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, H₂SO₄, NaCl.HNO₃, KOH, NaOH, HNO₃, AgNO₃, CuSO₄, 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 :

K =

Ka

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 -

N+ .

$$\frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}][\mathrm{H}_2\mathrm{O}]}$$

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,

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

 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

 $\begin{array}{ccc} & HA \ + \ H_2O & H^+ \ + \ A^- \\ \mbox{Initial concentration} & C & 0 & 0 \\ \mbox{Equilibrium} & (1 \ - \ \alpha)C & C\alpha & C\alpha \end{array}$

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

The degree of ionisation α is very small as compared to 1 means α <<< 1. So, 1 – α = 1

 $\alpha^2 = \frac{K_a}{C}$

Thus,
$$K_a = \alpha^2 c$$
;

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

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

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This equation is known as ostwald dilution law equation.

Similarly, for a weak base we have

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

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

Where,

 ${\rm K}_{\rm b}$ 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.

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 $\propto k_a$

$$\infty \frac{1}{pk_a}$$
$$\infty pk_b$$
$$\infty \frac{1}{k_b}$$

(g) Similarly basic strength of bases is directly proportional to $K_{\rm p}$.

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

Basic strength of base $\propto k_b$

$$\begin{array}{c}
\infty \quad \frac{1}{pk_{b}} \\
\infty \quad pk_{a} \\
\infty \quad \frac{1}{k_{a}}
\end{array}$$

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

Conduction of solution ∞ 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.

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

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 ∝ 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

 $\propto~$ 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 ∞ 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 CH₃COOH 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 ACID & **BASES:**

4.1 Postulates :-

(1) Acid - Proton (H⁺) donor (2) Base - Proton (H⁺) acceptor e.g. $HCI(aq) + H_2O(\ell)$ $H_2O^+(aq) + Cl^-(aq)$ Acid Base $HCl(aq) + NH_3(aq)$ $NH_{4}^{+}(aq) + CI^{-}(aq)$ Acid Base $HCl(aq) + CH_{3}COOH(aq)$ $CH_3COOH^+_2(aq)$ Base+ Cl⁻(aq) Acid

Note :- Here CH₃COOH has a less tendency to donate H⁺ than HCl, therefore CH₃COOH 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. $HCl(aq) + NH_3(aq)$ $NH_{a}^{+}(aq) + CI^{-}(aq)$ Acid₂ Base₂ Base₁ Acid₁ 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.

<u>Acid (or Base)</u> <u>Conjugate Base (or Acid)</u> (i) Weak Strong Weak (ii) Strong

e.g.

Strength order of acids. $HCIO_4 > H_2SO_4 > HCI > CH_2COOH$ strength order of conjugate bases $CIO_4^- < HSO_4^- < CI^- < CH_3COO^-$

5. IONIC PRODUCT WATER :

Pure water is a very weak electrolyte -

$$H_{2}O$$
 H^{+} + OH^{-}

on applying the law of mass action at equilibrium,

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

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

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

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 . $[H^+] [OH^-] = K_w$ So,

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

$$K_{\rm W} = 10^{-7} \times 10^{-7}$$

 $K_{\rm W} = 10^{-14}$

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 (°C) Value of K_w (1)0 0.11×10^{-14} 0.31×10^{-14} (2)10 (3)20-35 or 25° 1 \times 10⁻¹⁴ (Room temp.) (4)60 2.9×10^{-14} 5.6×10^{-14} (5)80 1×10^{-12} (6)90



$$K_{W} = [H^{+}] [OH^{-}]$$

$$-\log K_{W} = -\log [H^{+}] + (-) \log [OH^{-}]$$

$$pK_{W} = pH + pOH$$

$$14 = pH + pOH$$

The acidity and basicity depend upon the concentration of $\rm H^+$ and $\rm OH^-$ 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 = $55.5 \times 6.023 \times 10^{23}$ = 3.34×10^{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 H⁺ + OH⁻

$$\mathsf{K} = \frac{[\mathsf{H}^+][\mathsf{O}\mathsf{H}^-]}{[\mathsf{H}_2\mathsf{O}]}$$

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

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. H_2SO_4 + NaOH \rightarrow NaHSO₄ (Dibasic) 1 mole \downarrow H^{\oplus}

(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)CI, Mg(OH)CI, $Fe(OH)_2CI$ etc.

eg.
$$Ca(OH)_2 + HCI \rightarrow Ca(OH)CI + OH^-$$

1mol Basic salt
eg. $Mg(OH)_2 + HNO_3 \rightarrow Mg(OH)NO_3$
1mol Basic salt
eg. $AI(OH)_3 + HCI \rightarrow AI(OH)_2CI \rightarrow AI(OH)CI_2$
1mol Basic salt

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,

 $\rightarrow OH - CH - COONa$

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

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

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.

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

or 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 w	e know	[H+][(OH-] :	= K _w =	= 10 ⁻¹⁴	
or pH	+ pOH	= 14	4 at 2	25°C		
(iii) [H+]	[OH-]	pН	pOH I	Nature	of solut	ion
10°=1	10-14	0	14 9	Strongl	y Acidic	
10-2	10-12	2	12 /	Acidic		
10-5	10 ⁻⁹ 5	9	Weal	kly acio	dic	\mathbf{N}
10-7	10 ⁻⁷ 7	7	Neut	ral		
10 ⁻⁹	10 ⁻⁵ 9	5	Weak	<ly bas<="" td=""><td>ic</td><td></td></ly>	ic	
10-11	10-3 11	3	Basic	2		
10 ⁻¹⁴	10°=1	14	0 9	Strongl	y 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 \times 10⁻⁵ N HCl is twice concentrated as a 2 \times 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 = 10^{-2} N HCl [H⁺] = 10^{-2} M
- or $pH = -log(10^{-2}) = 2$
- **(b)** For 10^{-3} M NaOH = 10^{-3} N NaoH 10^{-14}

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

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

(c) For $10^{-2}M H_2SO_4 = 2 \times 10^{-2} N H_2SO_4$ $[H^+] = 2 \times 10^{-2}M$ or pH = $-\log (2 \times 10^{-2}) = 1.699$

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(d) For 10^{-3} M Mg(OH)₂ = 2 × 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

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

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

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

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

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

Salt + water 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 -

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(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	Weak	Strong	Weak
acids	acids	bases	bases
HCI	CH₃COOH	NaOH	NH₄OH
H_2SO_4	HCŇ KOH	LiOH	·
HÑO₃	H_2CO_3	RbOH	$Ca(OH)_2$
HClO₄	H ₃ PO ₄	CsOH	Be(OH) ₂
HI	H ₃ PO ₃	Ba(OH) ₂	Zn(OH) ₂
СООН	Fe(OH)₃ RNH₂		

COOH NH3

8.1 Hydrolysis of Salt of Strong acid and Strong base :

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 :

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 + BA BOH + HA Salt weak base strong acid B⁺ + A⁻ BOH + H⁺ + A⁻

Resultant eq. $B^+ + H_2O$ BOH + H^+ on applying the law of mass action

 $\mathsf{K} = \frac{[\mathsf{BOH}][\mathsf{H}^+]}{[\mathsf{B}^+][\mathsf{H}_2\mathsf{O}]}$

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

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

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

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

$$\begin{array}{l} \therefore \quad H_2O & H^+ + OH^- \\ K &= \frac{[H^+][OH^-]}{[H_2O]} \\ K & [H_2O] &= & [H^+] & [OH^-] \\ K_W &= & [H^+] & [OH^-] \\ [H^+] &= & \frac{K_W}{[OH^-]} \\ \end{array}$$
(2)

Similarly some part of BOH will be also ionized - \therefore BOH B⁺ + OH⁻

$$K_{b} = \frac{[B^{+}][OH^{-}]}{[BOH]}$$
$$B^{+}] = \frac{K_{b} \times [BOH]}{[OH^{-}]} \qquad \dots \dots (3)$$

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



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

$$B^+ + H_2 O BOH + H^+$$

Initial molar C 0 0
concentration
Molar concentration (1 - h)C hC hC

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

$$\therefore \quad \frac{1-h}{V} \qquad \frac{h}{V} \qquad \frac{h}{V}$$
$$K = \frac{[BOH][H^+]}{[B^+][H_2O]}$$
$$K[H_2O] = \frac{[BOH][H}{[B^+]}$$



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

Since, $h \ll 1$, therefore 1 - h = 1,

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

$$h^{2} = K_{h} \times V$$

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

 \therefore K_b = Hydrolysis constant

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

Hence, the degree of hydrolysis is directly proportional to the square root of volume, inversely proportional to the square root of C. $\therefore h^2 = K_h \times V$ $\therefore V = 1/C$

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

$$h = \sqrt{\frac{K_{h}}{C}}$$

on putting the value of K_h in the above equation

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 $[OH^-] = hC$
 $\therefore \qquad [H^+] = \frac{K_W}{hC}$
But $h = \sqrt{\frac{K_W}{K_HC}}$

$$[\mathsf{H}^+] = \mathsf{C}\sqrt{\frac{\mathsf{K}_{\mathsf{W}}}{\mathsf{K}_{\mathsf{b}}.\mathsf{C}}} = \sqrt{\frac{\mathsf{K}_{\mathsf{W}}\mathsf{C}}{\mathsf{K}_{\mathsf{b}}}} = \left(\frac{\mathsf{K}_{\mathsf{W}}\mathsf{C}}{\mathsf{K}_{\mathsf{b}}}\right)^{1/2}$$

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

$$pH = -\log \left(\frac{K_{W}C}{K_{b}}\right)^{1/2}$$

$$pH = -\frac{1}{2}\log K_{W} + \frac{1}{2}\log K_{b} - \frac{1}{2}\log C$$

$$pH = \frac{1}{2}pK_{W} - \frac{1}{2}pK_{b} - \frac{1}{2}\log C$$

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

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 :

CH₃COOH + NaOH on hydrolysis

$$CH_3COONa + H_2O$$

 $\begin{array}{rcl} \mathsf{CH}_3\mathsf{COONa} + \mathsf{H}_2\mathsf{O} & \mathsf{CH}_3\mathsf{COOH} &+ & \mathsf{NaOH} \\ \mathsf{Salt} & & \mathsf{Weak} \text{ acid strong base} \\ \mathsf{CH}_3\mathsf{COO}^- + & \mathsf{Na}^+ + & \mathsf{H}_2\mathsf{O} & \mathsf{CH}_3\mathsf{COOH} + & \mathsf{Na}^+ + \mathsf{OH}^- \end{array}$

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	cons	sider a s	alt -	BA	
H ₂ O	+	BA	BOH	+	HA	
Salt	: /		Strong	base	Weak	acid
B+	+ A	\-	B+ +	- OH-	+ HA	

Resultant equation :- $A^- + H_2O$ $OH^- + HA$ 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,
$$K[H_2O] = \frac{[HA][OH^-]}{[A^-]}$$

$$K_{h} = \frac{[HA][OH^{-}]}{[A^{-}]}$$
(1)

Some part of H_2O would be ionized otherwise reaction will not be reversible - $\therefore H_2O H^+ + OH^-$

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

$$K_{W} = [H^{+}] [OH^{-}]$$

 $[OH^{-}] = \frac{K_{W}}{[H^{+}]}$ (2)

Similarly some part of HA will be also ionized. \therefore HA H⁺ + A⁻

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$$
$$[A^{-}] = \frac{K_{a} \times [HA]}{[H^{+}]} \qquad \dots \dots (3)$$

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

$$K_{h} = \frac{K_{W}}{K_{a}}$$

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

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

hC

$$\therefore K_{h} = \frac{[OH][HA]}{[A^{-}]} = \frac{hC \times hC}{(1-h)C}$$
$$= \frac{h^{2}C}{(1-h)}$$

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

$$K_{h} = h^{2}C$$

$$h = \sqrt{\frac{K_{h}}{C}} \quad \because C = \frac{1}{V}$$

$$\therefore h = \sqrt{K_{h} \times V}$$

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 , $h = \sqrt{\frac{K_W}{K_aC}}$

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

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

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

but
$$h = \sqrt{\frac{K_W}{K_aC}}$$

...

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

Since, pH = - log [H⁺]

$$\log \left(\frac{\kappa_W.\kappa_a}{C}\right)^{1/2}$$

$$-\frac{1}{2}\log K_{\rm W} - \frac{1}{2}\log K_{\rm a} + \frac{1}{2}\log C$$

$$= \frac{1}{2} pK_{W} + \frac{1}{2} pK_{a} + \frac{1}{2} \log C$$

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 :

 $CH_3COOH + NH_4OH CH_3COONH_4 + H_2O$ on 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.

B⁺

(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

 $BA + H_2O HA +$ BOH Weak acid Weak base

$$+ A^{-} + H_2O$$
 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.

So, $K[H_2O] = \frac{[HA] [BOH]}{[B^+] [A^-]}$ $K_{h} = \frac{[HA] [BOH]}{[B^{+}] [A^{-}]}$(1)

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

HA H^+ + A^- BOH B⁺ + OH⁻

$$\therefore \quad \mathsf{K}_{\mathsf{a}} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

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

We know that,

$$K_W = [H^+] [OH^-]$$
(4)
Dividing (4) by (2) and (3) -

from equation (1) and (5)-

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 HA + BOH
Initial molar C C 0 0
concentration
Molar $(1 - h)C (1 - h)C$ hC hC
concentration
at equilibrium

$$\therefore \quad K_{h} = \frac{[HA] [BOH]}{[B^{+}] [A^{-}]}$$
$$= \frac{hC \times hC}{(1-h)C \times (1-h)C}$$
$$K_{h} = \frac{h^{2}}{(1-h)^{2}}$$

If h is very small as compared to 1 then (1 h) is equal to 1. Hence the above equation becomes, $K_h = h^2$

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

h

.....(2)

(3)

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)

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

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

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

on putting the value of h

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

We know that $pH = -\log [H^+]$

$$= -\log \sqrt{\frac{K_{W} \cdot K_{a}}{K_{b}}}$$

$$= -\log \left(\frac{K_{W} \cdot K_{a}}{K_{b}}\right)^{1/2}$$

$$= -\frac{1}{2}\log K_{W} - \frac{1}{2}\log K_{a} + \frac{1}{2}pK_{B}$$

$$= \frac{1}{2}pK_{w} + \frac{1}{2}pK_{A} - \frac{1}{2}pK_{b}$$

$$pH = 7 + \frac{1}{2}pK_{a} - \frac{1}{2}pK_{b}$$

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

(Salt hydrolysis)

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

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

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

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

CH₃COO ⁻ + H ⁺	CH3COOH
(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

 $NH_4^+ + OH^ NH_4OH$ (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 $(Na_2 B_4O_7)$

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

(a) $CH_3COOH H^+ + CH_3COO^-$

(Feebly ionised.)

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

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

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) 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)
 $CH_3COO^- + H_2O$

(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) $CH_3COOH CH_3COO^- + H^+$ (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 $[CH_3CO O^-]=[salt]$ and $[CH_3COOH]=[Acid]$ taken initially in buffer solution.

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

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

 $log[H^+] = logK_a + log[CH_3COOH] - log[CH_3COO^-] - log[H^+] =$

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

[CH_2COO^-]

 $pH = pK_a + \log \frac{1}{[CH_3COOH]}$

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

or $\mathbf{pH} = \mathbf{pK}_{a} + \log \frac{[Salt]}{[Acid]}$

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 N₂V₂ = 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.

9.2.2Basic Buffer

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

e.g.

(a) $NH_4OH + NH_4CI$

(b) Glycine (NH₂CH₂COOH) + +Glycine hydrochloride (CL NH₃CH₂COOH)

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

(a)
$$NH_4OH$$
 $NH_4^+ + OH^ (K_b)$
(b) NH_4CI \longrightarrow $NH_4^+ + CI^-$

(c) H_2O 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) 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) $NH_4^+ + H_2O$

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



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

(a) NH_4OH $NH_4^+ + OH^ (K_b)$ (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
$$K_b$$
 = $\frac{[OH^-][NH_4^+]}{[NH_4OH]}$
or $[OH^-]$ = $\frac{K_b[NH_4OH]}{[NH_4^+]}$
= $\frac{K_a[Base]}{[Salt]}$



or
$$\mathbf{pOH} = \mathbf{pK}_{\mathbf{b}} + \mathbf{log} \frac{[Salt]}{[Base]}$$

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)

Number of moles acid or base added to 11 sol.

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

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 CH₃COOH + CH₃COONa 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 $NH_aCI + NH_aOH$ buffer.

(iv) A buffer solution of NH_4Cl , NH_4OH and $(NH_4)_2$ CO₃ is used for precipitation of carbonates of Vth group.

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

Solubility of solute in gm / litre

= molecular weight of the solute

10.1 Solubility product (K_{SP}) :

nic 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,

AB	AB	A+ + B-
Insoluble	Unionised	Ions
Solute	(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 -

$$\mathsf{K}_1 = \frac{[\mathsf{A}^+][\mathsf{B}^-]}{[\mathsf{A}\mathsf{B}]}$$

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 $K_{\rm SP} \ > \ [{\rm A}^+] \ [{\rm B}^-] \label{KSP}$
 - i.e. more solute can be dissolved.
- (g) In a supersaturated solution $K_{sp} < [A^+] [B^-]$

i.e. precipitation will start to occur.

10.2Relationship between Solubility and Solubility Product :

The equilibrium for a saturated solution of a salt $A_{\rm x}$ $B_{\rm y}$ may be expressed as,

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

$$\begin{array}{rcrcrc} A_{x} & B_{y} & xA^{y+} & + & yB^{x-} \\ & & xs & ys \\ \text{So, } K_{\text{SP}} &= [xs]^{x} & [ys]^{y} \\ & & K_{\text{SP}} &= & x^{x} & y^{y}(s)^{x} + y \end{array}$$



(a) 1 : 1 types salts or AB type of salts : eg. AgCl, AgI, BaSO₄, PbSO₄, etc. AB A⁺ + Blet 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. Ag₂CrO₄, PbI₂, Ag₂CO₃, CaF₂, CaCl₂ etc. (i) AB_2 A^{2+} + $2B^{-}$

25 S let the solubility of AB₂ is 's' moles per litre So, $K_{SP} = [A^{2+}][B^{-}]^2 = s \times (2s)^2 = 4s^3$

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

(ii) $A_2B = 2A^+ + B^{2-}$ let s the solubility of A_2B So, A_2B 2A⁺ + B²⁻ 2s s $K_{SP} = [A^+]^2 [B^{-2}]$ $= (2s)^2 (s) = 4s^3$ s = $3\sqrt{\frac{K_{SP}}{4}}$

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

 $AB_3 = Valency of A = 3 \times Valency of B$ eg. FeCl₃, AlCl₃, PCl₃, Al(OH)₃, Fe(OH)₃ etc. $A_3B = 3 \times$ Valency of A = Valency of B eg. Na_3BO_3 , Na_3PO_4 , H_3PO_4 etc.

A³⁺ + 3B⁻ (i) AB₃ let the solubility of A_3B is 's' mole / litre.

$$AB_{3} \qquad A^{3+} + 3B^{-}$$

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

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

(ii) A₃B 3A⁺ + B⁻³

let the solubility of A_3B is 's' moles/litre. $A_{2}B \quad 3A^{+} \quad + \quad B^{-3}$

(d) 2 : 3 or
$$A_2B_3$$
 type of salts :
eg. $Al_2(SO_4)_3$
 $A_2B_2 \quad 2A^{+3} + 3B^{-2}$
let the solubility of salt A_2B_3 is 's' -
So, $A_2B_3 \quad 2A^{+3} + 3B^{-2}$
 $2s \quad 3s$
 $K_{SP} = [A^{+3}]^2 \quad [B^{-2}]^3$
 $= (2s)^2 \times (3s)^3$
 $= 4s^2 \times 27 \ s^3$
 $K_{SP} = 108 \ s^5$
 $s = 5\sqrt{\frac{K_{SP}}{108}}$

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 $Na^+ + Cl^-$ to left & causes the precipitation of NaCl.

B.In preparation of NaHCO₃ by solvay **method** : Precipitation of NaHCO₃ 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 H₂S 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_4CI . The presence of NH₄Cl 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_4CI . 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 CH₃COOH, it ionises as, CH₃COOH CH₃COO⁻ + H⁺

 $K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$

(b) What do we mean by this equilibrium and this equilibrium constant ? A stage will come such that concentration of CH₃COOH, CH₃COO⁻ 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 CH₃COO⁻ ions concentration since mathematical calculation will tend to change itself to change that equilibrium constant, electrolyte (CH₃COOH) will do same thing in order to keep K_a constant because it has to be a constant, it will reduce its ionisation. Thus [CH₃COOH] 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.

11.1Effect 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 A^+ + B

s

s

S $K_{SP} = S^2 = [A^+] [B^-]$(1) (Product should not exceed s² otherwise precipitation will start) Now. Let solubility of AB in CB be S.

$$CB = C^{+} + B^{-}$$

$$C = C = C$$

$$AB = A^{+} + B^{-}$$

$$s_{1} = s_{1}$$

$$[A^{+}] = s_{1}$$

$$[B^{-}] = s_{1} + C$$

$$K_{SP} = (s_{1}) (s_{1} + C)$$
If $s_{1} <<< C$

$$K_{SP} = s_{1}C = s^{2}$$
, from equation (1)
or $s_{1} = \frac{s^{2}}{C}$

So, solubility gets reduced.

С

	SOLVED P	ROBL	EMS
Ex.1 Sol.	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) pH = 13 -log [H ⁺] = 13 or [H ⁺] = 10 ⁻¹³ mole/litre [H ⁺] in 1 ml = 10 ⁻¹⁶ moles	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)
Ex.2	1 mole H ⁺ contains 6.023×10^{23} H ⁺ ions \therefore No. of H ⁺ ions in 10^{-16} moles $= 6.023 \times 10^{23} \times 10^{-16} = 6.023 \times 10^{7}$ The pH of a 0.05 M solution of H ₂ SO ₄ in water is nearly - (A) 0.05 (B)1 (C) -1 (D) 0	Sol.	Concentration of monobasic acid = 0.01 M pH = 4 If the acid is completely ionised the pH of the acid would be pH = $-\log 0.01$ = $-\log 10^{-2} = 2$
Sol.	$pH = -\log_{10} H^{+}$ The concentration of H ⁺ ions is expressed in gm equivalent Molarity of H ₂ SO ₄ = 0.05 \therefore Normality = 0.05 × 2 = 0.1 \therefore pH = -log 0.1	Ex.6	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. The dissociation constant of a monobasic N
	or $pH = 1$		acid which is 3.5% dissociated in $\frac{1}{20}$
Ex.3	A salt $M_2 X_3$ dissolves in water such that its solubility is x g. mole/litre. Its K_{SP} is -		(A) 3.5×10^{-2} (B) 5×10^{-3} (C) 6.34×10^{-5} (D) 6.75×10^{-2} (Ans C)
Sol.	(A) x^5 (B) $6x^2$ (C) 108 x^5 (D) $6x^5$ (Ans. C) Solubility of $M_2X_3 = x$ gm mole/litre $M_2 X_3 2M^{+3} + 3X^{-2}$ $\therefore [M^{+3}] = 2x$ $[X^{-2}] = 3x$ Solubility product $K_{SP} = (2x)^2 \cdot (3x)^3 = 108 x^5$	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
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		$= \frac{35}{100} = 0.035 = \alpha$ K _a = $\frac{C\alpha^2}{(1-\alpha)^2} = \frac{0.05 \times (0.035)^2}{1-0.025} = 6.34 \times 10^{-5}$
Sol.	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) (B) Solubility = Solubility Product Concentration of Common ion $\therefore S_1 = \frac{K_{SP}}{0.02} = 50 K_{SP}$ $S_2 = \frac{K_{SP}}{0.01} = 100 K_{SP}$	<i>Ex.7</i> Sol.	$(1-\alpha) \qquad 1-0.035$ Solubility product of AgCl is 2.8 × 10 ⁻¹⁰ at 25°C. 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) In 0.1 M AgNO ₃ AgNO ₃ Ag ⁺ + NO ₃ ⁻ AgCl Ag ⁺ + Cl ⁻
	$\begin{split} & S_3 = \frac{n_{sp}}{0.05} = 20 \ K_{SP} \\ & So, S_2 > S_1^{0.05} > S_3 \ Again \ solubility \ will \ be \\ & greatest \ in \ water. \ So, \ \mathbf{S_0} > \mathbf{S_2} > \mathbf{S_1} > \mathbf{S_3} \end{split}$		$K_{SP} = [Ag^+] [CI]$ Now $[Ag^+]$ can be taken as $[AgNO_3]$ while $[CI^-]$ is the solubility of AgCl

$$\begin{array}{l} \begin{array}{c} \begin{array}{c} \label{eq:constraints} \begin{array}{c} \label{eq:constraints} \\ \$$

	EQUILIBRIUM		
Sol.	Aniline ⁺ +Acetate ⁻ +H ₂ O Aniline +Acetic acid		Let solut havii
	1 1 0 0 After hydrolysis		∴ [
	1-h 1-h h h Let concen. salt be C mole litre ⁻¹		and
	$K_{h} = \frac{Ch \cdot Ch}{C(1-h) \cdot C(1-h)} = \frac{h^{2}}{(1-h)^{2}}$		Give a
	$\frac{h}{1-h} = \sqrt{\frac{K_w}{K_a.K_b}}$		∴ 5
	$= \sqrt{\frac{10^{-14}}{2 \times 10^{-6} \times 4 \times 10^{-10}}}$		 mole
	% hydrolysis = 54.95 % h = 0.035		= ∴ V
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	Ex.17	The 2 × Calc
Sol.	(Ans. D) Let V ml of acid and V ml of NaOH be used concentration of both acid and NaOH are same. CH_COOH + NaOH \rightarrow CH_COONa + H_O	Sol.	(A) Rela
	Concentration before reaction $\frac{0.1 \times V}{2V} = \frac{0.1 \times V}{2V}$		
	Concentration after reaction $0.1 \times V$ $0.1 \times V$		∴ Re
	$0 \ 0 \ -\frac{2V}{2V} \ -\frac{2V}{2V}$ [CH COONa] = $\frac{0.1}{2V}$ = 0.05 M		= Relat
	Now calculate pH by hydrolysis of CH_3COONa $CH_3COONa + H_2O$ $CH_3COOH + NaOH$	Ex.18	= Find 25m
	$[OH^{-}] = C.h = \sqrt{\frac{K_{w} \cdot C}{K_{a}}} = \sqrt{\frac{10^{-14} \times 0.05}{2 \times 10^{-5}}}$		0.5 (A) ((C) :
	= 5 × 10 ⁻⁶ = 6 × 0.699 = 5.301 = [14 -5.301] = 8.699 ≈ 8.7	Sol.	We k ∴ n n
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 $NH_2 = 2 \times 10^{-5}$		m.e. = total
	$NT_3 = 2 \times 10^{}$. N

(A) 3.248 g (B) 4.248 g (C) 1.320 g (D) 6.248 g $pOH = -\log K_{b} + \log \frac{[NH_{4}^{+}]}{[NH_{4}OH]}$ Sol.

'a' millimoles of NH_4^+ are added to a ion ng milli moles of $NH_aOH = 500 \times 0.2 = 100$ $[NH_4^+] = [salt] = \frac{a}{500}$ 100 $[NH_4OH] = [Base] = \frac{100}{500}$ en K_b for NH₄OH = 2 x10⁻⁵ and pH = 9 $= -\log 2 \times 10^{-5} + \log \frac{a/500}{100/500}$ a = 200 mili moles = 0.2 mol es of $(NH_4)_2$ SO₄ added $= \frac{a}{2} = 0.1 \text{ mol}$ $W_{(NH_4)_2 SO_4} = 0.1 \times 132$ = 1.32

 K_a for formic acid and acetic acid are 10^{-4} and 2×10^{-5} respectively. ulate the relative strength of acids same molar concentration -(-)

$$\sqrt{10}$$
 (B) $\sqrt{7}$ (C) $\sqrt{8}$ (D) $\sqrt{5}$ (Ans. A)

tive strength of weak acids

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

Relative strength = $\sqrt{\left(\frac{K_{a_1}}{K_{a_2}}\right)}$ (\because C₁ = C₂)

 $= \sqrt{\left(\frac{2 \times 10^{-5}}{2 \times 10^{-5}}\right)}$ tive strength for HCOOH to CH₃COOH = √<u>10</u>:1

the pH of solution prepared by mixing l of a 0.5 M solution of HCl, 10ml of a M solution of NaOH and 15ml of water 0.8239 (B) 1.0029 1.0239 (D) 1.8239

(Ans. A)

now that for HCl and NaOH, m.e. = m.e. n.e. of HCl = $0.5 \times 25 = 12.5$ n.e. of NaOH = $0.5 \times 10 = 5.0$ of HCl in the resultant mixture = 12.5 - 5.0 = 7.5 volume = (25 + 10 + 15) ml = 50 ml Normally of HCl = $\frac{\text{m.e.}}{\text{Vol(ml)}} = \frac{7.50}{50}$ **g** (Ans. C) \therefore Molarity = $\frac{7.50}{50}$ \therefore [H⁺] = [HCI] = $\frac{7.50}{50}$:. pH = $-\log \frac{7.50}{50} = 0.8239$

Ex.19 The solubility procduct of chalk is **Sol.** $pH = pK_a + log \frac{[Salt]}{[Acid]}$ 9.3×10^{-8} . Calculate its solubility in gram per litre - $= -\log(1.0 \times 10^{-5}) + \log \frac{(0.02 - 0.01)}{(0.03 + 0.01)}$ (A) 0.3040 gram / litre (B) 0.0304 gram / litre $= 5 + \log \left(\frac{1}{4}\right) = 5 - 0.6 = 4.4$ (C) 2.0304 gram / litre (Ans. B) (D) 4.0304 gram / litre $CaCO_{3}$ Ca^{2+} + CO_{3}^{2-} Sol. Ex.23 20 ml of 0.2 M NaOH is added to 50 ml, of Let the solubility of CaCO₃ be s mole per 0.2 M CH₃COOH to give 70ml, of the litre solution. What is the pH of the solution ? : $K_{SP} = [Ca^{2+}] [CO_3^{2-}] = s.s$ The ionization constant of acetic acid is \therefore s = $\sqrt{K_{SP}}$ = $\sqrt{9.3 \times 10^{-8}}$ 2 × 10⁻⁵ -= 0.000304 mole / litre (B) 5.568 (A) 4.522 Solubility in $g/I = mole/litre \times Molegular$ (C) 6.522 (D) 7.568 weight of CaCO₃ (Ans. A) $= 0.000304 \times 100$ The addition of NaOH converts equivalent Sol. = 0.0304 gram / litre amount of acetic acid into sodium acetate. Ex.20 Maximum Conductivity would be of -Hence, (A) K_3 Fe(CN)₆ [0.1 M solution] Concen. of acetic acid after the addition of (B) $K_2 Ni(CN)_4$ [0.1M solution] $NaOH = \frac{30}{70} \times 0.2 M$ (C) \overline{FeSO}_4 . $AI_2(SO_4)_3$.24 H_2O [0.1 M solution] Concen. of CH₂COONa after the addition of (D) $Na[Ag(S_2O_2)_3]$ [0.1 M solution] $NaOH = \frac{20}{70} \times 0.2 M$ (Ans. C) Double salt on ionization gives more ions. Sol. Hense, Using the expression One molecule of the salt gives Fe⁺², 2AI⁺³, pH = $pK_a + \log \frac{[Salt]}{[Acid]}$ = $-\log (2 \times 10^{-5}) + \log \left(\frac{20}{30}\right)$ $4SO_4^{-2}$ ions. Hence its conductance would be highest. Ex.21 What amount of sodium propanoate should be added to one litre of an = 4.699 - 0.177 = **4.522** aqueous solution containing 0.02 mole of Ex.24 The concentration of H⁺ ion in a 0.2 M propanoic acid ($K_a = 1.0 \times 10^{-5}$ at 25°C) solution of HCOOH is 6.4×10^{-3} mole ℓ^{-1} . to obtain a buffer solution of pH 6 -To this solution HCOONa is added so as to (A) 0.1 M (B) 0.2M (C) 0.3 M (D) 1.3 M (Ans. B) adjust the concentration of HCOONa to one Using the expression Sol. mole per litre. What will be the pH of this solution? K_a for HCOOH is 2.4 × 10⁻⁴ and $pH = pK_a + \log \frac{[Salt]}{[Acid]}$ the degree of dissociation of HCOONa is [Salt] 0.75 we get,6 = $-\log(1.0 \times 10^{-5}) + \log \frac{13}{[0.02 M]}$ (A) 3.19 (B) 4.19 [Salt] (C) 5.19 (D) 6.19 Which gives $6 = 5 + \log \frac{[Saij]}{[0.02 M]}$ (Ans. B) Assuming that the addition of HCOONa or $\frac{[Salt]}{[0.02 M]} = 10$ or [Salt] = 0.2 MSol. suppresses the ionization of HCOOH, we can use the expression Ex.22 What will be the pH of the solution, if 0.01 mole of HCl is dissolved in a buffer $pH = pK_a + log \frac{[Salt]}{[Acid]}$ solution containing 0.03 mole of propanoic to compute pH of the solution, since salt is acid ($K_a = 1.0 \times 10^{-5}$) and 0.02 moles of salt, at 25°C -75% dissociated we will get, (A) 3.699 (B) 4.699 0.75 $Ph = -\log(2.4 \times 10^{-4}) + \log \frac{0.73}{0.2}$ (D) 6.11 (C) 5.11 (Ans. B) = 3.62 + 0.57 = 4.19

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Ex.25 What amount of HCI will be required to Ex.27 Calculate the pH of a solution which contains 10 ml of 1M HCl and 10 ml of 2 prepare one litre of a buffer solution (containing NaCN and HCN) of pH 10.4 M NaOH using 0.01 mole of NaCN. (A) 11.7 (B) 12.7 Given K_{ion} (HCN) = 4.1 × 10⁻¹⁰ -(C) 13.7 (D) 10.7 (A) 8.55 × 10⁻³ mole (Ans. C) (B) 8.65 × 10⁻³ mole HCI + NaOH \rightarrow NaCl + H₂O Sol. (C) 8.75 × 10⁻³ mole Meq. before $10 \times 1 \quad 10 \times 2$ (D) 9.9 \times 10⁻⁴ mole (Ans. D) Reaction = $10 = 20 \ 0 \ 0$ Sol. The addition of HCl converts NaCN into HCN. Meg. After 0 10 10 10 Let x be the amount of HCl added. We will Reaction have. $[OH^{-}]$ left from NaOH = $\frac{10}{20}$ = 0.5 M [NaCN] = (0.01 - x)= x [HCN] $pOH = - \log OH^- = - \log 0.5$ pOH = 0.3 pH = 13.7 Substituting these values along with pH and K_a in the expression. Ex.28 Calculate pH of a solution of given $pH = -\log K_a + \log \frac{[Salt]}{[Acid]}$ mixture (0.1 mole CH₃COOH + 0.2mole CH₃COONa) in 100 ml of mixture. $K_a = 2 \times 10^{-5}$. We get (B) 5.6 (C) 6.6 (A) 4.6 (D) 7.6 $10.4 = -\log[4 \times 10^{-10}] + \log \frac{0.01 - x}{x}$ (Ans. A) We have Sol. or 10.4 = 9.4 + log $\frac{0.01 - x}{x}$ $pH = -\log K_a + \log \frac{[Salt]}{[A+i]}$ [Acid] or log $\frac{0.01 - x}{x} = 1$ $\frac{3 \times 1000 \text{ M}}{82 \times 100} = 0.366$ [Salt] = or $\frac{0.01-x}{x} = 10 \Rightarrow 11x = 10^{-2}$ or x = **9.9 x 10^{-4} M** $[Acid] = \frac{2 \times 1000}{60 \times 100} M = 0.333$ Ex.26 Calculate the pH of aqueous solution of 0.2×1000 1.0 M HCOONH₄ assuming complete $= -\log 2 \times 10^{-5} + \log \frac{100}{0.1 \times 1000}$ dissociation (pK_a of HCOOH = 3.8 and = 4.6 $pK_{b} = of NH_{3} = 4.8)$ -1000 (A) 3.5 (B) 4.5 (C) 5.5 (D) 6.5 (Ans. D) Ex.29 Calculate the pH of a buffer solution Ammonium formate undergoes hydrolysis as Sol. prepared by dissolving 10.6 of Na₂CO₃ in 500 ml of an aqueous solution containing $NH_4^+ + HCOO^- + H_2O$ NH₄OH + HCOOH 80 ml of 1M HCl. $K_{h} = \frac{K_{W}}{K_{a} \cdot K_{b}}$ K_a for $HCO_3^- = 6 \times 10^{-11} -$ (A) 8.6 (B) 9.6 (C) 11.6 (D) 12.6 Moreover in the solution we have (Ans. B) $[NH_4OH] = [HCOOH]$ Na₂CO₃ + HCl→NaCl+NaHCO₃ Sol. $K_{h} = \frac{[HCOOH]^{2}}{[HCOO^{-}]^{2}}$ Hence Meq. before $\frac{10.6}{106} \times 1000$ 80×1 $\frac{\mathsf{K}_{\mathsf{W}}}{\mathsf{K}_{\mathsf{a}}.\mathsf{K}_{\mathsf{b}}} = \frac{[\mathsf{H}^{+}]^{2}}{[\mathsf{K}_{\mathsf{a}}]^{2}}$ Reaction = 10080 0 0 or Meq. After 20 0 80 80 or $[H^+]^2 = \frac{K_w \cdot K_a}{K_b}$ Reaction The solution Na_2CO_3 and HCO_3^- and thus or 2pH = $pK_W + pK_a - pK_b$ acts as buffer $pH = -\log K_a + \log \frac{[CO_3^{-2}]}{[HCO_3^{-1}]}$ or pH = $\frac{1}{2}$ [pK_W + pK_a - pK_b] $=\frac{1}{2}$ [14 + 3.8 - 4.8] = 6.5 $= -\log 6 \times 10^{-11} + \log \frac{20}{80} = 9.6$ Sol.

Sol.





reaction with a strong base -(B) 10¹⁰ (C) 10¹¹ (D) 10¹² (A) 10⁹ (Ans. B)

Sol.	HA + weak s	BOH strong	BA	\ +	H ₂ O		
	or HA + E	8+ + OH-	-	B+ +	A⁻ +	H ₂ O	or
	HA⁻	A⁻ +	H ₂ O			-	
	· K =	[A ⁻]					
	·· · · [H	A][OH⁻]					
	Also for w	eak acio					
	HA	H+ +	A-				
	$K_{a} = \frac{[H^{+}][A]}{[HA]}$	$\frac{1}{K} = K_{w}$	or K =	$=\frac{K_a}{K_w}=$	$=\frac{10^{-4}}{10^{-14}}$	= 10) 10
Ex.33	Calculate	pH of a	solut	ion w	hose	100	ml
	contains	0.2 gm	NaOH	disso	lved	in it	-
	(A) 10.69 (C) 12 69	9	(B) (D)	11.6	99		
	(0) 12.05		(5)	15.0	(Ar	ns. C))
Sol. 🎽	100ml s	olution	of	NaO	Н`с	ontai	ns
	= 2.0gm N	laOH			<u>.</u>		
	= 2 am Na	mi solu aOH	tion c	or Na	он с	ontai	ns
				2	0.05	NI	
	Normality	of soluti	on =	40 =	0.05	N	
	∴ [H+] =	10 ⁻¹⁴					
		0.05	[10]	-14]			
	: - log[H	I ⁺] = -		05			
	= - [-	14 + 2	- 0.69	90] =	12.6	599	
Ex.34	Calculate	the rat	tio of	nH o	fas	oluti	on
	containin	g 1 mol	e of CH	<i>4</i> ₃COC)Na +	- 1 <i>m</i> c	ble
E.	of HCl po	er litre	and o	of ot	her s	oluti	on
	containing	g 1 mol d ner lit	e CH ₃ C re	COON	3 + 1	mole	of
	(A) 1 : 1		(B)	2:1			
	(C) 1 : 2		(D)	2:3	(Ar	is. C))
Sol.	Case I -	oH when	1mole	e CH ₃ (COON	a and	11
		are pres +HCl→Cŀ	ent Hacoor	++NaC	1		
	Before	1	130001	1	•	0	0
	reaction						
	After	0		0		1	1
	reaction	[CH2CC)OH] =	= 1M			
		L - 3	K]				
	∴ [H+] C	$\alpha = C. $	$\frac{R_a}{C} =$	√C.K _a		$\sqrt{K_{a}}$	
	∵ C =	1	-				
	∴ pH₁ =	$-\frac{1}{2}$ lo	og K _a				
	Case II -	2 pH who	en 1 m	iole Cl	1,00	DNa a	nd
	1 mole of	CH ₃ COC)H, a b	ouffer	solut	ion	

$$\therefore \text{ pH}_2 = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a$$

- Ex.35 Calculate pH of 0.002 N NH₄OH having 2% dissociation -(A) 7.6 (B) 8.6 (C) 9.6 (D) 10.6
 - 7.6 (B) 8.6 (C) 9.6 (D) 10.6 (Ans. C)
- **Sol.** NH₄OH is a weak base and partially dissociated

 $\begin{array}{ccc} \mathsf{NH}_4\mathsf{OH} & \mathsf{NH}_4^+ + \mathsf{OH}^-\\ \mathsf{Concentration} \ 1 & 0 & 0\\ \mathsf{before\ dissociation}\\ \mathsf{Concentration\ 1} - \alpha & \alpha & \alpha\\ \mathsf{after\ dissociation} \end{array}$

 $\therefore [OH^{-}] = C\alpha = 2 \times 10^{-3} \times \frac{2}{100}$ = 4 × 10^{-5} M pOH = - log[OH^{-}] = - log 4 × 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⁻, H₃O⁺ (B) Na⁺, Cl⁻, H₂O (C) Na⁺, Cl⁻, OH⁻ (D) H⁺, H₃O⁺ (Ans. B)

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. N₁V₁ = N₂V₂

$$50 \times \frac{N}{5} = N_2 \times 100$$

 $N_2 = \frac{50 \times N}{5 \times 100} = .1$ Hence, **pH = 1**

 $M NH_{3'} 0.40M NH_{4}Cl, K_{b} \text{ for ammonia} = 10$ (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 = $\frac{pK_{1} + pK_{2}}{2}$

Ex.38 Calculate the $pOH - pK_b$ for the buffer, 0.20

(D) $pH = 7 + \left(\frac{pK_a - pK_b}{2}\right)$ Sol. $HS^- + H_2O + H_2S + OH^-$

$$\therefore [OH^{-}] = Ch = \sqrt{\frac{K_{w} \cdot C}{K_{a}}}$$
$$\therefore [H^{+}] = \frac{K_{w}}{\sqrt{\frac{K_{w} \cdot C}{K_{a}}}} = \sqrt{\frac{K_{w} \cdot K_{a}}{C}}$$
$$or pH = \frac{1}{2} [pK_{w} + pK_{a} + \log C]$$

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 -

$$\alpha = \sqrt{\frac{K_a}{C}} \therefore \% \alpha = 100 \sqrt{\frac{K_a}{C}}$$
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 $\frac{(1-\alpha)}{\alpha}$
 $\therefore \frac{1-\alpha}{\alpha} = 10^{pK_a-pH}$
or $\frac{1}{\alpha} = 10^{pK_a-pH} + 1$
or $\alpha = \frac{1}{(1+10^{pK_a-pH})}$

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(Ans. A)