College of science for women
Department of Chemistry

Second Stage

Gravimetric Analysis

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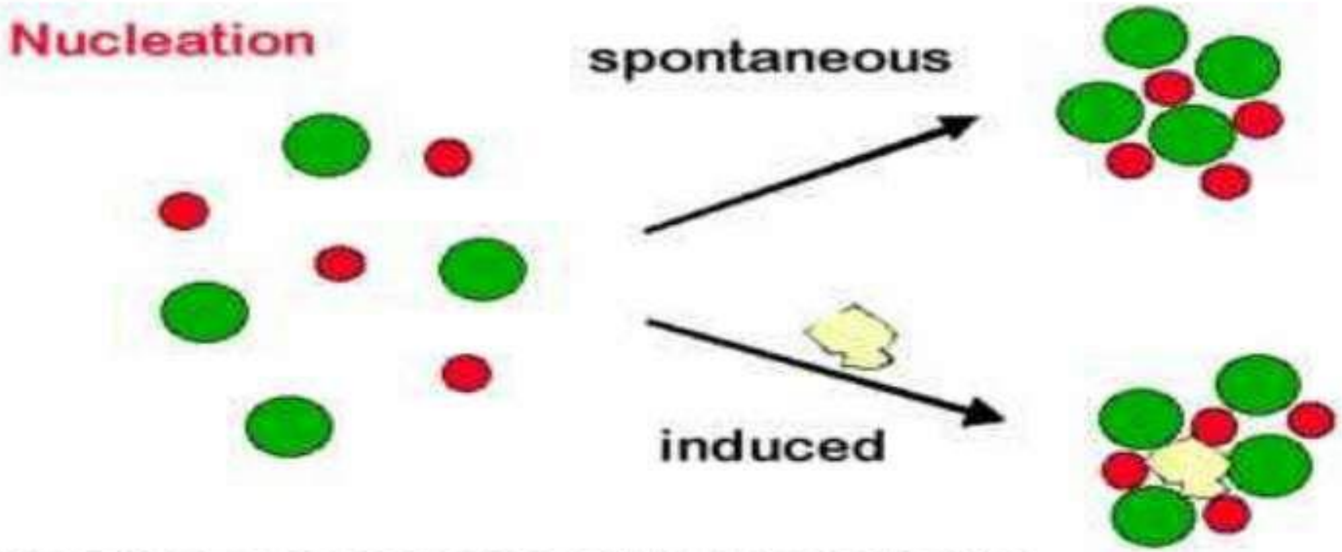
1. Mechanism of Precipitation

When a solution of precipitating agent is added to a test solution to form a precipitate,

such as in the addition of AgNO3 to a chloride solution to precipitate AgCl.

The actual precipitation occurs in a series of steps:

Mechanisms of precipitation



Spontaneous nucleation will occur on its own.

Induced nucleation requires a 'seed' particle to get things started (dust, another crystal, glass fragment, ...)

Mechanisms of precipitation

Particle growth

Once a nucleation site has formed, other ions are attracted to the site. This will result in the formation of large, filterable particles.

If done properly, it also reduces contaminates since they don't 'fit in' to the crystal structure.

1- Mechanism of Precipitation (cont.)

Important Notes

When a solution is super-saturated, it is in an unstable state and this favors rapid nucleation to form a large number of small particles.

A higher degree of supersaturation

A greater rate of nucleation

A greater number of nuclei formed per unit time

Precipitate is in the form of a large number of small nuclei

Increase total surface area of precipitate which increases the possibility of entrapment of impurities

Precipitate is not of filterable size

Degree of supersaturation

Von Weimarn discovered that the particles size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process

Relative supersaturation = $\frac{Q - S}{S}$

Q is the concentration of the solute at any instant.

S is its equilibrium solubility.

HIGH RSS → Many small crystals (Large Surface Area)

Low RSS → Fewer large crystals (Small Surface Area)

Low RSS is favorable.
How to achieve it?

During precipitation: ↓ Q ↑ S

- **Favorable conditions for precipitaion**
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- To decrease the value of Q
- 1-Precipitate from dilute solutions.
- 2-Add dilute precipitating agents slowly with constant stirring.
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- To increase the value of S
- 1-Precipitate from hot solution.
- 2-Precipitate at as low pH as possible.
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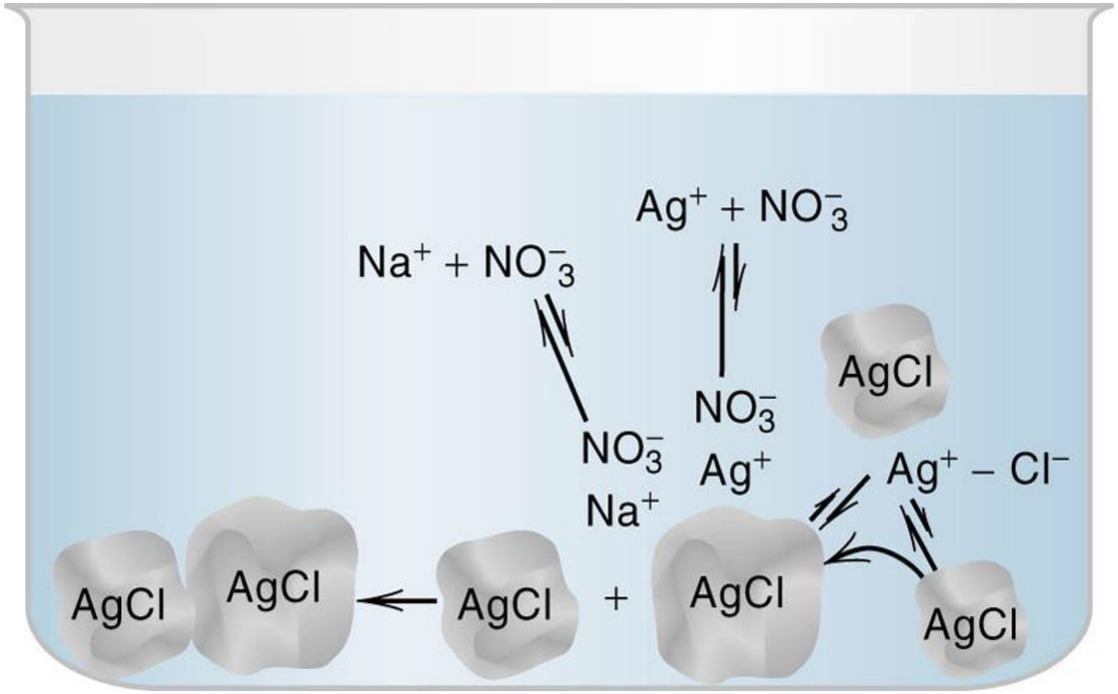
- **2. Digestion**
- Digestion is keeping the precipitate formed in contact with the mother liquor for a specified amount of time. Mother liquor (the solution from which it was precipitated).

In case of Colloidal precipitates:	In case of Crystalline precipitates:
Particle size (less than 100 m)	Particle size (more than 100 m)
Digestion is performed by allowing the precipitate to remain in contact with the mother liquor at high temperature for a couple of hours.	Digestion is performed by allowing the precipitate to remain in contact with the mother liquor for a long time.

- **Why is it important?**
- 1-The small particles tend to dissolve and re-precipitate on the surfaces of large crystal.
- 2- Individual particles tend to agglomerate together.
- 3- Imperfections of the crystals tend to disappear and adsorbed or trapped impurities tend to escape into solution.



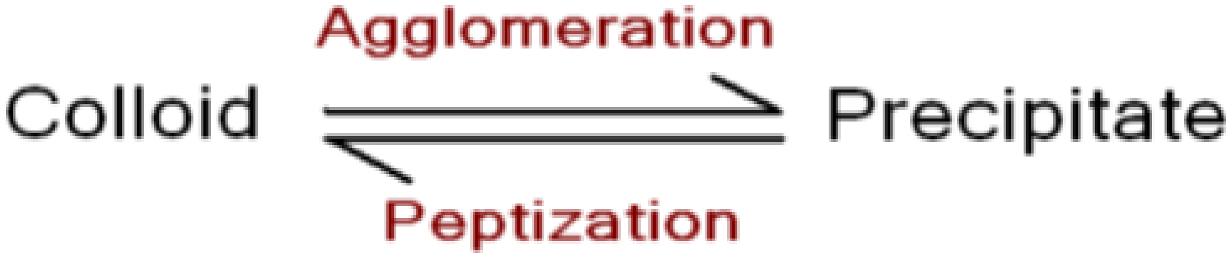
4. Filtering and Washing the Precipitate:

It is crucial to wash the precipitate very well in order to remove all adsorbed species which will add to weight of precipitate.

One should be careful **not to use** too much water since part of the precipitate may be lost.

Also, in case of colloidal precipitates we **should not use** water as a washing solution since ***peptization*** would occur.

In such situations dilute nitric acid, ammonium nitrate, or dilute acetic acid may be used. Usually, coagulated particles return to the colloidal state if washed with water, a process called ***peptization***, *re-dissolution of coagulated colloids by washing and removing inert electrolyte.*



- **Impurities in Precipitates**
- Impurities in Precipitates No discussion of gravimetric analysis would be complete without some discussion of the impurities which may be present in the precipitates. There are two typs of impurities :
- **a. Coprecipitation**
- This is anything unwanted which precipitates with the analyte during precipitation . Coprecipitation occurs to some degree in every gravimetric analysis (especially barium sulfate and those involving hydrous oxides). You cannot avoid it all what you can do is minimize it by careful precipitation and thorough washing :
- 1- **Surface adsorption**
- Here unwanted material is adsorbed onto the surface of the precipitate. Digestion of a precipitate reduces the amount of surface area and hence the area available for surface adsorption. Washing can also remove surface material.
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- 2- **Occlusion**
- This is a type of coprecipitation in which impurities are trapped within the growing crystal. And can be reduced by digestion and reprecipitation .

- b. **Postprecipitation**
- Sometimes a precipitate standing in contact with the mother liquor becomes contaminated by the precipitation of an impurity on top of the desired precipitate .To reduce postprecipitation filter as soon as the precipitation is complete and avoid digestion .
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