) 0

(Ans. B)

Sol. pH= $-\log_{10} H^+$

The concentration of H^+ ions is expressed in gm equivalent

Molarity of $H_2SO_4 = 0.05$

$\therefore$ Normality $= 0.05 \times 2 = 0.1$

$\therefore$ pH = –log 0.1

or pH **= 1**

Ex.3 A salt M_2X_3 dissolves in water such that its solubility is x g. mole/litre. Its K_{SP} is –

(A) x^5 (B) $6x^2$

(C) $108\ x^5$ (D) $6x^5$

(Ans. C)

Sol. Solubility of M_2X_3 = x gm mole/litre

$$M_2X_3 \rightleftharpoons 2M^{+3} + 3X^{-2}$$

$\because$ $[M^{+3}] = 2x$

$[X^{-2}] = 3x$

Solubility product $K_{SP} = (2x)^2.(3x)^3$ **$= 108\ x^5$**

Ex.4 The solubility of AgCl in water, in 0.02 M $CaCl_2$, in 0.01M NaCl and in 0.05 M $AgNO_3$ are S_0, S_1, S_2, S_3 respectively. Which of the following relationships between these quantities is correct –

(A) $S_0 > S_1 > S_2 > S_3$

(B) $S_0 > S_2 > S_1 > S_3$

(C) $S_0 > S_1 = S_2 > S_3$

(D) $S_0 > S_2 > S_3 > S_1$

(Ans. B)

Sol. (B) $\text{Solubility} = \dfrac{\text{Solubility Product}}{\text{Concentration of Common ion}}$

$$\therefore \quad S_1 = \frac{K_{SP}}{0.02} = 50\ K_{SP}$$

$$S_2 = \frac{K_{SP}}{0.01} = 100\ K_{SP}$$

$$S_3 = \frac{K_{sp}}{0.05} = 20\ K_{SP}$$

So, $S_2 > S_1 > S_3$ Again solubility will be greatest in water. So, $\mathbf{S_0 > S_2 > S_1 > S_3}$

Ex.5 The pH of a 0.01M solution of a monobasic acid is four. Which one of the following statement about the acid is incorrect –

(A) When a little NaOH is added, it will form a buffer solution

(B) It is a weak acid

(C) It's sodium salt will be acidic

(D) It's sodium salt will be basic

(Ans. C)

Sol. Concentration of monobasic acid = 0.01 M

pH = 4

If the acid is completely ionised the pH of the acid would be

pH = –log 0.01

$= -\log 10^{-2} = 2$

So it is a weak acid. The sodium salt of a weak acid when dissolved the anions will be hydrolysed giving rise to OH^- ion concentration. The solution will be basic. So statement (C) is incorrect.

Ex.6 The dissociation constant of a monobasic acid which is 3.5% dissociated in $\frac{N}{20}$ solution at 20ºC is –

(A) 3.5×10^{-2} (B) 5×10^{-3}

(C) 6.34×10^{-5} (D) 6.75×10^{-2}

(Ans. C)

Sol. Concentration of acid $= \frac{N}{20} = 0.05$ N

Out of 100 molecules, 3.5 molecules have been dissociated

$\therefore$ Out of 1 molecules the no. of dissociated molecules

$= \dfrac{35}{100} = 0.035 = \alpha$

$K_a = \dfrac{C\alpha^2}{(1-\alpha)}$

$= \dfrac{0.05 \times (0.035)^2}{1 - 0.035}$

$=$ **6.34×10^{-5}**

Ex.7 Solubility product of AgCl is 2.8×10^{-10} at 25ºC. Calculate solubility of the salt in 0.1 M $AgNO_3$ solution –

(A) 2.8×10^{-9} mole/litre
(B) 2.8×10^{-10} mole/litre
(C) 3.2×10^{-9} mole/litre
(D) 3.2×10^{-12} mole/litre

(Ans. A)

Sol. In 0.1 M $AgNO_3$

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$

$AgCl \rightleftharpoons Ag^+ + Cl^-$

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

Now $[Ag^+]$ can be taken as $[AgNO_3]$ while $[Cl^-]$ is the solubility of AgCl

$\therefore$ $Cl = \dfrac{K_{SP}}{[Ag^+]} = \dfrac{2.8 \times 10^{-10}}{0.1}$

$\therefore$ Solubility of AgCl

= **2.8×10^{-9} mole/litre**

Ex.8 What is the maximum concentration of Ni^{+2} ions in water (at 25ºC) that is saturated with H_2S (0.1M at 25ºC) and maintained at pH 3 with HCl . K_{SP} of NiS is 3×10^{-21}. H_2S dissociates in two steps, each with an equilibrium constant –

$H_2S \rightleftharpoons H^+ + HS^-$ $Ka_1 = 9.1 \times 10^{-8}$

$HS^- \rightleftharpoons H^+ + S^{-2}$ $Ka_2 = 1.1 \times 10^{-12}$

(A) 3×10^{-7} M   (B) 4×10^{-7} M
(C) 5×10^{-7} M   (D) 6×10^{-7} M

(Ans. A)

Sol. The overall dissociation of H_2S will be the product of K_{a_1} and K_{a_2}.

$K_a = K_{a_1} \times K_{a_2}$

$= (9.1 \times 10^{-8}) \times (1.1 \times 10^{-12})$

$= 1 \times 10^{-19}$

Saturated H_2S is approximately 0.1 M and dissociation of H_2S is very slight

So, $[H^+]^2\,[S^{-2}] = 1 \times 10^{-19} \times 10^{-1} = 10^{-20}$

Since, pH is 3, $[H^+] = 10^{-3}$ M

$[S^{-2}] = \dfrac{[H^+]^2[S^{-2}]}{[H^+]^2} = \dfrac{10^{-20}}{10^{-6}} = 10^{-14}$ M

Since NiS will precipitate, if the S.P. is exceeded, the highest value which $[Ni^{+2}]$ concentration can have is:

$[Ni^{+2}] = \dfrac{3 \times 10^{-21}}{10^{-14}} = 3 \times 10^{-7}$ M

Ex.9 Calculate the pH of solution having H^+ ion concentration of 5×10^{-4} mole/litre –

(A) 3.3   (B) 2.26
(C) 1.26   (D) 0.26

(Ans. A)

Sol. $[H^+]$ ion concentration $= 5 \times 10^{-4}$ mole/litre

pH $= -\log [5 \times 10^{-4}]$

$= -(\log 5 + \log 10^{-4})$

$= -0.7 + 4$

= 3.3

Ex.10 Suppose the change $HC_2O_4^- + Cl_2 \rightarrow CO_3^{-2} + Cl^-$ is to be carried out in basic solution. Starting with 0.1 mole of OH, 0.1 mole of $HC_2O_4^-$ and 0.05 mole of Cl_2, How many moles of Cl^- would be expected to be in the final solution –

(A) 3.04   (B) 2.04
(C) 1.04   (D) 0.04

(Ans. D)

Sol The equation for this reaction is

$HC_2O_4^- + Cl_2 + 5OH^- \rightarrow 2Cl^- + CO_3^{-2} + 3H_2O$

Here, OH^- is the limiting reagent and will be used up completely.

Since, 5 moles of OH^- produce 2 moles of Cl^-

0.1 mol of OH^- will produce 0.04 mole of Cl^-

$\therefore$ Moles of Cl^- in the final solution = 0.04

Ex.11 The dissociation constant of weak acid HA is 4.9×10^{-8}. After making the necessary approximations. Calculate pH in 0.1 M acid –

(A) 1.155   (B) 2.155
(C) 3.155   (D) 4.155

(Ans. D)

Sol. For weak acid $K_a = \alpha^2 .C$

$\therefore \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9 \times 10^{-8}}{0.1}}$

$= 7 \times 10^{-4}$

pH $= -\log H^+ = -\log \alpha C$

$= -\log 7\times10^{-4} \times 10^{-1}$

$= 4.1549$ **= 4.155**

Ex.12 K_a for cyanoacetic acid is 4×10^{-3}. What is the value of degree of hydrolysis of 0.4 M sodium cyano acetate solution ?

(A) 4.5×10^{-6} (B) 5.5×10^{-6}

(C) 2.5×10^{-6} (D) 3.5×10^{-6}

(Ans. C)

Sol. $K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{4\times10^{-3}}$

$= 0.25 \times 10^{-11}$

$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{0.25\times10^{-11}}{0.4}}$

$= 2.5 \times 10^{-6}$

Ex.13 Calculate the pH of solution obtained by mixing10ml of 0.1M HCl and 40ml. of 0.2M H_2SO_4–

(A) 0.3685 (B) 0.4685

(C) 1.3685 (D) 1.4684

(Ans. B)

Sol. Milli equivalent of H^+ from HCl = $10 \times 0.1 = 1$

Milli equivalent of H^+ from H_2SO_4

$= 40 \times 0.2 \times 2 = 16$

Total Meq of H^+ in solution = 1 + 16 = 17

$[H^+] = \frac{17}{50} = 3.4 \times 10^{-1}$ $[\because [H^+] = \frac{Meq}{V \text{ in ml}}]$

pH = – log $[H^+]$ = – log [0.34] = **0.4685**

Ex.14 The dissociation constants for aniline, acetic acid and water at 25ºC are 4×10^{-10}, 2×10^{-5} and 10^{-14} respectively. Calculate degree of hydrolysis of aniline acetate in a decinormal solution–

(A) 0.025 (B) 0.015

(C) 0.035 (D) 0.045

(Ans. C)

Sol. $Aniline^+ + Acetate^- + H_2O \rightleftharpoons$ Aniline +Acetic acid

Before hydrolysis

1 1 0 0

After hydrolysis

1–h 1–h h h

Let concen. salt be C mole litre^{-1}

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

$\frac{h}{1-h} = \sqrt{\frac{K_w}{K_a.K_b}}$

$= \sqrt{\frac{10^{-14}}{2\times10^{-6}\times4\times10^{-10}}}$

% hydrolysis = 54.95 %

h = 0.035

Ex.15 Calculate the pH at the equivalence point when a solution of 0.1M acetic acid is titrated with a solution of 0.1M NaOH, K_a for acid = 2×10^{-5}–

(A) 5.7 (B) 6.7

(C) 7.7 (D) 8.7

(Ans. D)

Sol. Let V ml of acid and V ml of NaOH be used concentration of both acid and NaOH are same.

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Concentration before reaction

$\frac{0.1\times V}{2V}$ $\frac{0.1\times V}{2V}$ 0 0

Concentration after reaction

0 0 $\frac{0.1\times V}{2V}$ $\frac{0.1\times V}{2V}$

$[CH_3COONa] = \frac{0.1}{2} = 0.05$ M

Now calculate pH by hydrolysis of CH_3COONa

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

$[OH^-] = C.h = \sqrt{\frac{K_w\,.\,C}{K_a}}$

$= \sqrt{\frac{10^{-14}\times0.05}{2\times10^{-5}}}$

$= 5 \times 10^{-6}$

p[OH] = $6 \times 0.699 = 5.301$

pH = [14 – 5.301] **= 8.699 ≈ 8.7**

Ex.16 Calculate the amount of $(NH_4)_2SO_4$ in gm which must be added to 500 ml of 0.2 M NH_3 to yield a solution of pH = 9, K_b for $NH_3 = 2 \times 10^{-5}$–

(A) 3.248 g (B) 4.248 g
(C) 1.320 g (D) 6.248 g

(Ans. C)

Sol. $pOH = -\log K_b + \log \frac{[NH_4^+]}{[NH_4OH]}$

Let 'a' millimoles of NH_4^+ are added to a solution

having milli moles of $NH_4OH = 500 \times 0.2 = 100$

$\therefore \quad [NH_4^+] = [\text{salt}] = \frac{a}{500}$

and $\quad [NH_4OH] = [\text{Base}] = \frac{100}{500}$

Given K_b for $NH_4OH = 2 \times 10^{-5}$
and pH = 9

$\therefore \quad 5 = -\log 2 \times 10^{-5} + \log \frac{a/500}{100/500}$

$\therefore$ a = 200 mili moles = 0.2 mol

moles of $(NH_4)_2\,SO_4$ added

$= \frac{a}{2} = 0.1$ mol

$\therefore \quad W_{(NH_4)_2\,SO_4} =$ **0.1 × 132**
= 1.32

Ex.17 The K_a for formic acid and acetic acid are 2×10^{-4} and 2×10^{-5} respectively. Calculate the relative strength of acids with same molar concentration–

(A) $\sqrt{10}$ (B) $\sqrt{7}$

(C) $\sqrt{8}$ (D) $\sqrt{5}$

(Ans. A)

Sol. Relative strength of weak acids

$$= \sqrt{\left(\frac{K_{a_1}}{K_{a_2}} \times \frac{C_1}{C_2}\right)}$$

$\therefore$ Relative strength $= \sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)}$ $(\because C_1 = C_2)$

$$= \sqrt{\left(\frac{2 \times 10^{-4}}{2 \times 10^{-5}}\right)}$$

Relative strength for HCOOH to CH_3COOH

$= \sqrt{10} : 1$

Ex.18 Find the pH of solution prepared by mixing 25ml of a 0.5 M solution of HCl, 10ml of a 0.5 M solution of NaOH and 15ml of water –

(A) 0.8239 (B) 1.0029
(C) 1.0239 (D) 1.8239

(Ans. A)

Sol. We know that for HCl and NaOH, m.e. = m.e.

$\therefore$ m.e. of HCl = 0.5 × 25 = 12.5
m.e. of NaOH = 0.5 × 10 = 5.0

m.e. of HCl in the resultant mixture
= 12.5 – 5.0 = 7.5

total volume = (25 + 10 + 15) ml = 50 ml

$\therefore$ Normally of HCl $= \frac{\text{m.e.}}{\text{Vol(ml)}} = \frac{7.50}{50}$

$\therefore$ Molarity $= \frac{7.50}{50}$

$\therefore \quad [H^+] = [HCl] = \frac{7.50}{50}$

$\therefore$ pH $= -\log \frac{7.50}{50}$ = **0.8239**

Ex.19 The solubility procduct of chalk is 9.3×10^{-8}. Calculate its solubility in gram per litre –

(A) 0.3040 gram / litre
(B) 0.0304 gram / litre
(C) 2.0304 gram / litre
(D) 4.0304 gram / litre

(Ans. B)

Sol. $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$

Let the solubility of $CaCO_3$ be s mole per litre

$\therefore \quad K_{SP} = [Ca^{2+}]\,[CO_3^{2-}] = s.s$

$\therefore \quad s = \sqrt{K_{SP}} = \sqrt{9.3 \times 10^{-8}}$
= 0.000304 mole / litre

Solubility in g/l = mole/litre × Moleqular weight of $CaCO_3$
= 0.000304 × 100
= 0.0304 gram / litre

Ex.20 Maximum Conductivity would be of –

(A) $K_3Fe(CN)_6$ [0.1 M solution]
(B) $K_2Ni(CN)_4$ [0.1M solution]
(C) $FeSO_4.Al_2(SO_4)_3.24H_2O$ [0.1 M solution]
(D) $Na[Ag(S_2O_2)_3]$ [0.1 M solution]

(Ans. C)

Sol. Double salt on ionization gives more ions. One molecule of the salt gives Fe^{+2}, $2Al^{+3}$, $4SO_4^{-2}$ ions. Hence its conductance would be highest.

Ex.21 What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mole of propanoic acid ($K_a = 1.0 \times 10^{-5}$ at 25ºC) to obtain a buffer solution of pH 6 –

(A) 0.1 M (B) 0.2M

(C) 0.3 M (D) 1.3 M

(Ans. B)

Sol. Using the expression

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

we get, $6 = -\log(1.0 \times 10^{-5}) + \log \frac{[Salt]}{[0.02\ M]}$

Which gives $6 = 5 + \log \frac{[Salt]}{[0.02\ M]}$

or $\frac{[Salt]}{[0.02\ M]} = 10$ or [Salt] = **0.2 M**

Ex.22 What will be the pH of the solution, if 0.01 mole of HCl is dissolved in a buffer solution containing 0.03 mole of propanoic acid ($K_a = 1.0 \times 10^{-5}$) and 0.02 moles of salt, at 25ºC -

(A) 3.699 (B) 4.699

(C) 5.11 (D) 6.11

(Ans. B)

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

$= -\log(1.0 \times 10^{-5}) + \log \frac{(0.02 - 0.01)}{(0.03 + 0.01)}$

$= 5 + \log \left(\frac{1}{4}\right) = 5 - 0.6$

= 4.4

Ex.23 20 ml of 0.2 M NaOH is added to 50 ml, of 0.2 M CH_3COOH to give 70ml, of the solution. What is the pH of the solution ? The ionization constant of acetic acid is 2×10^{-5} –

(A) 4.522 (B) 5.568

(C) 6.522 (D) 7.568

(Ans. A)

Sol. The addition of NaOH converts equivalent amount of acetic acid into sodium acetate. Hence,

Concen. of acetic acid after the addition of

NaOH = $\frac{30}{70} \times 0.2$ M

Concen. of CH_2COONa after the addition of

NaOH = $\frac{20}{70} \times 0.2$ M

Hense, Using the expression

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

$= -\log(2 \times 10^{-5}) + \log\left(\frac{20}{30}\right)$

$= 4.699 - 0.177 =$ **4.522**

Ex.24 The concentration of H^+ ion in a 0.2 M solution of HCOOH is 6.4×10^{-3} mole ℓ^{-1} . To this solution HCOONa is added so as to adjust the concentration of HCOONa to one mole per litre. What will be the pH of this solution? K_a for HCOOH is 2.4×10^{-4} and the degree of dissociation of HCOONa is 0.75 –

(A) 3.19 (B) 4.19

(C) 5.19 (D) 6.19

(Ans. B)

Sol. Assuming that the addition of HCOONa suppresses the ionization of HCOOH, we can use the expression

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

to compute pH of the solution, since salt is 75% dissociated we will get,

$pH = -\log(2.4 \times 10^{-4}) + \log \frac{0.75}{0.2}$

$= 3.62 + 0.57 =$ **4.19**

Ex.25 What amount of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 10.4 using 0.01 mole of NaCN. Given K_{ion} (HCN) = 4.1×10^{-10} –

(A) 8.55×10^{-3} mole

(B) 8.65×10^{-3} mole

(C) 8.75×10^{-3} mole

(D) 9.9×10^{-4} mole **(Ans. D)**

Sol. The addition of HCl converts NaCN into HCN. Let x be the amount of HCl added. We will have.

$[NaCN] = (0.01 - x)$

$[HCN] = x$

Substituting these values along with pH and K_a in the expression.

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

We get $10.4 = -\log[4 \times 10^{-10}] + \log \frac{0.01-x}{x}$

or $10.4 = 9.4 + \log \frac{0.01-x}{x}$

or $\log \frac{0.01-x}{x} = 1$

or $\frac{0.01-x}{x} = 10 \Rightarrow 11x = 10^{-2}$

or $x = \mathbf{9.9 \times 10^{-4}\ M}$

Ex.26 Calculate the pH of aqueous solution of 1.0 M $HCOONH_4$ assuming complete dissociation (pK_a of HCOOH = 3.8 and pK_b = of NH_3 = 4.8) –

(A) 3.5 (B) 4.5
(C) 5.5 (D) 6.5

(Ans. D)

Sol. Ammonium formate undergoes hydrolysis as

$NH_4^+ + HCOO^- + H_2O \rightleftharpoons NH_4OH + HCOOH$

$$K_h = \frac{K_W}{K_a . K_b}$$

Moreover in the solution we have

$[NH_4OH] = [HCOOH]$

Hence $K_h = \frac{[HCOOH]^2}{[HCOO^-]^2}$

or $\frac{K_W}{K_a . K_b} = \frac{[H^+]^2}{[K_a]^2}$

or $[H^+]^2 = \frac{K_W . K_a}{K_b}$

or $2pH = pK_W + pK_a - pK_b$

or $pH = \frac{1}{2}[pK_W + pK_a - pK_b]$

$= \frac{1}{2}[14 + 3.8 - 4.8]$ **= 6.5**

Ex.27 Calculate the pH of a solution which contains 10 ml of 1M HCl and 10 ml of 2 M NaOH

(A) 11.7 (B) 12.7
(C) 13.7 (D) 10.7

(Ans. C)

Sol.

	HCl +	NaOH →	NaCl +	H_2O
Meq. before	10 × 1	10 × 2		
Reaction	=10	=20	0	0
Meq. After Reaction	0	10	10	10

$[OH^-]$ left from NaOH$= \frac{10}{20} = 0.5$ M

$pOH = -\log OH^- = -\log 0.5$

$pOH = 0.3$

pH = 13.7

Ex.28 Calculate pH of a solution of given mixture (0.1 mole CH_3COOH + 0.2mole CH_3COONa) in 100 ml of mixture. $K_a = 2 \times 10^{-5}$.

(A) 4.6 (B) 5.6
(C) 6.6 (D) 7.6

(Ans. A)

Sol. We have

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

$$[Salt] = \frac{3 \times 1000\ M}{82 \times 100} = 0.366$$

$$[Acid] = \frac{2 \times 1000}{60 \times 100}\ M = 0.333$$

$$= -\log 2 \times 10^{-5} + \log \frac{\frac{0.2 \times 1000}{100}}{\frac{0.1 \times 1000}{1000}}$$

= 4.6

Ex.29 Calculate the pH of a buffer solution prepared by dissolving 10.6 of Na_2CO_3 in 500 ml of an aqueous solution containing 80 ml of 1M HCl. K_a for $HCO_3^- = 6 \times 10^{-11}$ –

(A) 8.6 (B) 9.6
(C) 11.6 (D) 12.6

(Ans. B)

Sol. $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

Meq. before	$\frac{10.6}{106}\times 1000$	80×1		
Reaction	=100	80	0	0
Meq. After Reaction	20	0	80	80

The solution Na_2CO_3 and HCO_3^- and thus acts as buffer

$$pH = -\log K_a + \log \frac{[CO_3^{-2}]}{[HCO_3^-]}$$

$$= -\log 6 \times 10^{-11} + \log \frac{20}{80}$$

$$\mathbf{= 9.6}$$

Ex.30 What volume of 0.1 M HCOONa solution should be added to 50ml of 0.05 M formic acid to produce a buffer solution of pH = 4.0, pK_a of formic acid = 3.7

(A) 50 ml (B) 40 ml
(C) 30 ml (D) 60 ml

(Ans. A)

Sol. Let V ml of 0.1 M HCOONa be mixed to 50ml of 0.05 M HCOOH

in mixture

$$[HCOONa] = \frac{0.1\times V}{(V+50)}$$

$$[HCOOH] = \frac{50\times 0.05}{(V+50)}$$

$$\therefore \quad pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$$

$$4.0 = 3.7 + \log \frac{(0.1\times V)/(V+50)}{2.5/(V+50)}$$

V = 50 ml

Ex.31 Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid respectively by formula HSaC. A 4×10^{-4} mole amount of Saccharin is dissolved in 200cc water of pH 3. Assuming no change in volume. Calculate the concentration of Sac. ions in the resulting solution at equilibrium -

(A) 2×10^{-12} M
(B) 3×10^{-12} M
(C) 4×10^{-12} M
(D) 5×10^{-12} M

(Ans. C)

Sol. $[HSaC] = \frac{4\times 10^{-4}}{200/1000} = 2 \times 10^{-3}$ M

The dissociation of HSaC takes places in the presence of $[H^+] = 10^{-3}$

	HSaC ⇌	H^+ +	SaC^-
conc. before dissociation	2×10^{-3}	10^{-3}	0

In presence of H^+ the dissociation of HSaC is almost negligible because of common ion effect. Thus at equilibrium

$[HSaC] = 2 \times 10^{-3}$, $H^+ = 10^{-3}$

$$K_a = \frac{[H^+][SaC^-]}{[HSaC]}$$

$$\therefore \quad 2 \times 10^{-12} = \frac{[10^{-3}][SaC^-]}{[2\times 10^{-3}]}$$

$$\therefore \quad [SaC^-] = \mathbf{4 \times 10^{-12}\ M}$$

Ex.32 A certain weak acid has $K_a = 1.0\times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base -

(A) 10^9 (B) 10^{10}
(C) 10^{11} (D) 10^{12}

(Ans. B)

Sol. $HA + BOH \rightleftharpoons BA + H_2O$
weak strong

or $HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$

or $HA^- \rightleftharpoons A^- + H_2O$

$$\therefore \quad K = \frac{[A^-]}{[HA][OH^-]}$$

Also for weak acid HA

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

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

$$\frac{K_a}{K} = K_W \quad \text{or} \quad K = \frac{K_a}{K_W} = \frac{10^{-4}}{10^{-14}}$$

$$\mathbf{= 10^{10}}$$

Ex.33 Calculate pH of a solution whose 100 ml contains 0.2 gm NaOH dissolved in it -

(A) 10.699 (B) 11.699
(C) 12.699 (D) 13.699

(Ans. C)

Sol. 100ml solution of NaOH contains = 2.0gm NaOH

$\therefore$ 1000 ml solution of NaOH contains = 2 gm NaOH

Normality of solution $= \frac{2}{40} = 0.05$ N

$\therefore \quad [H^+] = \frac{10^{-14}}{0.05}$

$\therefore \quad -\log[H^+] = -\log\left[\frac{10^{-14}}{0.05}\right]$

$= -[-14 + 2 - 0.6990]$ **= 12.699**

Ex.34 Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1mole of HCl per litre and of other solution containing 1 mole CH_3COONa + 1mole of acetic acid per litre.

(A) 1 : 1 (B) 2 : 1
(C) 1 : 2 (D) 2 : 3

(Ans. C)

Sol. **Case I** - pH when 1mole CH_3COONa and 1 mole HCl are present

$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

Before reaction	1	1	0	0
After reaction	0	0	1	1

$[CH_3COOH] = 1M$

$\therefore \quad [H^+]\ C\alpha = C.\sqrt{\frac{K_a}{C}} = \sqrt{C.K_a} = \sqrt{K_a}$

$\because \quad C = 1$

$\therefore \quad pH_1 = -\frac{1}{2}\log K_a$

Case II - pH when 1 mole CH_3COONa and 1 mole of CH_3COOH, a buffer solution

$\therefore \quad pH_2 = -\log K_a + \log\frac{[Salt]}{[Acid]} = -\log K_a$

$\because \quad [Salt] = [Acid] = 1M$

$\therefore \quad \frac{pH_1}{pH_2} = \frac{1}{2}$ or $pH_1 : pH_2$ **= 1 : 2**

Ex.35 Calculate pH of 0.002 N NH_4OH having 2% dissociation -

(A) 7.6 (B) 8.6
(C) 9.6 (D) 10.6

(Ans. C)

Sol. NH_4OH is a weak base and partially dissociated

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

Concentration before dissociation	1	0	0
Concentration after dissociation	$1-\alpha$	α	α

$\therefore \quad [OH^-] = C\alpha = 2 \times 10^{-3} \times \frac{2}{100}$

$= 4 \times 10^{-5}$ M

pOH $= -\log[OH^-]$

$= -\log 4 \times 10^{-5} = 4.4$

pH $= 14 - 4.4$

= 9.6

Ex.36 The present species in the resultant solution which is form by the neutralisation of HCl from NaOH is -

(A) Na^+, Cl^-, H_3O^+ (B) Na^+, Cl^-, H_2O
(C) Na^+, Cl^-, OH^- (D) H^+, H_3O^+

(Ans. B)

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

Ex.37 Which of the following has pH is equal to near about one -

(A) 100 ml $\frac{M}{10}$ HCl + 100ml $\frac{M}{10}$ NaOH

(B) 55 ml $\frac{M}{10}$ HCl + 44 ml $\frac{M}{10}$ NaOH

(C) 10 ml $\frac{M}{10}$ HCl + 90 ml $\frac{M}{10}$ NaOH

(5) 75 ml $\frac{M}{5}$ HCl + 25ml $\frac{M}{5}$ NaOH

(Ans. D)

Sol. 25 ml $\frac{M}{5}$ NaOH will be neutralise 25 ml $\frac{M}{5}$ HCl. Hence, 50 ml $\frac{M}{5}$ HCl get rest and to the mixing of both solution will give total 100 ml volume.

$N_1V_1 = N_2V_2$

$50 \times \frac{N}{5} = N_2 \times 100$

$N_2 = \frac{50 \times N}{5 \times 100} = .1$ Hence, **pH = 1**

Ex.38 Calculate the pOH – pK_b for the buffer, 0.20 M NH_3, 0.40M NH_4Cl, K_b for ammonia = 10 -

(A) 0.50 (B) 0.60
(C) 0.30 (D) 0.75

(Ans. C)

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

$pOH - pK_b = \log\frac{0.4}{0.2} = 0.30$

Ex.39 pH of 0.01 M HS^- will be -

(A) $pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$

(B) $pH = 7 - \frac{pK_a}{2} - \frac{\log C}{2}$

(C) $pH = \frac{pK_1 + pK_2}{2}$

(D) $pH = 7 + \left(\frac{pK_a - pK_b}{2}\right)$

(Ans. A)

Sol. $HS^- + H_2O \rightleftharpoons H_2S + OH^-$

$$\therefore \quad [OH^-] = Ch = \sqrt{\frac{K_w.C}{K_a}}$$

$$\therefore \quad [H^+] = \frac{K_w}{\sqrt{\frac{K_w.C}{K_a}}} = \sqrt{\frac{K_w.K_a}{C}}$$

or $$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

Ex.40 Percentage ionisation of weak acid can be calculated using the formula -

(A) $100\sqrt{\frac{K_a}{C}}$ (B) $\frac{100}{1+10^{(pK_a - pH)}}$

(C) Both (A) and (B) (D) None

(Ans. C)

Sol. For weak acid dissociation equilibria, degree of dissociation α is given as -

$$\alpha = \sqrt{\frac{K_a}{C}} \quad \therefore \quad \% \alpha = 100\sqrt{\frac{K_a}{C}}$$

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

$$\log K_a = \log H^+ + \log \frac{\alpha}{(1-\alpha)}$$

or $$pK_a = pH + \log \frac{(1-\alpha)}{\alpha}$$

$$pK_a - pH = \log \frac{(1-\alpha)}{\alpha}$$

$$\therefore \quad \frac{1-\alpha}{\alpha} = 10^{pK_a - pH}$$

or $$\frac{1}{\alpha} = 10^{pK_a - pH} + 1$$

or $$\alpha = \frac{1}{(1+10^{pK_a - pH})}$$