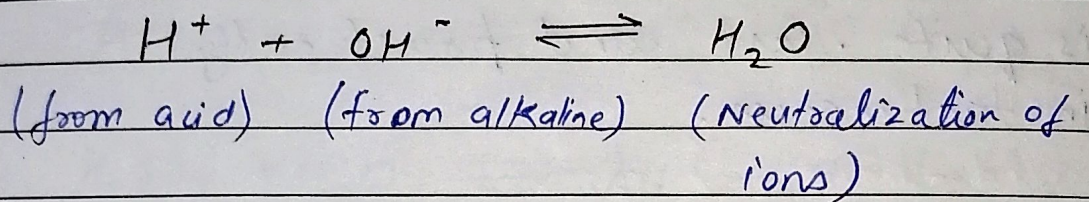


ACID BASE TITRATION:-

Chemical reaction between an acid and a base (alkaline) take place the reaction is based on the principle of neutralization.

Acidimetry :-

A substance acid solⁿ is used for quantitative determination of the base / alkali.

Alkalimetry :-

A standard solⁿ of base is used for quantitative determination of acid.

This acid base titration method is used for various volumetric determinations, which involves neutralization one another way.

eg. - Determination of salt like
- Na_2CO_3
- $\text{Na}_2\text{B}_4\text{O}_7$ etc.

- These salt have strongly alkaline reaction that's why they are titrated with acid solution.

★ Advantages of acid and base titration :-

- (a) The reaction between acid and base is quite fast and practically instantaneous.
- (b) The reaction in acid base titrations will be single without the side reaction.
- (c) The reaction will always reach to completion.
- (d) The reaction will always stoichiometric.

★ Acid - base concepts (Theories)

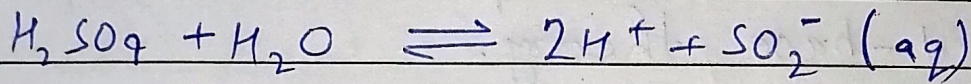
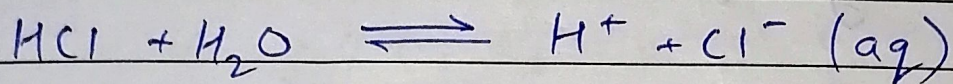
There are four theories proposed to understand the concept of acid-base titrimetric reaction:

① Arrhenius Theory [H^+ and OH^-]

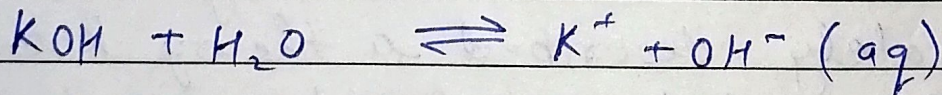
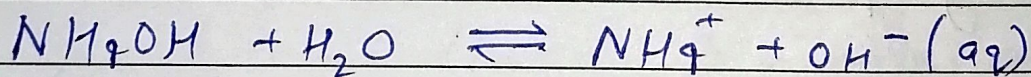
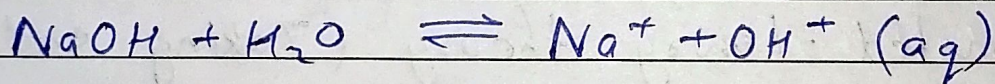
Arrhenius in 1884, first and foremost introduced a radical theory which rightly expatiates an adequate quantitative in an aqueous medium

specifically.

According to Arrhenius acid is any substance that ionizes (partially or completely) in water or aqueous medium to give hydrogen ions $[H^+]$



Base is any substance that ions (partially or completely) in water or aqueous medium to give hydroxyl ion $[OH^-]$.



Advantage :-

The concept explain the behaviour of an acid and base practically.

Limitation :-

- (a) In this concept acid and base is defined in aqueous medium only.
- (b) This concept fails to explain the stability of H^+ ions (s)
- (c) It does not explain the conjugate acid-base theory.
- (d) It does not able to define those acid and base O_2 and SO_2 (aq) which does not contain H^+ (OH^- ion eg. $\rightarrow NH_3$ and Na_2CO_3 (base)).

2. Brønsted-Lowry theory (Taking and giving proton).

In 1923 Brønsted and Lowry separately described a theory known as Brønsted-Lowry concept.

A/c to this theory :-

Acids are those compounds or species which have tendency to donate the proton (H^+) in any type of solvent by any method.

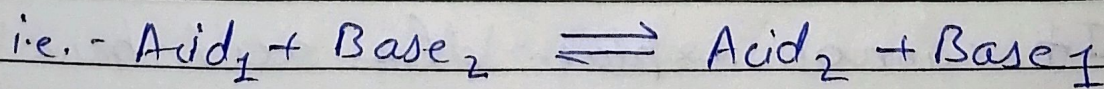
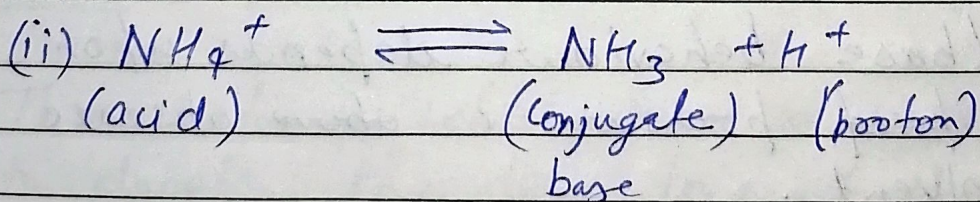
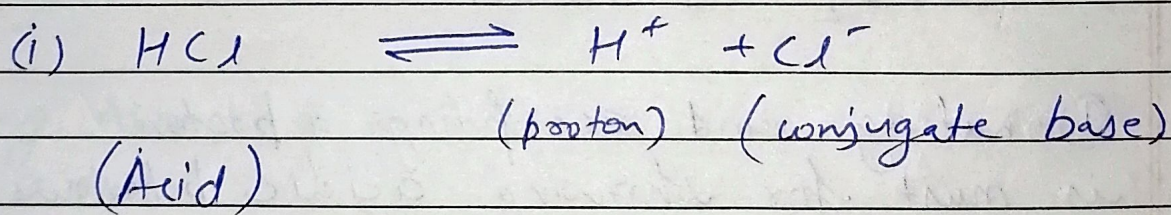
eg. H_2SO_4 , HCl , HClO_4 , CH_3COOH etc.

Bases are those compounds or species, which have tendency to accept the protons (H^+) in any type of solvent by any method.

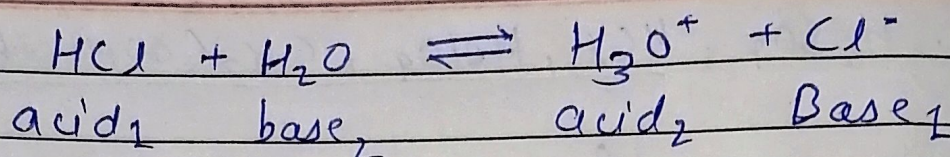
eg :- NaOH , KOH , HSO_4^- etc

Conjugate pairs :-

A pair of substance which can be formed from one another by the gain or loss of proton are called as conjugate base and every base has its conjugate acid.



where, $\text{Base}_1 =$ conjugate base of Acid 1
 $\text{Acid}_2 =$ conjugate acid of base 2



Advantage :-

This concept explain the acid base in any type of solvent.

This concept is able to explain the stability of proton.

Limitation :-

1. Behaviours of SO_2 , SO_3 and CO_2 as acids and behaviour of CaO and BaO_2 as bases.
2. Donating and accepting a proton is must for showing acidic behaviours.
3. Acid / base behaviour depends upon the ~~pref~~ pressure or ~~above~~ absence of solvent.
4. It cannot explain the acid-base reaction taking place in non-protic solvent, like BF_3 and AlCl_3 .

* Lewis theory [Taking and giving electrons] (lone pair of e^-)

- 1923, G.N. Lewis introduced the electronic theory of acid and base.
- In this concept he was defined an acid and base according to the electron proton donor-accept concept.

Acids :-

Those species which have self tendency to accept the lone pair of electrons.

Lewis acids are electrophils.

eg. $AlCl_3$, BCl_3 , $SnCl_2$, CO_2 , SO_2 etc.

Bases :-

Those species which have tendency to donate the lone pair of electron

Lewis bases nucleophils.

eg. $-NH_2$, $C_2H_5NH_2$, H_2O , SO_4^{--} , F^- ,
 Cl^- etc.

concept.

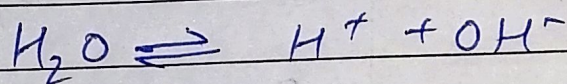
★ Hard and Soft acid Base concept:-

<u>Hard Acid.</u>	<u>Soft Acid.</u>
① High +ve charge	① Low +ve charge
② Relative small size	② Relative large size.
③ Unfilled valance orbitals	③ Filled valance orbitals.
④ eg - H^+ , L^+ , Mg^+ , K^+ etc	④ Cu^{2+} , Ag^+ , Au^+ , Hg^+ , I^- .

<u>Hard Base.</u>	<u>Soft Base.</u>
① High electronegative	① Low electronegative
② easily reduces	② easily oxidized.
③ low polarizability.	③ high polarizability.
④ Stable valance shell.	④ Unstable valance shell.
⑤ eg: - H_2O , OH^- , F^- , PO_4^{3-}	⑤ eg - Br^- , SO_3^-

○ Ionic product of water :-

Kohlrausch and Heydrouiller found in 1894 that the most highly purified water possesses a small and definite conductivity. So water must be highly ionized as per the equation :-



As per the law of mass action, the following equation is obtained at any given temp.

$$\frac{a_{\text{H}^+} \times a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{[\text{H}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]} \times \frac{\gamma_{\text{H}^+} \cdot \gamma_{\text{OH}^-}}{\gamma_{\text{H}_2\text{O}}}$$

Water is only slightly ionized, so the ionic concentration is small and their activity coefficient is unity. The activity of the unionised molecules is also taken as unity.

So the expression is :-

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \text{a constant.}$$

In pure water or in dilute solⁿ, the concentration of the undissociated water is considered constant.

$$\therefore [H^+] \times [OH^-] = K_w$$

K_w = Ionic product of water.

The ionic product of water varies with the temperature. At 25°C, its value is taken as 1×10^{-14} . The value is constant in dilute solⁿ. If the product of $[H^+]$ and $[OH^-]$ in aqueous solution exceeds the value, the excess ions will immediately combine to form water. On the contrary, if the product of two ionic concentrations is less than 10^{-14} more water molecules will dissociate until the equilibrium value is obtained.

★ Henderson - Hasselbalch Equation :-

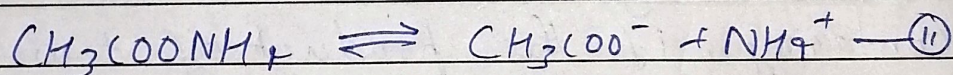
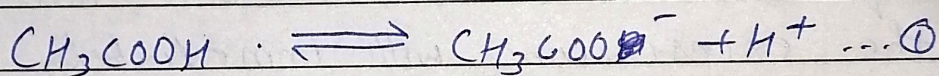
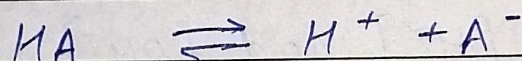
The change in pH upon the addition of an acid or base and the pH of a buffer solution is calculated by buffer equation

The buffer equation is calculated by considering the effect of a salt on the ionization of a weak acid if the salt

and the acid have an ion in common.

Henderson - Hasselbalch equation :-

The pH of an acidic/basic buffer solution can be calculated from the dissociation constant K_a of all acids/bases, concentration of the acid/base and salt used. The dissociation expression of weak acid may be represented as :-



According to law of mass action :-

$$K_a = \frac{[H^+][A^-]}{[HA]} \text{ or } [H^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]}$$

Where, $[CH_3COOH]$ = representing the total concentration of an acid in solution and $[CH_3COO^-]$ = representing the total concentration of acetate ion as most of them are entirely contributed by salt (CH_3COONH_4).

$$H^+ = K_a \frac{(\text{Acid})}{(\text{Salt})}$$

Expressing of negative logarithm on both side.

$$-\log [H^+] = -\log K_a - \log \frac{(\text{Acid})}{(\text{Salt})}$$

But, $-\log [H^+] = \text{pH}$ and

$$-\log K_a = \text{p}K_a$$

$$\text{pH} = \text{p}K_a - \log \frac{(\text{Acid})}{(\text{Salt})}$$

$$\text{pH} = \text{p}K_a + \log \frac{(\text{Salt})}{(\text{Acid})} \quad (\text{inverting the sign})$$

The relationship is called Henderson's Hasselbalch equation for acidic buffer. Similarly, the Henderson's Hasselbalch equation for a basic buffer can be derived as;

$$\text{pH} = \text{p}K_b + \log \frac{(\text{Salt})}{(\text{Base})}$$

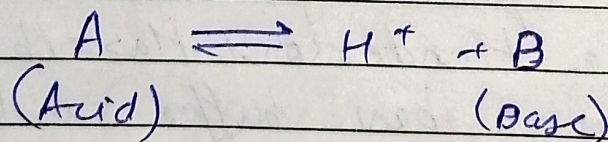
Significance:

1. The pH of the buffer solution can be calculated from the initial concentration of the weak acid and the salt provided K_a is given.
2. It allows calculation of the ~~ratio~~ ratio in which the weak acid and its salt must be mixed in order to get a buffer solution of known pH.

★ Strength of acids and bases:-

An acid is a substance which ionizes to yield hydrogen ions or protons.

Base is a substance which combines with hydrogen ions so, an acid is a proton donor and a base is a proton acceptor.

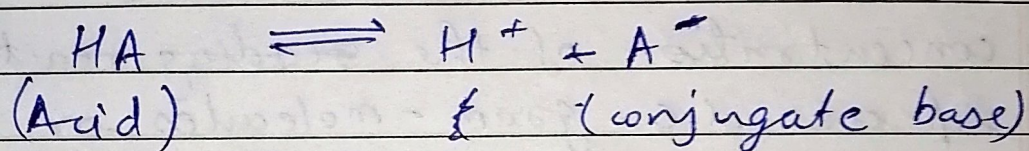


Strength of an acid is related to the concentration of hydrogen ions which it yield upon ionization and will depend upon the value of the degree of dissociation

α at any given concentration.

The acid dissociation constant K_a provides a relationship between α and the concentration. It is a measure of the acid strength.

Similarly, the strength of a base is related to its dissociation constant.



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{and} \quad K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$K_a K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$\therefore K_a K_b = [\text{H}^+][\text{OH}^-]$$

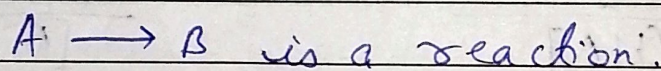
$$\therefore K_a K_b = K_w$$

Stronger acid the weaker its conjugated base.

* Law of mass action :-

This was first ~~coined~~ coined by Guldberg and Waage in 1867. The law is expressed as:-

The rate of a chemical reaction is proportional to the active masses of the reacting substance. In dil. solⁿ, the active mass is the concentration of the reacting species i.e. gram-molecules or gram-ions per litre. The constant of proportionality is the velocity constant. Here,

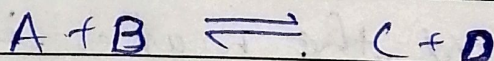


$$\text{Rate of reaction} = k[A]$$

$$[A] = \text{Concentration of A}$$

$$k = \text{Velocity constant}$$

A homogeneous reversible reaction is considered.



Acc to the law of mass action

$$V_f = k_1 [A] \cdot [B]$$

$$V_b = k_2 [C] \cdot [D]$$

V_f = velocity of forward reaction

V_b = velocity of backward reaction.

At equilibrium, $V_f = V_b$

$$k_2 [C] \cdot [D] = k_1 [A] \cdot [B]$$

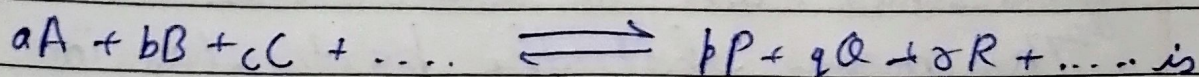
$$\frac{k_1}{k_2} = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

Since k_1 and k_2 are both constant the fraction k_1/k_2 must also be a constant.

$$\therefore k = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

k = Equilibrium constant of the reaction.

The equilibrium constant for the general reversible reaction is.



$$K = \frac{[P]^p \cdot [Q]^q \cdot [R]^r}{[A]^a \cdot [B]^b \cdot [C]^c}$$

Where, a, b, c and p, q, r are the no. of molecules of the reacting species.

Application of the law of mass action to solution of weak electrolytes :-

Strong electrolytes get completely dissociated even in less concentrated solution, so they do not constitute equilibrium system.

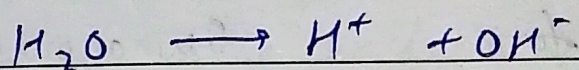
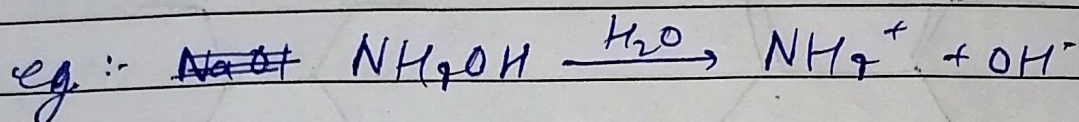
Weak electrolyte are only incompletely dissociated even in favourable ionization condition of dil. solⁿ - so an equilibrium is considered in terms of the law of mass action which occurs b/w undissociated molecules and ions. ∴

★ Common ion effect :-

The concentration of a particular ion in an ionic reaction is increased by the addition of a compound which gives that ion on dissociation.

This means that the particular ion

is thus obtained from the compound present in solution and is also obtained from the added reagent. That is why the name 'common ion' is given,



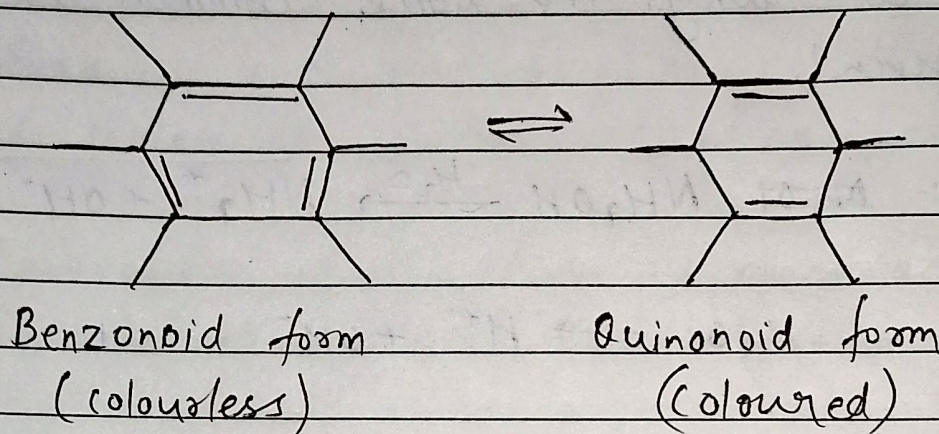
Here excess of OH^- ions is present. This system has excess of hydroxyl ion. Some of the hydroxyl ion combines with NH_4^+ ion to form ammonium hydroxide. OH^- ion is the common ion. This is the common ion effect.

* Theory of indicators :-

The theory suggests that the colour of organic compound is due to the ~~excess~~ presence of some ~~unsat~~ unsaturated 'chromophones' like $\text{C}=\text{O}$, $\text{C}=\text{C}$, $\text{N}=\dots$ and $\text{N}=\text{N}$.

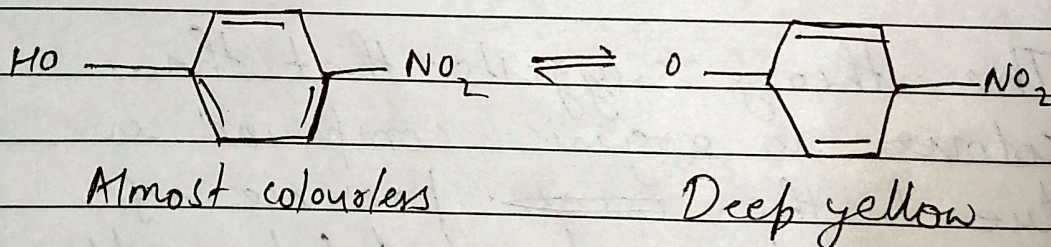
These chromophones are intensified by 'auxochromes' like NH_2 and OH group. The colour change of many indicators is due to the transformation of a benzoid structure into a

quinonoid and vice versa, along with the change in H^+ concentration of the solutions.



H.E. Armstrong explained this case by taking the examples of nitrophenols

In alkaline solution *p*-nitrophenol is present as the yellow ion. But in acid solution, it is found as colourless nitrocompound.



★ Choice of Acid-Base indicators :-

Methyl orange is used in the assay of strong acids and in reactions where CO_2 is evolved. CO_2 does

not affect this indicator. Methyl red is used in the assay of weak bases.

Eg. - Ammonia ~~am~~ and amines.

Phenolphthalein is used in the assay of weak acids.

The choice of some well known indicators along with their pH range, colour changes are summarized below.

1. Congo red :-

It is sodium salt of an azo compound.

Its pH range is 3-5 causes blue colour to become red.

2. Dimethyl red :-

It is 4-dimethylamino azobenzene. its pH range is 2.8 - 4.0 it turns red to yellow. It gives latter end-point is ~~is~~ strongly alcoholic solution. It is used in the determination of caovone.

3. Methyl orange :-

It is the sodium salt of 4-dimethylamino azobenzene - 4-sulphonic acid.

Its pH range is 2.8 - 4.0 it turns red colour to yellow.

A 0.04% aqueous solution alcoholic solution is used.

4. Methyl red :-

It is 4-dimethyl amino azobenzene-2-carboxylic acid. Its pH range is 4.2 - 6.3. It turns red colour to yellow colour. The preparation of this indicator is described in pharmacopoeia. This methyl red indicator is used in place of methyl orange in the titration of NH_3 and other weak bases where it gives a better end-point.

5. Phenolphthalein :-

It turns colourless to red. It acts in the pH b/w 8.3 - 10.3. The colour limit of red varies with the concentration of the indicator. Generally, a 1% solution in alcohol is used in titration.

* Mixed indicators:-

In some cases it is required to have a sharp colour change in a narrow and selected range of pH. This does not occur with an ordinary acid base indicator as the colour change extends over two units of pH. This condition is achieved by a mixture of indicators.

Mixed indicators are selected so that their pK_{in} values are close together and the overlapping colours are complementary at an intermediate pH value. The examples are given below.

(i) A mixture of equal parts of neutral red (0.1% solution in ethanol) and methylene blue (0.1% solution in ethanol) provides a sharp colour change from violet-blue to green. This occurs from acid to alkaline solⁿ at pH 7. This indicator is used to titrate acetic acid with NH_3 solution and vice-versa.

(ii) A mixture of thymol Blue (3 part of a 0.1% aqueous solⁿ of the sodium salt) and cresol red (1 part of a 0.1% aqueous solⁿ of the sodium salt) changes its colour from yellow to violet

at pH 8.3. This indicator is used for the titration of carbonate to hydrogen carbonate stage.

Buffer action in a solution of a weak acid and its salt is due ~~the~~ to the fact that ~~at~~ H^+ ions are removed by the anions of a weak acid to form unionized molecules.

Guess Question and Answer

Q1. Discuss principle of precipitation titration. Discuss Fajan method in detail. - (14) marks.

→ Principle of precipitation titration:-

The main principle of precipitation titrations is that the quantity of added precipitating reagent or precipitant is equivalent to the substance being precipitated.

Fajan's Method:-

This method was given by K. Fajan in 1924. The method employs adsorption indicators for the detection of

end point in precipitation titration.

The principle of fajan's method of precipitation titration is based on the fact that at the end point, the indicator get adsorbed by the precipitate resulting in a substance of different colour. commonly used indicators in fajan's method for the titration of halide and isocyanates silver nitrate are:

- (2 marks)
- ① Fluorescein
 - ② Dichlorofluorescein
 - ③ Eosin (Tetrabromo fluorescein)
 - ④ Erythrosine

Choice of adsorption Indicator

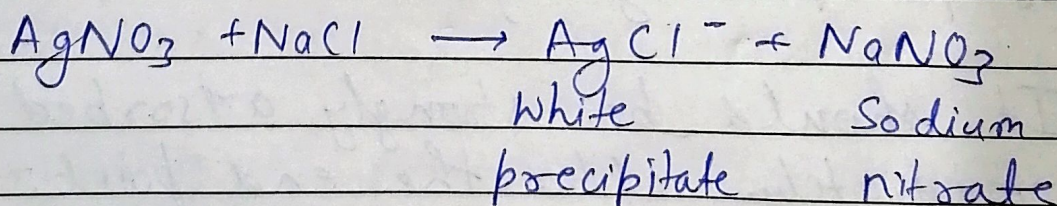
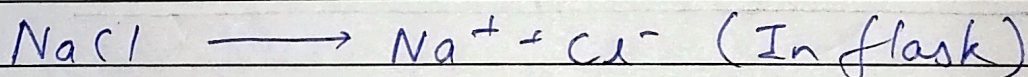
- Ⓐ The indicator ion (Fluoresceinate ion) must be an opposite charge to the ion of precipitating agent.
- Ⓑ It should be strongly adsorbed immediately after the end point.
- Ⓒ The indicator should not be adsorbed before the precipitate formation.

Principle of adsorption Indicator:

The principle of adsorption Indicator is based upon the phenomenon of adsorption. The phenomenon of concentration of molecules of gas or liquid at a solid surface is termed as adsorption. The substance that concentrates at the surface is called adsorbate and solid surface on which concentration occurs is known as adsorbent.

eg. Silver nitrate (AgNO_3) is titrated against sodium chloride (NaCl) solution.

In solution the ions present are.

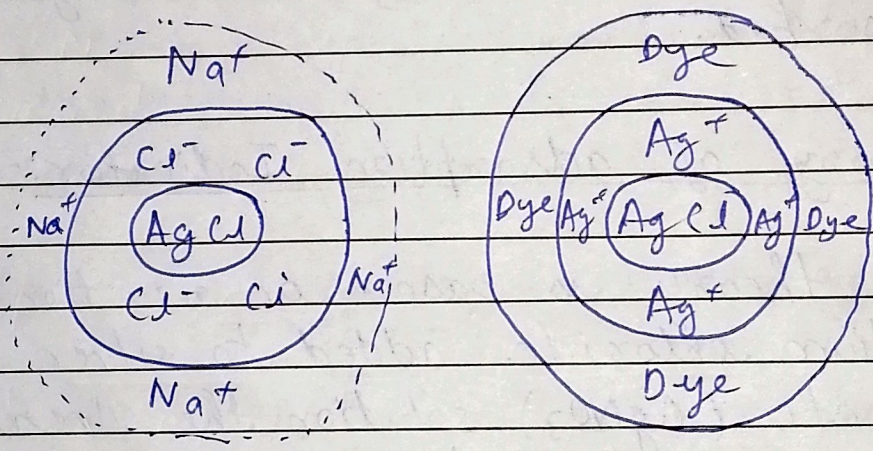


The precipitates of silver chloride (AgCl) adsorb chloride ion (Cl^-) to form a primary adsorbed layer. It will hold secondary adsorbed positively charged ions as Na^+ from solution present in the flask. At the end point Ag^+ ions are added from the burette which are not primary adsorbed and oppositely charged NO_3^- ions will form the secondary adsorbed layer. Now on the surface of first traces of Ag^+ ions the modified fluoresceinate ions of indicator get adsorbed.

Theory of adsorption Indicator:-

The theory is based on reaction of sodium chloride added to silver nitrate (AgNO_3) solution the silver chloride precipitate will adsorb chloride ions which are initially in excess. Thus the chloride ions form the primary adsorbed layer which in turn will hold the secondary adsorbed layer of oppositely charged Na^+ ions. Immediately after the equivalence point Ag^+ ions are in excess and hence silver chloride ions now adsorb Ag^+ ions as primary

adsorbed layer and NO_3^- as secondary adsorbed layer. Now if the sodium salt of fluorescein is also present in the solution then negatively charged fluorescein ions would be adsorbed instead of NO_3^- as secondary adsorbed layers and ~~there~~ this adsorption occurs along with a change to pink colour due to the formation of a pink coloured complex of Ag^+ and modified fluorescence ions.



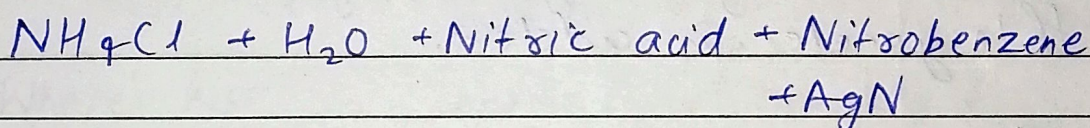
- (a) AgCl precipitated in presence of excess of Cl^- . (b) AgCl precipitated in presence of excess of Ag^+ .

Q.2. Discuss Valhard's method of precipitation titration :-

→ (Indirect method or residual titration)

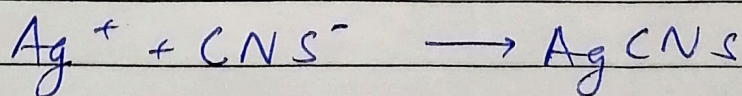
This method was given by Valhard in 1874. In this method the excess of silver nitrate (AgNO_3) is added to the solution of halide acidified with nitric acid. The unreacted silver nitrate (AgNO_3) is treated against standard ammonium thiocyanate (NH_4SCN) solution using ferric salt as indicator.

eg: - Assay of Ammonium chloride.

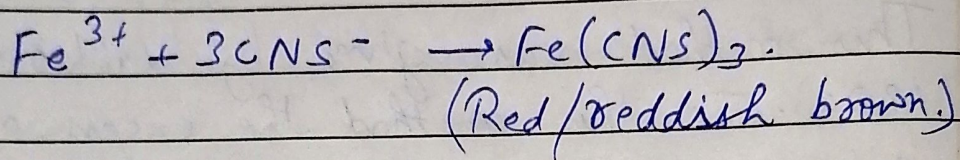


Shake vigorously for one minute and add ferric salt indicator → Titrate with 0.1N ammonium thiocyanate (NH_4SCN) till redish brown color is obtained.

When standard solution as NH_4SCN is added to a solution of silver salt a precipitate of silver thiocyanate (AgCNS) continues to be formed till the Ag^+ ions are not completely precipitated.



The addition of further drop of thiocyanate react with the ferric ions to form a reddish brown ferric thiocyanate complex.



When the end point is approached the solution of silver thiocyanate (AgCNS) should be vigorously agitated because a large amount of the Ag^+ ions are absorbed on the surface of AgCNS precipitate which get removed only very slowly when thiocyanate is added.

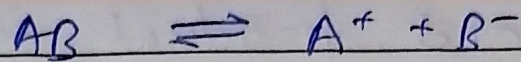
Application :-

It is employed in the determination of iodides, chlorides and thiocyanate ion.

Solubility product :-

7 marks

The process of gravimetric precipitation is completely based on the complex concepts of stability product let us consider a dissociation of slightly soluble salt AB.



Applying law of mass action.

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

The concentration of the AB in the solution remains constant in presence of undissolved AB i.e.)

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

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

Where K_{sp} is constant at constant temp. and is called solubility product of salt $[AB]$ and is defined as maximum product of concentration of its constituent ion solution.

$[A^+]$ and $[B^-]$ = Ionic concentration in standard solution.

If ionic product or ~~conc~~ concentration is ~~standard sol~~ greater than K_{sp} , precipitation will occur.

If the Ionic product or concentration is equal to K_{sp} solution remains ~~constant~~ consistent.

If the ionic product or concentration is less than K_{sp} precipitation do not occur.

Types of Acid-Base Titration / Neutralization Titration curves:

A titration curve is the plot of the pH of the analyte solution versus the volume of the titrant added as the titration progresses.

A. Aqueous Acid-Base Titration

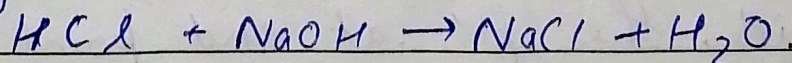
These are normal titration between acids and base dissolved in water. Hence, they are called aqueous acid-base titration.

1. Strong acid and Strong base :-

Strong acid reacts with a strong base to form salt and water. The reaction happens in stoichiometry means i.e. each molecule of acid reacts with corresponding molecule of base.

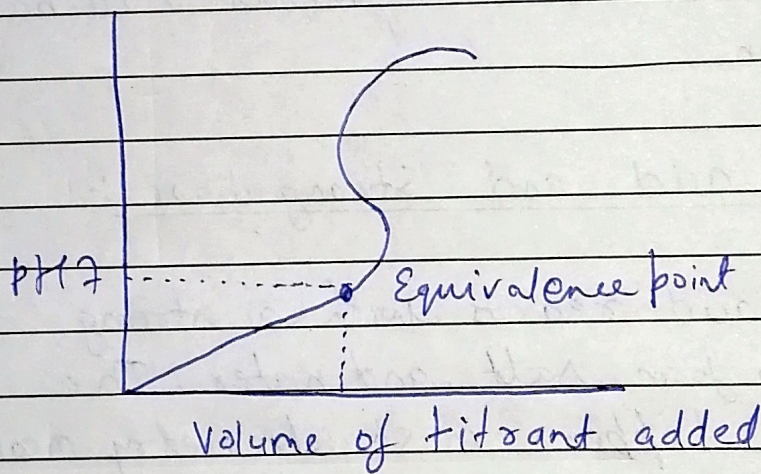
At the end of reaction acid and base are completely reacted to form salt. Hence the end point or equivalence point is precise and sharp.

eg. HCl as strong acid and NaOH strong base.



Initially, due to HCl, the pH of solution is less. As the NaOH added slowly, the dissociation of NaOH takes place and pH of solution increases.

At the equivalence point, HCl is completely reacted with NaOH to form water and salt. The pH of solution is 7. After the equivalence point the addition of NaOH, increases the concentration of OH^- ions as HCl is completely react. The pH of solution increases.

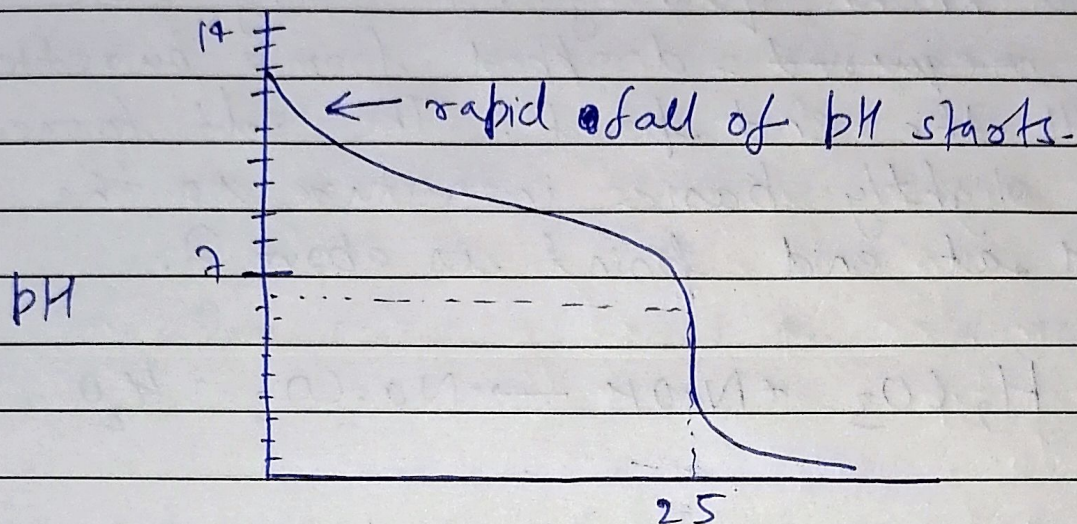
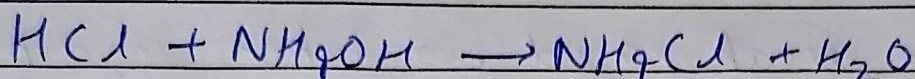


Titration curve for strong acid vs strong base.

(2) Strong acid vs Weak base :-

Here a strong acids reacts with weak base to form salt and water. But since, the reaction uses strong acid, the pH at end point will

be towards acidic i.e. below 7

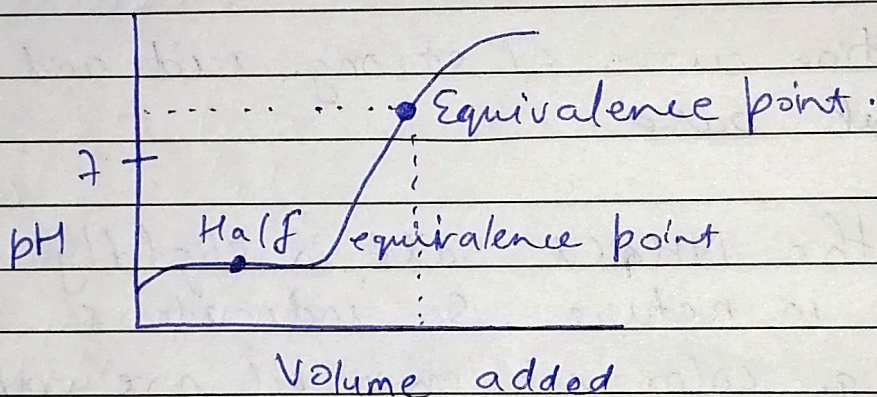
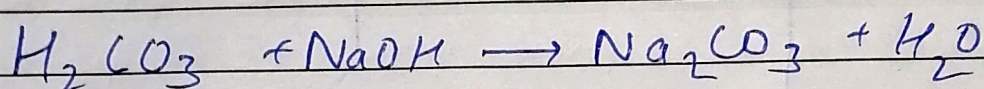


Titration curve of strong acid and weak base.

Here the NH_4Cl salt is slightly acidic in nature. So indicators changing color at lower pH are employed. During reaction known concentration of strong acid is taken in burette and allowed to react drop by drop with the base in beaker. Initially the pH of solution is high due to ammonia. After end point, further addition of HCl decreases pH of solution as there is no ammonia present in solution to react.

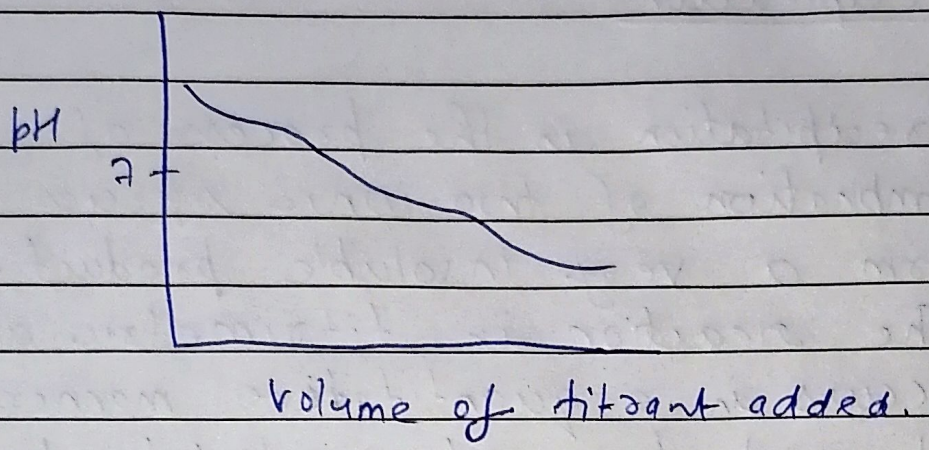
3. Weak acid vs Strong base.

The weak acid is taken in a beaker and known quantity of strong base is required, dropped from a burette till the end point. The salt formed is slightly basic in nature so the pH at end point is above 7.



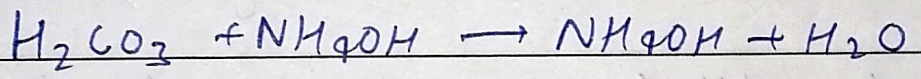
4. Weak acid vs Weak base.

Here both acid and base are weak. So mostly they are avoided due to imprecise end point. At the end point, the pH will be theoretically 7 but cannot be measured precisely as that is strong acid and strong base case.

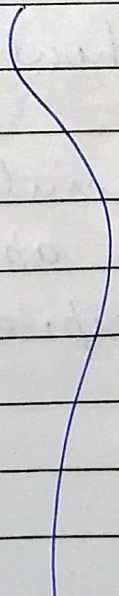


Titration curve of weak acid and weak base.

An extra amount of titrant is needed to reach the end point due to imprecise reaction.



The end point is neutral as the salt is neutral but due to excess titrant added the pH can be in favour of it.



Precipitation

Precipitation is the process of combination of two ionic species to form a very insoluble product.

The reaction in titrimetric analysis occurs in a quantitative manner.

It must proceed completely to form the product of the reaction.

This type of reaction is neutralization redox, completion and of precipitation reaction.

The reaction in titrimetric analysis must include the following requirements:

- i) The precipitate must be practically insoluble.
- ii) Precipitation reaction must occur in quantitative manner.
- iii) The reaction should be rapid.
- iv) The titration results must not be damaged due to absorption or any kind of co-precipitation effect.

- v) Determination of equivalence point during the titration must be detectable.

Principle of precipitation

Solubility depends on the solvent and temperature. It is the concentration of dissolved solute in moles per litre when the solution is in equilibrium with a solid solute.

In order to dissolve a solid the intermolecular forces of attraction must be overcome. i.e. solute-solute attraction is ~~replied~~ replaced by solute-solvent.

Here the solvent competes with crystal forces and overcome them. This means that the solvent environment must be similar to that provided by the crystal structure. i.e. like dissolves like but during precipitation opposite things happen here in precipitation, intermolecular forces between the molecules of product are high. so solute-solute forces replace the solute-solvent forces.