(Ionic Equilibrium)

— Electrolyte — An electrolyte is defined as a compound whose aqueous solution or melt conduct electricity. on the other hand, a compound whose aqueous solution or melt does not conduct electricity is called a non-electrolyte.

— Degree of ionization — The fraction of the total no. of molecules which dissociate into ions is called degree of dissociation or degree of ionization. and it is represented by α.

$$\alpha = \frac{\text{No. of mole dissociated}}{\text{Total no of mole taken.}}$$

— Strong electrolyte — It is defined as a substance which dissociate almost completely into ions in aqueous solution and hence is a very good conductor of electricity.
exam — NaOH, KOH, HCl, H_2SO_4, NaCl, KNO_3 etc.

— Weak electrolyte — It is defined as a substance which dissociates in to a small extent in aqueous solution and hence conduct electricity also to a small extent
ex. NH_4OH, CH_3COOH etc.

— Difference between dissociation and ionization — when an ionic compound dissolved in water, the ions which are already present in the solid compound seperate out. The process is called dissociation. On the other hand when a neutral molecule like a polar covalent compound which does not contain ion but when dissolved in water splits to produce ions in the solution, the process is called ionization.

Q. How dissociation occurs.

Ans. An ionic compound is a cluster of positively and negatively charged ions held together by electrostatic forces of attraction. When such ionic compound is put into water, the high dielectric constant of water reduces the electrostatic forces of attraction, thus ions become free to move in the solution. In case of weak electrolytes, the extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of the ions produce.

— Ionisation of weak electrolytes – Ostwald's Dilution Law.

When a weak electrolyte (Acetic acid) is dissolved in water, it dissociates partly into H^+ or H_3O^+ and CH_3COO^- ions and the equilibrium obtained.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

By the law of chemical equilibrium.

$$K = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

In dilute solution, $[H_2O]$ is constant and the product of K and $[H_2O]$ is denoted as K_a, the ionization constant or dissociation constant of the acid.

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \quad -①.$$

If 'c' is the initial concentration of the acid and α is the degree of dissociation then.

	$CH_3COOH + H_2O \rightleftharpoons$	CH_3COO^-	$+ H_3O^+$
Initial Conc.	c	0	0
Conc. at equ.	$c(1-\alpha)$	$c\alpha$	$c\alpha$.

$$\text{then } K_a = \frac{[c\alpha] \times [c\alpha]}{[c(1-\alpha)]} = \frac{c\alpha^2}{1-\alpha} \quad -②.$$

In case of weak electrolyte the value of α is very small.

and can be neglected in comparison to 1

then $K_a = c\alpha^2$

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{K_a V} \qquad \because c = \frac{1}{V}$$

Similarly, for a weak base

$$\alpha = \sqrt{\frac{K_b}{c}} = \sqrt{K_b V}$$

For a weak electrolyte, the degree of ionisation is inversely proportional to the square root of molar concentration or directly proportional to the square root of volume containing one mole of solute. This is called ostwald's dilution law.

– Various concepts of Acids and Bases.

a Classical concept of Acids and Bases.

Acid was defined as a substance whose aqueous solution have characteristics.

1. Conducts electricity.
2. reacts with active metals like zinc, magnesium etc. to give hydrogen.
3. Turns blue litmus red.
4. Has a sour taste.
5. whose acidic properties disapper on reaction with a base.

– Base was defined as a substance whose aqueous solution have characteristics.

1. Conducts electricity.
2. Turns Red litmus blue.
3. Has a bitter taste.
4. Has a soapy (slippery) touch.
5. whose basic properties are destroyed on reaction with acid.

The above definition of acids and bases are called operational definition.

b Arrhenius Concept of Acids and Bases:

- An acid is defined as a substance which contain hydrogen and which when dissolved into water gives hydrogen (H^+) ions.
- A base is defined as a substance which contains hydroxyl groups and which when dissolved into water gives (OH^-) ions.
- Arrhenius described neutralization as the process in which hydrogen ions and hydroxide ions combine to form unionized molecules of water.

limitation.

1. Nature of H^+ and OH^- ions - these ions cannot exist as such in aqueous solution but exist as hydrated ions.
2. Inability to explain acidic and basic character of certain substance.
3. Inability to explain the reaction between an acid and base in absence of water.

c. Bronsted - Lowery Concept of Acid and Base.

- An acid is defined as a substance which has the tendency to give a Proton (H^+) and a base is defined as a substance which has a tendency to accept a Proton. In other words an acid is a Proton donor whereas a base is a Proton acceptor.

Water acts both acid as well as a base and hence is called Amphoteric or Amphiprotic.

A conjugate pair of acid and a base differ by a Proton only

$$\text{Conjugate acid} \rightleftharpoons \text{Conjugate Base} + H^+$$

Advantages of Bronsted-Lowry Concept over Arrhenius Concept :-

1. Bronsted-Lowry Concept is not limited to molecules but includes even the ionic species to act as acids or Bases.
2. It can explain the basic character of substance which do not contain OH^- group on the basis that they are Proton acceptors.
3. It can explain the acid-base reactions in the non-aqueous medium or even in the absence of a solvent.

- Limitations.

1. It can not explain the reactions between acidic oxides and the basic oxides which take place even in the absence of the solvent.
2. Substance do not have any hydrogen and hence can not give a Proton but are known to behave as acids.

D. Lewis Concept of Acids and Bases.

An acid is defined as substance (atom, ion, or molecule) which is capable of accepting a pair of electron and a base is defined as a substance which is capable of donating an unshared (lone) pair of electron. In other words, an acid is an electron pair acceptor and a base is an electron donar.

Types of Lewis Bases :-

1. Neutral molecules like NH_3, $R-NH_2$, $R-OH$, H_2O, in which one of the atom has got at least one lone pair of electron.
2. All Negative ions like F^-, Cl^-, Br^-, I^-, OH^-, CN^- etc.

Types of Lewis Acids :-

1. Molecules having a central atom with incomplete octet.
2. Simple Cations. Ag^+, Cu^{+2}, Fe^{+3}.
3. Molecules having Central atoms with empty d-orbitals.

4. Molecules containing a multiple bond between two atoms of different electronegativities

— Strengths of Acids and Bases :- According to Arrhenius Concept Greater the number of H^+ ions Produced in the aqueous solution the Stronger is the acid, similarly greater the number of OH^- ions Produced in the aqueous solution, Stronger the base.

The relative Strength of two weak acids.

$$\frac{\text{Strength of the Acid } HA_1}{\text{Strength of the Acid } HA_2} = \sqrt{\frac{Ka_1}{Ka_2}}$$

where Ka is called the dissociation Constant of acid.

Similarly.

$$\frac{\text{Strength of the Base } (BOH)_1}{\text{Strength of the Base } (BOH)_2} = \sqrt{\frac{Kb_1}{Kb_2}}.$$

where Kb is called the dissociation Constant of base.

A Strong acid has a weak Conjugate base and a weak acid has a strong Conjugate base.

- Factor affecting Strength of hydroacids: The Strength of acids depends upon a number of factors but the main factor on which the dissociation of an acid depends is the Strength and Polarity of the H-A bond.

Weaker the H-A bond, more easily it dissociates to give H^+ ion and hence Stronger the acid, similarly, greater the Polarity of the H-A Bond, , more easily the bond break and hence greater is the acidity.

For element in the same group of Periodic table, the bond Strength dominates over the Polar Nature. Down the group As size of the atom increases, bond Strength decreases and hence acidic Strength increases.

However the Polarity of the H-A bond decided the acidic Strength, with increase in the electronegativity of A the.

Polarity of the bond increases and hence the acidic strength also increases.

— Dissociation Constant and ionic Product of water.

Pure water is Poor Conductor of electricity. this shows that water is a weak electrolyte, it is ionized to a very small extent as.

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

or $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

This ionization is called self ionization of water. then by the chemical equilibrium.

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

where K is called dissociation Constant of water.

$\because [H_2O]$ = Constant.

then $[H_2O]K = K_w = [H^+][OH^-] = [H_3O^+][OH^-]$

Ionic Product of water may be defined as the Product of the molar Concentration of H^+ ions and OH^- ions. As H^+ ions exist as H_3O^+ ions, therefore ionic Product may also be defined as the Product of molar Concentration of H_3O^+ and OH^- ions.

The ionic Product of water (K_w) increases with increase of temperature.

— Relationship between pH and pOH.

$$K_w = [H_3O^+][OH^-]$$

at 25°C $\quad 10^{-14} = [H_3O^+][OH^-]$.

$$\log 10^{-14} = \log[H_3O^+] + \log[OH^-]$$

$$-14 = \log[H_3O^+] + \log[OH^-]$$

$$14 = -\log[H_3O^+] - \log[OH^-]$$

$$14 = p(H) + p(OH)$$

— Relationship between K_a and K_b or pK_a and pK_b :- (between ionization constant of a weak acid that of its conjugate Base)

Consider the weak acid HF. Its conjugate base is F^-.

they dissociate as

$$HF \rightleftharpoons H^+ + F^-$$

$$K_a = \frac{[H^+] \times [F^-]}{[HF]} \quad \text{—①}$$

$$F^- + H_2O \rightleftharpoons OH^- + HF.$$

$$K_b = \frac{[OH^-][HF]}{[F^-]} \quad \text{—②}. \quad \because [H_2O] = 1$$

then by ① and ②.

$$K_a \times K_b = \frac{[H^+][F^-]}{[HF]} \times \frac{[HF][OH^-]}{[F^-]}$$

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

So $K_a \times K_b = K_w$.

$\log K_a + \log K_b = \log K_w$.

$-\log K_a - \log K_b = -\log K_w$.

$pK_a + pK_b = pK_w$.

Accurate measurement of PH of a solution is done with the help of an instrument called PH-meter. Approximate PH can be determined with the help of PH paper, which show different colours when dipped in solution of different PH.

— Salt hydrolysis — It is defined as the process in which a salt reacts with water to give back the acid and the base.

Salt hydrolysis may be considered as reverse of neutralization. All salts are strong electrolytes and thus ionize completely in the aqueous solution.

If the acid produced is strong and the base produced is weak, then the cation reacts with water to give an acidic solution.

This is called Cationic hydrolysis.

If the acid produced is weak and the base produced is strong then the anion reacts with water to give the basic solution. This is called anionic hydrolysis.

So, salt hydrolysis may be defined as the reaction of the cation or the anion of the salt with water to produce acidic or basic solution.

a Salts of strong acids and strong bases.

NaCl, $NaNO_3$, Na_2SO_4, KCl, KNO_3, K_2SO_4 etc.

The salt of strong acid and strong base do not undergo hydro- - lysis and the resulting solution is neutral.

b. Salts of weak acids and strong bases:-

CH_3COONa, Na_2CO_3, K_2CO_3, Na_3PO_4 etc.

The solution of such salts are alkaline in nature.

c. Salts of strong acids and weak bases:

NH_4Cl, $CuSO_4$, NH_4NO_3, $AlCl_3$, $CaCl_2$ etc.

The solution of such salts are acidic in nature.

d. Salts of weak acids and weak bases:

CH_3COONH_4, $(NH_4)_2CO_3$, $AlPO_4$ etc.

The solution of such salts are almost neutral.

— Hydrolysis Constant: The general equation of the hydrolysis of a salt (BA) may be written as.

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

then $$K = \frac{[HA][BOH]}{[BA][H_2O]}.$$

$$K[H_2O] = K_h = \frac{[HA][BOH]}{[BA]}.$$

where K_h is called the hydrolysis constant.

— Degree of hydrolysis: The degree of hydrolysis of a salt is defined as the fraction of the total salt which is hydrolysed.

$$h = \frac{\text{No. of moles of the salt hydrolysed}}{\text{Total no. of moles of the salt taken.}}$$

— Calculation of Hydrolysis Constant, Degree of hydrolysis and PH of salt solution.

1. Salt of weak acid and strong base.

a. Hydrolysis Constant.

$$BA + H_2O \rightleftharpoons \underset{\text{Strog.}}{BOH} + \underset{\text{weak}}{HA}$$

$$\downarrow \qquad\qquad \downarrow$$

$$B^+ + A^- + H_2O \rightleftharpoons B^+ + OH^- + HA.$$

$$A^- + H_2O \rightleftharpoons OH^- + HA.$$

It is a case of anion hydrolysis.

$$K_h = \frac{[OH^-][HA]}{[A^-]} \qquad -①$$

For the weak acid HA, the dissociation equilibrium is.

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

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad -②.$$

The ionic Product of water. $K_w = [H^+][OH^-]$ —③.

then.

$$\frac{K_a \times K_h}{K_w} = \frac{[H^+][A^-]}{[HA]} \times \frac{[OH^-][HA]}{[A^-]} \times \frac{1}{[H^+][OH^-]}$$

$$= 1$$

$$\text{So } K_h = \frac{K_w}{K_a}.$$

b. Degree of hydrolysis:- Let the original Concentration of the salt in the solution is C $\frac{mol}{liter}$ and h is its degree of hydrolysis at this Concentration. then.

	$A^- + H_2O \rightleftharpoons OH^- + HA$		
origional Concen.	C	0	0
molar Conc. at equilibrium.	$C(1-h)$	Ch	Ch

then $K_h = \frac{[OH^-][HA]}{[A^-]} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h}$.

If h is very small as compared to 1 then $1-h \approx 1$

$$K_h = Ch^2.$$

$$\text{or } h = \sqrt{\frac{K_h}{C}} \text{ or } \sqrt{\frac{K_w}{K_a \cdot C}}$$

c. pH —

	$A^- + H_2O \rightleftharpoons OH^- + HA$		
origional Conc.	C	0	0
Conc. at eq.	$C(1-h)$	Ch	Ch

$$[OH^-] = Ch.$$

$$H^+ = \frac{K_w}{[OH^-]} = \frac{K_w}{Ch} = \frac{K_w}{C}\sqrt{\frac{K_a \cdot C}{K_w}}.$$

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

$$\therefore pH = -\log[H^+] = -\log\sqrt{\frac{K_w \cdot K_a}{C}}$$

$$pH = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_c + \frac{1}{2}\log C$$

$$= \frac{1}{2}pK_w + \frac{1}{2}pK_c + \frac{1}{2}\log C$$

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

2. Salt of Strong acid and weak base —

a. Hydrolysis Constant :-

$$\underset{\text{Weak}}{BA} + H_2O \rightleftharpoons \underset{\text{Strog.}}{BOH} + HA$$

$$\downarrow \qquad\qquad \downarrow$$

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

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

It is a case of cation hydrolysis.

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

For the weak base BOH, the dissociation equilibrium-

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

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad -\text{②}.$$

$$K_w = [H^+][OH^-] \quad -\text{③}.$$

By ①, ② and ③.

$$\frac{K_b \times K_h}{K_w} = \frac{[B^+][OH^-]}{[BOH]} \times \frac{[BOH][H^+]}{[B^+]} \times \frac{1}{[H^+][OH^-]}$$

$$= 1$$

then $K_h = \frac{K_w}{K_b}$.

b. Degree of hydrolysis — Suppose the original concentration of the salt in solution is C mol/lit and h is its degree of hydrolysis at this concentration.

	$B^+ + H_2O \rightleftharpoons$	BOH	$+ H^+$
ori. conc.	C	0	0
	C(1-h)	Ch	Ch.

then.

$$K_h = \frac{[BOH][H^+]}{[B^+]} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h}.$$

If h is very small as compared to 1 then $1-h \approx 1$

so

$$K_h = Ch^2 \quad \text{or} \quad h = \sqrt{\frac{K_h}{C}}$$

then $h = \sqrt{\frac{K_w}{K_b \times C}}$.

c. pH. $[H^+] = ch.$

$$= c\sqrt{\frac{k_w}{k_b \times c}} = \sqrt{\frac{k_w \times c}{k_b}}.$$

$$-\log[H^+] = -\frac{1}{2}\log k_w - \frac{1}{2}\log c + \frac{1}{2}\log k_b.$$

$$pH = +7 - \frac{1}{2}\log c - \frac{1}{2}pk_b.$$

3. Salt of weak acid and weak base.

a. Hydrolysis Constant :- weak weak.

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

$$\downarrow.$$

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

It involves both anion hydrolysis as well as cation hydro-lysis

$$k_h = \frac{[BOH][HA]}{[B^+][A^-]} \quad \text{— ①}$$

For weak acid. $HA \rightleftharpoons H^+ + A^-$

$$k_a = \frac{[H^+][A^-]}{[A^-H]} \quad \text{— ②.}$$

For weak base $BOH \rightleftharpoons B^+ + OH^-$

$$k_b = \frac{[B^+][OH^-]}{[BOH]} \quad \text{— ③}$$

$$k_w = [H^+][OH^-] \quad \text{— ④.}$$

By ①, ②, ③ and ④.

$$\frac{k_h \times k_b \times k_a}{k_w} = \frac{[BOH][HA]}{[B^+][A^-]} \times \frac{[H^+][A^-]}{[HA]} \times \frac{[B^+][OH^-]}{[BOH]} \times \frac{1}{[H^+][OH^-]}$$

$$= 1$$

$$\text{so } k_h = \frac{k_w}{k_a \times k_b}.$$

b. Degree of hydrolysis: Let the origional Concentration of Salt in the solution is c mol/liter and h is its degree of hydrolysis.

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

orig. Conc.	c	c	0	0
Con. at eq.	c(1-h)	c(1-h)	ch	ch

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{ch \times ch}{c(1-h) \times c(1-h)} = \frac{h^2}{(1-h)^2} \quad \text{--- (1)}$$

the relationship between K_h and h does not involves c thus the degree of hydrolysis of such a Salt is independent of the Concentration of the solution.

If h is very small as Comparison to 1 then $1-h = 1$

then

$$K_h = h^2 \quad \text{or} \quad h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}}.$$

c. pH — For the weak acid

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

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

$$[H^+] = \frac{K_a.[HA]}{[A^-]} = K_a \frac{\times ch.}{c(1-h)}$$

$$= K_a \frac{h}{1-h}.$$

$$= K_a \sqrt{K_h}. \qquad \left[\because \frac{h}{1-h} = \sqrt{K_h}. \text{ by eq. } (1)\right]$$

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

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

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

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

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

- Solubility Product of an electrolyte at a specific temperature may be defined as the product of the molar concentrations of its ions in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte. In general for any electrolyte A_xB_y

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

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

- Common ion effect – If to an ionic equilibrium

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

a salt containing a common ion (AC or BD) is added, the equilibrium shifts in the backward direction. This is called common ion effect.

- Calculation of solubility of sparingly soluble salt :-
The relationship between solubility (S) in mol/L and solubility product K_{sp} depends upon the nature of the salt.

a. For salt of type AB (AgCl, $BaSO_4$, $PbSO_4$, $AlPO_4$ etc)

$$AB \rightleftharpoons A^+ + B^-$$
$$S \quad\quad S \quad S$$
$$K_{sp} = [A^+] \times [B^-] = S \times S = S^2$$

b. For salt of type AB_2 ($PbCl_2$, CaF_2 etc).

$$AB_2 \rightleftharpoons A^{+2} + 2B^-$$
$$S \quad\quad S \quad 2S$$
$$K_{sp} = [A^+][B^-]^2 = (S) \times (2S)^2 = 4S^3$$

c. For Salt of type AB_3 ($Fe(OH)_3$, $Al(OH)_3$ etc)

$$AB_3 \rightleftharpoons A^{+3} + 3B^-$$
$$S \qquad S \qquad 3S.$$

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

– If the ionic Product, the Product of the Concentration of ions in the solution exceeds the value of the Solubility Product of a sparingly soluble salt, the excess ions will Combine resulting in the formation of precipitate.

– Buffer Solution: It is defined as a solution which resists any change in its PH value even when small amounts of the acid or the base are added to it.

Types of buffer solution.

1. Solution of Single Substance — The solution of the salt of a weak acid and a weak base
2. Acidic buffer — It is the solution of a mixture of a weak acid and a salt of this weak acid with a strong base.
3. Basic buffer — It is the solution of a mixture of a weak base and a salt of this weak base with strong acid.

– Buffer action — The Property of a buffer solution to resist any change in its PH value even when small amounts of the acid or the base are added to it is called buffer action.

– Calculation of PH of a buffer mixture.

a. For Acidic buffer mixture:

If the weak acid is HA and its salt is BA then.

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

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

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$[H_3O^+] = K_a \cdot \frac{[HA]}{[A^-]}$$

$$= K_a \cdot \frac{[HA]}{[BA]} = K_a \frac{[Acid]}{[Salt]}$$

$$pH = -\log[H_3O] = -\log K_a - \log \frac{Acid}{Salt}$$

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

b. For basic buffer mixture:

$$pOH = pK_b + \log \frac{Salt}{Base}$$

— Buffer Capacity or Buffer index:- It is defined as the number of moles of an acid or a base required to be added to one liter of the buffer solution so as to change its pH by one unit.

— Importance of buffer solutions.

1. In biological Processes
2. In industrial Process.
3. In analytical chemistry.
4. In bacteriological research.

— pH of our blood is 7.4 and it remain constant because it is a buffer.