

CHAPTER IV : Solubility

1. Definitions

Solubility is the ability of a substance (**solute**) to dissolve in a liquid (**solvent**) to form a homogeneous solution. It is typically expressed as the maximum amount of solute that can dissolve in a given quantity of solvent at a specific temperature and pressure. Solubility (**S**) is expressed in $\text{mol}\cdot\text{L}^{-1}$ or $\text{g}\cdot\text{L}^{-1}$.

Examples

- **KNO₃ (Potassium Nitrate)**: $S \approx 10 \text{ mol}\cdot\text{L}^{-1}$, highly soluble in water.
- **Ca(OH)₂ (Calcium Hydroxide)**: $S \approx 0.02 \text{ mol}\cdot\text{L}^{-1}$, moderately soluble in water.
- **Mg(OH)₂ (Magnesium Hydroxide)**: $S \approx 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, slightly soluble in water.
- **NaCl (Sodium chloride)**: $S \approx 6 \text{ mol}\cdot\text{L}^{-1}$, highly soluble in water.

Note :

1. A solution is considered **saturated** with a compound **A** when its concentration exceeds the solubility limit, leading to the precipitation of this compound.

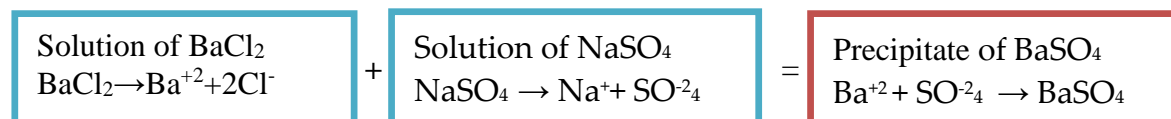
2. A chemical species is considered **sparingly soluble** when $s < 10^{-2} \text{ mol}\cdot\text{L}^{-1}$.

2. Precipitation Reaction

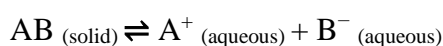
A **precipitation reaction** is a type of chemical reaction in which two aqueous solutions combine to form an insoluble solid, known as a **precipitate**. This reaction occurs when the ions in the two solutions interact and create a compound that cannot dissolve in water, resulting in the formation of a solid.

Example

When two solutions containing separately the ions **Ba²⁺** and **SO₄²⁻** of the slightly soluble compound **BaSO₄** are mixed, BaSO₄ precipitates during the mixing (provided that the solution reaches saturation with respect to BaSO₄).

3. Solubility product

For a solid ionic compound AB dissolving in water



The equilibrium constant K is given by

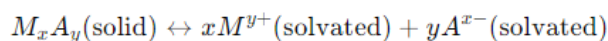
$$K = [\text{A}^+][\text{B}^-]/[\text{AB}_{(\text{solid})}]$$

Since the concentration of a pure solid (AB) is constant, it can be incorporated into the equilibrium constant to define the **solubility product constant (K_s)** :

$$K_s = [A^+]. [B^-]$$

General Case

For an ionic compound M_xA_y dissolving in water:



The solubility product K_s is given by:

$$K_s = [M^{y+}]^x [A^{x-}]^y$$

Where $[M^{y+}]$ and $[A^{x-}]$ are the concentrations of the dissociated ions in the solution, raised to the power of their respective stoichiometric coefficients.

$$pK_s = -\log(K_s)$$

Example

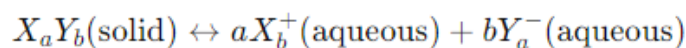
Table 1. Numerical values for solubility product (K_s) in Water at 25°C

Formula	Name	K_s
NaCl	Sodium chloride	38.98
PbCl ₂	Lead(II) chloride	1.6×10^{-5}
Ca(OH) ₂	Calcium hydroxide	5.5×10^{-6}
Cu(OH) ₂	Copper(II) hydroxide	2.2×10^{-20}
HgS	Mercury(II) sulfide	4×10^{-53}

4. Relation between molar solubility and solubility product (K_s)

The dissolution of an ionic compound with the general formula X_aY_b is represented as:

This means that for every mole of X_aY_b that dissolves, **a** moles of X_b^+ (cation) and **b** moles of Y_a^- (anion) are produced.



$$\text{à } t = 0 \quad \quad \quad S \quad \quad \quad 0 \quad \quad \quad 0$$

$$\text{à } t = t \quad \quad \quad 0 \quad \quad \quad aS \quad \quad \quad bS$$

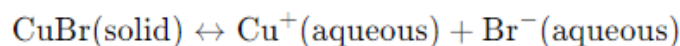
$$K_s = [X^{b+}]^a \cdot [Y^{a-}]^b = (aS)^a \cdot (bS)^b = (a)^a \cdot (b)^b S^{a+b}$$

$$S = (K_s / (a)^a \cdot (b)^b)^{1/a+b} \quad S = \sqrt[a+b]{\frac{K_s}{a^a \cdot b^b}}$$

Examples

2.1.1. An ionic compound of type XY

Consider that the Copper (I) bromide (CuBr), dissolves in water according to the equilibrium



$$\text{à } t = 0 \quad \quad \quad \text{S} \quad \quad \quad 0 \quad \quad \quad 0$$

$$\text{à } t = t \quad \quad \quad 0 \quad \quad \quad \text{S} \quad \quad \quad \text{S}$$

$$K_S = [\text{Cu}^+].[\text{Br}^-] = \text{S} \cdot \text{S} = \text{S}^2 \rightarrow \text{S} = (\text{K}_S)^{1/2}$$

$$\text{Given the value of } K_S \text{ for CuBr : } K_S = 5.3 \times 10^{-9} \rightarrow \text{S} = 7.2 \cdot 10^{-5} \text{ mole.L}^{-1}$$

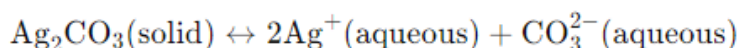
To find the **mass solubility** S_m of CuBr

$$S_m = S \times M = (7.2 \times 10^{-5} \text{ mol/L}) \times (143.45 \text{ g/mol})$$

$$S_m = 1.03 \times 10^{-2} \text{ g/L}$$

2.1.2. An ionic compound of type X₂Y

Consider that the silver carbonate (Ag₂CO₃) dissolves in water according to the following equilibrium. Given the value of K_S for Ag₂CO₃ : $K_S = 8.1 \times 10^{-18}$, Calculate the molar solubility (S) (mole.L⁻¹) and the mass solubility (S_m) (g.L⁻¹)



$$\text{à } t = 0 \quad \quad \quad \text{S} \quad \quad \quad 0 \quad \quad \quad 0$$

$$\text{à } t = t \quad \quad \quad 0 \quad \quad \quad 2\text{S} \quad \quad \quad \text{S}$$

$$K_S = [\text{Ag}^+]^2.[\text{CO}_3^{2-}] = (2\text{S})^2 \cdot \text{S} = 4\text{S}^3 \rightarrow \text{S} = (\text{K}_S/4)^{1/3}$$

$$\text{Given the value of } K_S \text{ for Ag}_2\text{CO}_3 : K_S = 8.1 \times 10^{-18} \rightarrow \text{S} = 1,26 \cdot 10^{-6} \text{ mole.L}^{-1}$$

$$M = 275,7 \text{ g/mol} \rightarrow S_m = 3,49 \cdot 10^{-4} \text{ g/L}$$

5. Factors Influencing Solubility

5.1. Effect of Temperature

The solubility of a chemical species depends on the value of its solubility constant (K_S), which in turn is influenced by temperature (T) according to Van 't Hoff's law:

$$\frac{d \ln K_S}{dT} = \frac{\Delta_{diss} H^0}{RT^2}$$

ΔH°_{diss} : The standard enthalpy of dissolution of the chemical species at 298 K.

In most cases, the dissolution of an electrolyte is an endothermic process. As a result, the solubility constant (K_S) generally increases with temperature (T), making solubility a rising function of temperature.

Solubility ($S \nearrow$) typically increases with temperature ($T \nearrow$).

Example

At $T=10^\circ\text{C}$, the solubility of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is $S_m=1.4\text{ g/L}$.

At $T=25^\circ\text{C}$, the solubility of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is $S_m=2.4\text{ g/L}$.

5.2. Effect of a common ion on solubility

What happens when a compound is dissolved in a solution that already contains one of its ions?

Example

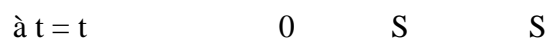
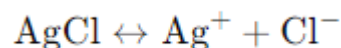
Consider the dissolution of silver chloride (AgCl) in a hydrochloric acid solution with a molar concentration of 0.1 M .

Solution

Hydrochloric acid is a strong acid and dissociates completely into H^+ and Cl^- ions



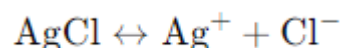
Solubility of AgCl in pure water is given by



$$K_s = [\text{Ag}^+].[\text{Cl}^-] = S \cdot S = S^2 \rightarrow S = (K_s)^{1/2}$$

Given the value of K_s for AgCl : $K_s = 1.8 \times 10^{-10} \rightarrow S = 1.35 \cdot 10^{-5} \text{ mole.L}^{-1}$

Solubility of AgCl in a 0.1 M hydrochloric acid solution



$$K_s = [\text{Ag}^+].[\text{Cl}^-]$$

Given

$$[\text{Ag}^+] = S' \text{ (the solubility of AgCl in the acid solution)}$$

$$[\text{Cl}^-] = S' + 0.1 \text{ (since there is already } 0.1\text{ M of } \text{Cl}^- \text{ from the hydrochloric acid)}$$

So the solubility product expression becomes:

$$K_s = S' \times (S' + 0.1)$$

We know that the solubility product K_s of AgCl is: $K_s=1.8 \times 10^{-10}$

Substituting this into the equation

$$1.8 \times 10^{-10} = S' \times (S' + 0.1)$$

We can make an approximation. Since S' (the solubility of AgCl in this solution) is very small compared to 0.1, we can approximate that $S' + 0.1 \approx 0.1$. This approximation simplifies the equation to

$$1.8 \times 10^{-10} \approx S' \times 0.1$$

$$\text{So : } S' = \frac{1.8 \times 10^{-10}}{0.1}$$

The solubility of AgCl in pure water is $S = 1.35 \times 10^{-5}$ mol/L

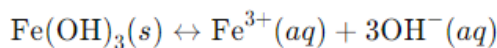
The solubility of AgCl in a 0.1 M hydrochloric acid is $S' = 1.8 \times 10^{-9}$ mol/L

Thus, the solubility of AgCl is significantly reduced in the presence of a common ion (chloride ion Cl^-).

Solubility ($S \searrow$) typically decreases with the addition of a common ion to the solubility equilibrium.

5.3. Influence of pH

Consider the equilibrium for iron(III) hydroxide dissolution



The solubility product K_s is

$$K_s = [\text{Fe}^{3+}][\text{OH}^-]^3$$

The autoionization of water is given by

$$K_e = [\text{OH}^-][\text{H}_3\text{O}^+] \quad [\text{OH}^-] = \frac{K_e}{[\text{H}_3\text{O}^+]}$$

$$K_s = [\text{Fe}^{3+}] \left(\frac{K_e}{[\text{H}_3\text{O}^+]} \right)^3$$

Let $S = [\text{Fe}^{3+}]$, the solubility of $\text{Fe}(\text{OH})_3$

$$K_s = S \left(\frac{K_e}{[\text{H}_3\text{O}^+]} \right)^3 \quad S = \frac{K_s \times [\text{H}_3\text{O}^+]^3}{K_e^3}$$

Solubility ($S \nearrow$) typically increases with the addition of H_3O^+ ions, which means the pH decreases ($\text{pH} \searrow$).

Example

Dissolution in an acidic medium of a salt of a weak acid, Silver Nitrite (AgNO_2)

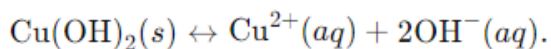
Solution

???

5.4. Effect of complexation on the solubility

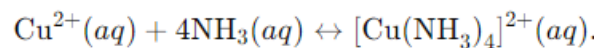
Example

The dissolution of $\text{Cu}(\text{OH})_2$ in pure water is given by the reaction:



The solubility product : $K_s = 2.2 \times 10^{-20}$.

In the presence of ammonia (NH_3), Cu^{2+} forms a soluble complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ via the reaction :



The formation constant of this complex is : $K_f = 1.0 \times 10^{13}$.

- 1) Calculate the solubility of $\text{Cu}(\text{OH})_2$ in pure water.
- 2) Explain how the addition of a 0.1 M solution of NH_3 affects the solubility of $\text{Cu}(\text{OH})_2$.

Solution

???