Gravimetric Methods of Analysis

- ***Gravimetric methods:*** The **quantitative methods** that are based on determining the **mass** of a **pure compound** to which the **analyte** is **chemically related**.

  - *Precipitation gravimetry*: The **analyte** is separated from a solution of the sample as a **precipitate** and is converted to a compound of known composition that can be weighed.

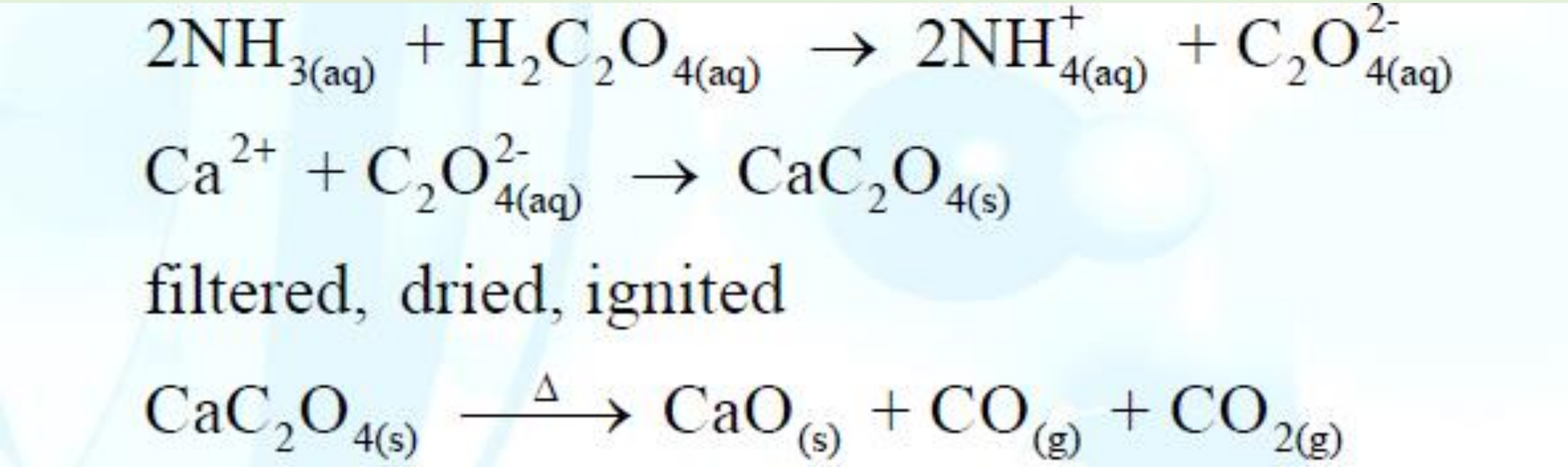
  - *Volatilization gravimetry*: The analyte is separated from other constituents of a sample by converting it to a gas of known chemical composition that can be weighed.

  - *Electrogravimetry*: The analyte is separated by deposition on an electrode by an electrical current.

A Precipitation gravimetry

- The analyte is converted to a **sparingly soluble precipitate** that is then **filtered**, **washed free of impurities** and converted to a product of **known composition** by suitable **heat** treatment and **weighed**.

Ex. for determining the $[Ca^{2+}]$ in water:



$$2NH_{3(aq)} + H_2C_2O_{4(aq)} \rightarrow 2NH^{+}_{4(aq)} + C_2O^{2-}_{4(aq)}$$

$$Ca^{2+} + C_2O^{2-}_{4(aq)} \rightarrow CaC_2O_{4(s)}$$

filtered, dried, ignited

$$CaC_2O_{4(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{(g)} + CO_{2(g)}$$

After cooling, the precipitate is weighed and the mass is determined.

1 Properties of Precipitates and Precipitating Reagents

- A gravimetric precipitating agent should react specifically or at least selectively with the analyte and give precipitates that is:

✓Enough particle size for retaining on filter paper

✓High purity (free of contaminants)

✓Low solubility that no significant loss of the analyte occurs during filtration and washing

✓Unreactive with air (stable)

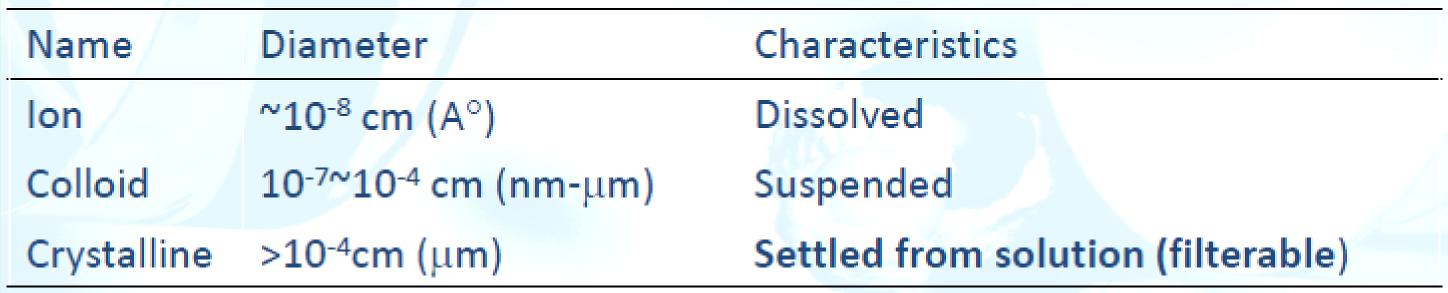
✓Known stoichiometric composition after it is dried or, if necessary, ignited

- Specific reagents: react only with a single chemical species.
- Selective reagents: react with a limited number of species.

2 Particle Size and Filterability of Precipitate

Characteristics of Ion, colloid and particle

- The particle size of solids formed by precipitation varies enormously. At one extreme are colloidal suspensions, whose tiny particles are invisible to the naked eye (10^{-7} to 10^{-4} cm in diameter). Colloidal particles show no tendency to settle from solution and are difficult to filter.
- At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a crystalline suspension tend to settle spontaneously and are easily filtered.



Name	Diameter	Characteristics
Ion	$\sim 10^{-8}$ cm (A°)	Dissolved
Colloid	$10^{-7} \sim 10^{-4}$ cm (nm-µm)	Suspended
Crystalline	$>10^{-4}$cm (µm)	**Settled from solution (filterable)**

- Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities.

Factors That Determine the Particle Size of Precipitates

- Precipitate formation has been studied for many years, but the mechanism of the process is still not fully understood. What is certain, however, is that the particle size of a precipitate is influenced by:

1.Precipitate solubility, 2. Temperature,
3. Reactant concentrations, and 4. The rate at which reactants are mixed.

- The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called **relative supersaturation**, where:

$$\boxed{RSS = \frac{Q - S}{S}}$$

Von Weimarn equation

Q: The concentration of the solute at **any instant**
S: The concentration solute **at equilibrium**

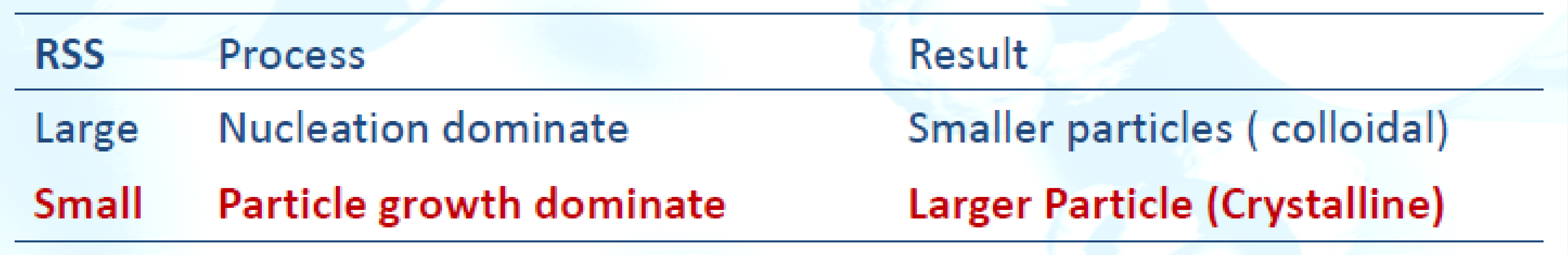
(The lower RSS value the larger particles)

Relative supersaturation (RSS)

A **supersaturated solution is an** unstable solution that contains a higher solute concentration than a saturated solution. As excess solute precipitates with time, supersaturation decreases to zero.

- ❖ Generally, precipitation reactions are slow so that, even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely.

- ❖ Experimental evidence indicates that the particle size of a precipitate varies inversely with the average relative supersaturation during the time when the reagent is being introduced. Thus, when (*Q - S)/S is large, the precipitate* tends to be colloidal, and when (*Q - S)/S is small, a crystalline solid is* more likely.



RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	**Particle growth dominate**	**Larger Particle (Crystalline)**

Mechanism of Precipitate Formation

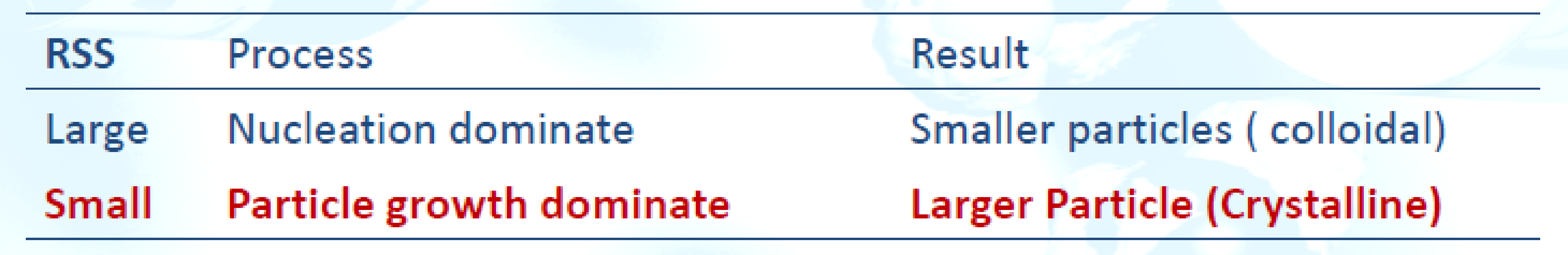
Nucleation and Particle growth

Nucleation: The initial formation process in which a minimum number of atoms, ions, or molecules join together to give a stable solid.

Often, these nuclei form on the surface of suspended solid contaminants, such as dust particles

Particle growth: The subsequent growth after nucleation.

- If nucleation predominates, a precipitate containing a large number of small particles results, and
- If growth predominates, a smaller number of larger particles is produced.



RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	Particle growth dominate	Larger Particle (Crystalline)

Experimental Control of Particle Size

***Increase S*:**

- Heating to increase solubility
- pH adjustment (If the solubility of the precipitate depends on pH)
- Adding complexing agent

***Decrease Q*:**

- Using dilute precipitating solution
- Adding precipitating agent slowly and stirring
- Using homogeneous precipitation technique
- Precipitation from Homogeneous Solution, generating the precipitating agent in the precipitation medium rather then adding it.

3 Colloidal Precipitate

Individual colloidal particles are so small that they are not retained by ordinary filters. Moreover, Brownian motion prevents their settling out of solution under the influence of gravity.

Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

(When liquid starts to thicken and become solid, it coagulates)

(agglomeration: a large group of many different things collected or brought together)

Coagulation of Colloids

Coagulation can be hastened by heating, by stirring, and by adding an electrolyte to the medium.

Why colloidal suspensions are stable and do not coagulate spontaneously?

Colloidal suspensions are stable because all of the particles of the colloid are either positively or negatively charged and thus repel one another. The charge results from cations or anions that are bound to the surface of the particles.

- We can show that ***colloidal particles are charged*** by placing them between charged plates where some of the particles migrate toward one electrode while others move toward the electrode of the opposite charge. The process by which ions are retained *on the surface of a solid is* known as **adsorption.**

4 Crystalline Precipitates

- Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids.

- Particle size of crystalline solids can often be improved significantly by:

  Minimizing Q (by using dilute solutions, and adding the precipitating reagent slowly, with good mixing) or Maximizing S (precipitating from hot solution or by adjusting the pH), or both.

- Digestion improves the purity and filterability of both colloidal and crystalline precipitates.

- The improvement in filterability undoubtedly results from the dissolution and recrystallization that occur continuously and at an enhanced rate at elevated temperatures.

- Recrystallization apparently results in bridging between adjacent particles, a process that yields larger and more easily filtered crystalline aggregates. This view is supported by the observation that little improvement in filtering characteristics occurs if the mixture is stirred during digestion.

5 Co-precipitation

Co-precipitation:

A process in which normally soluble compounds are carried out of solution by a precipitate. It may resulted in **impurities** within the desired precipitates.

Co-precipitated impurities may cause either negative or positive errors.

There are four types of co-precipitation:

A. **Surface adsorption,**
B. **Mixed-crystal formation,**
C. **Occlusion, and**
D. **Mechanical entrapment.**

How to Perform a Successful Gravimetric Analysis?

- **What steps are needed?**

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

1. Preparation of the Solution:

This may involve several steps including:

- *Adjustment of the pH of the solution* in order for the precipitate to occur quantitatively and get a precipitate of desired properties,
- *Removing interferences*,
- *Adjusting the volume of the sample* to suit the amount of precipitating agent to be added.

2. Precipitation:

- This requires **addition of a precipitating agent solution to the sample solution**.
- Upon addition of the first drops of the precipitating agent, **supersaturation occurs**, and **then nucleation starts to occur** where every few molecules of precipitate aggregate together forming a ***nucleous***.
- **At this point**, addition of extra precipitating agent will ***either*** form new nuclei ***or*** will build up on existing nuclei to give a precipitate.
- This can be predicted by ***Von Weimarn*** ratio where, according to this relation the particle size is inversely proportional to a quantity called the relative supersaturation where:

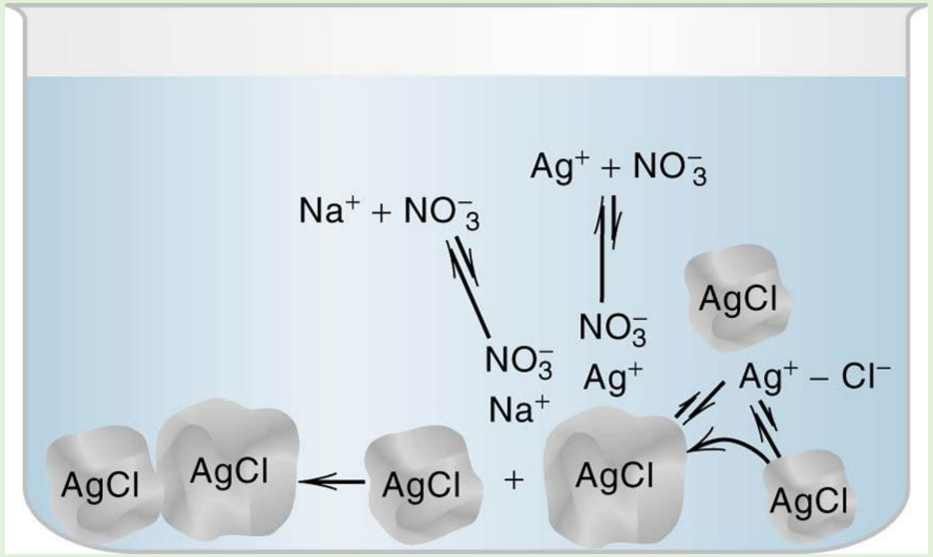
$$\text{Relative Supersaturation} = (Q - S)/S$$

- ***back to** Experimental Control of Particle Size*

3. Digestion of the Precipitate:

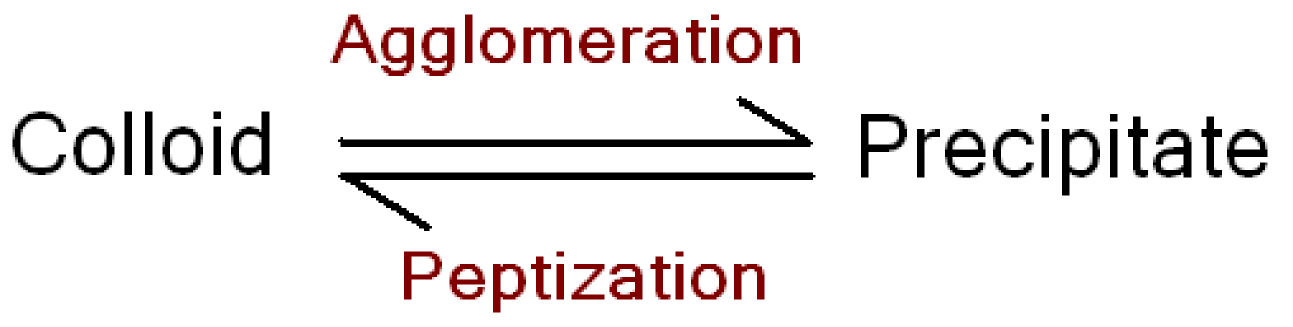
- The precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested.
- Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics. This process is called *Ostwald ripening*.
- An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate.
- Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption.
- **During digestion at elevated temperature:**

1. **Small particles tend to dissolve and reprecipitate on larger ones.**
2. **Individual particles agglomerate.**
3. **Adsorbed impurities tend to go into solution.**



4. Filtering and Washing the Precipitate:

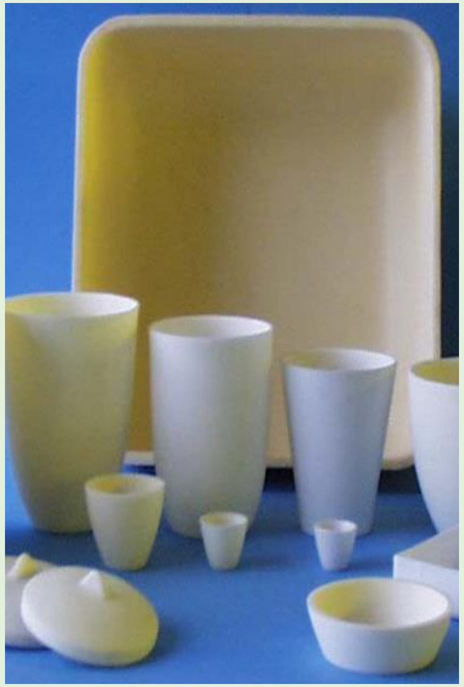
- It is crucial to wash the precipitate very well in order to remove all adsorbed species which will add to weight of precipitate.
- One should be careful **not to use** too much water since part of the precipitate may be lost.
- Also, in case of colloidal precipitates we **should not use** water as 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.*



$$\text{Colloid} \underset{\text{Peptization}}{\overset{\text{Agglomeration}}{\rightleftharpoons}} \text{Precipitate}$$

5. Drying and Ignition:

The purpose of drying (heating at about 120-150 ^{o}C in an oven) or ignition in a muffle furnace at temperatures ranging from 600-1200 ^{o}C is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined.



6. Calculations:

- The last step in the gravimetric procedure is performing the analytical calculations, as will be seen shortly.

Calculations of analyte content requires knowledge of :

1. Chemistry
2. Stoichiometry
3. Composition of precipitate