

« VOLUMETRIC ANALYSIS »

Chemical Analysis is carried out in two ways:-

i) Qualitative analysis

ii) Quantitative analysis

i) Qualitative analysis : It is detection of ions or radicals in an unknown inorganic salt.

ii) Quantitative analysis : It involves determination of quantity of a substance's component. It is carried out in two ways:-

i) Gravimetric Analysis

ii) Volumetric Analysis

* Gravimetric analysis : It is based on measurement of weight.

* volumetric analysis : It is based on measuring the volume of solution of a substance.

→ Terms used in titrimetric analysis.

i) Titration : Quantitative analysis carried out for determining the concn. of unknown solution which reacts with definite volume of standard volume.

ii) Titrant : The solution of known strength (soln. in burette).

iii) Titrand : The solution of unknown strength. (Analyte)

iv) Equivalence point : The point at which reaction is just complete.
(Theoretical or stoichiometric end point)

v) End point : The visual detection of end-point (equivalence) or
end-point is an observable physical change that occurs near equivalence point.

vi) Indicator : The substance which indicates end point of titration
Any compound which can undergo phys/chem. change to determine completion of rxn.

* **Strength:** The amount of substance dissolved in one litre of soln. when expressed in grams is termed as strength of soln.

It can be expressed in any of following ways:-

i) **Normality:** no. of gram equivalent of substance dissolved per litre of soln.

ii) **Molarity & molality.**

iii) **formality:** formula weight is involved used for ionic compounds.

* **Standard solutions :-** solution of known strength.

i) **Primary standards substance**

ii) **Secondary standard substance.**

* **Primary standard substance :-** Any substance whose standard soln. can be prepared directly by dissolving exact amount of it in water and making up the solution to a known volume by dilution with water.

Primary standard substance must possess the following characteristics:

- It should be easily available in pure state. Any impurity, if present, must be inert w.r.t substance which is to be titrated.
- Should have a high molar mass so that weighing error is min.
- Should be readily soluble in req. solvent or water.
- It should neither be hygroscopic nor efflorescent.
- It should be stable at oven temp. for drying.
- It should be stable & unaffected by air.
- Its composition should not change on standing.
- e.g.: Crystalline oxalic acid, anhydrous sodium carbonate, dried KCl, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ are used as primary standards.

NOTE: i) **Efflorescent:** Spontaneous loss of water by a hydrated salt. It occurs when aqueous vapour pressure of hydrate is $>$ partial pressure of water vapour in air.

e.g.: Washing Soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) & Glauber's salt.

- i> deliquescence : The process by which a substance absorbs moisture from atmosphere until it dissolves in absorbed water & forms a soln
- ii> hygroscopic : Absorbs moisture from atmosphere.

* Secondary standard solution : The substances which do not fulfill the above conditions and whose solution cannot be prepared directly by weighing.

Preparation of Secondary standard soln : an approximate weight of a substance is measured and dissolved in known volume of solvent (water). The exact strength of soln is determined by titrating it against some primary standard. This process is called standardisation.

e.g. Alkali hydroxides as they are hygroscopic and their weight keep on changing. NaOH & KOH etc.

KMnO₄, as it is always associated with MnO₂ & is not pure. MnO₂ catalyse the auto decomposition of permanganate soln. during standardization.

HCl, H₂SO₄ etc.

→ TYPES OF TITRATION

- i> Acid-Base or Neutralisation titrations
- ii> Redox titrations
- iii> Precipitation titrations.
- iv> Complexometric titrations.

* Criteria for titration to be carried out :

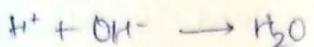
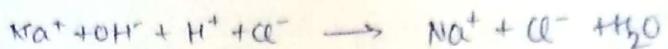
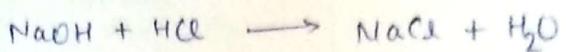
- i> reaction should be relatively fast.
- ii> simple chemical eqn should represent the rxn.
- iii> Proper indicator must be there to show that rxn has taken place

* Titration error : Smallest diff. b/w equivalence point & end point

* ACID-BASE TITRATIONS.

These are the titrations in which acid is titrated against an alkali or vice-versa. The titrations in aqueous solⁿ. are based on the rxn blue H⁺ & OH⁻ to form unionized water.

e.g.: Titration of sodium hydroxide against HCl.



Acidimetry: To find strength of an unknown acid with help of known base is called Acidimetry. OH⁻ of alkali combines with H⁺ of acid. The concentration of H⁺ gradually ↓ and pH of solution ↑. At a definite pH, end-point is reached.

Alkalimetry: To find strength of an unknown base with help of a known acid. H⁺ of acid combines with OH⁻ of alkali. concn. of H⁺ in solution increases and pH ↓. At definite pH, end-point is reached.

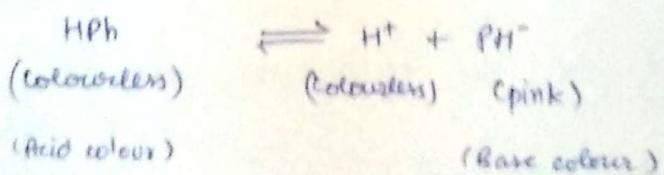
* ACID-BASE TITRATION AND INDICATORS.

The process of acid-base titrations is accompanied by change in pH. Substances which change colour according to pH are used to indicate end-point.

* THEORY OF ACID-BASE INDICATORS:

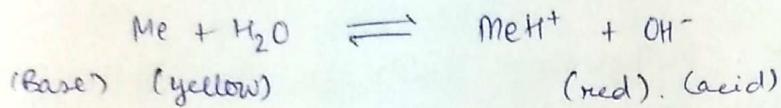
i> Ostwald's theory: Acc. to this theory, indicators are themselves weak acids and bases. They have diff. colour in ionized & unionized form.

Action of phenolphthalein: Phenolphthalein is a weak acid & is colourless in unionized form and pink in ionized form.



In presence of acid, there is increase in concentration of H^+ due to common-ion effect \therefore dissociation of HPh is suppressed and eqm shifts towards left and solution becomes colourless. whereas in presence of base, there is a decrease in concn. of H^+ , due to combination of H^+ with OH^- to form unionized water. Hence, eqm shifts towards right and solution turns pink.

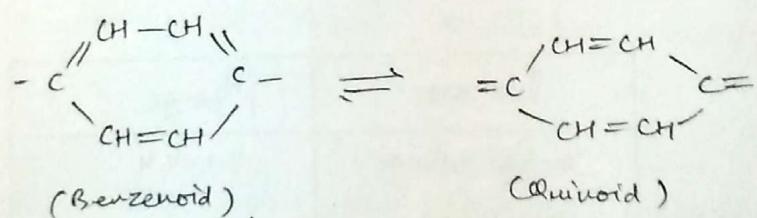
Action of methylorange : Methylorange is a weak base.



In presence of an acid, H^+ combines with OH^- and due to deficiency of OH^- , eqm shifts towards right and solution becomes red. whereas, in presence of a base, due to common ion effect, concn. of $OH^- \uparrow$ and hence eqm shifts towards left and colour of solution turns yellow.

i> MODERN QUINOID THEORY / BENZENOID THEORY.

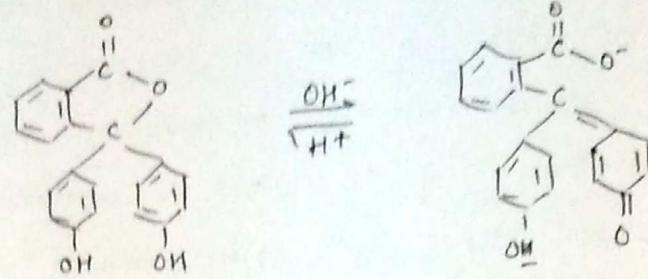
Acc. to this theory, acid-base indicators exists in two tautomeric forms. One is Benzenoid and other is quinoid form. The two forms have two different colours and usually quinoid form has deeper colour than Benzenoid form. One form exist in acidic medium and other in alkaline medium. pH conversion causes Benzenoid form to change in quinoid form and vice-versa.



- Action of Phenolphthalein : It possesses Benzenoid form in acidic medium and quinoid form in alkaline medium.
(pink).

Benzenoid form \rightarrow acid soln. (colourless)

Quinoid form \rightarrow basic soln (pink).

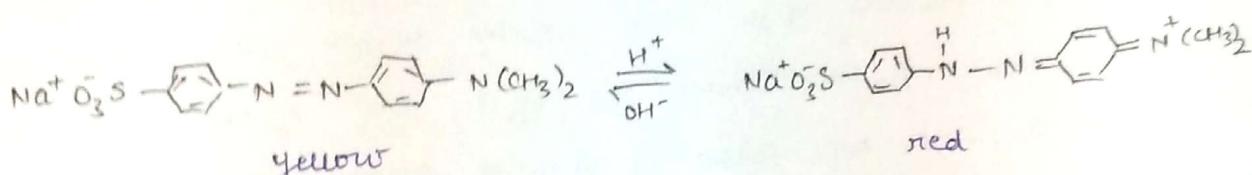


(Benzenoid form)
in acidic med.
colourless

(Quinonoid form)
in basic med.
red colour

- Action of Methyl orange: Methylorange exists in two tautomeric forms. In alkaline solⁿ, it exists in Benzenoid form & in acidic solⁿ, it exists in quinonoid form (red)

→ (yellow)



(Benzenoid form in alkaline medium)

(Quinonoid form in Acidic med.)

* SELECTION OF PROPER INDICATOR.

The pH value at the end point of titration depend upon relative strength of acid and base. Since diff. indicators have diff. ranges of pH within which they can be used, one should select an indicator which changes colour at approximately the pH at equivalence point of titration.

Indicator	pH range
Methyl orange	3.1 - 4.4
Methyl red	4.2 - 6.3
Litmus	4.5 - 8.3
Phenolphthalein	8.0 - 9.6.

* ACID-BASE TITRATION CURVES.

The addition of an alkali to an acid or vice versa is accompanied by change in H^+ conc. & hence pH of solution changes. During

A plot of pH against the volume of base or acid added from burette is called pH titration curve or acid-base Titration curve.

SIGNIFICANCE OF pH-TITRATION CURVE

It is used in detection of equivalence point and selection of suitable indicators. We select such an indicator whose colour changes at a pH close to that at equivalence point.

a) A titration of a strong acid with a strong base.

It is seen that pH changes very slowly at first & then increases rapidly at equivalence point. For even a very small addition of alkali, pH change is significant and there is a sharp increase. This sharp and sudden change in pH from 4 to 10 is very significant because all indicators which show colour change in this range can be used to detect end-point. Thus, methylorange, metylyred, Phenolphthalein all can be used. After equivalence pt., on further addition of alkali, pH changes very slowly.

NOTE: The equivalence point in all cases, for strong acid with base(s) remains the same i.e. 7.

b) titration of weak acid with strong base.

Suppose titration of CH_3COOH with NaOH is carried out. In this case, pH at equivalence point will not be 7, because hydrolysis of sodium acetate will take place. As sodium acetate is a salt of weak acid and strong base, it gives excess of OH^- and hence pH of solution at equivalence point will be beyond 7. Hence, phenolphthalein or thymol should be used as these indicators shows colour change at pH level > 7 .

* for titration of acids like boric acid against sodium hydroxide, the titration curve does not show any sharp \uparrow in pH. This is because, the salt so formed undergoes hydrolysis to a much greater extent and results in alkaline medium. \therefore there is a gradual increase in pH.

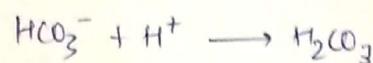
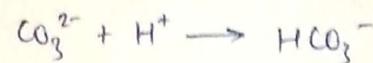
(c) Titration of weak base with a strong Acid :

Suppose titration of NH_3OH and HCl is carried out. Due to formation of salt NH_4Cl , which undergoes hydrolysis releasing H^+ ions, solution becomes acidic at equivalence point. pH change in at eq. lies in range 6 to 4. The indicators having pH range on acidic side i.e. methyl red & methyl orange can be used successfully.

(d) Titration of weak acid by a weak base :

There is no sharp pH change in this case. no indicator is suitable. however, a mixed indicator may be used.

(e) Titration of Na_2CO_3 with hydrochloric acid : when Na_2CO_3 is titrated with a strong acid i.e. HCl, carbonate ions are first converted to Bicarbonate ions, and then to carbonic acid.



There are two equivalence points. (\because neutralisation occurs in two steps)

- The first equivalence point corresponds to neutralisation of CO_3^{2-} to HCO_3^- stage. Equivalence pt is reached at $\text{pH} = 8.5$. so phenolphthalein can be used.
- The second equivalence point corresponds to neutralisation of HCO_3^- to H_2CO_3 stage. This rxn gets completed at 4.3.

Thus, methylorange can be used as an indicator.

Titrations	Approximate pH range at Equiva. pt.	Suitable indicators.	pH at colour change of indicator.
1. Strong acid & strong Base	4 to 10.	Methyl orange litmus phenolphthalein	3.1 - 4.4 4.5 - 8.3 8.0 - 9.6
2. Strong acid & weak base.	3.5 to 7 .	methyl orange methyl red.	3.1 - 4.4 4.2 - 6.3
3. Weak Acid & strong Base	6.5 to 10	phenolphthalein	8.0 - 9.6 .
4. weak Acid & weak Base.	No sharp eq.pt .	None satisfactory	-

2> REDOX - TITRATIONS.

Titration in which reducing Agent is titrated against oxidising Agent or vice-versa are called redox titrations.

* REDOX TITRATIONS AND INDICATORS.

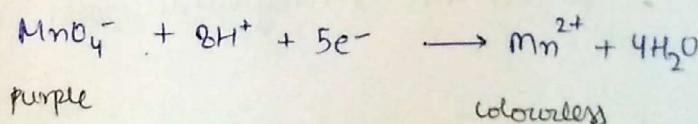
Redox indicators are those substance whose oxidised form is of diff. colour than reduced form. The oxidation and reduction of indicator must be readily reversible. The change in pH occurs according to the electrode potential of system. Hence, electrode potential of indicator should lie within that of system. (colour)

* TYPES OF REDOX INDICATORS ,

- i > Self-indicator
 - ii > Internal indicator
 - iii > External indicator

* SELF-Indicator : If the solution is strongly coloured and decolourises or undergoes change in colour at the end point by the substance to be determined then, it is called self-indicator.

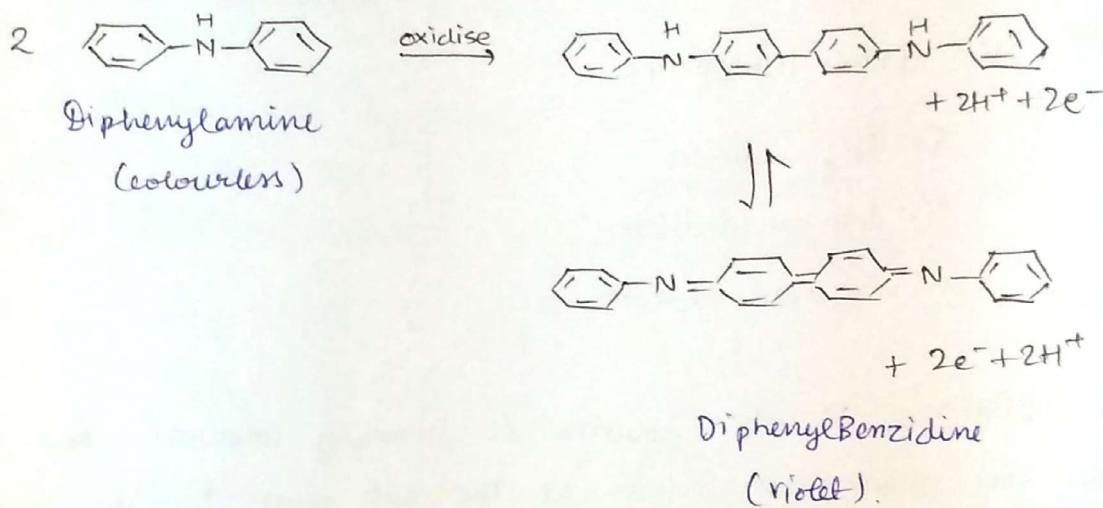
Potassium permanganate is purple in oxidised form & colourless in reduced form.



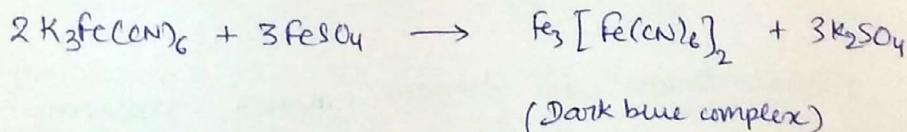
when potassium permanganate is titrated using reducing agent oxalic acid, then MnO_4^- gets reduced to Mn^{2+} giving rise to colourless solution. When whole of reducing agent is consumed up, then addition of an extra drop of $KMnO_4$ will give its own pink colour to solⁿ. This marks the end-point of titration.

No additional indicator is added.

* Internal indicators: Those substances which are added in the titration flask in which titration is carried out are called internal indicators. e.g. Phenolphthalein, methyl orange etc. In redox titration, diphenylamine is one of the first internal indicator discovered by Knop. It is used in titration of Fe^{2+} ions using $\text{K}_2\text{Cr}_2\text{O}_7$. Fe^{2+} ions are oxidized to Fe^{3+} by $\text{K}_2\text{Cr}_2\text{O}_7$. When whole of Fe^{2+} are oxidised, then an addition of another drop of $\text{K}_2\text{Cr}_2\text{O}_7$ with oxidise Diphenylamine giving blue-violet colour to solution. This marks the end of Titration.



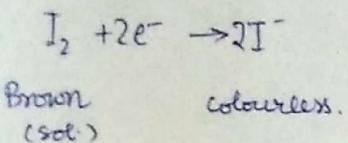
* External indicators: These are not added to the titration flask but are used externally. In titration of $\text{K}_2\text{Cr}_2\text{O}_7$ using ferrous Ammonium sulphate, potassium ferricyanide acts as external indicator.



Konium ferricyanide reacts with Fe^{2+} to form dark Blue complex ferrous ferricyanide. When whole of Fe^{2+} are oxidised to Fe^{3+} by $\text{K}_2\text{Cr}_2\text{O}_7$, then blue colour will no longer be obtained.

* The drops of external indicator are placed on groove tyle. During titration, drops of solution are taken out at regular intervals & are mixed with drops of external indicator. The end-point is reached when blue colour disappears.

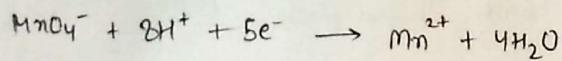
- * Adsorption indicator.
- Sometimes, change in colour at end point is not so distinct.



As iodine is reduced, pale yellow colour is obtained and is difficult to differentiate b/w pale yellow colour and colourless iodide ion. So, starch is used as an indicator, which absorbs iodine molecule & imparts blue colour to solution. When whole iodine is removed, (reduced to I^-) , Blue colour changes to colourless. This marks the end point.

* KMnO₄ Titration

- KMnO₄ is not a primary standard ∴ It should be standardise first with help of standardised reducing Agent.
- Potassium permanganate can work in all medium. (Acidic, Basic & Neutral).
- H₂SO₄ is used for Acidification.
- HCl should not be used for Acidification because HCl is oxidised & releases Cl₂ gas.
- HNO₃ is a very strong oxidising Agent. and will affect both OA & RA and will interfere in quantitative Analysis.



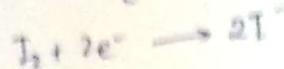
- used to estimate strength of reducing Agents like oxalic acid, Mohr's salt and sodium thiosulphate.
- It acts as a self-indicator.

* K₂Cr₂O₇ Titration

- Excellent primary standard.
- does not act as self-indicator.
- used to estimate strength of RA.
- Internal indicator such as Diphenyl Amine is used.

* IODINE TITRATIONS.

Iodine is a mild-oxidising Agent.



- Iodine is a much weaker oxidising Agent than $K_2Cr_2O_7$ & K_2CrO_7 and is used to estimate strength of weak reducing Agents like sodium thiosulphate, sodium sulphite etc.
- It is also used to find strength of oxidising Agents as well.

So, it is of two types

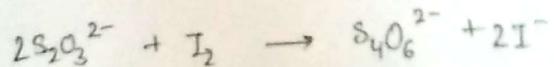
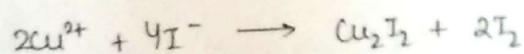
i) Iodimetry

ii) Iodometry

i) Iodimetry : It involves direct titration of iodine with reducing agents. It is used to determine strength of reducing Agents like sodium thiosulphate, etc. (ferrous salts). in neutral or acidic (moderately) medium.

ii) Iodometry : Iodine is liberated due to oxidation of I^- by an oxidising Agent. The liberated I_2 is then titrated with reducing agent. in neutral or Acidic medium. Iodometry is used to estimate strength of oxidising Agents.

Estimation of Cu^{2+} with Thiosulphate :

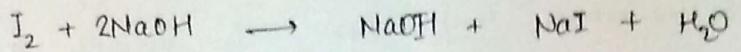


INDICATOR: Starch solution is used as an internal indicator in this type of titration.

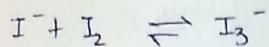
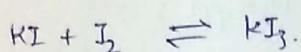
IODOMETRIC TITRATIONS

- This type of Titration should be performed in cold. Because of volatile nature of I_2 and starch also loses its sensitivity at high temp.

- It cannot be performed in strongly alkaline solutions. The reason being that I_2 reacts with alkalis to form hypoiodites. Hypoiodites being strong oxidising Agents may oxidise thiosulphate ions.

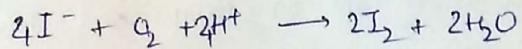


- Always use excess of KI: I_2 is volatile and hence to keep it in titration flask, KI is added which makes an unstable complex salt, KI_3 . This soluble complex will release iodine slowly.



when free iodine is used up in the reaction with thiosulphate, eqm shifts towards left releasing more I_2 .

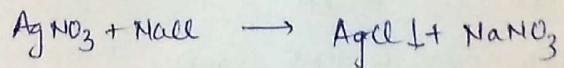
- The rxn mixture should be kept in dark before titrating. This is due to reason that light catalyses oxidation of I^- ions to I_2 by O_2 in atmosphere.



- Starch should be added only when 99% of titration is completed.

* PRECIPITATION TITRATIONS

The titrations accompanied by the formation of sparingly soluble salts, when solutions of two reacting substances are mixed with each other.

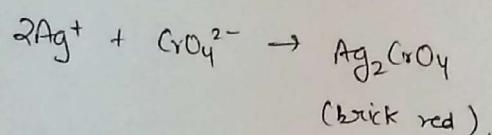
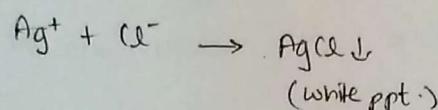


- These reactions involves presence of $AgNO_3$ sol (these are limited to) & hence called Argentometric titrations.
 - Precipitate forms only when ionic product exceeds solubility product.
 - Precipitate must be insoluble.
 - Precipitate formation should be rapid.
 - Equivalence sh pt should be easily detectable.
- } conditions for occurrence of ppt. titration.

1 > Indicators: Indicators are used depending on formation of coloured ppt
Argentometric titrations are of two types:-

i) Mohr's Method: used for estimation of chlorides.

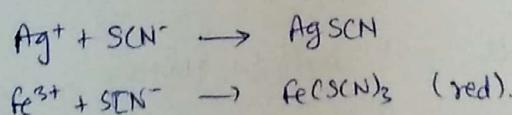
When AgCl is titrated with AgNO_3 in presence of K_2CrO_4 indicator, ppt. of AgCl is formed first. When all AgCl^- are precipitated, then the extra drop of AgNO_3 reacts with Ag^{+} K_2CrO_4 to form Ag_2CrO_4 (red brick) colour. This is because solubility product of AgCl is reached first and Ag_2CrO_4 is reached later. At equivalence point, solution acquires a brick-red colour.



* LIMITATIONS OF MOHR'S METHOD.

- i) Ag_2CrO_4 is soluble in acidic soln. and hence soln to be titrated should be neutral. If it is acidic, first neutralise by adding CaCO_3 .
- ii) If soln is alkaline, AgNO_3 is ppt. as AgOH and hence it is neutralised by adding dil HNO_3 .
- iii) not suitable for determination of iodides.
- iv) pH range \rightarrow 7 to 10.

ii VOLHARD'S METHOD: used for estimation of silver.



When standard solution of pot. or ammonium thiocyanate is titrated against AgNO_3 in presence of dil. HNO_3 & indicator ferric salt, then first AgSCN is precipitated. When whole Ag^+ are consumed, then an additional drop of SCN^- will form a red complex with Fe^{3+} & marks the end point.
(estimation of Bromides is also possible)

LIMITATIONS OF VOLHARD'S METHOD.

- i> Not applicable in case of coloured solⁿ i.e. copper halides etc.
- ii> In case of determination of Cl⁻, red colour disappears on stirring & hence end point cannot be achieved.
- iii> The solⁿ must be free from OA which may oxidise SCN⁻.

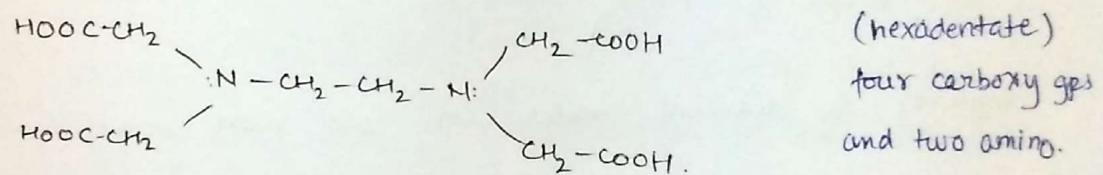
* COMPLEXOMETRIC TITRATIONS.

These are the titrations which involves formation of soluble complex between metal ion and a complexing Agent.

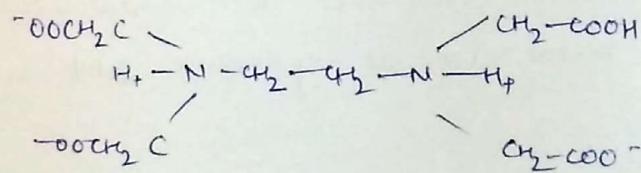
The metal ion is called central atom and Complexing Agent is called Ligand.

- Ligand can be unidentate, Bidentate or polydentate. The polydentate ligands forms more stable complexes because of formation of ring-like structures called chelates.
- EDTA is most widely used ligand.

Structure of EDTA :



- Zwitter-ion formation



- Various EDTA species are abbreviated as: H₄Y, H₃Y⁻, H₂Y²⁻, HY³⁻, Y⁴⁻

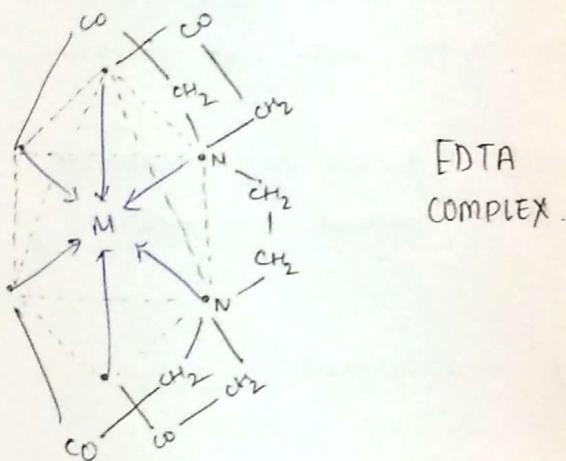
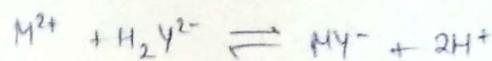
At pH > 12 , Y⁴⁻

pH ≥ 8 , HY³⁻

pH ~ 5 , H₂Y²⁻

- The free acid H₄Y is not used for prepn. of standard solⁿ, due to its limited solubility. But Na₂H₂Y is most commonly used because it can be obtained in highly pure state.

* Reactions of EDTA with Metal ions: Irrespective of charge on metal ion, it combines with metal in 1:1.

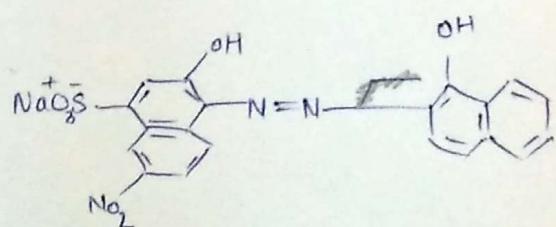


* Complexes of divalent metal ions are more soluble in Ammonical soln.

* INDICATORS USED IN EDTA TITRATIONS.

These indicators are organic colouring substances that undergoes change in colour when it forms complexes with metal ions. The indicator releases metal ion at equivalence point and results in change in colour.

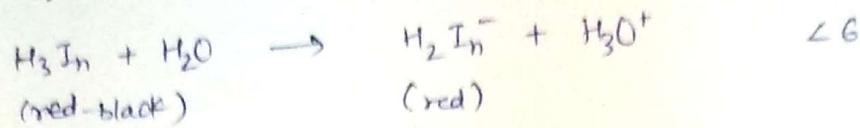
* ERIOCHROME BLACK T (EBT) (mostly used indicator).



1-(hydro-2-naphthylazo)-6-Nitro-2-naphthol-4-sulphonate.

It is abbreviated as H₃In

Dissociation of EDTA is as follows:



Depending on extent of dissociation, it exhibits diff. colours i.e. at diff. pH it exhibits diff. colours which signifies that it is a pH-sensitive indicator.

At	$\text{pH} < 6$	H_2In^-	(red)
	$\text{pH} > 7$	HIIn^{2-}	(blue)
	$\text{pH} > 10$	In^{3-}	(orange).

* full Action: EDTA titrations are performed at 8-10 pH range. As the metallic salt is added., the indicator forms a slightly stable complex with metal ion & hence colour changes from Blue to red. At the end point is reached, EDTA form complex with metal ion & the indicator will be set free and colour changes from red to blue.

