

Subject: Analytical chemistry UOMU027011 Lecturer: Zahraa Salah Hadi 1sterm – Lect 10

#### **Equilibrium in Precipitation**

**Precipitation** is a process where dissolved ions in a solution combine to form a solid, called a precipitate. The process can be described by an equilibrium between the ions in solution and the solid precipitate.

At equilibrium, the rate at which the precipitate forms (precipitation) is equal to the rate at which the solid dissolves back into the solution (dissolution). This equilibrium can be represented as:

Dissolution: AB (solid) 
$$\rightleftharpoons$$
 A<sup>+</sup>(aq) + B<sup>-</sup>(aq)

Where AB is the solid precipitate, and A<sup>+</sup> and B<sup>-</sup> are the ions in solution.

The equilibrium constant for this reaction is called the **solubility product constant (Ksp)**, which is specific to the compound in question.

#### Solubility

**Solubility** refers to the maximum amount of a solute that can dissolve in a solvent to form a saturated solution at a given temperature and pressure. When the concentration of dissolved ions reaches a level at which the solution is in equilibrium with the solid precipitate, the system is considered to be saturated.

For a salt AB dissociating into ions, the solubility product expression is:

$$K_{sp}=[\mathrm{A}^+][\mathrm{B}^-]$$

Where:

- [A<sup>+</sup>] and [B<sup>-</sup>] are the molar concentrations of the ions in solution at equilibrium.
- Ksp is the solubility product constant, which is a measure of how much of the solid can dissolve in water.



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If the concentration of either ion exceeds the value that would make the product equal to the Ksp, the solution is considered supersaturated, and precipitation will occur.

### Precipitation

**Precipitation** occurs when the concentration of ions in a solution exceeds the solubility limit, meaning the product of their concentrations is greater than the solubility product constant (Ksp). In this case, the excess ions combine to form a solid precipitate.

This is governed by the relationship:

$$Q = [\mathbf{A}^+][\mathbf{B}^-]$$

Where  $\mathbf{Q}$  is the ion product. If  $\mathbf{Q} > \mathbf{Ksp}$ , precipitation occurs, and solid AB will form. If  $\mathbf{Q} = \mathbf{Ksp}$ , the solution is saturated and no further precipitation occurs. If  $\mathbf{Q} < \mathbf{Ksp}$ , no precipitation occurs because the solution is unsaturated.

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#### **Partial Precipitation**

**Partial precipitation** occurs when one of the ions in a mixture of two or more salts reaches its solubility limit and precipitates out, while the other ions remain dissolved in the solution. This is a common phenomenon when dealing with mixtures of salts that have different solubilities.

For example, consider a solution containing both AgCl and PbCl<sub>2</sub>. If the concentration of chloride ions increases, AgCl will precipitate first because its Ksp is smaller than that of PbCl<sub>2</sub>. Only after all of the Ag<sup>+</sup> ions have precipitated out will PbCl<sub>2</sub> begin to precipitate.

#### **Conditions for Partial Precipitation**

Partial precipitation depends on:

- 1. The relative solubility products (Ksp) of the salts. A salt with a lower Ksp will precipitate first.
- 2. **The concentration of common ions**. If one of the ions (e.g., Cl<sup>-</sup> in the example above) is present in large excess, it will affect the precipitation of the other salts.

In practice, **partial precipitation** is used in **fractional crystallization**, a technique where selective precipitation of ions is used to separate different substances from a mixture.



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## **Summary**

- Equilibrium in Precipitation: Precipitation occurs when the ion product (Q) exceeds the Ksp. At equilibrium, the rate of dissolution equals the rate of precipitation.
- **Solubility**: The maximum amount of solute that can dissolve in a solvent, expressed as the solubility product constant (Ksp).
- Precipitation: The process when ions in a solution combine to form a solid when their concentrations exceed the solubility limit.
- Partial Precipitation: Occurs when one ion