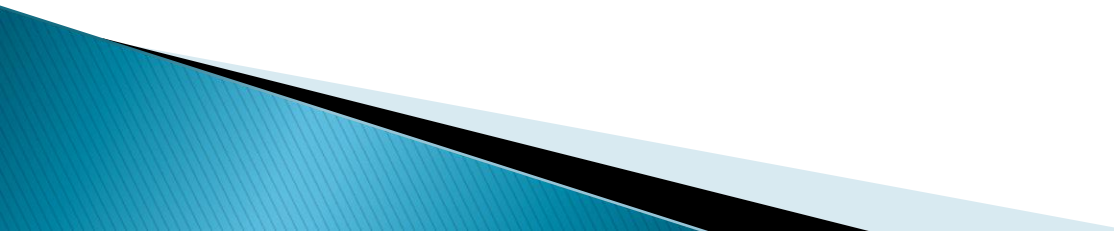# Gravimetric Analysis

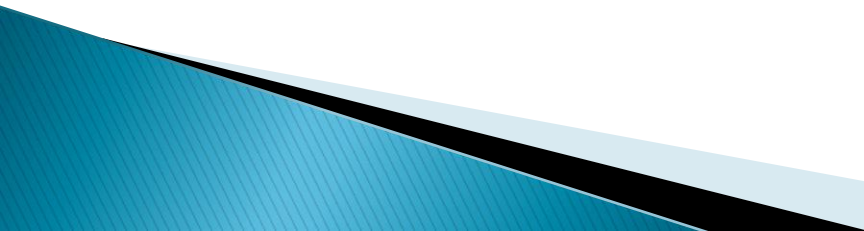# Defination

- Gravimetric analysis is a quantitative determination of the amount of analyte through a precipitation process, precipitate isolation, and determination of isolated product weight.

- Gravimetry = analytical methods that measure the mass or mass changes by highly accurate analytical balance
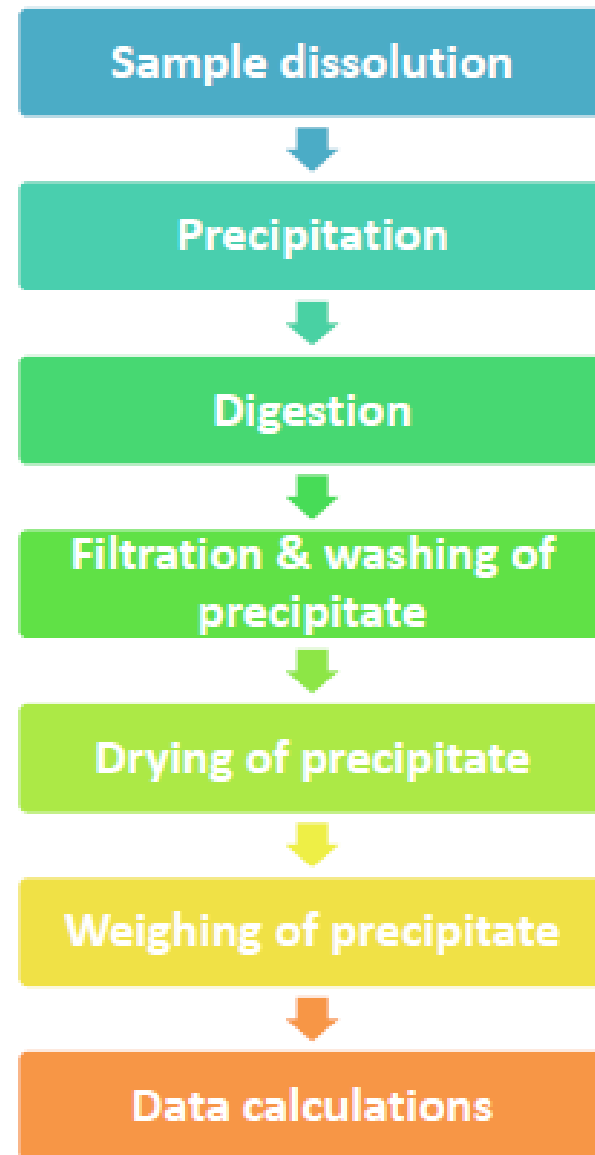
TYPES OF GRAVIMETRIC METHODS

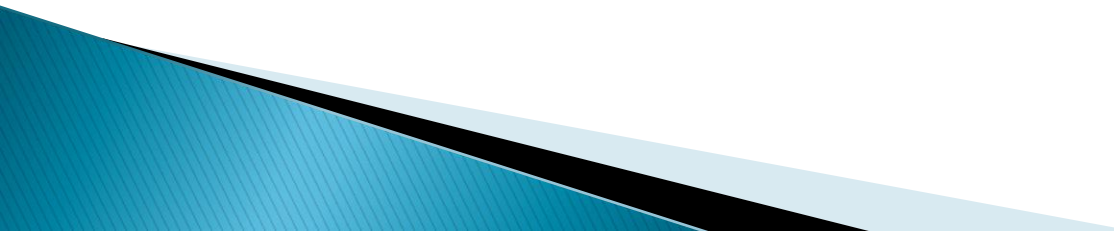| Gravimetric methods	Definition	Application
Precipitation gravimetry	A gravimetric method in which the signal is the **mass** of a precipitate	Suspended solid: determination of Cl^- by $AgNO_3$ precipitating to $AgCl$ (filtration)
Electrogravimetry	A gravimetric method in which the **signal is the mass of an electrodeposit** on the cathode or anode in an electrochemical cell	Aqueous ion: determination of Pb^{2+} by oxidizes to PbO_2 and deposited on Pt anode (chemical converting)
Volatilization gravimetry	A gravimetric method in which the **loss of a volatile species** gives rise to the signal (remove the volatile species)	Moisture: determination of water in food content by heat or thermal or chemical energy (heating)
Particulate gravimetry	A gravimetric method in which the **mass of a particulate analyte** is determined following its separation from its matrix	Suspended solid: determination of solid that can be separated from the sample (filtration or extraction)

PRECIPITATION GRAVIMETRY

- Appearance of insoluble compounds in a solution containing our analyte when a precipitating reagent/precipitant is added.
- The precipitate is then
  - filtered and washed (impurities removal)
  - converted to a product (known composition)
  - weighed

STEPS IN GRAVIMETRIC ANALYSIS

- Dissolve a sample after weighing.
- A precipitating agent with excess amount is added to this solution.
- The resulting precipitate is filtered, dried (or ignited) and weighed.
- Determine the amount of the original ion from the mass of the precipitate (known composition).
- Stoichiometry is important (write down the chemical equation!).

Sample dissolution

↓

Precipitation

↓

Digestion

↓

Filtration & washing of precipitate

↓

Drying of precipitate

↓

Weighing of precipitate

↓

Data calculations

Ideal precipitate for Gravimetric Analysis

- Easily filtrable (large particle size, smaller total surface area (minimize impurities))
- Insoluble or low solubility
- Known composition
- Pure

TYPES OF PRECIPITATING REAGENTS

Precipitating Reagent or precipitant : A reagent that causes the precipitation of a soluble species.

1. **Selective** (react with a few analytes)
   - Example: $AgNO_3$
   - $Ag^+ + Halides\ (X^-) \rightarrow AgX_{(s)}$
   - $Ag^+ + CNS^- \rightarrow AgCNS_{(s)}$

2. **Specific** (react with 1 analyte only)
   - Example: Dimethylglyoxime (DMG) that precipitates only Ni^{2+} from alkaline solutions
   - $2\ DMG + Ni^{2+} \rightarrow Ni(DMG)_{2(s)} + 2\ H^+$

Morden Analytical Chemistry– David Harvey
Refer Table no. 8.1 to 8.5

Solubility Rules

ALMOST
(always SOLUBLE)

Nitraes (NO_3^-)

Acetates ($C_2H_3O^-$)

Group 1 (Li^+, Na^+, K^+, etc)

Sulfates (SO_4^{2-})

Ammonium (NH_4^+)

Group 17 (F^-, Cl^-, Br^-, etc)

EXCEPTIONS (2 groups)

1. "PMS"
   - P → Pb^{2+} (lead)
   - M → Mercury (Hg_2^{2+})
   - S → Silver (Ag^+)
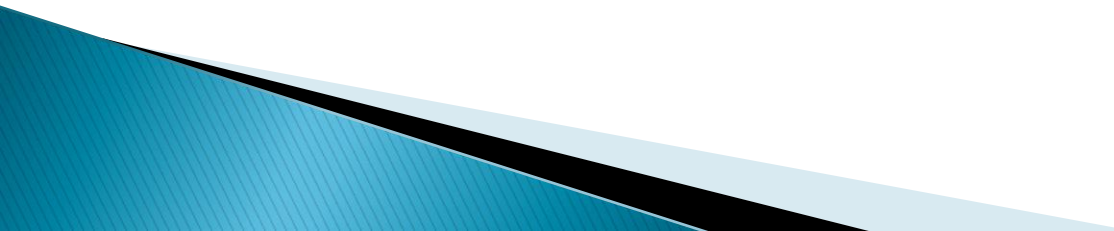
2. Castro Bear
   - Ca^{2+}, Sr^{2+}, Ba^{2+}

TYPES OF PRECIPITATE FORMED

- **Colloidal suspensions**

  - Normally remain suspended
 - 10^{-7} to 10^{-4} cm diameter
  - Very difficult to filter

- **Crystalline suspensions**
  - Normally settle out spontaneously
  - > tenths of mm diameter
 - Readily filterable

MECHANISM OF PRECIPITATE FORMATION

➢ **Nucleation** : Individual ions/atoms/molecules coalesce to form "nuclei" (join together to give a stable solid)

  ▸ If nucleation predominates, a large number of small particles result

Nucleation

spontaneous

induced
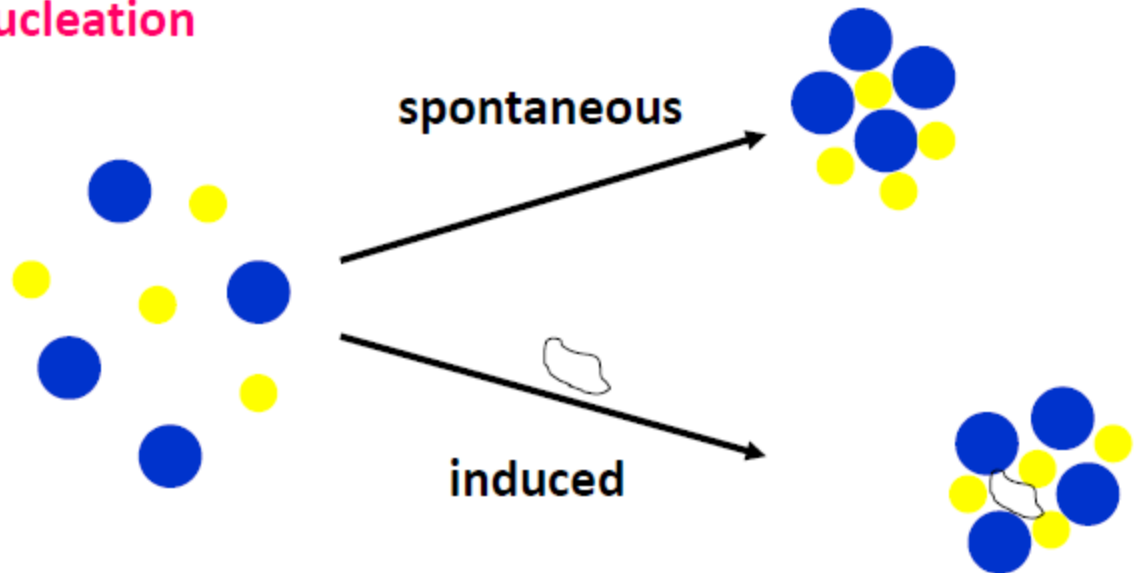
▸ **Particle growth :** Ions/atoms/molecules are added to the nucleus to form larger particles.

  ◦ If particle growth predominates, a smaller number of large particles result

Particle growth

| Formation of nucleation site | → | The site attract other ions | → | Formation of large, filterable particles |
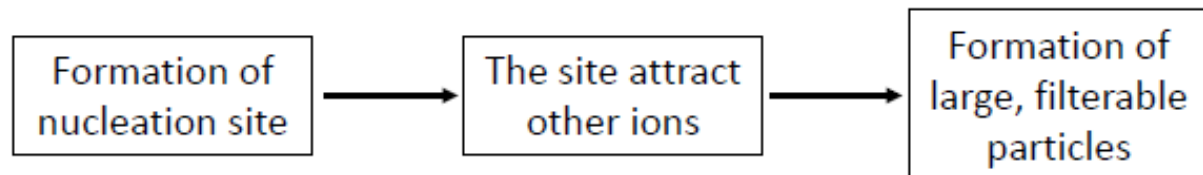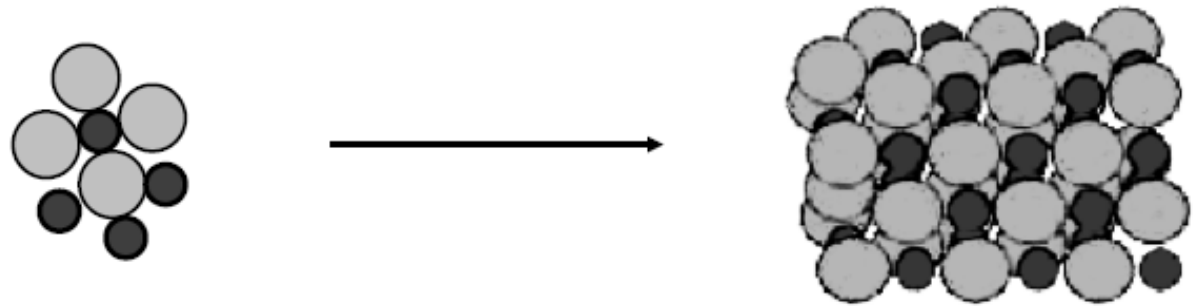
CONDITIONS FOR ANALYTICAL PRECIPITATION

- Saturation = Q – S

- Relative supersaturation = (Q – S) / S
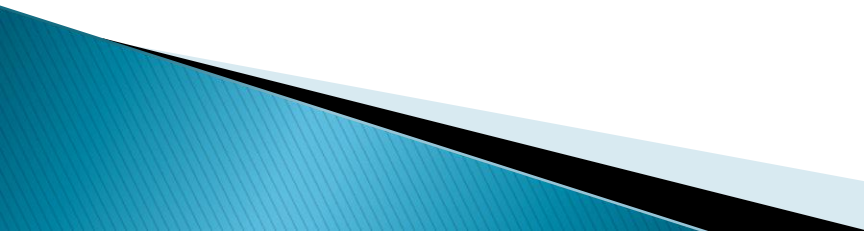
  Q = solute concentration

  S = solute solubility

For best possible results: **Q should be as low** as possible and **S should be relatively large**.

- $Q\uparrow$, $S\downarrow$: high supersaturation →fine particles
- $Q\downarrow$,$S\uparrow$: low supersaturation → large particles

Optimum precipitation conditions with low supersaturation

- Use dilute solutions - decrease Q
- Add precipitating agent slowly - keep Q low
- Stirring during the above addition - keep Q low
- Use hot solution - increase solubility
- Adjust the pH - increase S
- Add precipitating agent with excess amount

Mechanism of Precipitation

▸ Consider, for instance, the precipitation of AgCl from a solution of $AgNO_3$, using NaCl as a precipitant.

▸ Early in the precipitation, when NaCl is the limiting reagent, excess Ag^+ ions chemically adsorb to the AgCl particles, forming a positively charged primary adsorption layer .

▸ Anions in solution, in this case NO_3^- and OH^-, are attracted toward the surface, forming a negatively charged secondary adsorption layer that balances the surface's positive charge.

> ‣ The solution outside the secondary adsorption layer remains electrically neutral.
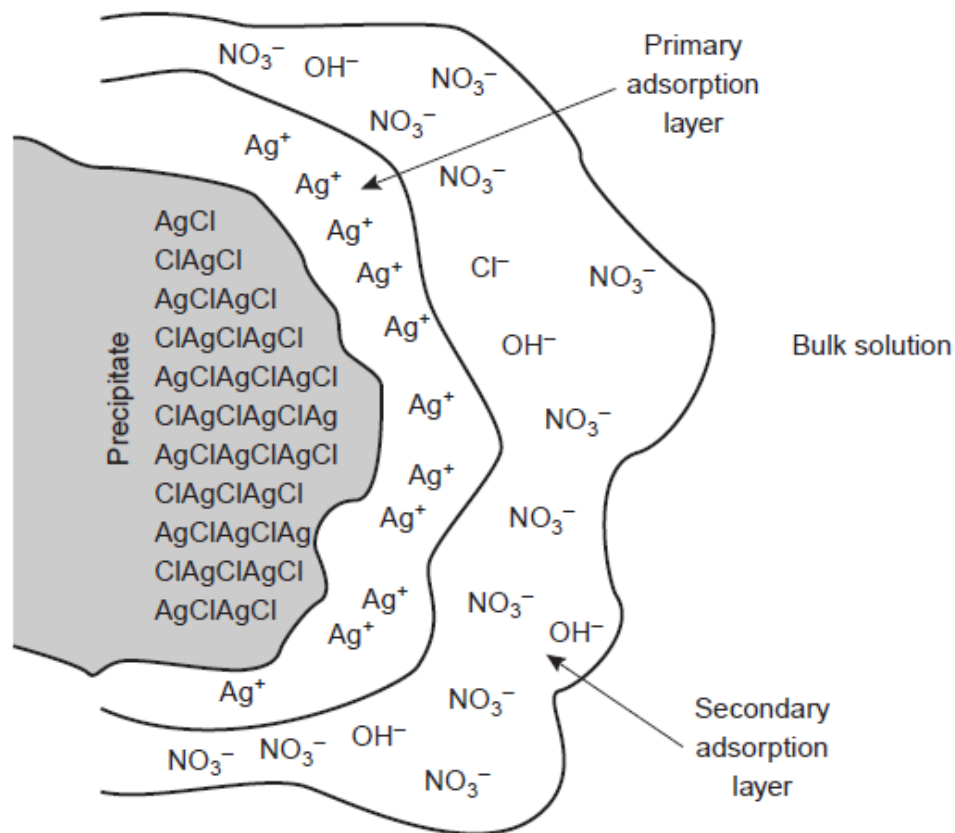
CO-PRECIPITATION: IMPURITIES IN PRECIPITATES

- Co-precipitation is a process where the impurity is precipitated along with the desired precipitate.
- Example: barium sulfate, hydrous oxides compounds.
- Normally soluble compounds carried down with insoluble precipitate
  - Surface adsorption
  - Occlusion (pockets of impurities that are trapped inside the rapidly growing cryctal)
  - Inclusion (impurity ions replaces an ion in the crystal lattice)
  - Mechanical entrapment (crystals lie close together during growth)
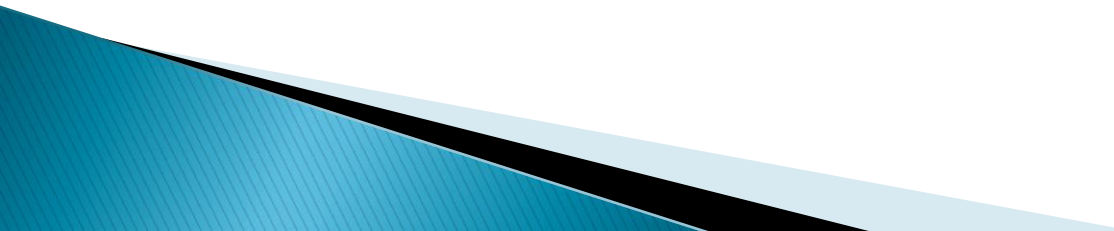
Theory of Precipitation gravimetry

▸ Solubility of precipitate is an important parameter of precipitation gravimetery.

▸ Precipitate should be least soluble for ideal precipitation gravimetery process.

▸ Hence there are two important factors affecting on solubility of ppt.

   1. Equilibrium concentration of precipitant

   2. pH of reaction condition

Equilibrium concentration of precipitant

▸ For example, Ag^+ can be determined gravimetrically by adding Cl^- as a precipitant, forming a precipitate of $AgCl$.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

▸ If this is the only reaction considered, we would falsely conclude that the precipitate's solubility, S_{AgCl}, is given by
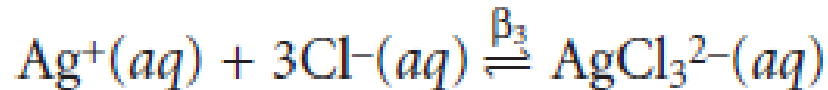
$$S_{AgCl} = [Ag^+] = \frac{K_{sp}}{[Cl^-]}$$

▸ and that solubility losses may be minimized by adding a large excess of Cl^-.
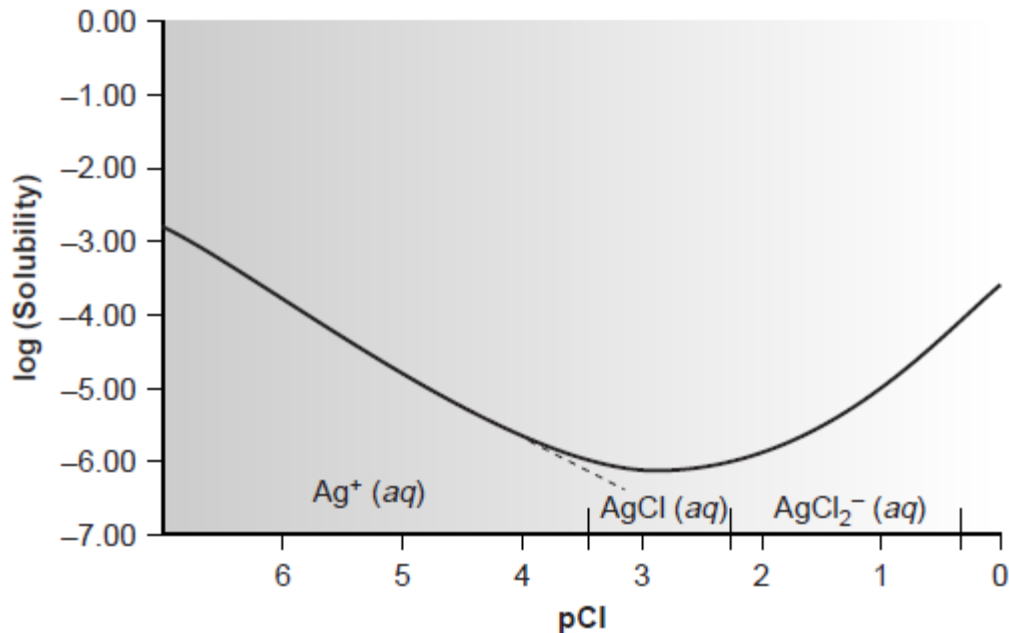
Solubility of AgCl as a function of pCl.

- Practically, as shown in Figure 8.1, adding a large excess of Cl– eventually increases the precipitate's solubility.
- To understand the pattern of this graph we must discuss the following reactions in which series of soluble chloro-complexes are forms

$$Ag^+(aq) + Cl^-(aq) \overset{K_1}{\rightleftharpoons} AgCl(aq)$$

$$Ag^+(aq) + 2Cl^-(aq) \overset{\beta_2}{\rightleftharpoons} AgCl_2^-(aq)$$

$$Ag^+(aq) + 3Cl^-(aq) \overset{\beta_3}{\rightleftharpoons} AgCl_3^{2-}(aq)$$
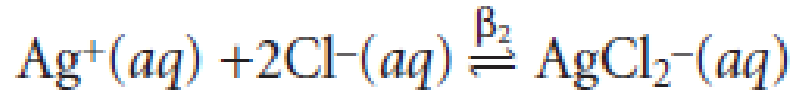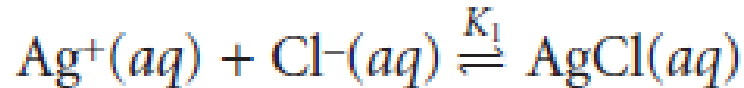
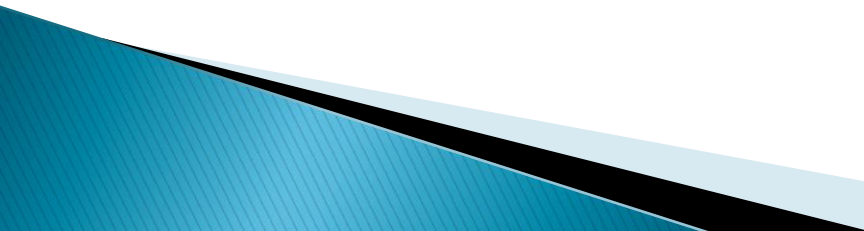The solubility of AgCl, therefore, is the sum of the equilibrium concentrations for all soluble forms of Ag+.

$$S_{AgCl} = [Ag^+] + [AgCl(aq)] + [AgCl_2^-] + [AgCl_3^{2-}]$$
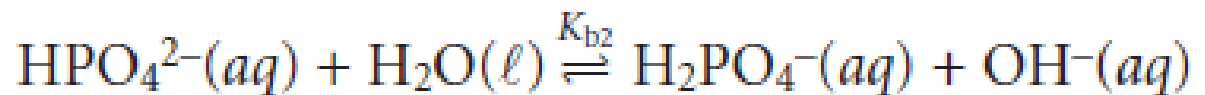
Substituting the equilibrium constant expressions for reactions

$$S_{AgCl} = \frac{K_{sp}}{[Cl^-]} + K_1 K_{sp} + \beta_2 K_{sp}[Cl^-] + \beta_3 K_{sp}[Cl^-]^2$$

- From this final equation we can assume that initially by increasing concentration of Cl ion the solubility of ppt. is decreases but after certain concentration or equilibrium concentration of reaction if more Cl ions are added solubility of ppt increase drastically due to formation of chloro-complexes.
- Hence, the equilibrium concentration of chloride is an important parameter if the concentration of silver is to be determined gravimetrically by precipitating AgCl.
- In particular, a large excess of chloride must be avoided.

pH of reaction condition

- Another important parameter that may affect a precipitate's solubility is the pH of the solution in which the precipitate forms.

- For example, hydroxide precipitates, such as $Fe(OH)_3$, are more soluble at lower pH levels at which the concentration of OH^- is small.

- The effect of pH on solubility is not limited to hydroxide precipitates, but also affects precipitates containing basic or acidic ions.

- The solubility of $Ca_3(PO_4)_2$ is pH-dependent because phosphate is a weak base.

$$Ca_3(PO_4)_2(s) \overset{K_{sp}}{\rightleftharpoons} 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$PO_4^{3-}(aq) + H_2O(\ell) \overset{K_{b1}}{\rightleftharpoons} HPO_4^{2-}(aq) + OH^-(aq)$$

$$HPO_4^{2-}(aq) + H_2O(\ell) \overset{K_{b2}}{\rightleftharpoons} H_2PO_4^-(aq) + OH^-(aq)$$

$$H_2PO_4^-(aq) + H_2O(\ell) \overset{K_{b3}}{\rightleftharpoons} H_3PO_4(aq) + OH^-(aq)$$
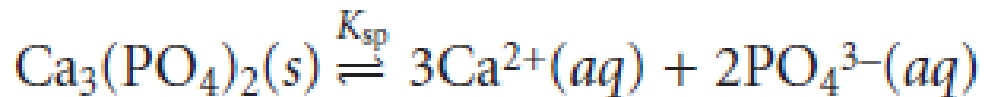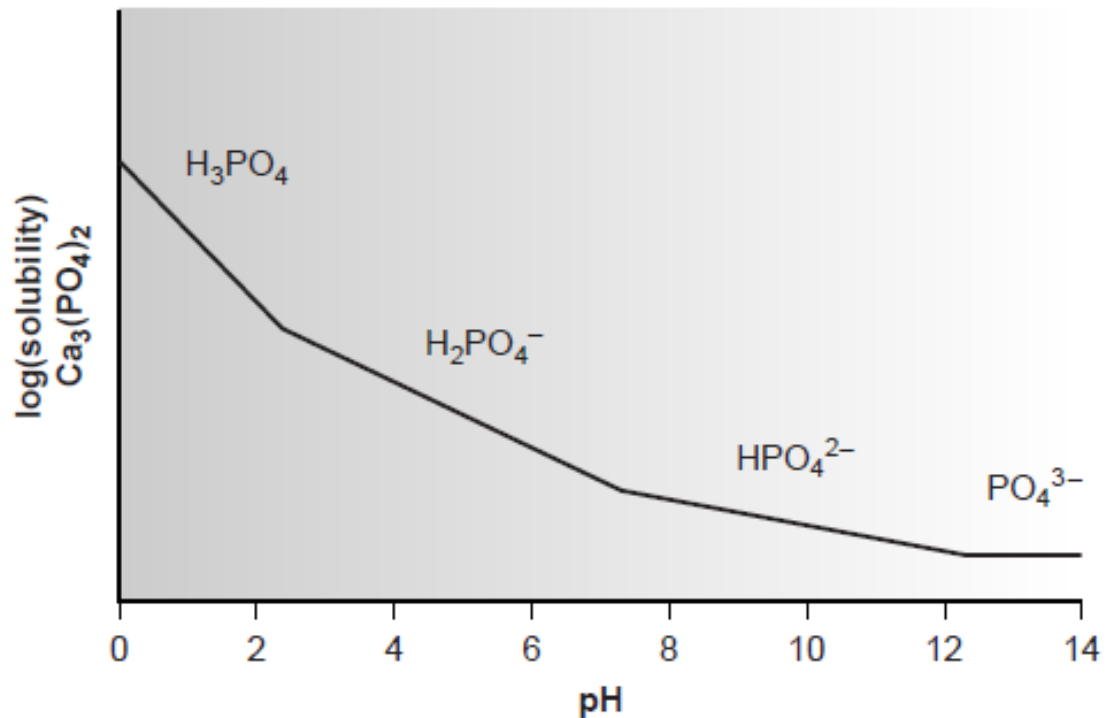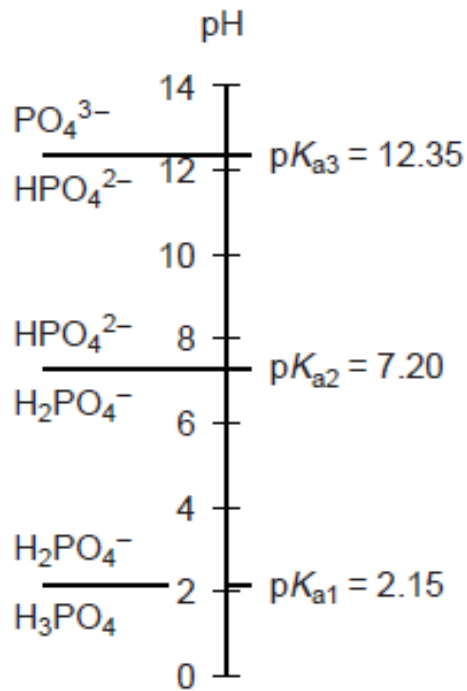
- The ladder diagram for phosphate, shown in Figure provides a convenient way to evaluate the pH-dependent solubility of phosphate precipitates.
- When the pH is greater than 12.4, the predominate phosphate species is PO_4^{3-}, and the solubility of $Ca_3(PO_4)_2$ will be at its minimum because
- As the solution becomes more acidic, the solubility of $Ca_3(PO_4)_2$ increases due to the contributions of remaining reactions.
- As in these all reaction HPO_4^{2-}, H_2PO^{4-}, or H_3PO_4 species are form which can increase the acidity of solution and lower the pH of reaction.

GRAVIMETRIC FACTOR

- The precipitate obtained is usually different from the weight of the analyte we want to report.

- The gravimetric factor (GF): weight of analyte per unit weight of precipitate.

$$GF = \frac{FW\ analyte\ (g/mol)}{FW\ precipitate\ (g/mol)} \times \frac{a}{b}\ (mol\ analyte/mol\ precipitate)$$

EXAMPLE 1

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
NaCl	AgCl

$$g \, \frac{NaCl}{AgCl} = \frac{FW \, NaCl \, (g/mol)}{FW \, AgCl \, (g/mol)} \times \frac{1}{1} \, (mol \, NaCl/mol \, AgCl)$$

$$GF = \frac{1}{1} \times \frac{58.44 \, g/mol}{143.32 \, g/mol} = 0.4078 \, g \, NaCl/mol \, AgCl$$

EXAMPLE 2

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
$2K_2HPO_4$	$Mg_2P_2O_7$

$$g \frac{K_2HPO_4}{Mg_2P_2O_7} = \frac{FW \ K_2HPO_4 \ (g/mol)}{FW \ Mg_2P_2O_7 \ (g/mol)} \ x \ \frac{2}{1} \ (mol \ _2HPO_4 / \ mol \ Mg_2P_2O_7)$$

$$GF = \frac{2}{1} \ x \ \frac{174.2 \ g/mol}{222.6 \ g/mol} = 1.565 \ g \ _2HPO_4 / \ mol \ Mg_2P_2O_7$$

EXAMPLE 3

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte:	Precipitate:
Bi_2S_3	$3BaSO_4$

$$g \frac{Bi_2S_3}{BaSO_4} = \frac{FW\ Bi_2S_3\ (g/mol)}{FW\ BaSO_4\ (g/mol)} \times \frac{1}{3}\ (mol\ Bi_2S_3\ /\ mol\ BaSO_4)$$

$$GF = \frac{1}{3} \times \frac{514.16\ g/mol}{233.43\,g/mol} = 0.734\ g\ Bi_2S_3\ /\ mol\ BaSO_4$$

An ore containing magnetite, Fe_3O_4, was analyzed by dissolving a 1.5419-g sample in concentrated HCl, giving a mixture of Fe^{2+} and Fe^{3+}. After adding HNO_3 to oxidize any Fe^{2+} to Fe^{3+}, the resulting solution was diluted with water and the Fe^{3+} precipitated as $Fe(OH)_3$ by adding NH_3. After filtering and rinsing, the residue was ignited, giving 0.8525 g of pure Fe_2O_3. Calculate the %w/w Fe_3O_4 in the sample.

SOLUTION

This is an example of a direct analysis since the iron in the analyte, Fe_3O_4, is part of the isolated precipitate, Fe_2O_3. Applying a conservation of mass to Fe, we write

$$3 \times \text{moles } Fe_3O_4 = 2 \times \text{moles } Fe_2O_3$$

Using formula weights, FW, to convert from moles to grams in the preceding equation leaves us with

$$\frac{3 \times \text{g } Fe_3O_4}{\text{FW } Fe_3O_4} = \frac{2 \times \text{g } Fe_2O_3}{\text{FW } Fe_2O_3}$$

which can be solved for grams of Fe_3O_4 and %w/w Fe_3O_4 in the sample.

$$\frac{2 \times \text{g } Fe_2O_3 \times \text{FW } Fe_3O_4}{3 \times \text{FW } Fe_2O_3} = \frac{2 \times 0.8525 \text{ g} \times 231.54 \text{ g/mol}}{3 \times 159.69 \text{ g/mol}} = 0.82405 \text{ g } Fe_3O_4$$

$$\frac{\text{g } Fe_3O_4}{\text{g sample}} \times 100 = \frac{0.82405 \text{ g}}{1.5419 \text{ g}} \times 100 = 53.44\% \text{ w/w Fe}$$

Volatilization Gravimetry

- Mostly use for determining water (moisture) carbon dioxide and other volatile compounds.

- DIRECT METHOD: Analyte vapour is collected on any of several solid desiccants (adsorbents), and its mass is determined from the mass gain of desiccants (adsorbents).

- INDIRECT METHOD: Amount of water is determined by the loss of mass of the sample during heating, is less satisfactory because it must assumed that the water is the only component volatilized.
- This method is also known as *Thermogravimetry*

▸ **Thermogravimetry :** It is the method for determining the products of a thermal decomposition is to monitor the sample's mass as a function of temperature. (Mass Vs Temp.)

Thermogram of $CaC_2O_4 \cdot H_2O$ obtained by heating a sample from room temperature to 1000°C at a rate of 20°C/min
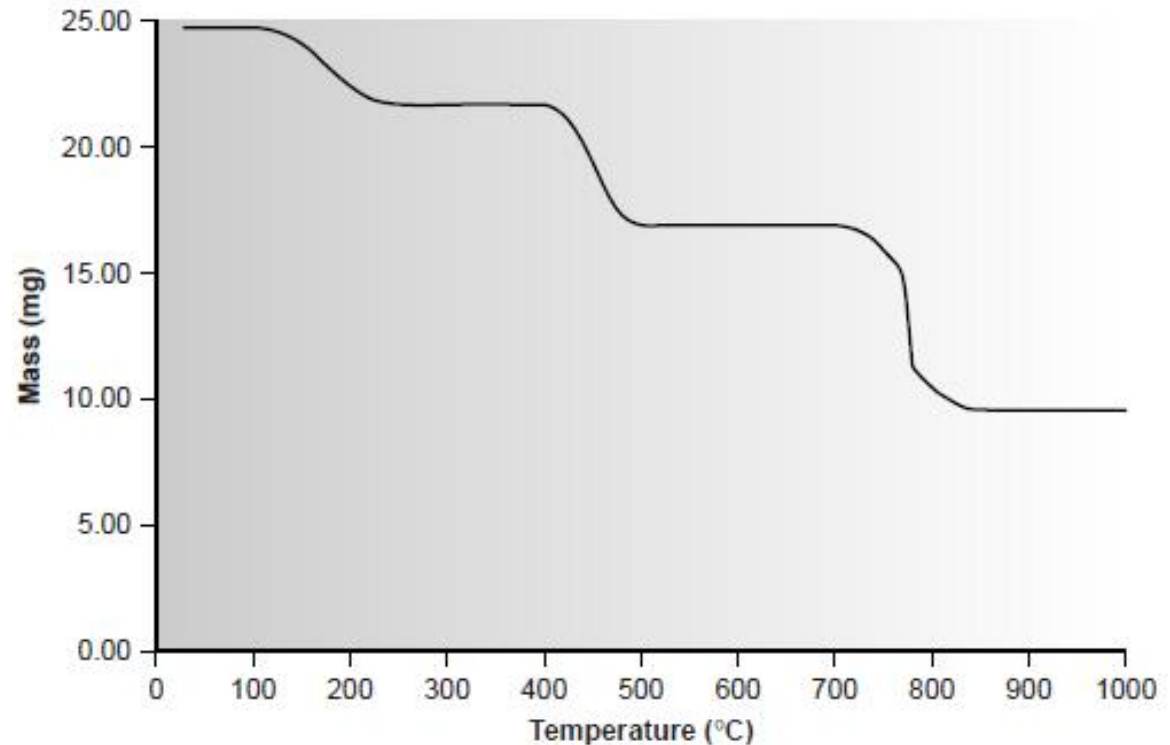
The thermogram in Figure 8.9 shows the change in mass for a sample of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$. The original sample weighed 24.60 mg and was heated from room temperature to 1000 °C at a rate of 5 °C min. The following changes in mass and corresponding temperature ranges were observed:

Loss of 3.03 mg from 100–250 °C

Loss of 4.72 mg from 400–500 °C

Loss of 7.41 mg from 700–850 °C

Determine the identities of the volatilization products and the solid residue at each step of the thermal decomposition.

Hence, there must be **3 volatilization product**.

The loss of 3.03 mg from 100–250 °C corresponds to a 12.32% decrease in the original sample's mass.

$$\frac{3.03 \text{ mg}}{24.60 \text{ mg}} \times 100 = 12.32\%$$

In terms of $CaC_2O_4 \cdot H_2O$, this corresponds to a loss of 18.00 g/mol.

$$0.1232 \times 146.11 \text{ g/mol} = 18.00 \text{ g/mol}$$

The product's molar mass, coupled with the temperature range, suggests that this represents the loss of H_2O. The residue is CaC_2O_4.

The loss of 4.72 mg from 400–500 °C represents a 19.19% decrease in the original mass of 24.60 g, or a loss of

$$0.1919 \times 146.11 \text{ g/mol} = 28.04 \text{ g/mol}$$

This loss is consistent with CO as the volatile product, leaving a residue of $CaCO_3$.

Finally, the loss of 7.41 mg from 700–850 °C is a 30.12% decrease in the original mass of 24.60 g. This is equivalent to a loss of

$$0.3012 \times 146.11 \text{ g/mol} = 44.01 \text{ g/mol}$$

suggesting the loss of CO_2. The final residue is CaO.

A sample of slag from a blast furnace is analyzed for SiO_2 by decomposing a 0.5003-g sample with HCl, leaving a residue with a mass of 0.1414 g. After treating with HF and H_2SO_4 and evaporating the volatile SiF_4, a residue with a mass of 0.0183 g remains. Determine the %w/w SiO_2 in the sample.

SOLUTION

In this procedure the difference in the residue's mass before and after volatilizing SiF_4 gives the mass of SiO_2 in the sample. Thus the sample contained

$$0.1414\ g - 0.0183\ g = 0.1231\ g\ SiO_2$$

The %w/w SiO_2, therefore, is

$$\frac{g\ SiO_2}{g\ sample} \times 100 = \frac{0.1231\ g}{0.5003\ g} \times 100 = 24.61\%\ w/w\ SiO_2$$
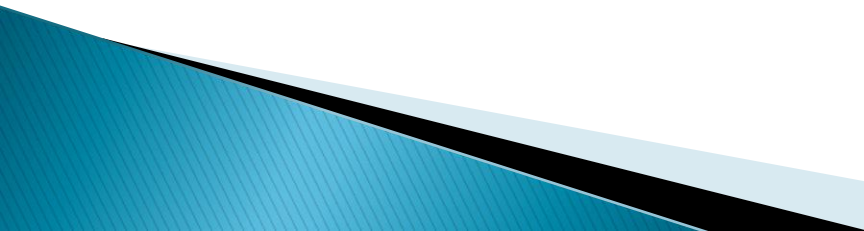
Application of Thermogravimetry

Inorganic Analysis

◦ Determining the inorganic ash content of an organic material, such as a polymer, is an example of a direct volatilization gravimetric analysis.

◦ The determination of dissolved solids (TDS) in natural waters and wastewaters.
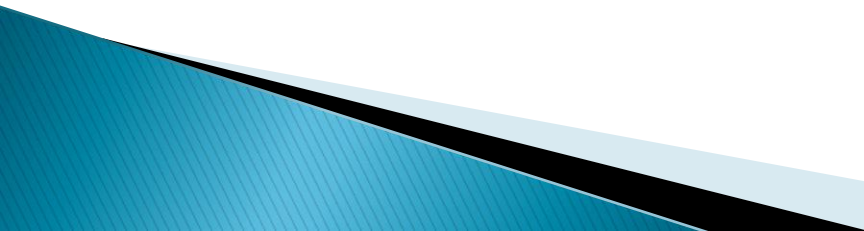
◦ Determining silica in waters by indirect method

Organic Analysis

◦ The most important application of volatilization gravimetry is for the elemental analysis of organic materials.

◦ To determine biomass in waters and wastewaters.

Particulate Gravimetry

- Two approaches :

- Filtration – solid particulates are separated from their gas, liquid or solid matrix

- Extraction – can be extracted from its matrix with a suitable solvent

APPLICATION OF PARTICULATE GRAVIMETRY

▶ Microbiological testing of water

▶ Determination of suspended solid in river water

▶ Total airborne particulates by using high-volume air sample.

▶ Grain size distributions for sediments and soils

Definations

Gravimetry : Any method in which the signal is a mass or change in mass.

Precipitation gravimetry: A gravimetric method in which the signal is the mass of a precipitate.

Electrogravimetry: A gravimetric method in which the signal is the mass of an electrodeposit on the cathode or anode in an electrochemical cell.

Volatilization gravimetry: A gravimetric method in which the loss of a volatile species gives rise to the signal.

Particulate gravimetry : A gravimetric method in which the mass of a particulate analyte is determined following its separation from its matrix.

Homogeneous precipitation: A precipitation in which the precipitant is generated in situ by a chemical reaction.

Relative supersaturation: A measure of the extent to which a solution, or a localized region of solution, contains more dissolved solute than that expected at equilibrium (RSS).

Digestion: The process by which a precipitate is given time to form larger, purer particles.

Occlusion: A coprecipitated impurity trapped within a precipitate as it forms.

Inclusion : A coprecipitated impurity in which the interfering ion occupies a lattice site in the precipitate.

Thermogram: A graph showing change in mass as a function of applied temperature.

Thermogravimetry: A form of volatilization gravimetry in which the change in a sample's mass is monitored while it is heated.

Peptization: The reverse of coagulation in which a coagulated precipitate reverts to smaller particles.

Supernatant: The solution that remains after a precipitate forms.

Coagulation: The process of smaller particles of precipitate clumping together to form larger particles.