Analytical Chemistry

GRAVEMMETRIC ANALYSIS

Sawa University

College of Pharmacology

First Stage

جامعـــــة ســـــــاوة الأهلية

كلية الصيدلة

المرحلـــــــــــة الاولى

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Solubility and Solubility Equilibria

Solubility is a fundamental concept in chemistry that describes the ability of a .substance to dissolve in a solvent

Understanding solubility is essential for analytical chemistry, especially precipitation and gravimetric analysis

Definition of Solubility

Solubility is defined as the maximum amount of a solute that can dissolve in a given amount of solvent at a specific temperature to form a .saturated solution

This definition emphasizes that solubility is not a fixed value but depends on experimental conditions

Saturated, Unsaturated, and Supersaturated Solutions

Unsaturated solution is the solution that contains less solute than the maximum possible amount.

Saturated solution is the solution that contains the maximum amount of solute that can dissolve at equilibrium.

Supersaturated solution is the solution that

Solubility as an Equilibrium Process

When a solid dissolves in water, dissolution and .precipitation occur simultaneously

At equilibrium, the rate of dissolution equals the rate of precipitation, resulting in a constant concentration of dissolved ions

Acording to Solubility, thereis two types of substances

Solubile Salts .1

Solubile Salts .1

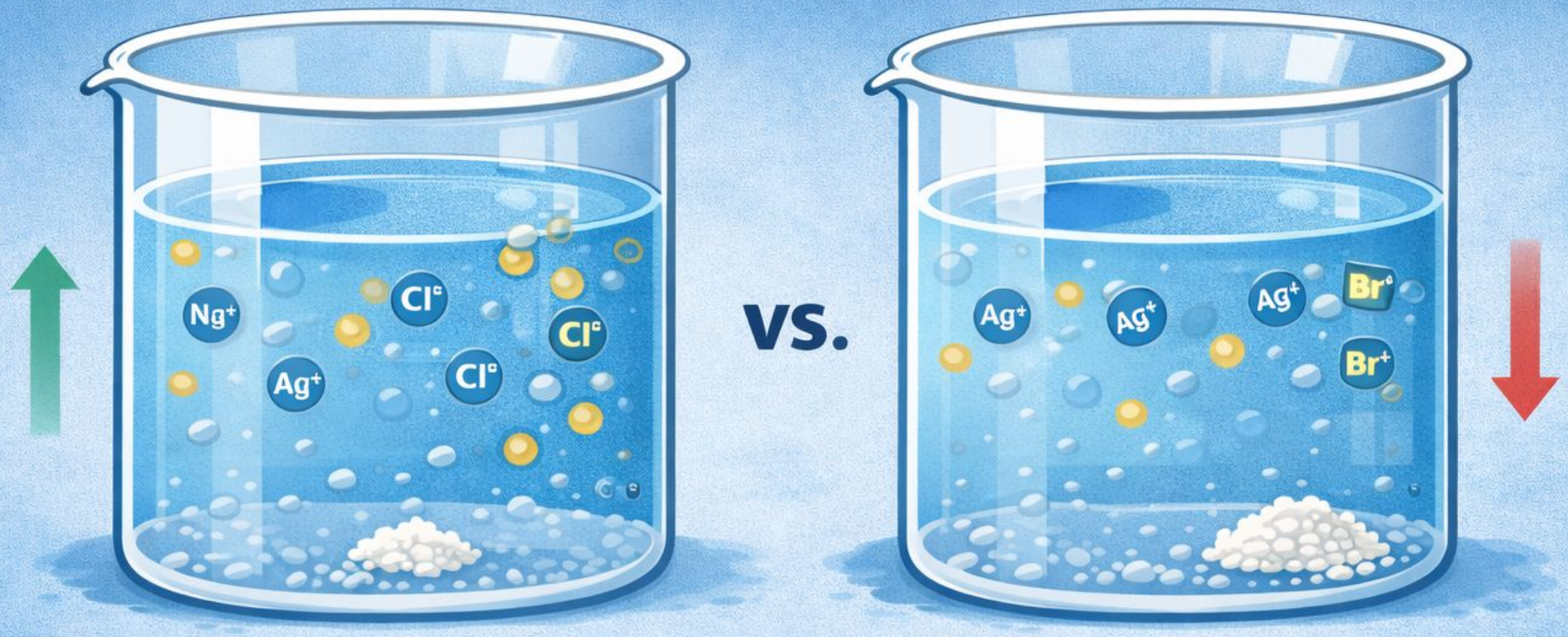
For ionic solids, solubility involves the separation of ions from the crystal lattice and their interaction with water molecules. This process depends on **lattice energy** and **hydration energy**

Slightly Soluble Salts .2

Many salts are described as slightly soluble rather .than completely insoluble

Note/ Even highly insoluble compounds

Soluble or Insoluble?



Soluble Salt (NaCl)

Dissolves easily

(Common Ion Effect)

Insoluble Salt (AgBr)

Does not dissolve easily

(No Common Ion Effect)

Solubility Product Constant (Ksp)

The solubility product constant, Ksp, **is the equilibrium constant for the dissolution of a sparingly soluble ionic compound**. It quantitatively expresses the extent of solubility.

Expression of Ksp

For a general salt:

$$A_mB_n(s) \rightleftharpoons mA^{n+} + nB^{m-}$$

$$K_{sp} = \left[A^{n+}\right]^m \left[B^{m-}\right]^n$$

The concentration of the solid does not appear in the Ksp expression

Example: Silver Chloride

For silver chloride:

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

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

The small value of Ksp explains why AgCl is considered a sparingly soluble salt

Example: Calcium Phosphate – A Sparingly Soluble Salt with Multiple Ions

Dissolution Equilibrium

Calcium phosphate is a sparingly soluble salt that dissociates into **multiple ions** when it dissolves in water:

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

$$K_{sp} = \left[Ca^{2+}\right]^3 \left[PO_4^{3-}\right]^2 = 2 * 10^{-26}$$

Relationship Between Ksp and Solubility

Although related, Ksp and solubility are not the same. Solubility refers to the amount dissolved, while Ksp is an equilibrium constant. The stoichiometry of the salt determines the mathematical relationship between them

Problem Statement

Calculate the molar solubility of silver chloride (AgCl) .in pure water at 25 °C

$$K_{sp}\ (AgCl) = 1.8 \times 10^{-10}$$

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

.AgCl dissociates into two ions

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

.Let the molar solubility be s mol L^{-1}

$$s = [^{+}Ag]$$

$$s = [^{-}Cl]$$

Substitution into Ksp

$$Ksp = (s)(s) = s^2$$

$$s^2 = 1.8 \times 10^{-10}$$

$$s = \sqrt{(1.8 \times 10^{-10})}$$

$$s = 1.34 \times 10^{-5} \text{ mol } L^{-1}$$

The molar solubility of AgCl in water is: $1.34 \times 10^{-5} M$

Problem Statement

Calculate the molar solubility of calcium fluoride (CaF2) in .pure water at 25 °C

$$K_{sp}\ (CaF_2) = 3.9 \times 10^{-11}$$

$$CaF_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2\ F^{-}\ (aq)$$

.This salt dissociates into multiple ions

$$K_{sp} = [Ca^{2+}][F^{-}]^2$$

.The exponents come from stoichiometry

.Let the molar solubility be s mol L^{-1}

$$s = [^{+}Ca^{2}]$$

$$2s = [^{-}F]$$

Substitution into Ksp

$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$4s^3 = 3.9 \times 10^{-11}$$

$$s^3 = 9.75 \times 10^{-12}$$

$$s = \sqrt[3]{(9.75 \times 10^{-12})}$$

$$s = 2.14 \times 10^{-4} \text{ mol } L^{-1}$$

The molar solubility of CaF2 in water is: 2.14×10^{-4} M

Common Ion Effect

The solubility of a salt decreases in the presence of a common ion. This effect is explained by Le Chatelier's principle and is extremely important in gravimetric analysis

Effect of Temperature on Solubility

For most solids, solubility increases with temperature. However, this behavior is not universal and depends on whether dissolution is endothermic or exothermic

Problem

Calculate the **molar solubility of AgCl** in a **0.10 M NaCl solution** at 25 °C.

Given:

$$K_{sp}(AgCl) = 1.8 \times 10^{-10}$$

Step 1 – Dissolution Equilibrium

Silver chloride dissociates according to the equilibrium:

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

$$\mathrm{NaCl}(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Step 2 – Ksp Expression

$$K_{sp} = [Ag^+][Cl^-]$$

Effect of the Common Ion

In pure water:

$$[Ag^+] = [Cl^-] = s$$

But in **0.10 M NaCl solution**:

Chloride ions are already present

$$[Cl^-] \approx 0.10\ M$$

The additional chloride from AgCl dissolution is negligible

$$[Cl^-] = s + 0.10 \approx 0.10$$

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

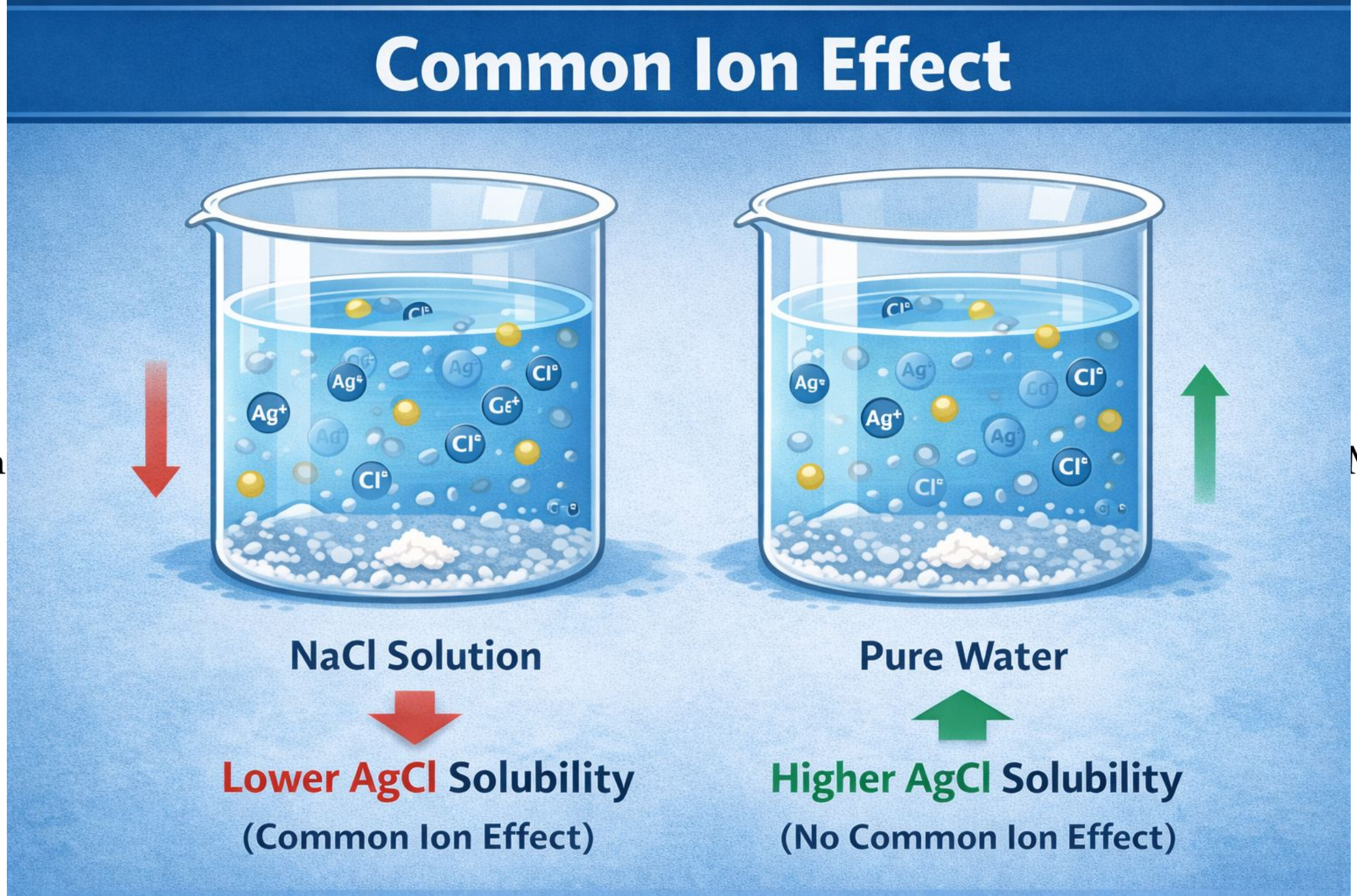
$$K_{sp} = s * 0.1$$

$$1.8 \times 10^{-10} = 0.10\ s$$

$$s = 0.18 \times 10^{-10}$$

The molar solubility of AgCl in water in presance 0.1 M of NaCl is: 0.18×10^{-10} M

Th M


Common Ion Effect
NaCl Solution
Pure Water
Lower AgCl Solubility
(Common Ion Effect)
Higher AgCl Solubility
(No Common Ion Effect)

Solubility and Gravimetric Analysis

Low solubility and a very small Ksp value are essential requirements for gravimetric precipitation. Loss of analyte due to solubility leads .to systematic **negative errors** in gravimetric results

Gravimetric Analysis

Gravimetric analysis is a classical quantitative analytical method .based on precise mass measurements

Despite the development of modern instrumental techniques, gravimetric methods remain fundamental due to their **accuracy and strong theoretical basis**

Definition

Gravimetric analysis is a quantitative analytical technique in which the analyte is converted into a solid compound of known and constant .composition

The amount of analyte is determined by accurately measuring the mass of this solid compound

Fundamental Principle

The fundamental principle of gravimetric analysis is based on .stoichiometry

1. **A known chemical reaction converts the analyte into a stable solid form.**
2. **The mass of this solid is directly related to the amount of analyte present in the original sample**

Why Mass Measurement is Reliable

Mass measurements are among the most accurate physical .measurements in chemistry

Unlike color intensity or electrical signals, **mass does not depend on external calibration when using a properly calibrated analytical balance**

General Requirements of Gravimetric Methods

For a gravimetric method to be valid, The final weighed compound must be chemically

Pure -1

,Stable upon drying or ignition -2

Have a known chemical composition, and -3

Classification of Gravimetric Analysis

According to standard textbooks, gravimetric analysis is classified into

1. **Precipitation gravimetry,**
2. **Volatilization gravimetry, and**
3. **Electrogravimetry.**

Among these, precipitation gravimetry is the most widely applied in routine analysis

Precipitation Gravimetry

In precipitation gravimetry, the analyte reacts with a suitable reagent to form an insoluble precipitate. This precipitate is

Difference Between Analyte and Weighed Compound

In most gravimetric methods, the compound that is finally weighed is **not the analyte itself**. Instead, the analyte is chemically transformed into a different compound that has .more suitable properties for isolation and weighing

This transformation is essential **because many analytes are**

- Soluble,
- Unstable, or
- Difficult to isolate directly.

Gravimetric analysis overcomes this limitation **by converting the analyte into a stable, insoluble form**

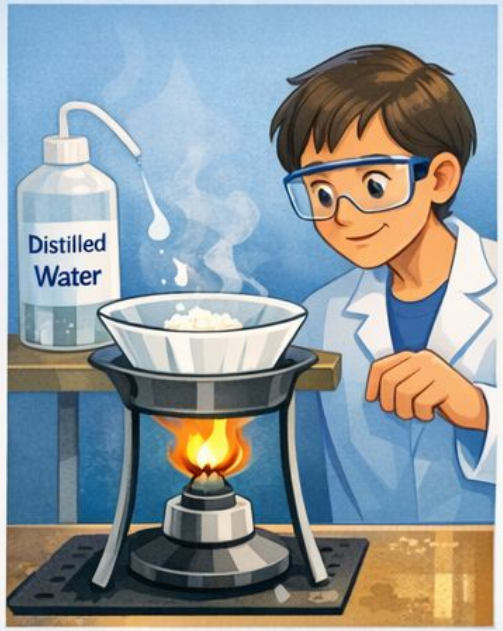
Steps of Gravimetric Analysis (Overview)

A typical gravimetric procedure involves

1. **Precipitation,**
2. **Digestion,**
3. **Filtration,**
4. **Washing,**
5. **Drying or ignition, and**
6. **accurate weighing.**

Each step must be carefully controlled to minimize error

Gravimetric Analysis Steps



Precipitation → **Filtration** → **Washing** → **Drying** → **Weighing**

Precipitate Formation → Filter & Funnel → Rinse with Water → Heat & Dry → Final Mass

with continuous stirring.

This promotes uniform crystal growth and prevents the formation of colloidal particles.

2- Digestion of the Precipitate

Digestion involves heating the precipitate in contact with the mother liquor. This process allows smaller particles to dissolve and recrystallize onto larger ones, improving purity and filterability

3- Filtration

Filtration separates the solid precipitate from the liquid phase. Depending on the nature of the precipitate, filter paper or a glass crucible may be used

4- Washing the Precipitate

Washing removes adsorbed impurities from the precipitate. The

Drying and Ignition -5

- **Drying** removes physically adsorbed water
- **Ignition** converts the precipitate into a stable form of known composition.
- **Heating** is repeated until a constant mass is achieved

Accurate Weighing -6

.The final mass is measured using an analytical balance
Constant mass confirms that the precipitate has reached a stable composition suitable for calculation

Concept of Gravimetric (Weight) Factor

To relate the mass of the weighed compound to the mas
of the analyte, a conversion factor known as the
.**gravimetric factor** is used

Definition of Gravimetric Factor

The gravimetric factor is defined as the ratio between
the molar mass of the analyte and the molar mass of the
weighed compound obtained from the analysis

$$GF = \frac{Molar\ mass\ of\ analyte * n\ of\ analyte}{Molar\ mass\ of\ weighed\ compound}$$

Classical Example: Sulfate Determination

One of the most important gravimetric determinations described in textbooks is the determination of sulfate ions by precipitation as barium sulfate.

Example:

What is the mass of sulfate ion that was present in the original solution if 0.466 g of barium sulfate was obtained

Chemical Reaction for Sulfate

$$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$$

In this method, sulfate is the analyte, while barium sulfate is the weighed compound.

Why $BaSO_4$ is Suitable

- Barium sulfate has **extremely low solubility**,
- **forms dense crystals**, and
- is **chemically stable upon ignition**, making it ideal for gravimetric determination

Gravimetric Factor for Sulfate

Molar mass of SO_4^{2-} = 96.06 g/mol

Molar mass of $BaSO_4$ = 233.39 g/mol

$$GF = \frac{96.06}{233.39} = 0.4116$$

$$\text{Mass of } SO_4^{2-} = 0.4116 \times 0.466$$
$$= 0.192 \text{ g of } SO_4^{2-}$$

Problem

A solution containing iron was treated to .precipitate iron as ferric hydroxide

After filtration and ignition, 0.500 g of Fe_2O_3 .was obtained

Calculate the mass of iron present in the original sample

Precipitation reaction:

$$Fe^{3+}(aq) + 3\,OH^{-}(aq) \rightarrow Fe(OH)_3(s)$$

Ignition reaction:

$$2\,Fe(OH)_3(s) \xrightarrow{\Delta} Fe_2O_3(s) + 3\,H_2O(g)$$

The compound finally weighed is **Fe_2O_3**.

Molar mass of Fe = **55.85 g/mol**

Molar mass of Fe_2O_3:

$$(2 \times 55.85) + (3 \times 16.00) = 159.70\ g/mol$$

Calculate the Gravimetric Factor

The gravimetric factor (GF) relates the mass of iron to the mass of Fe_2O_3:

$$GF = \frac{Molar\ mass\ of\ analyte * n\ of\ analyte}{Molar\ mass\ of\ weighed\ compound}$$

$$GF = \frac{2 \times 55.85}{159.70}$$

$$\boxed{GF = 0.699}$$

Calculate the Mass of Iron

Given:

$$\text{Mass } of\ Fe_2O_3 = 0.500\ g$$

$$Mass\ of\ Fe = GF \times Mass\ of\ Fe2O3 = 0.699 \times 0.500 = 0.350$$

Common Sources of Error

Errors in gravimetric analysis may arise from

- incomplete precipitation,
- coprecipitation,
- loss of precipitate during filtration, or
- insufficient drying or ignition

Problem 1 – Element Appears More Than Once in the Precipitate
A solution containing aluminum ions was analyzed gravimetrically. Aluminum was precipitated as aluminum hydroxide and, after ignition, converted to **aluminum oxide (Al_2O_3)**. If the mass of Al_2O_3 obtained was **0.510 g**, calculate the mass of aluminum present in the .original sample

Problem 2 – Common Ion Effect (Different Materials)
Calculate the molar solubility of **calcium fluoride (CaF_2)** in a solution that already contains **0.020 M sodium fluoride (NaF)** at 25 ° .C

Problem 3 – Percentage Composition (Gravimetric Analysis)
A **1.250 g** solid sample containing calcium was analyzed

Problem 4 – Gravimetric Determination Using a Different Precipitate

A sample containing magnesium ions was analyzed gravimetrically by precipitation as magnesium ammonium phosphate. After ignition, the precipitate was converted to **magnesium pyrophosphate ($Mg_2P_2O_7$)**, and its mass was **0.365 g**. Calculate the mass of .magnesium present in the original sample

Problem 5 – Percentage of Analyte with a Different Element

A **0.985 g** sample containing chloride ions was analyzed gravimetrically by precipitation with silver nitrate to form **silver chloride (AgCl)**. The mass of AgCl obtained after drying was **0.812 .g**. Calculate the **percentage of chloride ion** in the original sample

Problem 6 – A 2.000 g solid sample contains a mixture of calcium sulfate and inert material. The sample was dissolved and sulfate ions were precipitated gravimetrically as barium sulfate ($BaSO_4$) by the addition of excess barium chloride. The precipitation was carried out in the presence of 0.050 M sodium sulfate solution to reduce solubility losses. After digestion, filtration, washing, and ignition, 0.842 g of $BaSO_4$ was obtained