ACIDS AND BASES

Topic-1
Lowry - Bronsted and Lewis theory of acids and bases with examples and applications

VERY SHORT ANSWER QUESTIONS

1. What is bronsted acid and base give one example?
Ans:

Strength of bronsted acids and bronsted bases will depend on the ability to donate or to accept proton.

Strong acids: which have more ability to donate protons.
Eg: $HClO_4$, HCl, H_2SO_4

Weak acids: which have fewer tendencies to donate proton.
Eg: HF, CH_3COOH, H_2CO_3, HCN

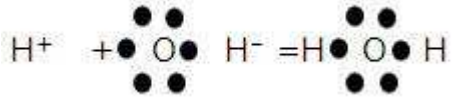
Strong bases: which have greater tendency to accept protons
Eg: OH^- CH_3COO^- CH_3^- etc.

Weak bases → which have fewer tendencies to accept the proton.
Eg: Cl^- ClO_4^- Br^- I^- NH_3…..etc

2. What is a Lewis acid and base?
Ans:

According to this concept, a base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons. The acid is also known as electron acceptor or electrophile while the base is electron donor or nucleophile.

A simple example of an acid-base is the reaction of a proton with hydroxyl ion.



Acid **Base**

$H_3N: + BF_3 = H_3N \rightarrow BF_3$

Base **Acid**

SHORT ANSWER QUESTIONS

1. What is conjugate acid-base pair?

Ans:

Conjugate acid – base pairs:

The acid base pair which differs by a proton is called conjugated acid base pair.

Acid $\xrightarrow{-H^{\oplus}}$ conjugate base

Base + $H^{\oplus}$ = conjugate acid

Eg :	**Acid**	**Base**
	HCl	Cl^-
	H_2SO_4	HSO_4^-
	HSO_4^-	SO_4^{2-}
	H_2S	HS^-
	C_2H_2	$CH \equiv C^-$

2. Give two examples of Lewis acid and Lewis base?

Ans: Lewis theory of acids – bases:

Acid: which accepts electron pair.

All electrophiles are Lewis acids

Lewis acid must contain suitable vacant orbitals.

Eg: BF_3, BCl_3, $AlCl_3$, H^+, Ag^+ etc.

Base: which donates e^- pair.

All nucleophiles are Lewis bases

Lewis base must contain 1 or more lone pairs of electrons.

Eg: $\ddot{N}H_3, \dddot{P}H_3, R-\ddot{N}H_2$,

$\ddot{N}H_2-\ddot{N}H_2$, OH^-, $\dddot{Cl}^-$, $H_2\ddot{O}$

LONG ANSWER QUESTIONS

1. **Explain the concept of Bronsted acids and Bornsted bases. Illustrate the answer with examples?**

Ans:

Bronsted – Lowry theory of Acids and bases: This is also called protonic theory .

Acid: which donates proton

Eg: HCl, H_2SO_4, HNO_3 etc.

Base: which accepts proton

Eg: NH_3, PH_3, N_2H_4, R – NH_2 etc.

Bronsted acid could be a neutral molecule, anion, cation.

Neutral molecule → HCl, HNO_3, H_2SO_4 etc

Cations → H_3O^+, NH_4^+

Anions → HSO_4^-, HCO_3^-, $H_2PO_4^-$, $H(PO_4)^{2-}$, $H_2(PO_3)^-$ Bronsted base could be neutral, cation or anion

Neutral → $\underset{\sim}{N}H_3$, $\underset{\sim}{P}H_3$, N_2H_4 etc.

anions → C$\underset{\cdot\cdot}{N}$B$\underset{\cdot\cdot}{r}\underset{\cdot\cdot}{I}O\underset{\cdot}{H}$etc.

Cations → $[Al(H_2O)_5OH)]^{2+}$, $[Fe(H_2O)_5OH$

- **Merits of Bronsted – Lowery theory :**

1) It could explain acid base behaviour in non – aqueous solvents also.
   Eg: liquid SO_2, liquid NH_3
2) It could explain the basic nature of substances like NH_3.
3) It could explain the acidic nature of HCl gas.
4) It is more generalized than Arrhenius theory.

- **Limitations of Bronsted – Lowery theory :**

1) This theory explains behaviour of acids only when there is a base (or) It explains behaviour of base only when there is a acid. (Acid base pairs must be present)
2) It fails to explain the acidic nature of electron deficient compound like BF_3, $AlCl_3$ etc.

2. **What are conjugate acids and conjugate bases? Give two examples**?

Ans:

Conjugate acid – base pairs: The acid base pair which differs by a proton is called conjugated acid base pair.

Acid $\tilde{}$ $H^{\oplus}$ = conjugate base

Base + $H^{\oplus}$ = conjugate acid

Eg :	**Acid**	**Base**
	HCl	$\tilde{Cl}$

H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
H_2S	HS^-

In any conjugate acid base pair, if the acid is stronger, the base is weak and if base is stronger, the acid is weak.
Eg:
1. HCl is strong acid, Cl^- is weak conjugate base.
2. CH_3COOH is weak acid $CH_3COO^-$is strong base
3. NH_3 is weak base, NH_4^+ strong acid
4. $HClO_4$ is strongest acid, ClO_4^- weak base

Strength of bronsted acids and bronsted bases will depend on the ability to donate or to accept proton.

Strong acids: which have more ability to donate protons
Eg: $HClO_4$, HCl, H_2SO_4

Weak acids: which have fewer tendencies to donate proton.
Eg: HF, CH_3COOH, H_2CO_3, HCN
Among Hydracids HCN is the weakest acid

Strong bases: which have greater tendency to accept protons
Eg: OH^- CH_3COO^- CH_3^- etc.

Weak bases $\rightarrow$ which have fewer tendencies to accept the proton.
Eg: Cl^- ClO_4^- Br^- I^- NH_3…..etc.

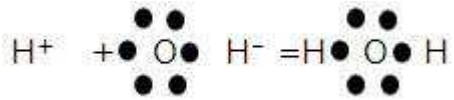
3. **Explain Lewis Acid-Base Theory?**

Ans:

<u>Lewis concept of Acids and bases :</u>

This concept was proposed by G.N. Lewis, in 1939. According to this concept, a base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons. The acid is also known as electron acceptor or electrophile while the base is electron donor or nucleophile.

A simple example of an acid-base is the reaction of a proton with hydroxyl ion.



Acid Base

Some other examples are:

$H_3N: + BF_3 = H_3N \rightarrow BF_3$

Base Acid

$H^+ +: NH_3 = [H \leftarrow NH_3]^+$

Acid Base

$BF_3 + [F]^- = [F \rightarrow BF_3]^+$

Acid Base

Lewis concept is more general than the Bronsted Lowry concept.

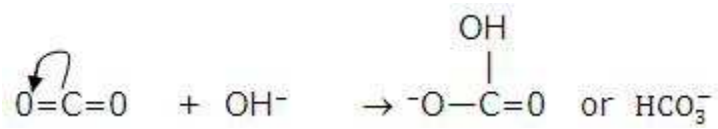
According to **Lewis concept**, the following species can act as **Lewis acids**.

(i) Molecules in which the central atom has incomplete octet: All compounds having central atom with less than 8 electrons are **Lewis acids**, e.g., BF_3, $BC1_3$, $A1C1_3$, $MgCl_2$. BeCL. etc.

(ii) Simple cations: All cations are expected to act as
Lewis acids since they are deficient in electrons. However, cations such as Na^+, K^+, Ca^{2+}, etc., have a very little tendency to accept electrons, while the cations like H^+, Ag^+, etc., have greater tendency to accept electrons and, therefore, act as **Lewis acids**.

(iii) Molecules in which the central atom has empty d-orbitals: The central atom of the halides such as SiX_4, GeX_4, $TiCl_4$, SnX_4, PX_3, PF_5, SF_4, SeF_4, $TeCl_4$, etc., have vacant d-orbitals. These can, therefore, accept an electron pair and act as **Lewis acids**.

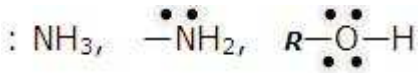
(iv) Molecules having a multiple bond between atoms of dissimilar electronegativity: Typical examples of molecules falling in this class of **Lewis acids** are $C0_2$, $S0_2$ and $S0_3$. Under the influence of attacking Lewis base, one -electron pair will be shifted towards the more negative atom.



Lewis acid Lewis base

The following species can act as **Lewis bases**.

(i) Neutral species having at least one lone pair of electrons: For example, ammonia, amines, alcohols, etc., act as **Lewis bases** because they contain a pair of electrons



(ii) Negatively charged species or anions: For example, chloride, cyanide, hydroxide ions, etc., act as **Lewis bases**.

CN^-, Cl^-, OH^-

It may be noted that all Bronsted bases are also **Lewis bases** but all Bronsted acids are not **Lewis acids**.

Limitations:

Since the strength of the **Lewis acids and bases** is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

The choice of which definition of acids and bases one wishes to use in a particular instance depends largely on the sort of chemistry that is studied. But Arrhenius concept is perfectly satisfactory and simplest for dealing with reactions in aqueous solutions. It explains satisfactorily the strength of acids and bases in aqueous solutions, neutralisation, salt hydrolysis, etc.

ACIDS AND BASES

Topic-2
Ionisation of acids and bases, ionic product of and concept of P^H

VERY SHORT ANSWER QUESTIONS

1. Explain the ionic product of water?

Ans:

Ionic Product of Water:

Pure water is a very weak electrolyte and ionises according to the equation

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

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

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

$$\mathbf{or\quad [H^+][OH^-] = K[H_20]}$$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_20]$, may be regarded as constant. Thus, the product $\#[H_20]$ gives another constant which is designated as K_w. So,

$$\mathbf{[H^+][OH^-] = K_w}$$

The constant, K_w, is termed as ionic product of water.

2. Define P^H.

Ans: The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

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

or $pH = \log 1/[H^+$

SHORT ANSWER QUESTIONS

1. Define ionic product of water?
Ans;

Ionic Product of Water:

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Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_20]$, may be regarded as constant. Thus, the product $\#[H_20]$ gives another constant which is designated as K_w. So,

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

The constant, K_w, is termed as ionic product of water.

The product of concentrations of H1 and OH ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature (°C)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14}. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

2. **Define P^H. What is the value of P^H of blood?**

Ans: The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

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

or $pH = \log 1/[H^+]$

pH of a solution is, thus, defined as **the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains or pH of the solution is the logarithm of the reciprocal of H^+ ion concentration.**

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, i.e.,

pOH = -log [OH-] Considering the relationship,

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

Taking log on both sides, we have

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

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

or $pH + pOH = PK_w^* = 14$

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at 25°C. The above discussion can be summarised in the following manner:

3. **What is degree of ionisation of a weak acid and base**?

Ans:

P^H of weak acids and weak bases:

Ionisation of weak acid (HA):

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ C & & 0 & & 0 \end{array}$$

$$\begin{matrix} C - C\alpha & C\alpha & C\alpha \end{matrix}$$

$$K_a = \frac{C\alpha . C\alpha}{C - C\alpha} = \frac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C \quad (\because \ \alpha \text{ is very less})$$

$$K_a = \alpha^2 C; \ \alpha^2 = K_a / C$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a . V} \ = \left(\frac{1}{c} = v\right)$$

4. **Explain the hydrolysis of the salt of weak acid and strong base?**

Ans: <u>Salt of a weak acid and a Strong base:</u>

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a **weak acid** and OH^- ions.

$A^- + H_2O; \ \leftrightarrow \ HA + OH^-$

Weak acid

Consider, for example, the salt CH_3COONa. It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a **weak acid**, CH_3COOH and OH^- ions.

$CH_3COO^- + H_2O \ \leftrightarrow \ CH_3COOH + OH^-$

$C(1-x) \qquad\qquad Cx \qquad Cx$

Thus, OH^- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$K_h = [CH_3COOH][OH^-]/[CH_3CO^-] = (Cx \times Cx)/C(1-x) = (Cx^2)/(1-x)$) ..... (i)

Other equations present in the solution are:

$CH_3COOH \leftrightarrow CH_3COO^- + H^+, \qquad K_a = [CH_3COO^-][H^+]/[CH_3COOH]$ ..... (ii)

$H_2O \leftrightarrow \ H^+ + OH^-, \qquad K_w = [H^+][OH^-]$ ..... (iii)

From eqs. (ii) and (iii),

$\log [OH^-] = \log K_w - \log K_a + \log[salt]/[acid]$

$-pOH = -pK_w + pK_a + \log[salt]/[acid]$

$pK_w - pOH = pK_a + \log[salt]/[acid]$

$pH = pK_a + \log[salt]/[acid]$

Considering eq. (i) again,

$K_h = cx^2/(1-x)$ or $K_h = Ch^2/(1-h)$

When h is very small, $(1-h) \rightarrow 1$

or $h^2 = K_h/C$

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

$[OH^-] = h \times C = \sqrt{(CK_h)} = \sqrt{(C*K_w/K_a)}$

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

$= K_w/\sqrt{(C*K_w/K_a)} = \sqrt{(K_a*K_w)}/K_c$

$-\log [H^+] = -1/2\log K_w - 1/2\log K_a + 1/2\log C$

$pH = 1/2pK_w + 1/2pK_a + 1/2\log C$

$= 7 + 1/2pK_a + 1/2\log C.$

LONG ANSWER QUESTIONS

1. Explain the concept of ionisation acid and base?

P^H of weak acids and weak bases:

Ionisation of weak acid (HA):

$$\begin{array}{ccccc} \mathbf{HA} & \rightleftharpoons & \mathbf{H^+} & + & \mathbf{A^-} \\ \mathbf{C} & & \mathbf{0} & & \mathbf{0} \\ \mathbf{C - C\alpha} & & \mathbf{C\alpha} & & \mathbf{C\alpha} \end{array}$$

$$\mathbf{K_a} = \frac{C\alpha.C\alpha}{C - C\alpha} = \frac{\alpha^2 C}{(1-\alpha)} = \alpha^2 C \quad (\because \ \mathbf{\alpha \text{ is very less}})$$

$$\mathbf{K_a = \alpha^2 C;\ \alpha^2 = K_a / C}$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a.V} \ = \left(\frac{1}{c} = v\right)$$

Ostwald's law of dilution explains the variation of degree of ionisation with concentration. The degree of ionisation is inversely proportional to its square root of its concentration (or) directly proportional to square root of its dilution.

$$[H^+] = C\alpha$$

$$[H^+] = C\sqrt{\frac{k_a}{C}}\ ;\ [H^+] = \sqrt{K_a.C}$$

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

$$\log[H^+] = \frac{1}{2}\log K_a + \frac{1}{2}\log C$$

Ostwald's law of dilution is applicable for weak electrolytes (weak acid and weak base) it is not applicable to strong electrolytes because they completely ionise at moderate concentration. The behaviour of strong electrolytes is explained by Debye – Huckel's theory.

$$-\log [H^+] = -\frac{1}{2}\log k_a - \frac{1}{2}\log C$$

$$p^H = \frac{1}{2}p^{k_a} - \frac{1}{2}\log C$$

Ionisation of weak bases (MOH):

$$MOH \rightleftharpoons M^+ + OH^-$$

C	0	0
(C – Cα)	Cα	Cα

$$K_b = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

$$K_b = \frac{\alpha^2 C}{(1-\alpha)}\ (\because\ \alpha \text{ is very less})$$

$$K_b = \alpha^2 C\ ; \qquad \alpha^2 = \frac{K_b}{C}$$

$$\alpha = \sqrt{\frac{K_b}{C}} \Rightarrow \alpha = \sqrt{K_b.v}\ \left(\frac{1}{c} = v\right)$$

$$[OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}}$$

$$[OH^-] = \sqrt{K_b.C}$$

$$-\log[OH]^- = -\frac{1}{2}\log K_b - \frac{1}{2}\log C$$

$$p^{OH} = \frac{1}{2}p^{K_b} - \frac{1}{2}\log C$$

$$p^H = K_w - p^{OH}$$

$$p^H = k_w - \frac{1}{2}p^{K_b} + \frac{1}{2}\log C$$

For weak acids:

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

$$\alpha = \sqrt{\frac{K_a}{C}}$$

For weak bases:

$$[OH^-] = C\alpha\ ;\ [OH^-] = \sqrt{K_b.C}$$

$$\alpha = \sqrt{\frac{K_b}{C}}$$

For strong acids; $[H^+]$ = N of acid
For weak acids; $[H^+]$ < N of acid
For strong bases; $[OH^-]$ = N of base
For weak bases; $[OH^-]$ < N of base

2. .**Explain Ionic product of water.**

Ionic Product of Water:

Pure water is a very weak electrolyte and ionises according to the equation

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

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

$K = [H^+]\,[OH^-]/[H_2O]$

or $[H^+][OH^-] = K[H_20]$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_20]$, may be regarded as constant. Thus, the product #$[H_20]$ gives another constant which is designated as K_w. So,

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

The constant, K_w, is termed as ionic product of water.

The product of concentrations of H1 and OH ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature (°C)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14}. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

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

or $[H^+][OH^-]=x^2= 1 \times 10^{-14}$

or $x = 1 \times 10^{-7}\ M$

or $[H^+] = [OH^-] = 1 \times 10^{-7}\ mol\ litre^{-1}$

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product, $[H^+][OH^-]$, remains constant, i.e., equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, i.e.,

$[H^+] > [OH^-]$; (Acidic solution)

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,

i.e., $[OH^-] > [H^+]$; (Alkaline or basic solution)

In neutral solution, $[H^+] = [OH^-] = 1 \times 10^{-7}\ M$

In acidic solution, $[H^+] > [OH^-]$

or $[H^+] > 1 \times 10^{-7}\ M$

and $[OH^-] < 1 \times 10^{-7}\ M$

In alkaline solution, $[OH^-] > [H^+]$

or $[OH^-] > 1 \times 10^{-7}\ M$

and $[H^+] < 1 \times 10^{-7}\ M$

Thus, if the hydrogen ion concentration is more than 1×10^{-7} M, the solution will be acidic in nature and if less than 1×10^{-7} M, the solution will be alkaline.

$[H^+] = 10^{-0}\ \ 10^{-1}\ 10^{-2}\ 10^{-3}\ \ 10^{-4}\ 10^{-5}\ 10^{-6}$ (Acidic)

$[H^+] = \quad 10^{-7}$ (Neutral)

$[H^+] = 10^{-14}\ 10^{-13}\ 10^{-12}\ 10^{-11}\ 10^{-10}\ 10^{-9}\ 10^{-8}$ (Alkaline)

We shall have the following table if OH^- ion concentration is taken into account.

$[OH^-] = 10^{-14}\ \ 10^{-13}\ 10^{-12}\ 10^{-11}\ 10^{-10}\ 10^{-9}\ 10^{-8}$ (Acidic)

$[OH^-] = \ \ 10^{-7}$ (Neutral)

$[OH^-] = 10^{-0}\ 10^{-1}\ 10^{-2}\ 10^{-3}\ 10^{-4}\ 10^{-5}\ 10^{-6}$ (Alkaline)

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25°C. If one increases, the other decrease accordingly so that the product remains 1×10-14 at 25° C.

If $[H^+] = 10^{-2}$ M, then $[OH^-] = 10^{-12}$ M; the product, $[H^+][OH^-] = 10^{-2} \times 10^{-12} = 10^{-14}$; the solution is acidic.

If $[H^+] = 10^{-10}$ M, then $[OH^-] = 10^{-4}$ M; the product, $[H^+][OH^-] = 10^{-10} \times 10^{-4} = 10^{-14}$; the solution is alkaline.

3. Explain the concept of P^H in detail?

Ans:

<u>HYDROGEN ION CONCENTRATION-pH SCALE:</u>

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since H^+ ion concentration can vary within a wide range from 1 mol per litre to about 1.0×10^{-14} mol per litre, a logarithmic notation has been devised **by Sorensen**, in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

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

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

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

or $pH = \log 1/[H^+]$

pH of a solution is, thus, defined as the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains or pH of the solution is the logarithm of the reciprocal of H^+ ion concentration**.**

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, i.e.,

pOH = -log [OH-] Considering the relationship,

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

Taking log on both sides, we have

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

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

or $pH + pOH = PK_w^* = 14$

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at 25°C. The above discussion can be summarized in the following manner:

	$[H^+]$	**$[OH^-]$**	**pH**	**pOH**
Acidic solution	$>10^{-7}$	$<10^{-7}$	<7	>7
Neutral solution	10^{-7}	10^{-7}	7	7
Basic solution	$<10^{-7}$	$>10^{-7}$	>7	<7

ACIDS AND BASES

Topic-3
Hydrolysis of salts, buffer solutions and common ion effect and its applications and uses

VERY SHORT ANSWER QUESTIONS

1. What is Buffer solution?

Ans: 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 the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

2. Give one example each of acid and base buffer solution?

Ans: Acid buffer solution is formed by mixing a weak acid with its salt with a strong base,

eg;

(a) $CH_3COOH + CH_3COONa$

(b) Boric acid + Borax

(c) Phthalic acid + Potassium acid phthalate

(ii) Base buffer solution is formed by mixing a weak base with its salt with a strong acid,

e.g;

(a) $PNH_4OH + NH_4Cl$

(b) Glycine + Glycine hydrochloride

3. Explain the hydrolysis of salt?

Ans: When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis.** It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.**

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.

$M^+ + H_2O \leftrightarrow MOH + H^+$

Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.

$A^- + H_2O \leftrightarrow HA + OH^-$

Weak acid

4. What is solubility product of a salt?

Ans: The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:

$A_xB_y \leftrightarrow xA^{y+} + yB^{x-}$

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

Let 's' mole per litre be the **solubility** of the salt, then

$AxBy \leftrightarrow xA^{y+} + yB^{x-}$

xs ys

So $K_s = [xs]x[ys]y$

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

SHORT ANSWER QUESTIONS

1. What is a common ion efffect? Illustrate?

Ans: COMMON ION EFFECT:

Let AB to the weak electrolyte. Considering its dissociation,

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

and applying law of mass action we have

$K = [A^+][B^-]/[AB]$

The equilibrium constant, K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increases the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increases, i.e., the equilibrium will shift to the left hand side.

In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or NaOH to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH^-_4 or OH^-.

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

2. **Give any two applications of solubility product?**

<u>Applications of solubility product</u>

(i) Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

$$NaCl \leftrightarrow Na^+ + Cl^-$$

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

The concentration of Cl^- ions increases considerably in solution due to ionization HCl. Hence, the ionic product $[Na^+][Cl^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

C_nH_{2n+1} COONa ↔ C_nH_{2n+1} COO^- + Na^+

Soap

NaCl ↔ Na^+ + Cl^-

Thus, the concentration of Na+ ions increases considerably on addition of NaCl solution. Hence, the ionic product [$C_nH_{2n+1}COO^-$] [Na^+] exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda):

In Solvay's soda process. CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.

$NH_4OH + CO_2 \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl, NH_3HCO_3 and NaCl.

Thus, baking soda ($NaHCO_3$) can be quantifiably estimated.

LONG ANSWER QUESTIONS

1. **Explain the concept of Common ion effect?**

OMMON ION EFFECT:

Let AB to the weak electrolyte. Considering its dissociation,

AB ↔ A^+ + B^-

and applying law of mass action we have

K = [A^+][B^-]/[AB]

The equilibrium constant, K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increases the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increases, i.e., the equilibrium will shift to the left hand side.

In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or NaOH to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH^-_4 or OH^-.

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

2. **Explain the conscept of Hydrolysis of salt?**

Ans: <u>Salt Hydrolysis:</u>

Pure water is a weak electrolyte and neutral in nature, i.e., H^+ ion concentration is exactly equal to OH" ion concentration

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

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis.** It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.**

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.

$$M^+ + H_2O \leftrightarrow MOH + H^+$$

Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.

$$A^- + H_2O \leftrightarrow HA + OH^-$$

Weak acid

The process of **salt hydrolysis** is actually the reverse of neutralization.

Salt + Water ↔ Acid + Base

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.

Examples: $FeCl_3$, $CuCl_2$, $AlCl_3$, NH_4Cl, $CuSO_4$, etc.

(ii) Salt of a strong base and a weak acid.

Examples: CH_3COONa, NaCN, $NaHCO_3$, Na_2CO_3, etc.

(iii) Salt of a weak acid and a weak base.

Examples: CH_3COONH_4, $(NH_4)_2CO_3$, NH_4HCO_3, etc.

(iv) Salt of a strong acid and a strong base.

Examples: NaCl, K_2SO_4, $NaNO_3$, NaBr, etc.

3. Explain the hydrolysis of salt of strong acid and weak base?

Ans:

<u>Salt of a strong acid and a weak base:</u>

The solution of such a salt is acidic in nature. The cation of the salt which has come from **weak base** is reactive. It reacts with water to form a **weak base** and H^+ ions.

$B^+ + H_2O \leftrightarrow BOH + H^+$

Weak base

Consider, for example, NH_4Cl. It ionises in water completely into NH_4 and CF ions. ions react with water to form a **weak base** (NH_4OH) and H^+ ions.

$NH^+_4 + H_2O \leftrightarrow NH_4OH + H^+$

C(1-x) Cx Cx

Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$K_h = [H^x][NH_4OH]/[NH_4^+] = (Cx.Cx)/C(1-x) = (x^2 C)/((1-x))$ ..... (i)

where C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are

$NH_4OH \leftrightarrow NH^+_4 + OH^-$, $K_b = [NH^+_4][OH^-]/[NH_4Oh]$ .... (ii)

$H_2O \leftrightarrow H^+ + OH^-$, $K_b = [H^+][H^-]$ ..... (iii)

From eqs. (II) and (iii)

$K_w/K_b = [H^+][NH^4 OH]/[NH_4^+] = K_h$ .... (iv)

$[H^+] = [H^+][NH_4^+]/[NH_4OH] = K_w/K_b \times [NH_4^+]/[NH_4 OH]$

$\log [H^+] = \log K_w - \log K_b + \log[salt]/[base]$

$-pH = -pK_w + pK_b + \log[salt]/[base]$

$pK_w - pH = pK_b + \log[salt]/[base]$

$pOH = pK_b + \log[salt]/[base]$

Relation between Hydrolysis constant and Degree of hydrolysis

The extent to which **hydrolysis** proceeds is expressed as the degree of **hydrolysis** and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as *h* or *x*.

h = (Amount of salt hydrolysed)/(Total salt taken)

Considering again eq. (i),

$K_h = x^2C/(1-x)$ or $K_h = h^2C/(1-h)$

When h is very small $(1-h) \rightarrow 1$,

$H_2 = K_h \times 1/c$

or $h = \sqrt{(K_h/C)}$

$= \sqrt{(K_w/K_b * C)}$

$[H^+] = h \times C = \sqrt{(C*K_h)}/K_b$

$\log [H^+] = 1/2 \log K_w + \mathbf{1}\ 1/2\log C - 1/2\log K_b$

$pH = 1/2pK_w - 1/2 \log C - 1/2\ pK_b$

$= 7 - 1/2\ pK_b - 1/2\log C$

4. **Explain the concept of hydrolysis of salt of weak acid and srong base?**

Salt of a weak acid and a Strong base:

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a **weak acid** and OH^- ions.

$A^- + H_2O; \leftrightarrow HA + OH^-$

Weak acid

Consider, for example, the salt CH_3COONa. It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a **weak acid**, CH_3COOH and OH^- ions.

$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

$C(1-x) \qquad Cx \qquad Cx$

Thus, OH^- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$K_h = [CH_3COOH][OH^-]/[CH_3CO^-] = (Cx \times Cx)/C(1-x) = (Cx^2)/(1-x)$) ..... (i)

Other equations present in the solution are:

$CH_3COOH \leftrightarrow CH_3COO^- + H^+, \qquad K_a = [CH_3COO^-][H^+]/[CH_3COOH]$ ..... (ii)

$H_2O \leftrightarrow H^+ + OH^-, \qquad K_w = [H^+][OH^-]$ ..... (iii)

From eqs. (ii) and (iii),

$\log [OH^-] = \log K_w - \log K_a + \log[salt]/[acid]$

$-pOH = -pK_w + pK_a + \log[salt]/[acid]$

$pK_w - pOH = pK_a + \log[salt]/[acid]$

$pH = pK_a + \log[salt]/[acid]$

Considering eq. (i) again,

$K_h = cx^2/(1-x)$ or $K_h = Ch^2/(1-h)$

When h is very small, $(1-h) \rightarrow 1$

or $h^2 = K_h/C$

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

$[OH^-] = h \times C = \sqrt{(CK_h)} = \sqrt{(C*K_w/K_a)}$

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

$= K_w/\sqrt{(C*K_w/K_a)} = \sqrt{(K_a*K_w)}/K_c$

$-\log [H^+] = -1/2\log K_w - 1/2\log K_a + 1/2\log C$

$pH = 1/2pK_w + 1/2pK_a + 1/2\log C$

$= 7 + 1/2pK_a + 1/2\log C.$

5. **Explain the concept of hydrolysis of salt of weak acid and weak base?**

Salt of a weak acid and a weak base:

neutral but it can be either slightly acidic or slightly alkaline if both the reactions take reactive and react with water to produce H^+ and OFT ions. The solution is generally

Maximum **hydrolysis** occurs in the case of such a salt as both the cation and anion are place with slightly different rates. Consider, for example, the salt CH_3COONH_4. It gives CH_3COO^- and ions in solution. Both react with water.

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

Weak base

or $CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + OH^-$

Weak acid

Both the reactions occur with same speeds. The solution is neutral

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

C(1-h) C(1-h) Ch Ch

$$Kh = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

Other equilibria which exist in solution are:

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$, $K_a = [CH^3COO^-][H^+]/[CH_3COOH]$ ..... (i)

$NH_4OH \leftrightarrow NH^+_4 + OH^-$, $Kb = [NH^+_4][OH^-]/[NH_4OH]$ ..... (ii)

$H_2O \leftrightarrow H^+ + OH^-$, $K_w = [H^+][OH^-]$ ..... (iii)

From Eqs. (i), (ii) and (iii),

$K_h = Kw/K_a.K_b = [CH_3COOH][NH_4OH]/[CH_3COO^-][NH^+_4]$ .... (iv)

Let C be the concentration and h be the degree of **hydrolysis**

$K_h = h^2/(1-h)^2$

When h is small, (1-h) → 1.

$K_h = h^2$

$h = \sqrt{Kh} = \sqrt{K_w/K_a * K_b}$

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

$= K_a \times \sqrt{K_w/K_a * K_b}$

$= \sqrt{K_w * K_a/K_b}$

$-\log [H^+] = -1/2\log K_a - 1/2\log K_w + 1/2\log K_b$

$pH = 1/2pK_a + 1/2pK_w - 1/2pK_b$

$= 7 + 1/2pK_a - 1/2pK_b$

When $pK_a = pK_b$, pH = 7, i.e., solution will be neutral in nature.

When $pK_a > pK_b$. The solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case $pK_a < pK_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7

6. **Explain the concept of buffer solutions and its preparation?**

<u>BUFFER SOLUTIONS:</u>

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is

observed that solutions and even pure water (pH = 7) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

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 the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

General characteristics of a buffer solution

(i) It has a definite pH, i.e., it has reserve acidity or alkalinity.

(ii) Its pH does not change on standing for long.

(iii) Its pH does not change on dilution.

(iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

(i) by mixing a weak acid with its salt with a strong base,

eg;

(a) $CH_3COOH + CH_3COONa$

(b) Boric acid + Borax

(c) Phthalic acid + Potassium acid phthalate

(ii) by mixing a weak base with its salt with a strong acid,

e.g;

(a) $PNH_4OH + NH_4Cl$

(b) Glycine + Glycine hydrochloride

(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, e.g., $Na_2HPO_4 + Na_3PO_4$, or a salt of weak acid and a weak base, such as CH_3COONH_4.

The first and second type is also called acidic and basic buffers respectively.

Explanation of buffer action

(i) Acidic buffer:

Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH_3COOH molecules, CH_3COO^- ions, Na^+ ions, H^+ ions and OH^- ions. Thus, we have the following equilibria in solution:

$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$ (Feebly ionised)

$CH_3COONa \leftrightarrow Na^+ + CH_3COC^-$ (Completely ionised)

$H_2O \leftrightarrow H^+ + OH^-$ (Very feebly ionised)

When a drop of strong acid, say HCl, is added, the H^+ ions furnished by HCl combine with CH_3COO^- ions to form feebly ionised CH_3COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H^+ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.

$$CH_3COOH + OH^- \leftrightarrow CH_3COO^- + H_2O$$

Thus, OH^- ions furnished by a base are removed and pH of the solution is practically unaltered.

(ii) Basic buffer:

Consider the case of the solution containing NH_4OH and its salt NH_4Cl. The solution will have NH_4OH molecule, ions, Cl^- ions, OH^- ions and H^+ ions

$NH_4OH \leftrightarrow NH^+_4 + OH^-$ (Feebly ionized)

$NH_4Cl \leftrightarrow NH_4 + Cl^-$ (Completely ionized)

$H_2O \leftrightarrow H^+ + OH^-$ (Very feebly ionized)

When a drop of NaOH is added, the added OH^- ion combine with NH_4 ions to form feebly ionised NH_4OH whose ionisation is further suppressed due to common ion effect. Thus pH is not disturbed considerably.

$NH_4 + OH^- \; NH_4OH$

(From strong base)

When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.

$NH_4OH + H^+ \leftrightarrow NH^+_4 + H_2O$

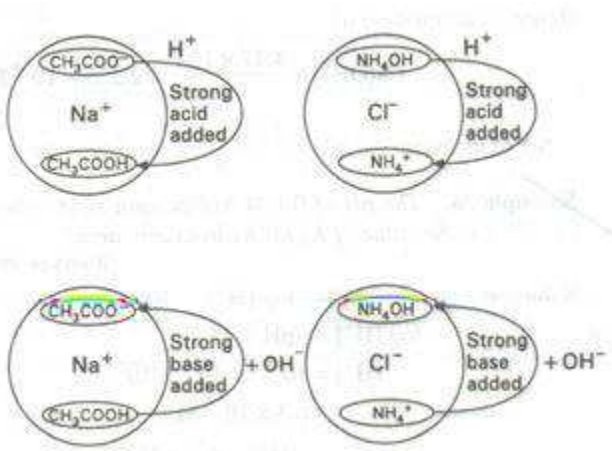
(From strong acid)

Thus pH of the buffer is practically unaffected.

Diagrammatic Representation of Buffer Action

Acid Buffer ($CH_3COOH + CH_3COONa$)

Base Buffer ($NH_4OH + NH_4Cl$)



7. Explain the Henderson's equation of P^H of buffer?

Ans:

<u>Henderson's Equation (pH of a buffer):</u>

(i) Acidic buffer:

It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation

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

Applying law of mass action,

$K_a = H^+A^-/[HA]$

It can be assumed that concentration of A^- ions from complete ionisation of the salt ***BA*** is too large to be compared with concentration of A^- ions from the acid HA.

$BA \leftrightarrow B^+ + A^-$

Thus, ***[HA]*** = Initial concentration of the acid as it is feebly ionised in presence of common ion

and ***$[A^-]$*** = Initial concentration of the salt as it is completely ionised.

So $[H^+] = Ka . [Acid]/[Salt]$ ..... (iii)

Taking logarithm and reversing sign,

$-\log [H^+] = -\log K_a - \log[Acid]/[Salt]$

or $pH = \log[Salt]/[Acid] - \log K_a$

or $pH = pK_a + \log[Salt]/[Acid]$ ..... (iv)

This is known as Henderson's equation.

When [Salt]/[Acid] = 10 , then

$pH = 1 + pK_a$

and when [Salt]/[Acid] , then

$pH = pK_a - 1$

So weak acid may be used for preparing buffer solutions having pH values lying within the ranges $pK_a + 1$ and $pK_a - 1$. The acetic acid gas a pK_a of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the ranges 3.8 to 5.8.

(ii) Basic offer:

It consists of a weak base and its salt with strong acid. Ionization of a weak base, BOH, can be represented by the equation.

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

Applying law of mass action,

$K_b = [B^+][OH^-]/[BOH]$ ..... (i)

or $[OH^-] = K_b [BOH]/[B^+]$ ..... (ii)

As the salt is completely ionized, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.

$BA \leftrightarrow B^+ + A^-$ (Completely ionised)

So $[OH^-] = K_b[Base]/[Salt]$ .... (iii)

or pOH = log[Salt]/[Base] log K_b

or pOH = pKb + log[Salt]/[Base] ..... (iv)

Knowing pOH, pH can be calculated by the application of the formula.

pH + pOH = 14

NUMERICALS

The value of Kp, if the value of Kc is $2x10^{-3}$ for H_2 (g) +I_2 (g) ↔ 2HI (g) at 27^0c

Sol: Kp = Kc $[RT]^{\Delta n}$

H_2 + I_2 ↔ 2HI

(g) (g) (g)

Δn = [(no. of moles of gaseous products) – (no .of moles of gaseous reactants)]

= [2 – (1+1)]

= 2 - 2

Δn = 0

If Δn = 0 then, Kp = Kc

Given Kc = $2x\ 10^{-3}$

∴ Kp = $2\ x\ 10^{-3}$

4. **How many grams of NaOH are present per litre if the pH of NaOH solution is 10** ?

Sol: $\therefore$ The Ph Value of NaOH is = 10

$\therefore$ pOH = 14 – 10 = 4 (pH +,pOH = 14)

$\therefore$ $[OH] = 10^{-4}$ N

$\therefore$ Normality (N) = 10^{-4} N

$\therefore$ Weight of NaOH = Normality x eq. wt

$= 10^{-4} \times 40$

$= 4 \times 10^{-3}$ grams

5. **What is the P^H of 0.1 M NaOH ?**

Sol: Molarity of NaOH = $0.1 = 10^{-1}$

Since $NaOH \rightarrow Na^+ + OH^-$

$\therefore$ $[OH] = 10^{-1}$

$p^{OH} = -\log [10^{-1}] = 1$

$p^{OH} = 1$

$p^H = 14 - p^{OH}$

$= 14 - 1$

$= 13$

6. Find the pH of 0.05 M Ba $(OH)_2$ aqueous solution?

Sol: Since $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

$\therefore$ $[OH^-] = 2[Ba(OH)_2]$

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

$[OH^-] = 10 \times 10^{-2} = 10^{-1}$

$p^{OH} = - \log [OH^-]$

$= - \log [10^{-1}]$

$pOH = 1$

$p^{OH} = 14 - p^{OH}$

$= 14 - 1$

$p^H = 13$

7. Find the p^H of10^{-8} M HCL solution?

Sol: The given acid solution is very dilute. Hence the H^+ obtained from the acid and water must be taken into consideration.

H^+ Ion concentration of acid is 10^{-8} M

H^+ Ion concentration of water is 10^{-7} M

Total $[H^+] = 10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$ or 1.1×10^{-7} M

$\therefore p^H = - \log 1.1 \times 10^{-7}$

$= 7 - \log 1.1 = 7 - 0.0414 = 6.995$

8. 0.1825% HCL solution would have a p^{Hn} of ----------?

Sol: 0.1825% HCL solution means 100 ml solution contain 0.1825 g. of HCL

$$\text{Normality (N)} = \frac{W}{EW} \times \frac{1000}{V} \times \frac{0.1825}{36.5} \times \frac{1000}{100} \quad 0.05N$$

$\therefore [H^+] = 0.05N$

$\therefore p^H = -\log [H^+] = -\log [0.05] = -\log [5 \times 10^{-2}] = 2 - \log 5 = 2 - 0.692$

$\therefore p^H = 1.308$

9. **The p^H of solution is 5.4 . What is the hydrogen ion concentration?**

Sol: $p^H = -\log [H^+]$

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

$= 10^{-5.4}$

$= 10^{-6 + 0.6}$

$=$ Antilog (0.6) $\times 10^{-6}$

$= 3.981 \times 10^{-6}$ moles/litre

10. **50 ml of 0.2 NH_2SO_4 were added to 100 ml of 0.2 N HNO_3. Then the solution is diluted to 300 ml. What is the p^p of the solution?**

Sol: $N = [H^+] = \dfrac{(50 \times 0.2) + (100 \times 0.2)}{300}$

$= \dfrac{10 + 20}{300}$

$= \dfrac{30}{300} = 0.1$ N

$[H^+] = 0.1$ N $= 10^{-1}$N

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

$= -\log [10^{-1}]$

$= 1$

$\therefore p^H = 1$

11 At a certain temperature, the ionic product of H_2O is 9.55 x10^{-14} moles^2/lit^2. Then what is the of the p^H solution?

Sol: Since $K_w = [H^+]\ [OH^-]$

$K_w = 9.55 \times 10^{-14}$ moles^2/lit^2

$[H^+]\ [OH^-] = 9.55 \times 10^{-14}$ moles^2/lit^2

$\therefore [H^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7}$ moles^2/lit^2

$p^H = -\log [H^+] = -\log [3.09 \times 10^{-7}]$

$= -[\log 3.09 + \log 10^{-7}]$

$= -[0.49 - 7]$

$p^H = 7 - 0.49 = 6.51$

12. The K_a for a 0.2M CH3 COOH is 2 x 10^{-5} what is its p^H? (Assume CH_3 COOH as a strong acid)

Sol: Given that CH_3 COOH is strong acid. So, complete ionisation takes place.

$CH_3 COOH \rightarrow CH_3 COO^- + [H^+]$

0.2M 0.2M

$[H^+] = 0.2\ M = 2 \times 10^{-1}\ M$

$p^H = -\log [H^+] = -[2 \times 10^{-1}] = 1 - \log 2 = 1 - 0.3010 = 0.6990$

13. Find the p^H of 0.5 M NH_4OH solution. K_b for NH_4OH is 2 x 10^{-5}(If NH_4OH is assumed as a strong base.)?

Sol: Given that NH_4OH is strong base. So, complete ionisation takes place.

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

0.5 M 0.5 M

$[OH^-] = 0.5\ M = 5 \times 10^{-1}\ M$

$pOH = -\log [OH^-] = -\log [5 \times 10^{-1}] = 1 - \log 5 = 1 - 0.6989 = 0.3011$

$p^H = 14 - pOH = 14 - 0.311 = 13.69$

14. What is the pH of HCl solution containing 3.65g in 250 ml?

Sol: Molarity of HCl $= \dfrac{\text{Weight of HCl}}{\text{Molecular weight}} \times \dfrac{1000}{250}$

$= \dfrac{3.65}{36.5} \times \dfrac{1000}{250} = 0.4\ M$

Since HCl is strong acid $[H^+] = 0.4\ M$

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

$= -\log [0.4]$

$= -\log [4 \times 10^{-1}]$

$= 1 - \log 4$

$= 1 - 0.6020$

$= 0.398\ (\approx 0.4)$

15. A litre of buffer solution contains 0.1 mole of acetic and 1 mole of sodium acetate. Find its p^H if pK_a at CH_3COOH = 4.8. ?

Sol: For an acid buffer $pH = pK_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

$$p^H = 48 + \log \frac{1}{0.1}$$

$$= 48 + \log 10$$

$$p^H = 48 + 1$$

$$\Rightarrow p^H = 5.8$$

16. 20ml of 0.2 M CH_3 COOH and 20 ml of 0.4M sodium acetate were mixed together to form a buffer. What is the p^H? (CH_3 COOH has pK_a of 4.8)

Sol: For an acid buffer $pH = pK_a + \log \frac{[salt]}{[acid]}$

$$p^H = pK_a + \log \frac{\frac{20 \times 0.4}{30}}{\frac{20 \times 0.2}{30}}$$

$$\Rightarrow p^H = 4.8 + \log 2$$

$$= 4.8 + 0.3010$$

$$= 5.1$$

17. Find the hydrolysis constant at 01M sodium acetate K_a of CH_3 COOH =2 x 10^5.

Sol: The hydrolysis constant $K_h = \frac{K_w}{K_a}$

$$\Rightarrow K_h = \frac{1 \times 10^{-14}}{}$$

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

$$\Rightarrow K_h = 0.5 \times 10^{-9}$$

$$\Rightarrow K_h = 5 \times 10^{-10}$$

18. What is the p^H of a buffer formed by mixing 20 ml of 0.1 M NH_4Cl and 2 ml of 0.1 M NH_3 ? pK_b for NH_4OH = 4.8.

Sol: For a basic buffer $pH = pK_w \{pK_b + \log \frac{[salt]}{[acid]}\}$

$$pH = 14 - 4.8 - \log \frac{\frac{20 \times 0.1}{22}}{\frac{2 \times 0.1}{22}}$$

$$= 14 - 4.8 - \log \frac{0.090}{0.0090}$$

$$= 9.2 - \log 10$$

$$= 9.2 - 1$$

$$= 8.2$$

19. The hydrolysis constant for NH4Cl solution is 0.5 x 10^{-9} . Then what is the dissociation constant of the base ?

Sol: The hydrolysis constant $K_h = \frac{K_w}{K_a}$

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

$$= \frac{1 \times 10^{-14}}{0.5 \times 10^{-9}}$$

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

Dissociation constant of NH4OH is 2×10^{-5}

20. The dissociation constants of NH4OH and CH_3 COOH are 2 x and 1.8 x respectively. Find the hydrolysis constant of ammoium acetate?

Sol: Since ammonium acetate is a salt of weak acid and weak base $K_h = \frac{K_w}{K_a K_b}$

$$K_h = \frac{1 \times 10^{-14}}{2 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

$$= \frac{1 \times 10^{-14}}{2 \times 1.8 \times 10^{-10}}$$

$$= 0.277 \times 10^{-4}$$

$$K_h = 2.77 \times 10^{-5}$$

21. 50 Ml of 1 M CH_3 COOH solution, when added to 50 ml of 0.5 M NaOH gives a solution with pH value 'X'. Find the value of 'X' (pK_a of CH_3 COOH = 4.8)

Sol: Acetic acid reacts with sodium hydroxide to form sodium acetate.

$$CH_3 COOH + NaOH \rightarrow CH_3 COONa + H_2O$$

No.of millimoles of CH_3 COOH = 50 x 1 = 50

No.of millimoles of NaOH = 50 x 0.5 = 25

No.of millimoles of CH_3 COOH remained unreacted = 50– 25 = 25

Total Vol. of solution = 50 + 50 = 100ml

No.of millimoles of CH_3 COONa formed = 25

$$\therefore \text{ Molarity of } CH_3COONa = \frac{25}{100} = .25M$$

$$\text{Molarity of } CH_3\,COOH = \frac{25}{100} = .25M$$

$$pH = pK_a + \log \frac{[salt]}{[\text{ acid }]}$$

$$= 4.8 + \log \frac{.25}{.25} = 4.8 + \log (1)$$

$\therefore$ pH of solution = 4.8 + 0 = 4.8

22. What is the pH of solution formed by mixing 50ml 1 M HCl and 50ml 0.1M NaOH?

Sol: $N_a V_a = 50 \text{ x } 1 = 50$

$N_b V_b = 50 \text{ x } 0.1 = 5$

$\therefore \quad N_a V_a > N_b V_b$

$$[H^+] = \frac{N_a V_a - N_b V_b}{V_a + V_b} = \frac{50 - 5}{100} = \frac{45}{100}$$

$$[H^+] = 4.5 \times 10^{-1}$$

$$pH = -\log [H^+] = -\log [4.5 \times 10^{-1}]$$

$$= 1 - \log 4.5]$$

$$= 0.35$$

23. 0.005 M monobasic acid has a pH of 5. What is the degree of dissociation?

Sol: pH = 5

$\therefore [H^+] = 10^{-5}$

Concentraion (C) = 0.005 M = 5×10^{-3} M

$$[H^+] = C\alpha$$

α = degree of dissociation per mole = ?

$$\therefore \alpha = \frac{[H^+]}{C} = \frac{[H^+]}{5 \times 10^{-3}} = \frac{10^{-5}}{5 \times 10^{-3}} = \frac{1}{5} \times 10^{-2} = 0.2 \times 10^{-2}$$

Percentage of degree of dissociation = $0.02 \times 10^{-2} \times 100 = 0.2\ \%$