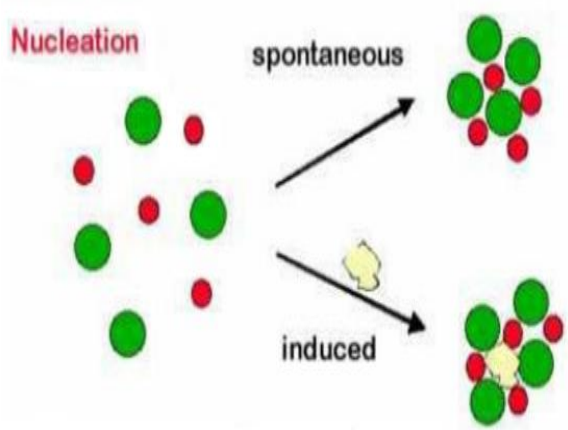
Mechanism of Precipitation (how particles are formed?)

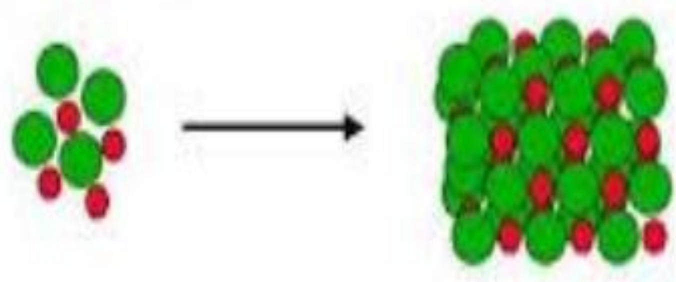
- Supersaturated solution formed ... *The ionic product of concentrations ≥ the solubility product.*
- Nucleation ...*a few atoms, ions or molecules join together to give a stable solid called nuclei.*
- Particle growth ...*the process where more ions are added to the nucleus to form colloids with sizes in the range of 1-100nm in diameter.*

When a solution of a precipitating agent is added to a test solution to form a precipitate, such as in the addition of $AgNO_3$ to a chloride solution to precipitate AgCl, the actual precipitation occurs in a series of steps. The precipitation process involves heterogeneous equilibria and, as such, is not instantaneous.
First, **supersaturation occurs**, that is, the solution phase contains more of the dissolved salt than it can carry at equilibrium. This is a metastable condition, and the driving force will be for the system to approach equilibrium (saturation). This is started by **nucleation**.

For nucleation to occur, a minimum number of particles must come together to produce microscopic nuclei of the solid phase. The higher the degree of supersaturation, the greater the rate of nucleation. The formation of a greater number of nuclei per unit time will ultimately produce more total crystals of smaller size. The total crystal surface area will be larger, and there will be more danger that impurities will be adsorbed. Although nucleation should theoretically occur spontaneously, it is usually induced, for example, on dust particles, scratches on the vessel surface, or added seed crystals of the precipitate (not in quantitative analysis).



Following nucleation, the initial nucleus will grow by depositing other precipitate particles to form a crystal of a certain geometric shape. Again, the greater the supersaturation, the more rapid the crystal growth rate. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.



How particle size is controlled ?

1. Precipitate from **dilute solution**. This keeps Q low.
2. Add dilute precipitating reagents slowly, with effective **stirring**. This also keeps Q low. Stirring prevents local excesses of the reagent.
3. Precipitate from **hot solution**. This increases S. The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be coold to make the precipitation quantitative.
4. Precipitate at as **low a pH** as is possible to maintain quantitative precipitation. Many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate (which comes from a weak acid) combines with protons in the solution.

VonWeimarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process:

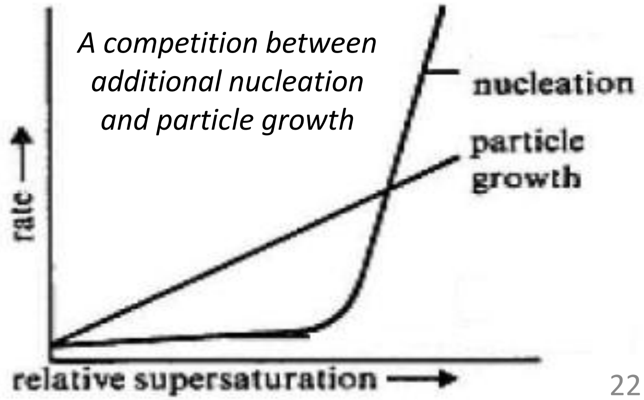
Where:

Q *is the concentration of the mixed reagents before precipitation occurs, S is the* solubility of the precipitate at equilibrium,

Q* – *S *is the degree of supersaturation.*

The ratio, ***(Q* – *S)/S***, *relative supersaturation, is also called the VonWeimarn ratio.*

When a solution is supersaturated, it is in a state of metastable equilibrium, and this favors rapid nucleation to form a large number of small particles. That is, Obviously, then, we want to keep *Q low and S high* during precipitation



A competition between additional nucleation and particle growth

- Solubility of the precipitate *... Increase solubility by precipitating from hot solution or adjusting the pH*
- Relative Supersaturated (RSS) *...as small as possible*

RSS = (Q-S)/S (Von Weimarn ... Particles size inversely RSS)

Q: conc. of the solute
S: equilibrium solubility
(Q-S) is a measure of the degree of supersaturation

- Solutions *...as diluted as possible*
- Addition of precipitating agent *...as slow as possible*

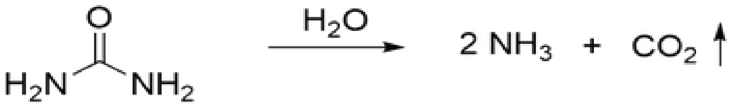
Large particle size (**crystalline solid**) ⇨ S ↑ + RSS ↓ + Q ↓ (dil. & slow)

Small particle size (**colloid**) ⇨ S ↓ + RSS ↑+ Q ↑ (conc. & fast)

Precipitation from homogeneous solution

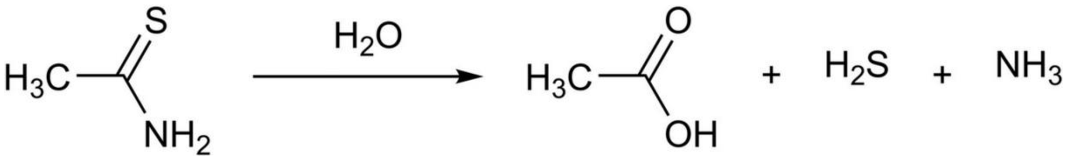
Homogeneous precipitation is a process in which a precipitate is formed by slow generation of an precipitating reagent homogeneously throughout a solution. Solids formed by homogeneous precipitation are generally purer and larger in size.

Hydrolysis of urea



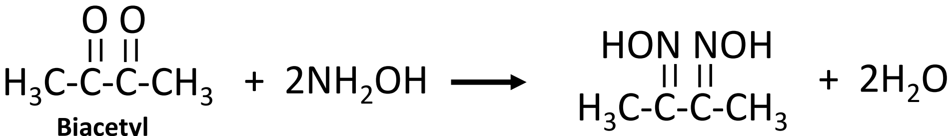
Urea

Hydrolysis of thioacetamide



Thioacetamide Acetic acid Hydrogen sulfide Ammonia

Formation of DMG



$$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 + 2NH_2OH \longrightarrow H_3C-\overset{\overset{HON}{\|}}{C}-\overset{\overset{NOH}{\|}}{C}-CH_3 + 2H_2O$$

Biacetyl
(2,3-diketobutane) Hydroxylamine Dimethylglyoxime

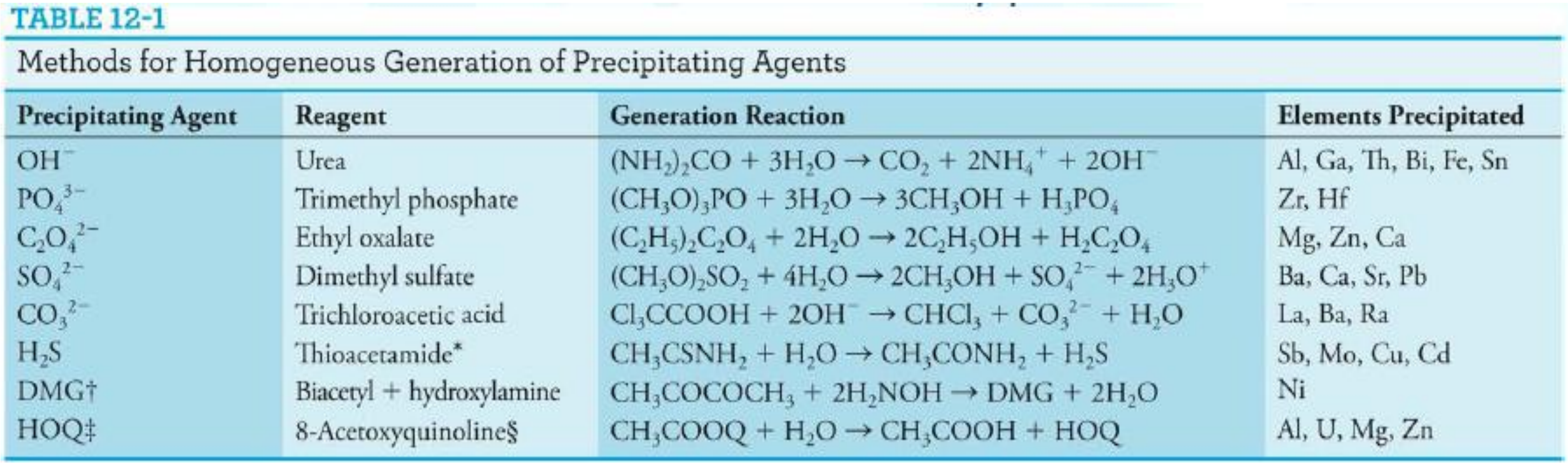


TABLE 12-1

Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

Types of precipitates

There are two types of precipitates, according to the size of the formed particles

1. colloidal (1- 100 μm diameter) or amorphous.
2. crystalline (> 100 μm diameter) precipitates

Colloidal particles are very small (1 to 100 nm) and have a very large surface to-mass ratio, which promotes surface adsorption. They are formed by virtue of the precipitation mechanism. As a precipitate forms, the ions are arranged in a fixed pattern.

Primary adsorption layer:

- It will have a positive or negative charge, depending on the excess reagent.
- If the excess reagent is the cation of the solute, then the overall charge will be positive. For example, excess silver nitrate added to sodium chloride. The primary adsorption layer will be predominately silver ions.

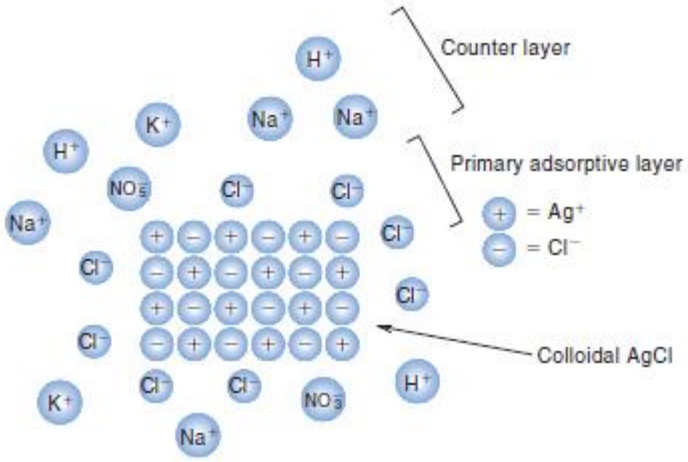
Counter-ion layer:

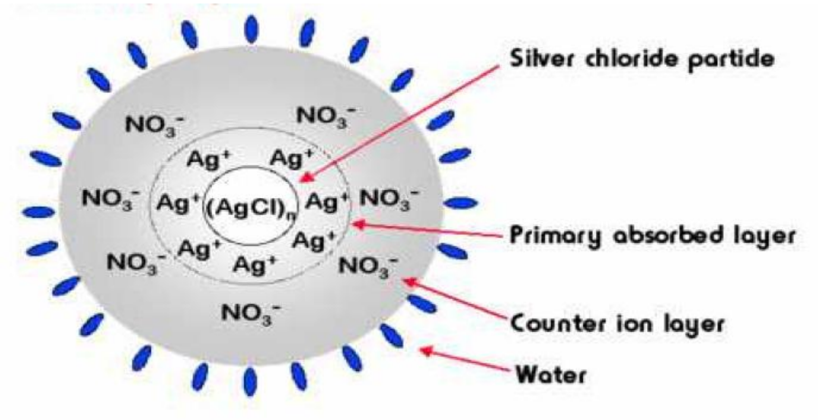
- Because of the overall charge of the adsorption layer, a second layer called the counter-ion layer forms.
- This is also composed of the excess reagent along with other ions in solution.
- It will impart the opposite overall charge to the entire colloidal particle.
- So if the adsorption layer is positive, the counter-ion layer will be negative.

Electrical double layer:

Together, the two layers comprise what is called an electrical double layer surrounding a solid core.

In AgCl, for example, there will be alternating Ag^+ and Cl^- ions on the surface (see figures below). While there are localized + and − charges on the surface, the net surface charge is zero. However, the surface does tend to adsorb the ion of the precipitate particle that is in excess in the solution, for example, Ag^+ if precipitating Cl^- with an excess of Ag^+; this imparts a charge. (With crystalline precipitates, the degree of such adsorption will generally be small in comparison with particles that tend to form colloids.) The adsorption creates a **primary layer** that is strongly adsorbed and is an integral part of the crystal. It will attract ions of the opposite charge in a **counter layer or secondary layer** so the particle will have an overall neutral charge. There will be solvent molecules interspersed between the layers. Normally, the counter layer completely neutralizes the primary layer and is close to it, so the particles will collect together to form larger particles; that is, they will **coagulate**. However, if the secondary layer is loosely bound, the primary surface charge will tend to repel like particles, maintaining a colloidal state.





Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to some extent.

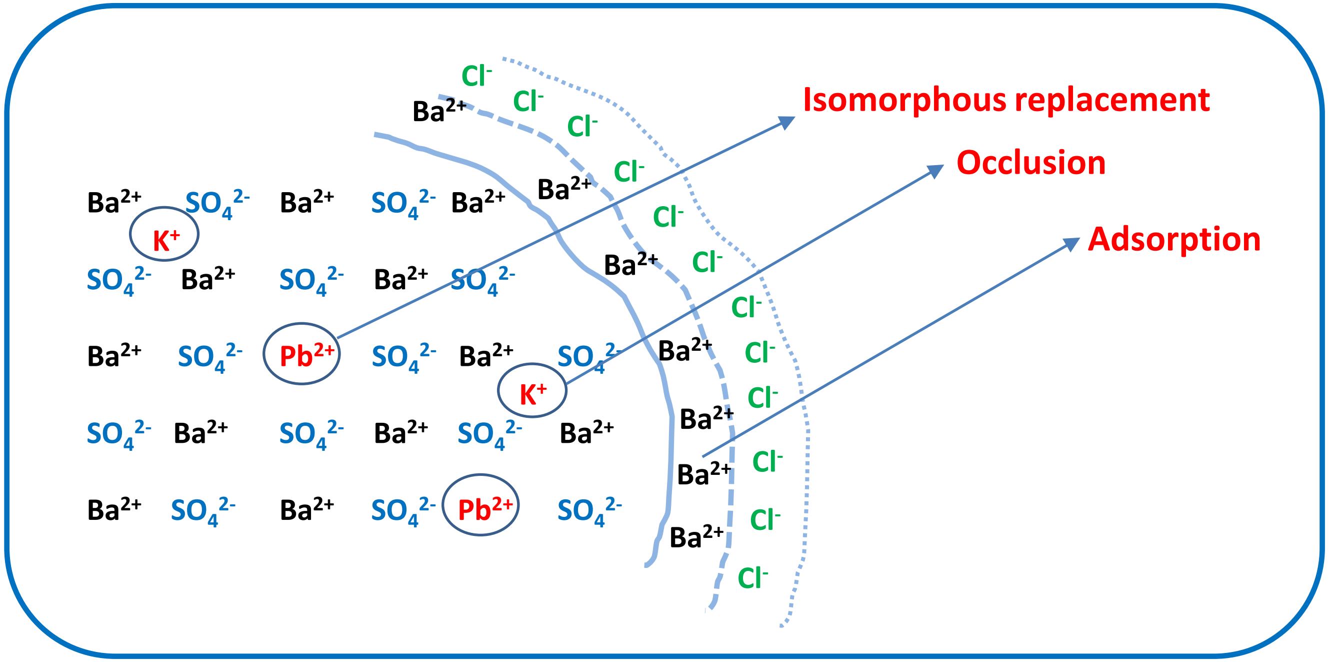
Impurities in Precipitates

Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to become contaminated. This process is called **coprecipitation.** The process may be equilibrium based or kinetically controlled.

There are a number of ways in which a foreign material may be coprecipitated.

1. Co-precipitation

- Inclusion ... *trap a pocket of solution*
- Occlusion ...*impurities trapped inside the growing crystal*
- Surface adsorption ...*on the surface*
- Isomorphous replacement (mixed crystal) ...*occupy crystal lattice*



An example of Co-precipitation of $PbSO_4$ in $BaSO_4$

Occlusion

In the process of occlusion, material that is not part of the crystal structure is trapped within a crystal. For example, water may be trapped in pockets when $AgNO_3$ crystals are formed, and this can be removed to a degree by dissolution and recrystallization. If such mechanical trapping occurs during a precipitation process, the water will contain dissolved impurities.

Inclusion

Inclusion occurs when ions, generally of similar size and charge, are trapped within the crystal lattice (isomorphous inclusion, as with K_+ in NH_4MgPO_4 precipitation). These are not equilibrium processes.

Occluded or included impurities are difficult to remove. Digestion may help some but is not completely effective. The impurities cannot be removed by washing. Purification by dissolving and re-precipitating is helpful.

Surface adsorption

The surface of the precipitate will have a primary adsorbed layer of the lattice ions in excess. This results in surface adsorption, the most common form of contamination. For example, after barium sulfate is completely precipitated, the lattice ion in excess will be barium, and this will form the primary layer. The counter ion will be a foreign anion, for example, nitrate two for each barium. The net effect then is an adsorbed layer of barium nitrate, an equilibrium-based process. These adsorbed layers can often be removed by washing, or they can be replaced by ions that are readily volatilized. Gelatinous precipitates are especially troublesome, though. Digestion reduces the surface area and, therefore, the adsorbed amount.

Isomorphous replacement

Two compounds are said to be isomorphous if they have the same type of formula and crystallize in similar geometric forms. When their lattice dimensions are about the same, one ion can replace another in a crystal, resulting in a mixed crystal. This process is called isomorphous replacement or isomorphous substitution. For example, in the precipitation of Mg^{2+} as magnesium ammonium phosphate, K^+ has nearly the same ionic size as NH_4^+ and can replace it to form magnesium potassium phosphate. Isomorphous replacement, when it occurs, causes major interference, and little can be done about it. Precipitates in which it occurs are seldom used analytically.

2. Post-precipitation

Sometimes, when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent. This is called **postprecipitation.** For example, when calcium oxalate is precipitated in the presence of magnesium ions, magnesium oxalate does not immediately precipitate because it tends to form supersaturated solutions. But it will precipitate if the solution is allowed to stand too long before being filtered. Similarly, copper sulfide will precipitate in acid solution in the presence of zinc ions without zinc sulfide being precipitated, but eventually zinc sulfide will precipitate.