



Unit-III

Chapter-3

GRAVIMETRIC ANALYSIS

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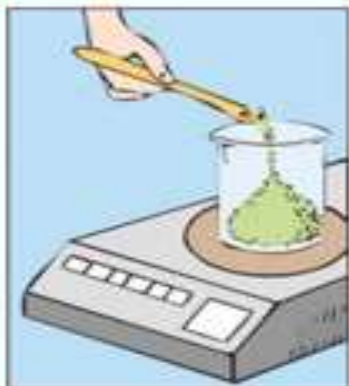
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Gravimetric Analysis

- It is quantitative analysis in which the end product is weighed and from that weight composition of analyte is determined.
- Hence gravimetric analysis is based upon the measurement of the weight of a substance of known composition which is chemically related to the analyte.

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.



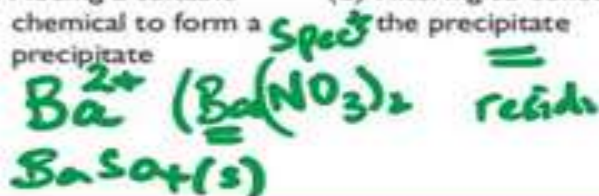
(a) Weighing the sample to be analysed



(b) Dissolving this sample in water



(c) Adding a suitable chemical to form a precipitate



(d) Filtering to collect the precipitate



(e) Repeated drying and weighing until a constant mass of precipitate is obtained

Principle:

The principle involved in this method is that the sample is dissolved in a solvent and then the precipitating agent is added. The resulting precipitate is filtered dried and weighed.

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

- Precipitation method: In this method the sample is completely precipitated.
- Volatilization method: In this method the sample is completely volatilized.
- Electro-analytical methods: In this method the sample deposited on an electrode.
- Extraction and chromatographic methods: Here, the sample is separated from the matrix after precipitation.

The following steps are needed for gravimetric analysis:

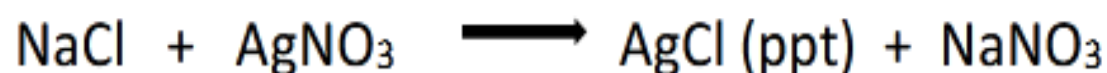
1. Preparation of the sample solution.
2. Separation of the desired constituent as precipitate.
3. Weighing of the isolated constituent.
4. Calculating the amount of the particular constituent in sample from the observed weight.



Theory:

The procedure is nothing but the sample is dissolved in the appropriate solvent and then the excess amount of the precipitating agent is added. Followed by the formation of the precipitate, it is filtered through the filter paper. The obtained precipitate is commonly known as residue. This residue is dried and weighed.

For example, soluble sodium chloride is estimated by converting them into insoluble silver chloride by adding silver nitrate reagent. The precipitate of the silver chloride is isolated, purified and weighed.

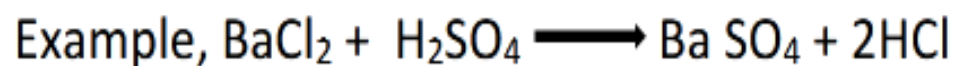


The principle and theory involved in the gravimetric analysis are the following:

- I. Law of Mass Action and reversible reaction.
- II. Principle of solubility product.
- III. Common ion effect.

Law of mass action:

The law of mass action states that the rate of reaction is directly proportional to the concentrations of the reacting substances.



Rate of Forward reaction,

$$\text{Rate} = [\text{BaCl}_2] [\text{H}_2\text{SO}_4] K$$

K = ionisation constant.

Principle of solubility product

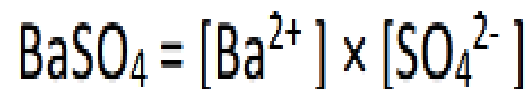
This is mainly useful for the difficultly soluble salts, precipitation and dissolution of the substances. The solubility product is defined as the product obtained by the dissociation of the practically insoluble salts.



$$\text{BaSO}_4 = [\text{Ba}^{2+}] \times [\text{SO}_4^{2-}]$$

Common ion effect

When BaCl is added to the HSO₄, the sulphate ion exceeds and the barium sulphate is precipitated.



At the equilibrium, the barium ions concentration is equal to that of the sulphate ion concentration. The supernatant liquid contains a saturated solution of BaSO₄. The equilibrium gives an idea of the ionisation constant and is written as,

$$\frac{[\text{Ba}^{2+}] [\text{SO}_4^{2-}]}{[\text{BaSO}_4]} = K$$

Types of Gravimetric Analysis:

- I. **Precipitation Gravimetry:** This involves chemical precipitation of the constituents.
- II. **Volatilization Gravimetry:** In this method, the constituents are decomposed due to volatilization at a suitable temperature.
- III. **Electrogravimetry:** This involves the electrochemical reduction of the metal ions at the cathode and simultaneous deposition of the metal ions at the cathode
- IV. **Thermogravimetry:** In this type, the sample is heated and with the change in temperature changes in mass of the sample are recorded.

PRECIPITATION GRAVIMETRY

Introduction:

- ⊙ Precipitation method is a process of weighing an element or radical in the form of precipitates which is separated by filtration from solution.
- ⊙ Precipitation method is affected by some factors i.e..
 1. Precipitated compound must be convertible into a pure compound by ignition or by simple evaporation.
 2. Precipitated compound must be free from soluble impurities.
 3. Precipitated compound must be **insoluble in solution.**
 4. Precipitated compound must be readily separated from the solution by **filtration process.**

Precipitates:

○ During this gravimetry precipitate is formed which of mainly three types.

1. Crystalline Precipitate: This precipitate is relatively pure and easily filterable.

2. Curdy Precipitate: This precipitate is colloidal particle size but are filterable.

3. Gelatinous Precipitate: This precipitate is flocculated colloids. The particle size is smaller than curdy precipitate and difficult to filter.

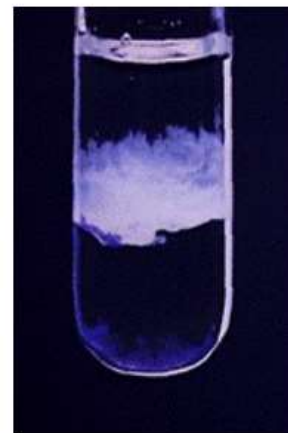


Crystalline



AgCl - curdy white precipitate

Curdy



Gelatinous



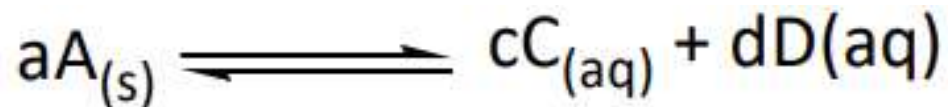
Properties of precipitates:

- The precipitate formed should be insoluble.
- The physical nature of the precipitate should be such that it can be easily removed by filtration.
- The precipitate should be stable to atmospheric temperature.
- The precipitate should be convertible to pure compound.

Conditions for Precipitation:

- Precipitation is an ionic reaction of mixing of +ve ions of one substance and -ve ions of another substance to form a sparingly soluble substance.
- The completeness of a precipitate depends on equilibrium solubility of a precipitate.
- The solubility of any substance is defined as the amount of the substance dissolved in a solvent at a given temperature and is expressed in $\text{gram} / \text{dm}^3$ or mol / dm^3 .

- ◉ Solubility product is defined as the product of concentration of the constituent ions raised to the appropriate power depending on the number of ions present in a molecule of the compound. (Saturated solution)



$$K_{sp} = [C]^c [D]^d$$

- ◉ Both the solubility and solubility product are temperature dependent. If temperature is increases, solubility and solubility product is also increases.
- ◉ Most important condition for precipitation is that the ionic product (product of the concentration of the salt at any concentration) must be greater than the solubility product of the salt.

When,

Ionic product > Solubility product = Precipitate formation

Ionic product = Solubility product = Saturated solution

Ionic product < Solubility product = Unsaturated solution

Factors affecting the solubility, solubility products and completeness of a precipitates:

1. Common Ion Effect: Presence of an ion common with ions of the salt decreases the solubility of the salt. The solubility of the salt is less in presence of a common ion compared to pure water. This effect is known as the common ion effect.

2. Diverse Ion Effect: If the solubility of sparingly soluble salt increases in presence of foreign ions, that ions are not common to those of the salt. This effect is known as diverse ion effect or salt effect or activity effect.

Example: Solubility of BaSO_4 is increased by 70% in 0.1M solution of potassium nitrate than in water.

3. Temperature: Solubility of any salt increases with increase in temperature. The increase in solubility of two salts with increase in temperature may be different.

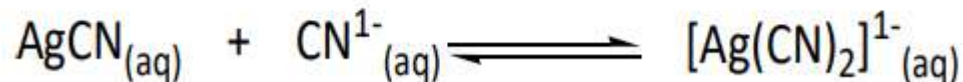
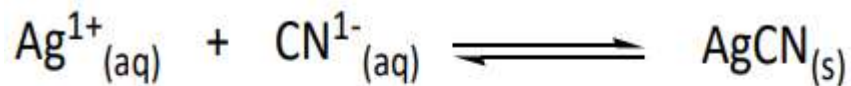
Example: Solubility of AgCl in water increases 12 times when temperature is increases from 273K to 383K. While at the same increase of temperature the solubility of BaSO_4 in water is doubled only.

4. pH: The solubility of substance depends on pH of the solution from which that is precipitated. The change in pH is brought by addition of strong acid or a base. If the salt is of strong acid or strong base type, then addition of acid or base will produce diverse ion effect. This increases the solubility to small extent. On the other hand, if the salt is of weak acid or weak base then solubility is increases to high extent.

Example: Consider a salt of weak acid, a strong acid is added to change pH. The hydrogen ion from the added strong acid react with anion of salt and form the weak undissociated acid, to maintain the solubility equilibrium more and more salt dissolves.

5. Complexation: In many cases precipitating agent itself may act as complexing agent dissolving the precipitate by converting it in to a complex.

Example: The cyanide ions act as precipitating agent for silver ions forming precipitate of AgCN. But the AgCN is dissolved in excess of the cyanide ions forming a complex $[\text{Ag}(\text{CN})_2]^{1-}$



6. Nature of the solvent: Polar solvents like water will always favour dissolution of the polar or ionic solute but nonpolar solvent not favour dissolution.

Example: Solubility of a salt like calcium sulphate in water can be decreased by addition of a less polar solvent like ethanol to it.

THE PRECIPITATION PROCESS

- i. Nucleation:** Collision of ions in supersaturated solution to yield primary nuclei.
- ii. Formation of Colloidal Particles:** Aggregation of ions around primary nuclei forming colloidal particles.
- iii. Growth of Colloidal Particles:** Growth of Colloidal particles to form particles which settle as precipitate.

Ions (10^{-1} nm)



Nucleation (10^1 to 1 nm)



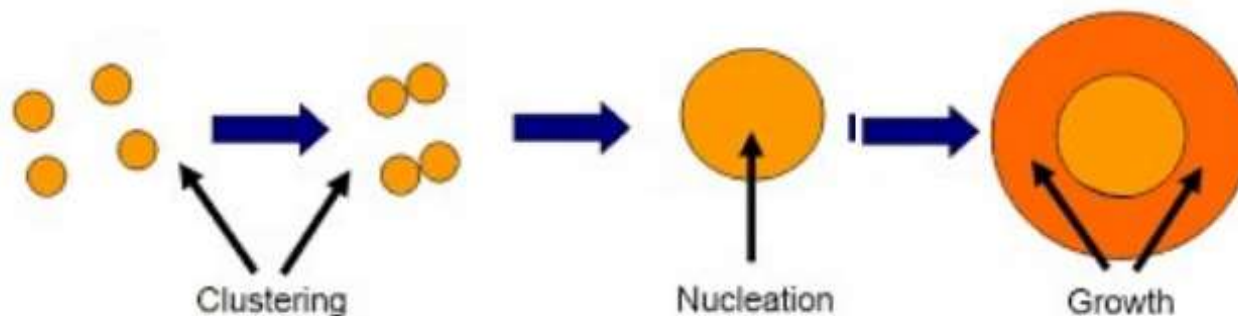
Colloidal particle (1 nm to 10^3 nm)



Precipitate ($> 10^3$ nm)

1. Nucleation:

- Precipitation is beginning with the attraction of ions towards each other due to electrostatic forces between them.
- This results in to formation of ion pairs.
- These ion pairs grow further by the addition of ions or ions pairs to form ion clusters.
- The ion pair and ion cluster formation takes place even when ionic concentration has not exceeded the solubility product of the substance which has to be precipitated.
- The ion clusters can be separated easily into ion pairs till they attain some minimum size known as critical size.
- Once the critical size is attained, the ion cluster becomes the nucleus (Nucleation) and continues to grow to form crystal.



There are two types of Nucleation process.

- i. Heterogenous Nucleation Process:** In this process nuclei formed by clustering of ions around another particle.
- ii. Homogenous Nucleation Process:** In this process nuclei formed by clustering of ions, by themselves and arranging in a definite pattern. According to Von Weimarn, if particle size is small the faster is precipitation. He found super saturation plays an important role in determining the particle size of a precipitate.

$$\text{Relative Supersaturation} = \frac{Q - S}{S}$$

Where,

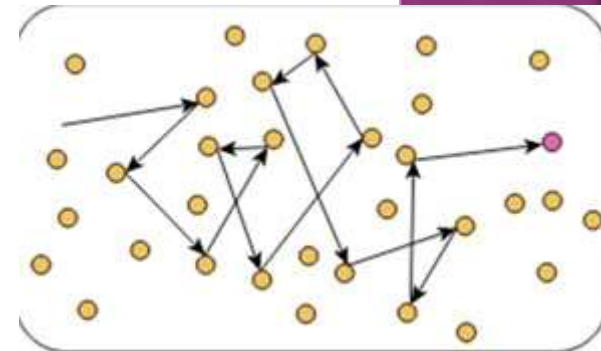
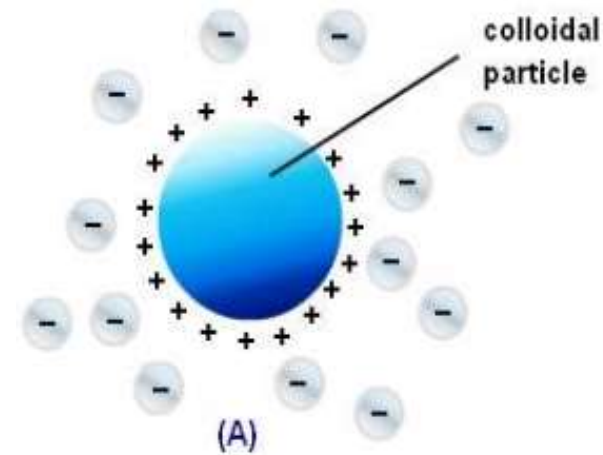
$Q - S$ = is the super saturation at the moment precipitation starts

Q = molar concentration of mixed reagents

S = molar solubility of a precipitate at equilibrium

2. Colloidal State:

- The colloidal state has particle size ranging from 1 nm to 10^3 nm.
- Charge on colloidal particles arises due to adsorption of ions on the surface of the catalyst.
- Due to charge, these particles migrate in an applied electrical field, and colloidal particles scatter light. The scattering effect is known as the Tyndall effect.
- Colloidal particles are involved in the random motion or zig-zag movement in a colloidal solution which is known as **Brownian movement**.
- These particles absorb ions from the solution which are present in large concentration in the solution.



- **Tyndall Effect (Reflection and light scattering)** : Tyndall effect is the ability of a colloid to scatter light. The beam of light can be seen through the colloid.



Impurities in the Analytical Precipitate:

- Once the precipitate is formed, it has to be treated as it can be contaminated.
- The contamination of a precipitate is due to two reasons:
 1. **Co-precipitation:** The phenomenon in which the impurity is soluble and it is precipitated along with the main precipitate causes the contamination of precipitate is known as co-precipitation.
 2. **Post- precipitation:** The phenomenon in which an impurity which occurs on the surface of the first precipitate after appreciable time is known as post-precipitation.

Co-Precipitation

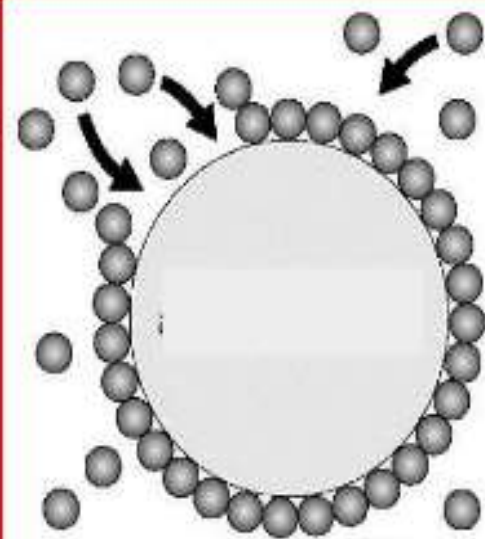
It is the simultaneous precipitation of more than one compound or substance from the solution. In gravimetric analysis, co-precipitation is a problem because undesired impurities often co-precipitate with the analyte, resulting in excess mass of the final product. This problem can be overcome by the digestion process.

There are four main mechanisms of co-precipitation

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

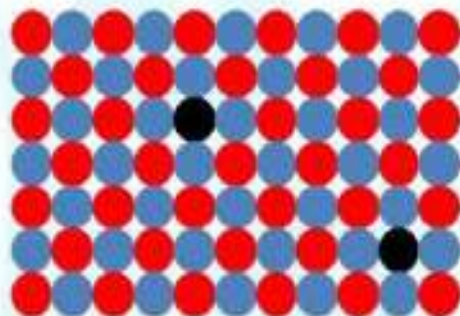
1. Surface adsorption

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.



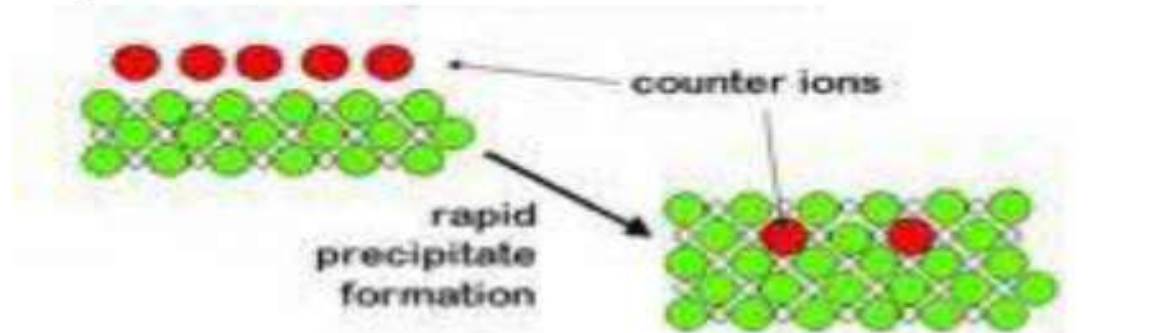
2. Mixed crystal formation

Is it 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%.



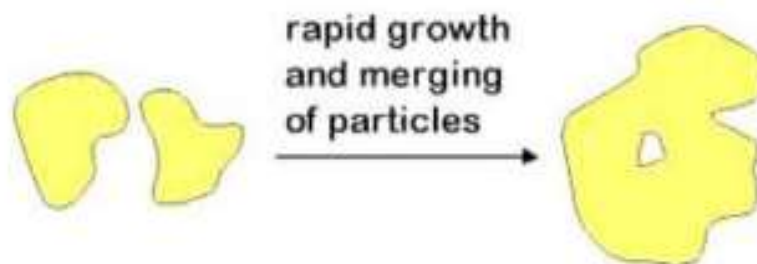
3. Occlusion

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 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. Hence, 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

Sometimes when the precipitate is allowed to stand in presence of mother liquor the second substance will form the precipitate with the precipitating reagent. The process by which an impurity is deposited after the precipitation of the desired substance is termed as post precipitation. Longer the precipitate remain in the mother liquor solution, greater is the chance for post precipitation.

Example : if Mg^{2+} is present as an impurity along with Ca^{2+} , then there during the synthesis of calcium oxalate, there are chances of the post precipitation of Magnesium oxalate. This can be avoided by maintaining a high pH.

Gravimetric Analysis



weigh sample



Add precipitating agent



Heat

Filter and dry



Calculations



JA Neron
Weigh precipitate

Steps Involved in Gravimetric Analysis

Gravimetric analysis is one of the few analytical methods that do not require standard solutions as the weight of the precipitate is the only important parameter in analyte determination.

The following steps should be followed for gravimetric procedure:

1. Preparation of the solution.
2. Precipitation.
3. Digestion of the precipitate.
4. Filtering and washing of the precipitate.
5. Drying and ignition.
6. Weighing and calculation.

PROCEDURE FOR GRAVIMETRIC ANALYSIS

Analyte (or) Sample

↓ (selectively convert)

Precipitate form (Insoluble form)

↓

Filtration (Separate the precipitate)

↓

Drying

↓

Igniting

↓

Weighing

↓

Calculations

1. Preparation of Sample:

- ⊙ Sample solution is prepared for the analysis; precipitation should be carried out in dilute solution(s).
- ⊙ Adjustment of the volume, appropriate pH and getting the desired properties of the solution for the precipitate is taken care in this step.

2. Precipitation:

- ⊙ This step requires addition of the precipitating agent in the form of solution to the sample solution. After addition of the first drop of the precipitating agent, super saturation occurs, and nucleation starts to occur, where molecules of precipitate aggregate together and forms a nucleus.

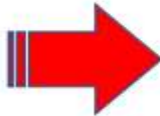
3. Digestion: (Ageing or Ostwald Ripening):

- ⊙ When the precipitation is carried out from the concentrated solution, the particles of precipitate (colloids) obtained have imperfect structure and size.
- ⊙ Such crystals are difficult to filter. This can be resolved by keeping such precipitate for digestion.

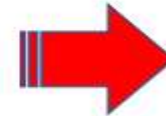
- ◉ Digestion is the process in which the precipitate is allowed to stand for an hour or more in contact with hot solution from which it is formed. During this process, smaller particles dissolve and the solution becomes saturated with larger particles.
- ◉ The dissolved particles get redeposited on larger particles.
- ◉ This increases the average particle size. This process is called digestion or ageing or Ostwald's ripening.
- ◉ As the particle size is increased, the surface area is decreased and hence the concentration of co-precipitated impurities adsorbed on precipitate is also decreased.
- ◉ The occluded impurities are also exposed to the solution during digestion and they pass into the solution.



Before Digestion



Digestion



After Digestion

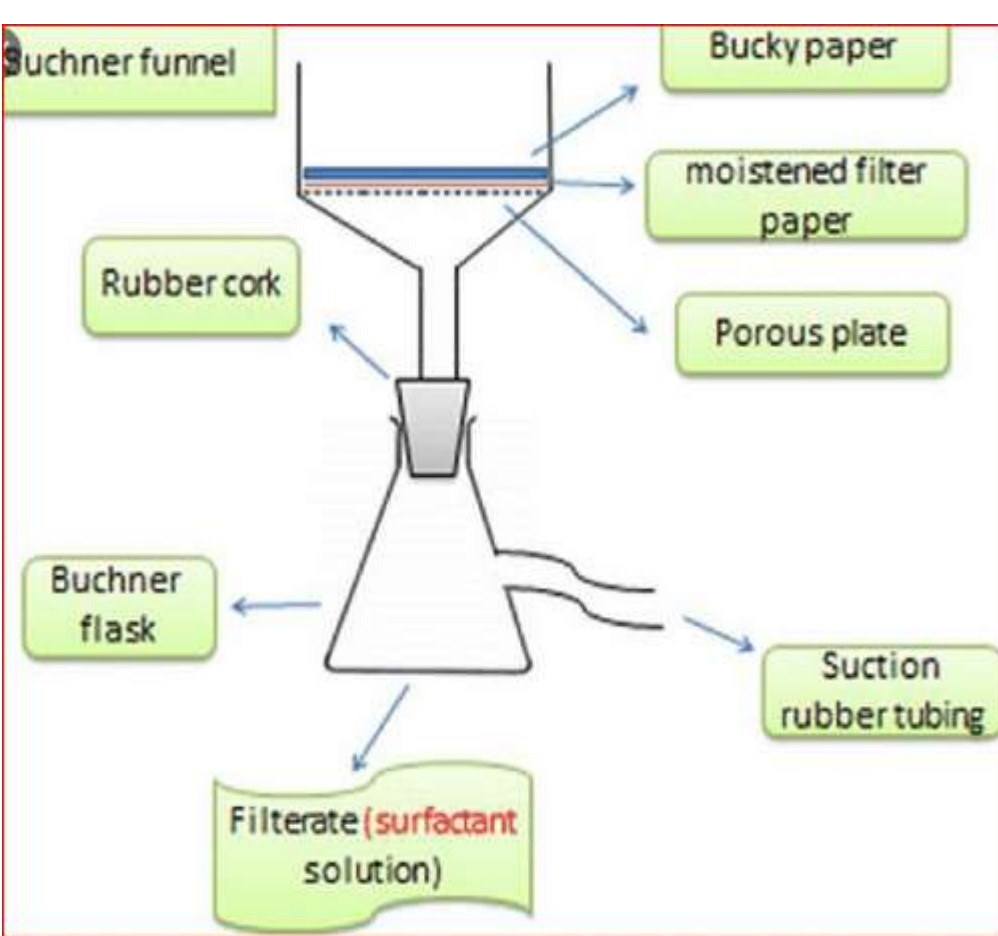
4. Filtration:

- Filtration is the separation of precipitate from the mother liquor. The main object of this is to obtain the precipitate free from solution. Filtration is carried out by two ways.
- Filtration by using Filter Paper: Whatman filter paper which is ash less is used for the filtration. Three qualities of filter papers are generally made, one for fine particles, second for average precipitate of medium sized particles and third for gelatinous and coarse particles. The precipitate collected on filter paper is further dried and ignited to a constant weight.



- ◉ Filtration by Counterpoise method: In this method, sintered glass crucible is used for the filtration. The sintered glass crucibles are made up of resistance glass and have a porous disc of sintered ground glass fused at the bottom of the crucible.
- ◉ During the filtration, a previously weighed sintered crucible is connected to vacuum pump and filtration is carried, precipitate is washed with appropriate wash solution. After filtration, the crucible with precipitate is dried in an electric oven at a constant temperature. Finally, the weight of crucible with precipitate is recorded from which weight of precipitate is obtained which used for further calculation.





5. Washing:

- ⦿ Most of precipitates are obtained in presence of one or more soluble compound or contaminants. As these are non-volatile at the temperature at which the precipitated is dried, it is necessary to wash the precipitate to remove such substance completely.
- ⦿ Characteristics of washing solution:
 - i. It should have no action on the precipitate but capacity to dissolve the impurity.
 - ii. It should not form any volatile or insoluble substance with precipitate
 - iii. It should be volatile at the temperature of drying of precipitate
- ⦿ Water is mostly used as a wash solution if precipitate is insoluble in water. If precipitate is soluble in water then an electrolyte containing common ion is added in water and then it is used as wash solution.

6. Drying and Ignition of Precipitate:

- ⦿ Heating of precipitate below 250°C is referred as drying. The purpose of drying and ignition of precipitate is to obtain a compound of known and constant composition.
- ⦿ During this drying, the water associated with the precipitate is also get remove.
- ⦿ The drying is depending on the way in which he filtration is carried out.
 - i. If the filtration is carried out in a sintered glass crucible then the drying will be done in an oven with the temperature range of 100 to 150°C and weighed to a constant weight.



ii. If the filtration is carried out with Whatman Filter paper then the filter paper along with the precipitate is dried on a cone with care that the filter paper does not charred in the process. The precipitate along with the filter paper is ignited to white ash in a crucible. The crucible is cooled to room temperature and then transferred to a desiccator and finally weighed to a constant weight.



7. Weighing and Calculations:

- Weight of analyze is calculated front the weight of precipitate. The weight of analyte in the sample is calculated by using Gravimetric factor.

Gravimetric factor is the ratio of the formula weight of the substance sought to that of the substance weighed.

$$\begin{aligned} \textit{gravimetric factor (GF)} \\ = \frac{\textit{Formula weight (FW)(substance sought)}}{\textit{Formula weight (FW)(substance weighed)}} \end{aligned}$$

The weight of the specific analyte in the weighed precipitate can be found using the formula,

$$\% \textit{ analyte} = \frac{\textit{weight precipitate (g)} \times \textit{GF} \times 100}{\textit{weight of sample (g)}}$$

ESTIMATION OF BARIUM SULPHATE

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.



- A white gelatinous precipitate is obtained which is filtered, washed, dried, ignited and weighed as barium sulphate.

Requirements:

- Barium chloride (BaCl_2) solution (12.57 g in 1000 ml of distilled water), precipitating agent (3 ml of concentrated H_2SO_4 in 100 ml of distilled water), wash solution (hot distilled water), volumetric flask, conical flask, burette, pipette etc.

Experiment:

- Pipette out 2.5 ml of given solution of barium chloride (BaCl_2) in 500 ml beaker. Add 0.5 ml of concentrated Sulphuric acid (H_2SO_4) and 100 ml of distilled water.

- ◉ Heat the resulting solution to boiling. To this hot solution, add dilute Sulphuric acid (H_2SO_4) solution drop wise with constant stirring until the precipitation is not complete.
- ◉ Allow the precipitate to settled down and test the supernatant liquid for complete filter. precipitation. Now, filter the precipitate by decanting method through Whatman filter.
- ◉ Wash the precipitate 3-4 times with hot water and dry it by placing the funnel in on oven. After drying, transfer the filter paper containing precipitate to the pre- constantly weighed crucible and ignite it till all the carbonaceous matter is not burnt off.
- ◉ Now, cool the crucible and add one drop of each of concentrated hydrochloric acid (HCl) and concentrated Sulphuric acid (H_2SO_4). Cool the crucible by placing in a desiccator and weigh it.
- ◉ Precipitation should be carried out in a dilute hot solution and in the presence of 0.05N HCl , which helps to increase the size of the precipitate particles.

Calculations:

- Let the constant weight of barium sulphate (BaSO_4) precipitate be x g



$$233.42 = 137.36$$

233.42 g of BaSO_4 Contains 137.36 g of Ba^{+2} ions

$$\therefore X \text{ g of } \text{BaSO}_4 \text{ Contains } \left(\frac{137.36 \times X}{233.42} \right) \text{ g of } \text{Ba}^{+2} \text{ ions}$$

ADVANTAGES OF GRAVIMETRIC ANALYSIS

1. Analysis can be done accurately.
2. No instrumental error.
3. Do not require calibration.
4. Simple and cheap. They do not require expensive equipment.
5. Very precise method when compared to other analytical techniques.
6. Filtrate can be examined for completion of reaction.

APPLICATIONS OF GRAVIMETRIC ANALYSIS

1. Extensive number of inorganic ions can be easily determined.
2. It is the most widely applicable analytical procedure.
3. A variety of organic substances can be easily determined like lactose in milk products, cholesterol in cereals etc.
4. To determine atomic mass of many elements.
5. Elemental analysis of the organic compound can be done. The composition of the elements of the compound can be done.
6. The analysis of rocks, ores, soils etc and other inorganic samples for their major components can be carried out,

THANK YOU.....

