Chapter:

Volumetric Analysis

Titrations

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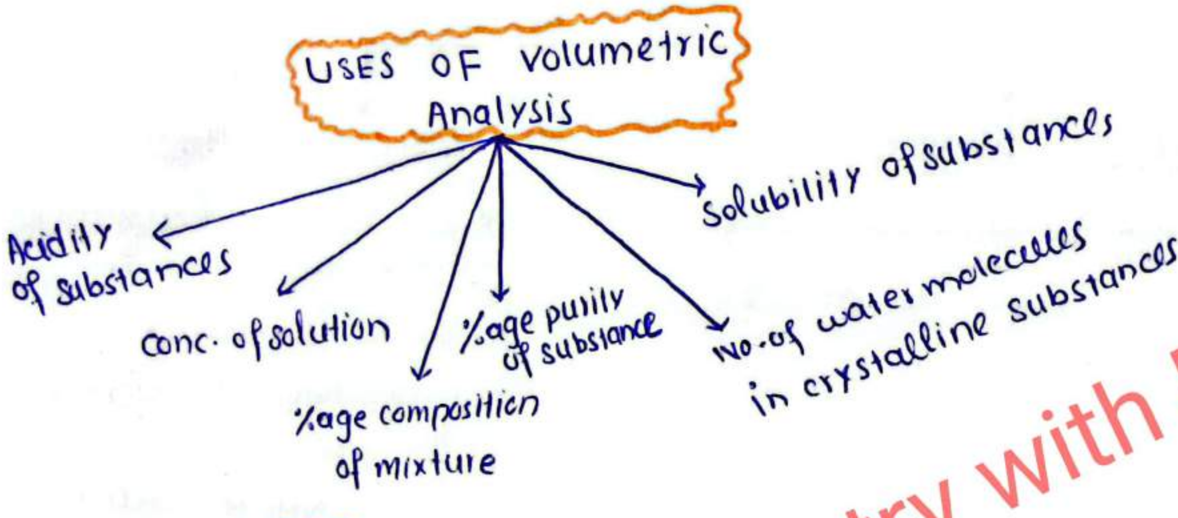
CHAPTER: Volumetric Analysis

TITRATIONS

Volumetric Analysis:

It is the quantitative analysis, involves the measurement of the volume of a known solution required to bring about the completion of Reaction with a measured volume of unknown solution whose concentration is to be determined. Volumetric Analysis is also termed as titrimetric Analysis.



ADVANTAGES:

- No side Reaction occurs
- Reaction is so Rapid
- Suitable standard solution is available
- indicator → shows the completion of Reaction
- Apparatus is easy to handle
- Analysis could be done at small Laboratory
- Level.

Important terms :

Titration:
process of Addition of Known solution from biurette to the measure volume of solution of the substance to be estimated until the Reaction B/w the two is just complete known as Titration.

Titrant: → The reagent whose solution is empolyed to estimate the concentration OF unknown solution is called tirant.

Titrant → Generally, taken in Biurette

Primary titrants
- Can be Accuratel y weighed
- No need to Standardised Before to USE.

e.g oxalic acid
$K_2Cr_2O_7$, $AgNO_3$
Ferrous Ammonium Sulphate
Sod. Thiosulphate etc.

Secondary titrants
- can not be Accuralely weighed
- It is necessary to standardized it Before the USE

e.g NaOH, KOH
HCl, H_2SO_4, Iodine
$KMnO_4$ etc.

Titrand / Titrate: solution consisting the substance to be estimated / whose conc is to be determined
↳ Generally taken in a conical FLASK.

standard Solution:

Solution of exactly known concentration of the titrant called standard solution

primary-standard solution

→ Nature does not change by environmental conditions

→ No need to standardized

secondary-standard solution

↳ nature changes

↳ necessary to standardize

indicator:

The substance used for the detection of completion of titration or detection of end point.

e.g phenolphthalein, starch etc.

End point	Equivalence point
The point where indicator changes the colour.	The point where the amount of titrant & Analyte (titrand) are chemically Equivalent
Its Related to colour change	It is determined stochiometrically.

- The difference B/W end point & Equivalence point should be very small and this difference is called titration error

$$\text{Titration error} = (E_t) = V_{e.p} - V_{eq.point}$$

$V_{end.p}$ = The Actual volume used to get the end point

$V_{eq.p}$ = The Theoretical value (→ Determine by stochiomatric moles) of Reagent required to reach the end point

CONCENTRATIONS FOR MAKING SOLUTIONS:

- % solution
- Molar solutions (M)
- Normal solution (N)
- Molal solutions (m)
- ppm solutions (ppm)

∴ Their calculations are important to perform the titrations (we have discussed in detail in (solution chemistry)

V.Imp : CLASSIFICATION OF Titrations:

A) Acid Base Titrations
- Strong Acid - Strong Base
- W. Acid - S. Base
- S. Acid - W. Base
- W. Acid - W. Base

B) Redox Titrations
- permanganometry
- Dichrometry
- Iodometry OR Iodimetry

C) precipitation titrations (Argentometric)
- Mohar Method
- Volhard's Method
- Argentometric titration
- Fajan's Method

D) complexometric titrations
- Back-Titration
- Replacement Titration
- Direct-Tit
- Indirect Tit-

A) Acid- Base Titration:

Acidimetry
Base conc. is determined by Acid

Alkalimetry
Acid-concentration is determined by BASE.

Acid-Base indicators:

in the selection of indicators for titration, Following informations are important.

(i) pH Range of indicator

(ii) pH change near the equivalence point in titration

Theories OF Indicators:-

Indicator:

An indicator is a substance which is used to determine the endpoint in a titration.

1) Acid Base Indicators:

↳ Generally organic substances (weak Acids or weak BASES) used as Acid-BASE indicators.

They change in colour at specific pH.

indicatoRS	PH Range	(Acid → BASE) ★ color ★
* Methyl orange	→ 3.2—4.5 →	~~pink~~ Red to yellow
* Litmus ↳(natural)	→ 5.5 — 7.5 →	Red to Blue
* phenolphthalein	→ 8.3— 10.5 →	colourless to pink

★ PPSC

Two theories were proposed to explain the change in colour OF Acid-BasE indicators.

a) Ostwald's Theory:

This Theory says that colour change is due to the ionization OF The Acid-BasE indicators. unionized form has different colour than the ionized form.

ionization of the indicator is largely affected in acids and Bases either it is weak Acid or weak Base

* If indicator is a weak Acid ⟶ its ionization is very low in Acids due to common H^+ while fairly ionised in alkalies.

* If indicator is a weak Base ⟶ ionization↑ in Acids & lower in Bases

* phenolpthalein (weak Acid)
* Methyl orange (weak Base)

* **phenolpthalein: (W. Acid)**

$$HPh \rightleftharpoons H^+ + Ph^-$$

HPh: W. Acid (colourless); Ph^-: (pink)

Acidic solution;
↳ Acidic ⟶ $H^{\oplus}$

Reaction go back and phenolpthalein ionization suppressed thus it gives no colour in Acidic solution

Basic solution;

$$HPh \rightleftharpoons H^+ + Ph^{\ominus}$$

Alkali ⟶ $OH^{\ominus}$

$$H^+ + OH^{\ominus} \longrightarrow H_2O$$

Thus Equilibrium shift forward

* $H^{\oplus}$ are used by $OH^{\ominus}$ → Thus conc. of $Ph^{\ominus}$ increases → impart pink colour

* **Methyl orange: (Weak Base)**

$$MeOH \rightleftharpoons Me^+ + OH^-$$

MeOH: (yellow); Me^+: (Red)

in Basic solution;
*↳ MeOH ⟶ Dissociation suppressed since solution Remains *yellow in colour (undissociated molecules)

in Acidic solution;
↳ $H^+ + OH^{\ominus} \longrightarrow H_2O$ ⟶ Forward ⟶ Red colour is due to cation

h) Quinonoid Theory:

↳ According to this Theory Acid Base indicators are exist in two tautomeric forms having different structures

Two forms are in Equilibrium;

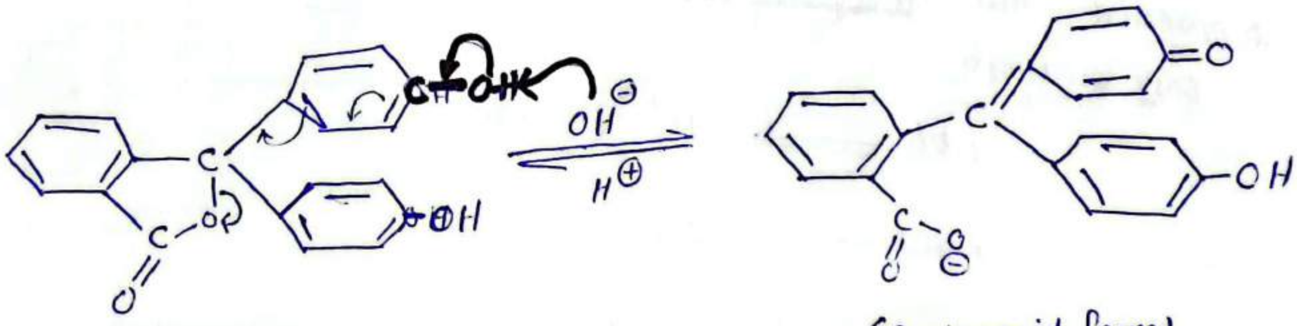
Benzenoid Form ← Two forms → Quinonoid form

* Two forms have different colours. Colour change is due to the interconversation of one tautomeric form to another tautomeric form.

* One form mainly exist in Acidic medium and other in Alkaline medium.

phenolpthalein (w. Acid)

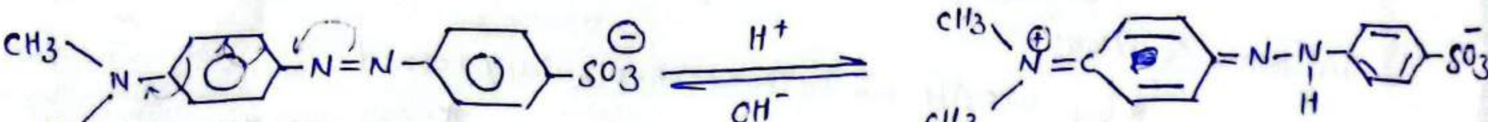
- ~~Its benzied~~
- It gives benzenoid form in Acidic medium
  colourless
- It gives Quinonoid form in Alkaline Medium
  ↳ pink colour



Benzenoid form (colourless) | (Quinonoid form) (pink)

Methyl orange:

- It gives the Quinonoid form in Acidic solution
  ↳ Red
- It gives the Benzenoid form in Basic solution
  ↳ yellow



Benzenoid form (yellow) | Quinonoid form (Red)

Types of Acid-Base Titration

(i) Strong Acid + Strong Base Titration:

($HCl + NaOH$)

- Equivalence point lies in the pH range of 4–10
- So suitable indicators are phenolpthalein (8.3–10) & Methyle Red, Methyl orange

phenolpthalein → Most commonly used

(ii) Weak Acid + Strong Base:

($CH_3COOH + NaOH$)

∴ Equivalence point = B/W 7.5–10 OR >7

7.5–10 → transition Range of indicator

So, suitable indicator is phenolpthaleine pH=(8.3–10)

(iii) Weak Base + Strong Acid:

↳ phenolpthalene not used ✗

($NH_4OH + HCl$)

∴ Equivalence point B/W 4–7

- Suitable indicator = Methyl orange OR methyl Red

Methyl orange → (3.2–4.5) → most commonly used

methyl Red → (4.2–6.3)

(iv) Weak Acid + Weak Base:

($CH_3COOH + NH_4OH$)

Equivalence point at ~7 (6.5–7.5)

↓

But no sharp change in pH is observed

↓

So no simple indicator is used

B) Redox-Titrations:

Oxidemetry

To determine the strength of Reducing agent by titration with a standard solution of an oxidizing agent ↓(Biurette)

Reductimetry

To determine the strength of an oxi Agent by standard solution of Reducing Agent. ↓(Biurette)

TYPES OF Redox-Titrations:

(i) permagnometry: ($KMnO_4$ - titration)

- potassium permangnate is taken as a Standard
- Taken in the biurette.
- $KMnO_4$ itself indicator, so no need to the indicator
- End point ⟶ light pink

$$2KMnO_4 + 5\begin{matrix}COOH\\|\\COOH\end{matrix}\cdot 2H_2O + 3H_2SO_4\,(dil)$$

$$\downarrow$$

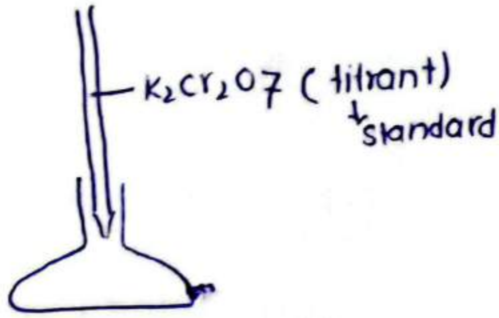
$$K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O$$

NOTE

- in this titration, we use dil. H_2SO_4 not the Nitric Acid & HCl B/C
- Nitric Acid itself oxidizing Agent → so no need to this
- If HCl used, it react with $KMnO_4$ & produce chlorine (oxidizing Agent) → so we avoid from this.

(ii) Dichrometry: ($K_2Cr_2O_7$ - Titration) → oxidizing Agent

- $K_2Cr_2O_7$ is weak oxi. Agent than $KMnO_4$, still widely used in Redox titrations
- It is available in high purity and highly stable



★ Dichromate ions (Cr-VI) reduces to chromium(III) ions in this titration

★ Brucine is Also used as an indicator.

$$K_2Cr_2O_7 + 6Fe(NH_4)_2(SO_4)_2 + 7H_2SO_4$$
$$\downarrow$$
$$3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 6(NH_4)_2SO_4 + 7H_2O$$

oxidation ($Fe^{2+} \rightarrow Fe^{3+}$)

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(+6) Reduction ($Cr_2O_7^{2-} \rightarrow Cr^{3+}$)

INDICATORS

Also some others 3 → indicators can be used in Dichrometery.

1. Diphenyl amine
2. Diphenyl Benzedine
3. Diphenyl amine sulfonate

} Green (with iron) to violet (END point)

(iii) Iodine-titration:

- Iodimetry → (Direct Titration)
- Iodometry → (indirect titration)

Iodimetry: (Direct Titration)

It is a redox-titration. Iodine (I_2) solution act as an oxidizing agent can be titrated against sod. thiosulphate soln (Red. Agent)

indicator = starch

End point = Blue to colourless

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + NaI$$

I_2 ↓ (oxi. Agent) $Na_2S_2O_3$ ↓ (R. Agent)

Iodometry: (Indirect Titration)

- In Iodometric titration, an oxidizing Agent is Allowed to react with excess of KI in neutral or Acidic medium to liberate Free Iodine.
- Liberated free Iodine is titrated against a standard solution $Na_2S_2O_3$ (Red. Agent)

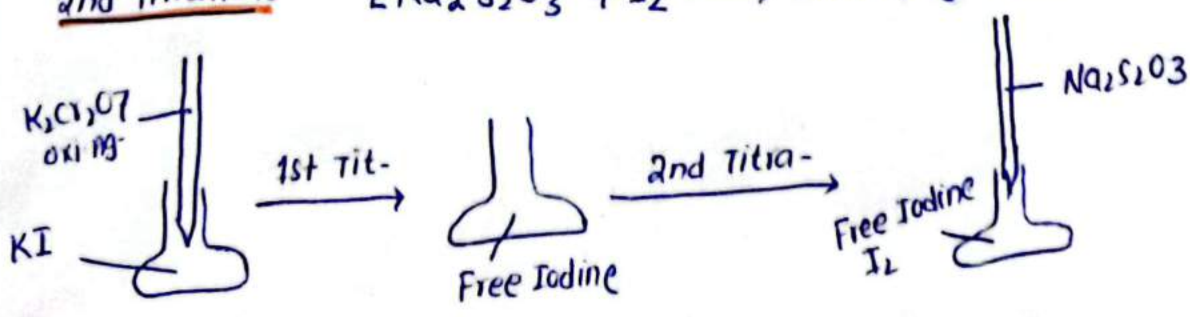
Used oxidizing Agent: $K_2Cr_2O_7$, $KMnO_4$, H_2O_2, Br_2, Cl_2
↓ For Liberation of I_2

Starch indicator

1st Titration:

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4H_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$$

2nd titration: $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$



c) Precipitation titrations:

Two types of Indicators:
- coloured precipitates
- Adsorption indicators

Also Called ↳ **Argentometric titrations**

Titrant reacts with the Analyte & Forms insoluble precipitates

(i) Mohar's Method: → Given by Freidric Mohar

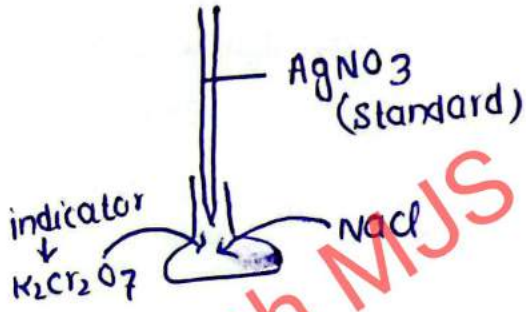
↳ Analysis of chloride by using $AgNO_3$ as a standard solution.

PH = Neutral

indicator = $K_2Cr_2O_7$

$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + NaNO_3$

(white ppt) (primary ppt)



$AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4\downarrow + KNO_3$

K_2CrO_4 ↓ Soluble chromate salt act as indicator.

Ag_2CrO_4 (Reddish brown) ↓ ppt (2^o-ppt)

(ii) Volhard Method: → coloured precipitate indicator

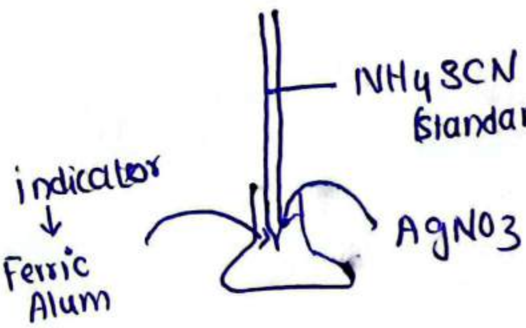
in this method $AgNO_3$ is used as an Analyte (titrand)

PH = Acidic b/c in Basic Medium Ferric Alum will be hydrolyzed

indicator = Ferric Alum

$AgNO_3 + NH_4SCN \longrightarrow AgSCN + NH_4NO_3$

white (ppt)



$NH_4SCN + Fe(SCN) \longrightarrow$ Reddish yellow ppt

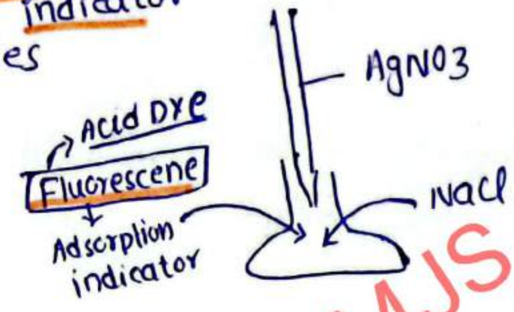
↓

(end point)

(iii) Fajan's Method: → Adsorption indicator

↳ Analysis of chlorides

indicator Adsorbed on the surface of precipitates & change the colour of precipitates



$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$
(white ppt)

Fluorescene Adsorb on white ppt of AgCl & change its colour to pink → indicates the end point.

Imp Note:

Argentometric Titration (Argentometry → derived from a Latin word Argentum, mean silver, it involves the formation of silver ion so called Argentometry.

Mohar's, Fajan's & volhard's → these are Argentometric titrations

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D) Complexometric titrations:

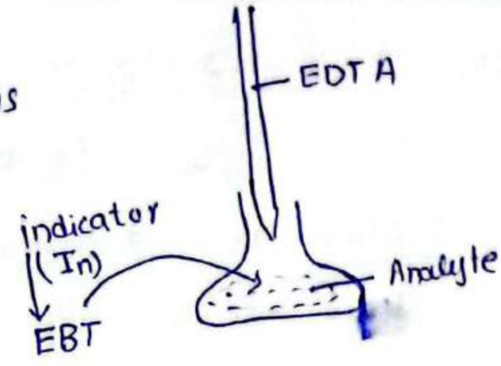
- Complexometric titrations rely on the formation of a complex B/W the Analyte & titrant.
- The Equivalent point is determined by metal indicator

TYPES

- Direct titration
- indirect titration
- Replacement titration
- Back Titration.

General Equation / Principle

Indicator (EBT) bind with metal ions loosely while EDTA binds with metal ions strongly, so when All metal ions bounded to EDTA, EBT Remains Free in The sample & solution turns Blue.



let $MgIn^- + H_2Y^{2-} \longrightarrow MgY^{2-} + HIn^{2-} + H^{+}$

(Red) — $MgIn^-$; (colourless) ↓ (EDTA) — H_2Y^{2-}; (Blue) — HIn^{2-}

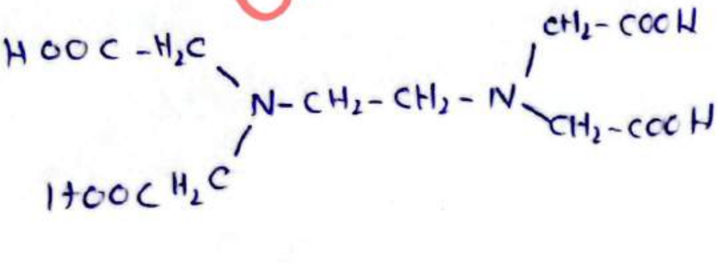
pH Range = 0—12
↓
EDTA Titration

(i) Direct titration:

↳ Most commonly used

- This is the direct determination of metal ion by Adding standard (EDTA) → titrant to the Sample solution.
  - some time solution is precipitated at Basic pH so we add the Buffer to maintain the pH For Example;
  - Some Auxiliary complexing Agent such as tartarate can be Added to prevent the precipitation of the hydroxide of Metal ion
  - Cu^{2+}, Ni^{2+}, Zn^{2+} can be determined by Direct titration.

EDTA



(ii) Indirect titration:

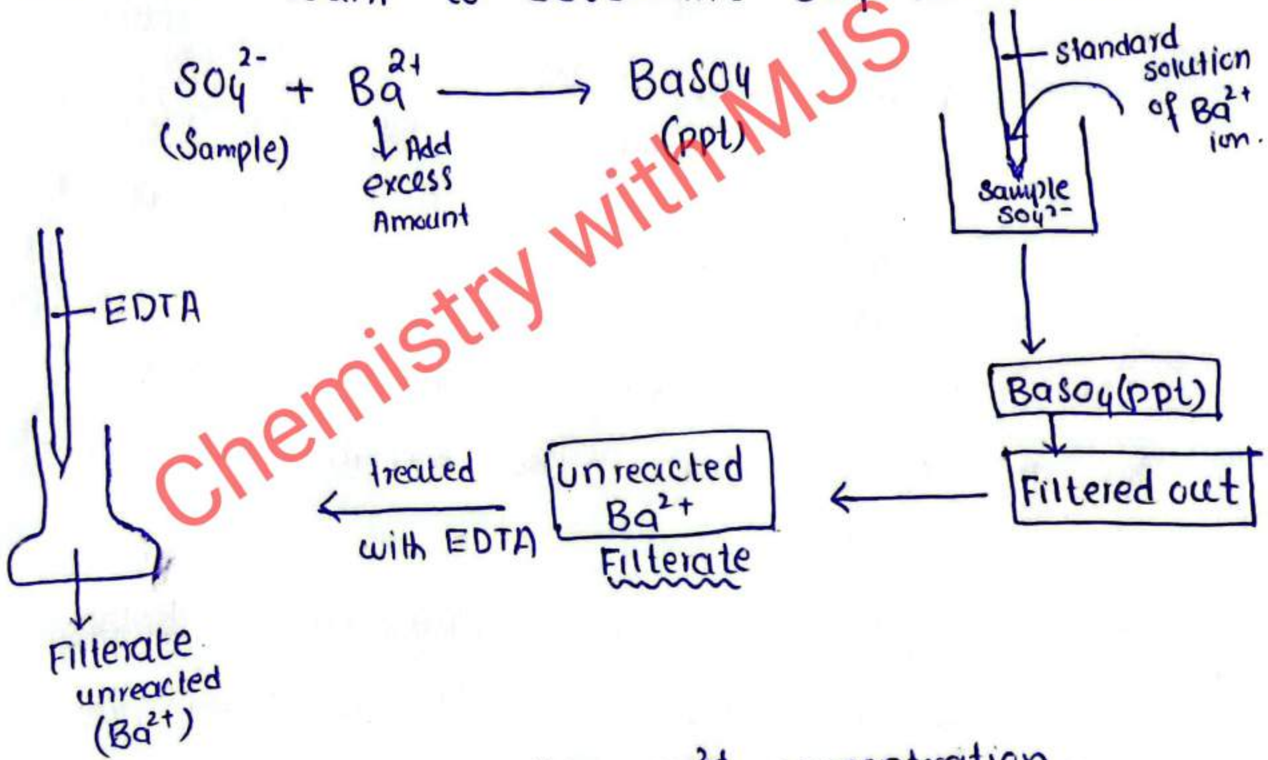
This method is used to determine the ions such as halides, phosphates, & sulphates that do not form complex with EDTA.
B/C These ions have -vely charged & EDTA also donar.

Example: How to Quantify?

Let we want to determine SO_4^{2-} ion in solution.

$$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4$$

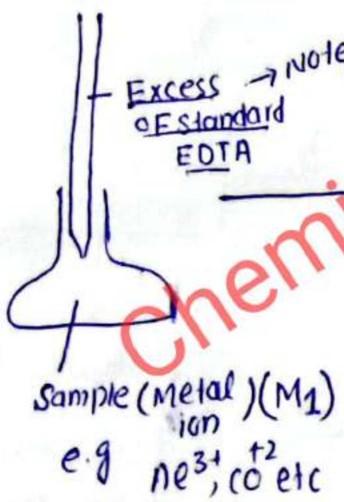
(Sample) ↓ Add excess Amount (ppt)



* Thus we determine the Ba^{2+} concentration
* we know Ba^{2+} & SO_4^{2-} are in the same moles Ratio. thus in this way we determine the Amount of SO_4^{2-} ions present in the sample solution called indirect method.

(iii) Back titration:

- Back titration is used for such type of ions, which makes complex with EDTA but have no sharp end point.
- In this method, an excess of standard EDTA (→ Addition EDTA After end point) is added to the sample solution of metal ion.
- The Resulting solution will contain unreacted EDTA which is then back titrated with Standard metal ion solution in the presence of indicator.
  - ↳ Having sharp End point. e.g $ZnCl_2$, $ZnSO_4$, $MgCl_2$, $MgSO_4$ — Sharp End point
- Al^{3+}, Co^{+2}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Ni^{+2} → no sharp end points so estimated by Back titration.



→ [Metal-EDTA complex M_1-EDTA + unreacted Standard EDTA (→ Extra/Additional)]

↓ titrated against standard Metal ion M_2 e.g $ZnCl_2$, $MgCl_2$

[Metal-EDTA complex M_2-EDTA]

↳ Note the volume USED, Let 1·8 mL used

Let initial volume Added = 12mL

volume used After 2nd titration = 1·8mL

Actually Volume Required to make complex with M1 = 12 − 1·8 = 10·2mL → Some Estimate

iv) Replacement titration:

Also called Substitution OR Displacement

- This is used for such type of metals whose end point can not be determined exactly.
- Generall, used for Ca^{2+} ions.
- In this method weak EDTA complex of another metal ion (M_2) is added to the solution of metal ion (M_1) to be determined.
  - Mg-EDTA & Zn-EDTA → Generally weak EDTA complex
- Weaker EDTA complex is replaced with stronger EDTA complex.
- The equivalent amount of M_2 freed from the weaker complex can be treated with standard EDTA solution.

جتنے Zn^{2+} / Mg^{2+} فری ہوتے ہیں۔
اتنے Ca^{2+} ← EDTA کے
ساتھ Bond بناتے ہیں۔ so.
جتنی Amount (M_2) کی calculate
ہو گی اتنی ہی M_1 کی ہو گی - اور Sample
estimate ہو جائے گا -

: indicators used in complexometric titration:

1. Eriochrome Black T:

When metal ions form complex with EDTA colour shifts from Blue to wine Red

2. Murexide:

purple to green colour

3. Calmagite: (wine Red)

wine Red to Blue

: some Natural indicators:

Turmeric:

in Basic solutions & yellow ~~to Red~~)
↓ Red colour ↳ Acidic solution

China Rose:

Acidic solution (Dark pink

Basic (Green)

Natural indicator { Red cabbage, Grape Juice, curry powder, cherries, beetroots, onion, tomato

universal indicator: (pH indicator)

It is a mixture of indicators which give different colours at different pH value of entire scale.

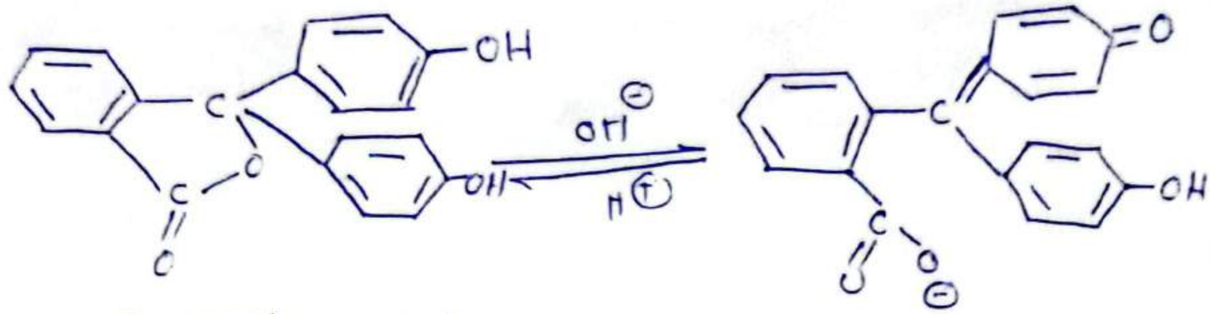
★ common indicators → cannot give us the strength of Acid & Base, so we need a universal indicator.

★ in Acidic Medium → Red, orange, yellow colour

★ In Basic Medium → Blue, violet or purple.

: IMPORTANT INDICATORS & Structures:

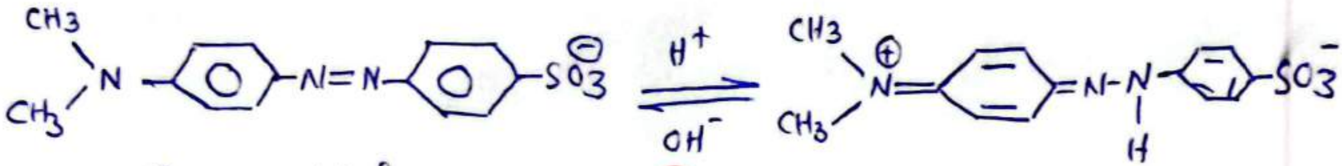
Phenolphthaleine



Benzenoid Form (colourless)

Quinonoid Form (pink)

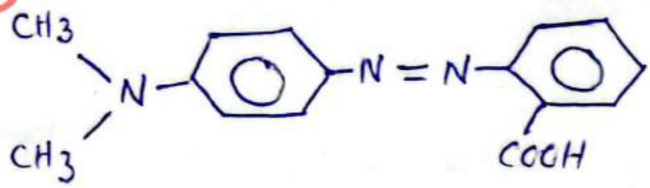
Methyl orange:



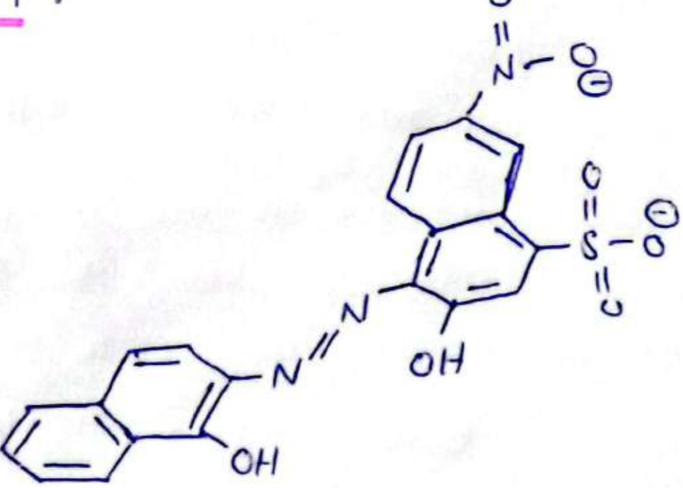
Benzenoid form (yellow)

Quinonoid form (Red)

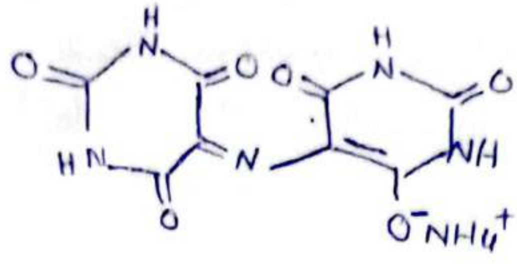
Methyl Red:



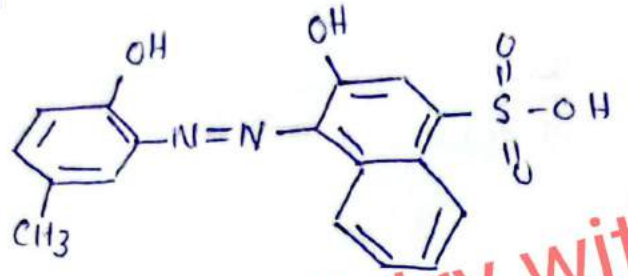
EBT :



Murexide:



Calmagite:



∴ Some others important TYPES OF Titrations

★ Coulometric titration:

- It measures the Quantity of electricity (I) required to complete a reaction/electrolyze the substance
- Total charge passed during the titration, used to determine the quantity of substance/Analyte/titrand
- Titrant is generated electrochemically
- We use titration cell with 3 electrodes working, Reference & counter electrode.

  voltage/potential is applied on working electrode

Applying current ← $I \propto$ Amount of titrant produced

(I = passing through the cell)

End point:

Monitor the current passing through the cell. The end point is reached when the amount of titrant generated is stochiometrically equalent to the Analyte.

Total charge is Recorded

~~Columb~~ Faraday's law is used;

$$n = \frac{Q}{F}$$

n → moles of titrant

F → Faraday constant.

★ Amperometric titration:

↳ It measure the current produced in Reaction while in coulometric current is Applied.

produced current ∝ Amount of Analyte

★ Karl Fischer titration:

↳ It is a type of coulometric titration.

- specifically used to measure/determine the amount of water in a sample
- commonly this is used in industries where moisture levels are critical such as pharmaceuticals, petroleum & Food production.

principle:
Titration Based on reaction b/w Iodine & SO_2. water reacts with iodine & SO_2 to form SO_3 & HI. End point is reached when all water consumed.

BEST OF LUCK
MJS