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UNIT-III

- **Precipitation titrations**: Mohr's method, Volhard's, Modified Volhard's, Fajans method, estimation of sodium chloride.
- **Complexometric titration**: Classification, metal ion indicators, masking and demasking reagents, estimation of Magnesium sulphate, and calcium gluconate.
- **Gravimetry**: Principle and steps involved in gravimetric analysis. Purity of the precipitate: co-precipitation and post precipitation, Estimation of barium sulphate.

- Basic Principles,methods and application of diazotisation titration.

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GRAVIMETRIC ANALYSIS

- Theodore W. Richard first proposed the technique of gravimetric analysis for the determination of chlorine and silver ions.
- Gravimetric analysis is a process of precipitation, isolation and weighing of the isolated product.
- It is mainly based on the measurement of the analyte.
- For example, in progesterone injection, the content of progesterone is quantitatively determined by this method.

Principle

It is based on the principle that it involve the conversion of ions/element to its pure form by precipitation reaction, which can be easily weigh and quantify.

The separation of the sample is carried out by the following principle methods:

1. **Precipitation Method:** In this method the sample is completely precipitated.
2. **Volatilization Method:** In this method the sample is completely volatilized.
3. **Electro-analytical Methods:** In this method the sample deposited on an electrode.
4. **Extraction and chromatographic Methods:** Here, the sample is separated from the matrix after precipitation.

Gravimetric Analysis

The following steps are needed for gravimetric analysis:

1. Preparation of the sample solution.
2. Separation of the desired constituent as precipitate.
3. Weighing of the isolated constituent.
4. Calculating the amount of the particular constituent in sample from the observed weight.

Steps involved in Gravimetry

It involves the several steps:-

1. Sampling-preparation of solution
2. Precipitation
3. Digestion/ Ostwald ripening
4. Filteration
5. Washing
6. Drying/ Ignition
7. Weighing
8. Calculation

1. Sampling

- Firstly we have to prepare solution by dissolving of substance in a solvent in which it dissolved and reaction take place.
- The suitable substance/ sample is withdrawn form the bulk material.

Eg:- $BaCl_2$ + conc. H_2SO_4 ⟶ $BaSO_4$ + 2HCl↓

(barium chloride)

(barium sulphate ppt.)

2. Precipitation

- Now, for preparation of precipitate, we have to add precipitating reagent for make a precipitate of substance in a solution.
- Precipitation is a process of formation of a solid in a solution, when a chemical reaction take place.
- Precipitation is necessary to convert substance into its pure form.

Eg:- dil. H_2SO_4

3. Digestion/ Ostwald ripening

- It is a process, in which the smaller particles of precipitate is converted into larger one by allowing a precipitate to stand in the presence of mother liquor.
- Mother liquor is a solution that contain precipitate.
- In this precipitate is allowed to stand for 12-24hr at room temperature.
- To increase the rate of digestion, temperature is raised.

5. Washing

Now, during this process, precipitate are contaminated with some impurities. So, we have to wash that precipitate by using warm water or with suitable solvent for remove the impurities from the precipitate.

6. Drying

- Drying or ignition is used to remove the water from the precipitate which occurs during washing.
- The drying can be done by heating at 110^{o}C to 120^{o}V for 1 to 2hr.
- Ignition can be done at much higher temperature which is usually required if precipitate must be converted to a more suitable form for weighing.

7. Weighing

After drying, take residue (precipitate) in room temperature and weigh accurately on analytical balance.

8. Calculation

$$\text{\% purity of substance} = \frac{E \times S \times 100}{W}$$

Where,

E = weight of residue (precipitate)

S = Gravimetric factor

W = weight of sample

Advantage of Gravimetric Titration

a. No Calibration required
b. No instrumental error.
c. Simple and cheap. They do not require expensive equipment.
d. Filtrate can be examined for completion of reaction.
e. Ppt. dissolve (when we maintain pH)
f. Analysis can be done accurately.

Disadvantage

Time consuming

Purity Of Precipitate

When the precipitate is separate out from the solution, it is not always pure i.e. the precipitate is contaminated with some amount of impurities.

These amount of impurities depends upon the nature and condition of precipitate.

It is mainly of two types:-

1. Co-precipitation
2. Post-precipitation

Co-precipitation

Simmentaneously precipitation of other ion/radicle with desired one.

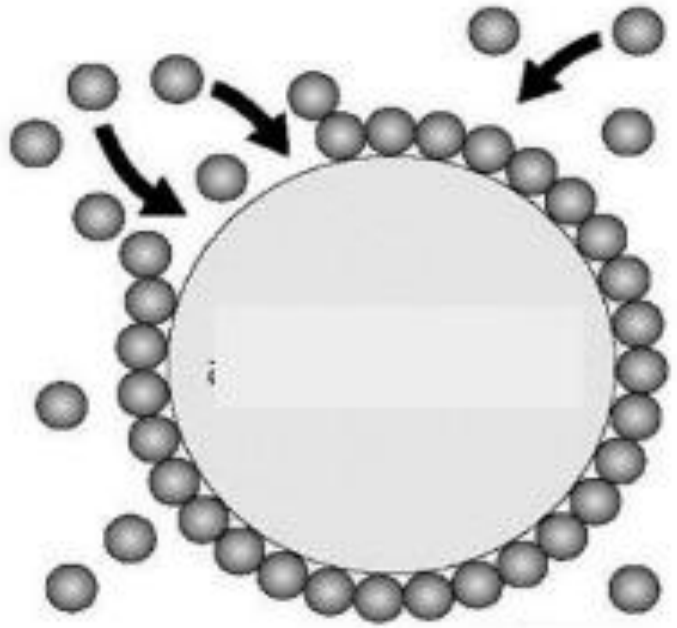
It is a condition/process in which the precipitate is contaminated during gravimetry by those substance which are soluble in mother liquor.

It is mainly of four types:-

1. Surface adsorption
2. Mixed crystal formation
3. Occlusion
4. Mechanical entrapment

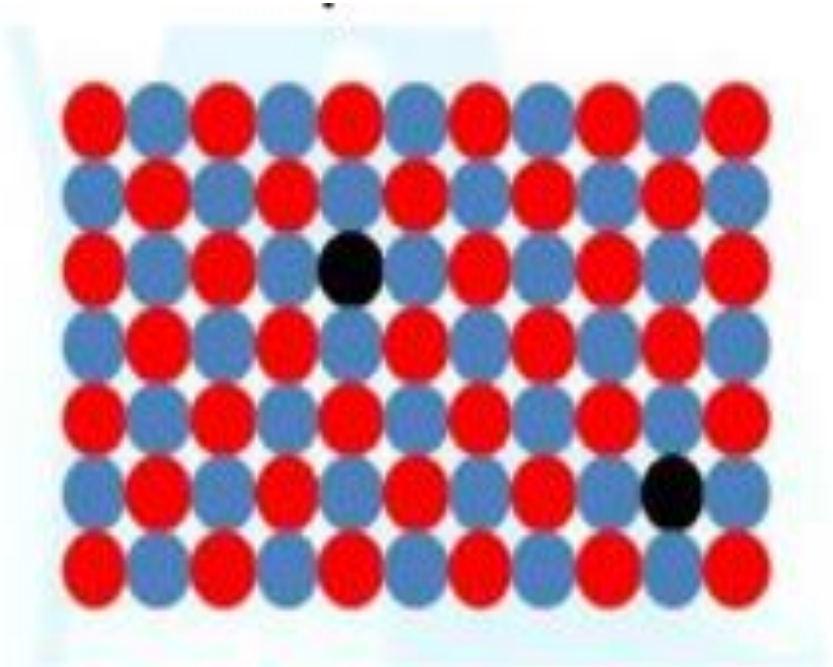
1. Surface Adsorption

- Adsorption is a common source of co-precipitation.
- It causes significant contamination of the precipitates.
- Adsorption does not occur in crystalline solids.
- The adsorption process can be overcome by the desorption.
- Desorption is the process in which the adsorbed ion from the surface of the precipitate enter into the solution.



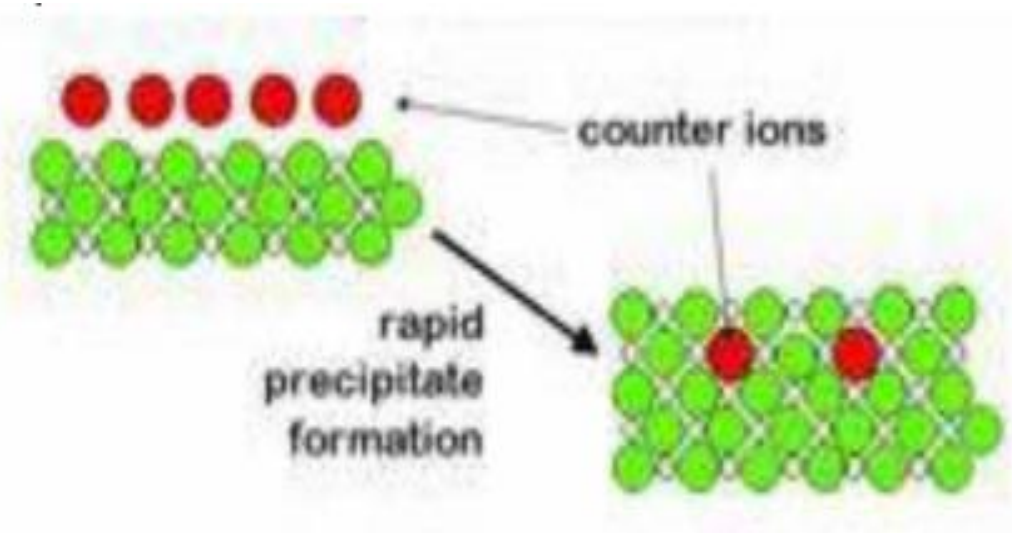
2. Mixed Crystal Formation

- It is troublesome phenomenon, in which one of the ions in the crystal lattice of the solid is replaced by an ion of another element.
- If such change should occur, then both the ions must have the same charge and their sizes must not differ by more than about 5%.



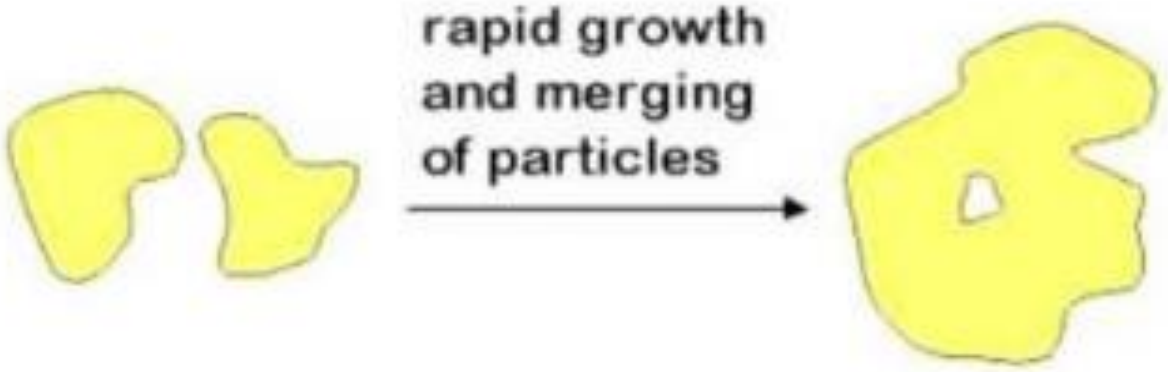
3. Occlusion

- Occlusion is a type of co-precipitation in which a compound is trapped within a pocket formed during rapid crystal growth, material that is not a part of the crystal structure is trapped within a crystal.
- When crystal growth occurs rapidly then the counter ions (impurities) do not have time to escape from the surface.



4. Mechanical Entrapment

- Mechanical entrapment occurs when the crystals lie close together during growth.
- Several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.
- Mechanical entrapment is low when the rate of precipitate formation is slow.



Post Precipitation

- It is a condition/ process in which the impurities get adsorbed on the surface of precipitate after its formation.
- It mainly occurs when the precipitate is allow to stand in presence of mother liquor.

Estimation of Barium Sulphate

In gravimetry analysis, the amount of sulphate is estimated quantitatively as barium sulphate.

Molecular formula:- $BaSO_4$

Molecular weight:- 233.4g/mol

Principle

When dilute sulphuric acid (H_2SO_4) is added to the dilute solution of barium chloride ($BaCl_2$), a white precipitate of barium sulphate ($BaSO_4$) is formed.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

Procedure

1. Pipette out 25ml of $BaCl_2$ solution into 500ml beaker.
2. Add 0.5ml of conc. H_2SO_4 in a solution and make volume upto 100ml with distilled water.
3. Now, heat the solution and make solution hot.
4. Add dil. H_2SO_4 dropwise in a solution until the precipitate is not separated out.
5. Now, filtered washed and dried it.

Calculation:

$$\%\text{purity of substance} = \frac{E \times S \times 100}{W}$$

Applications of Gravimetry

- Used in analysis of standard solutions.
- Used in analysis requiring accuracy i.e. it is time consuming but show better accuracy (accurate result).
- Used in determination of

➢ Chloride as silver chloride

➢ Lead as chromate etc.…

Diazotization Titration

These are those titration which are used for the determination of 1° aromatic amines.

In this reaction, primary aromatic amines are reacts with sodium nitrite in acidic medium to form diazonium salt.

[Also known as Nitrite/ sodium nitrite titration].

This reaction is carried out in ice bath at a temp. 0°C - 5°C (approx. 15°C)

Principle

This first involved is addition of sodium nitrate to hydrochloric acid cause formation of nitrous acid.

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

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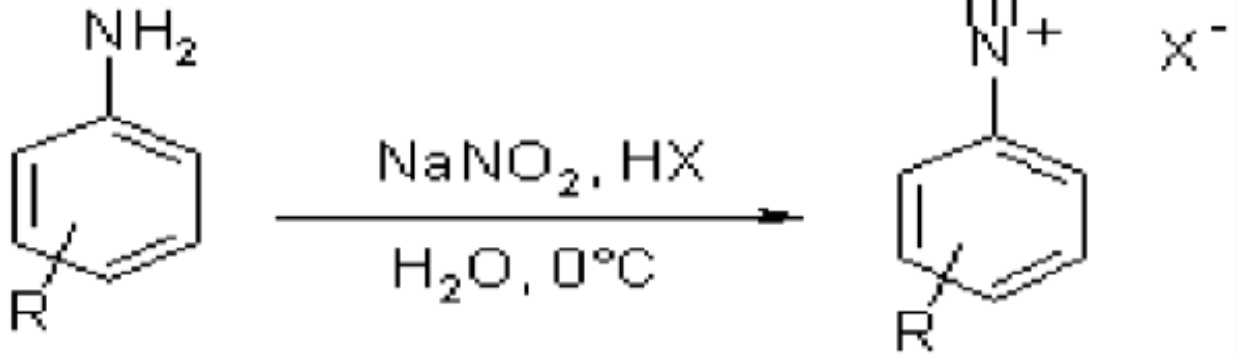
- This nitrous acid diazotizes the aromatic amino group

$$R-NH_2 + NaNO_2 + HCl \longrightarrow R-N^+\equiv N-Cl^- + NaCl + ..$$

- Diazonium salt is formed by
- diazotization of nitrous acid and
- Aromatic primary amino group.



- Direct titration with nitrous acid and aromatic primary amine is not possible because nitrous acid is unstable and formed in-situ.
- Nitrous acid is unstable so it readily breaks into nitric oxide and nitrogen dioxide.

$$2\,HNO_2 \longrightarrow NO + NO_2 + H_2O$$

- After the end point, excess nitrous acid formed is shown by instant formation of blue colour with starch iodide paper.

$$KI + HCl \longrightarrow HI + KCl$$

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

$$2HI + 2HONO \longrightarrow I_2\uparrow + 2NO + 2H_2O$$

- Starch iodide paper is prepared by immersing a filter paper in starch mucilage and potassium iodide solution.
- The iodine formed reacts with starch mucilage to give the blue colour.

$$I_2 + \text{Starch} \longrightarrow \text{blue color (end point)}$$

- The end point can also be determined by dead stop end point and potentiometric technique.

IMPORTANT NOTE

- It is important to check the acidity at the end of the titration.
- If there is no excess of acid present in the solution, starch-iodide paper will not detect excess HNO_2 and so will not indicate the end point.

END POINT

1. **External Indicator:-** This is starch iodide paper. The end point is marked by the formation of a blue color with starch iodide paper, which is prepared by dipping the filter paper in the starch mucilage and potassium iodide solution.
2. **Potentiometrically Indicator:-** It is used as electrometric method. In this, end point is determined with the help of instrument potentiometer.

Methods

1. **Direct Method:-** In this, the amino group containing drug with the acid solution, then the resulting solution is immersed in ice water bath (0-5^{o}C), which then titrated with sodium nitrite solution and the end point is determined by external indicator.
2. **Indirect Method:-** In this, the nitrous acid is added to the titration in excess amount, which is back titrated with other appropriate titrant. This method is used for insoluble diazonium salts.
3. **Other Method:-** Used for those compound in which oxide group are present, which is not give sharp end point with other two methods.

APPLICATIONS

- Assay of sulpha drugs containing free amino group
- E.g.:- Sulphacetamide sodium, Sulphadoxine, Sulphadiazine, Sulphaguanidine.
- Assay of drugs like benzocaine, dapsone, procaine HCl, procainamide HCl.