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 **mol·L⁻¹** or **g·L⁻¹**.

Examples

- **KNO_3 (Potassium Nitrate)**: $S \approx 10$ mol.L^{-1}, highly soluble in water.
- **$Ca(OH)_2$ (Calcium Hydroxide)**: $S \approx 0.02$ mol.L^{-1}, moderately soluble in water.
- **$Mg(OH)_2$ (Magnesium Hydroxide)**: $S \approx 10^{-4}$ mol.L^{-1}, slightly soluble in water.
- **NaCl(**Sodium chloride**)**: $S \approx 6$ mol.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 $s < 10^{-2}$ mol.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 **Ba^{2+}** and **SO_4^{2-}** of the slightly soluble compound **$BaSO_4$** are mixed, $BaSO_4$ precipitates during the mixing (provided that the solution reaches saturation with respect to $BaSO_4$).

Solution of $BaCl_2$
$BaCl_2 \rightarrow Ba^{+2} + 2Cl^-$

+

Solution of $NaSO_4$
$NaSO_4 \rightarrow Na^+ + SO^{-2}_4$

=

Precipitate of $BaSO_4$
$Ba^{+2} + SO^{-2}_4 \rightarrow BaSO_4$

3. Solubility product

For a solid ionic compound AB dissolving in water

$AB_{(solid)} \rightleftharpoons A^+_{(aqueous)} + B^-_{(aqueous)}$

The equilibrium constant K is given by

$K = [A^+][B^-]/[AB_{(solid)}]$

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

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

General Case

For an ionic compound M_xA_y dissolving in water:

$$M_xA_y(\text{solid}) \leftrightarrow xM^{y+}(\text{solvated}) + yA^{x-}(\text{solvated})$$

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 (Ks) 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 (Ks)

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.

$$X_aY_b(\text{solid}) \leftrightarrow aX_b^+(\text{aqueous}) + bY_a^-(\text{aqueous})$$

à t = 0	S	0	0
à t = t	0	aS	bS

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

$$S = (K_S/(a)^a. (b)^b)^{1/a+b} \qquad S = \sqrt[a+b]{\frac{K_S}{a^a.b^b}}$$

Examples

2.1.1. An ionic compound of type XY

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

$$\mathrm{CuBr(solid)} \leftrightarrow \mathrm{Cu^{+}(aqueous)} + \mathrm{Br^{-}(aqueous)}$$

à t = 0	S	0	0
à t = t	0	S	S

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

Given the value of Ks for CuBr : $Ks = 5.3\times10^{-9} \rightarrow S = 7{,}2.10^{-5}$ mole.L^{-1}

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

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

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

2.1.2. An ionic compound of type X_2Y

Consider that the silver carbonate (Ag_2CO_3) dissolves in water according to the following equilibrium. Given the value of Ks for Ag_2CO_3 : $Ks = 8.1\times10^{-18}$, Calculate the molar solubility **(S)** (mole.L^{-1}) and the mass solubility (**S_m**) (g.L^{-1})

$$\mathrm{Ag_2CO_3(solid)} \leftrightarrow \mathrm{2Ag^{+}(aqueous)} + \mathrm{CO_3^{2-}(aqueous)}$$

à t = 0	S	0	0
à t = t	0	2S	S

$K_S = [Ag^+]^2.[CO_3^{2-}] = (2S)^2\ .\ S = 4S^3 \rightarrow S = (Ks/4)^{1/3}$

Given the value of Ks for Ag_2CO_3 : $Ks = 8.1\times10^{-18} \rightarrow S = 1{,}26.10^{-6}$ mole.L^{-1}

M = 275,7 g/mol → $S_m = 3{,}49.10^{-4}$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 (Ks), which in turn is influenced by temperature (T) according to Van 't Hoff's law:

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

$\Delta H°_{diss}$: 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 (Ks) generally increases with temperature (T), making solubility a rising function of temperature.

Solubility (**S** ↗) typically increases with temperature (T↗).

Example

At T=10° C, the solubility of benzoic acid (C_6H_5COOH) is S_m =1.4 g/L.

At T=25° C, the solubility of benzoic acid (C_6H_5COOH) is S_m=2.4 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

$$\mathrm{HCl} \rightarrow \mathrm{H}^+ + \mathrm{Cl}^-$$

Solubility of AgCl in pure water is given by

$$\mathrm{AgCl} \leftrightarrow \mathrm{Ag}^+ + \mathrm{Cl}^-$$

à t = 0	S	0	0
à t = t	0	S	S

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

Given the value of Ks for AgCl : $Ks = 1.8 \times 10^{-10} \rightarrow S = 1.35.10^{-5}$ mole.L^{-1}

Solubility of AgCl in a 0.1 M hydrochloric acid solution

$$\mathrm{AgCl} \leftrightarrow \mathrm{Ag}^+ + \mathrm{Cl}^-$$

à t = 0	S′	0	0
à t = t	0	S′	S′ + 0.1

$K_S = [Ag^+].[Cl^-]$

Given

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

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

So the solubility product expression becomes:

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

We know that the solubility product Ks of AgCl is: $Ks=1.8\times10^{-10}$

Substituting this into the equation

$1.8\times10^{-10} = S'\times (S' + 0.1)$

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≈ 0.1. This approximation simplifies the equation to

$1.8\times10^{-10} \approx S' \times 0.1$

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

The solubility of AgCl in pure water is **S** $=1.35\times10^{-5}$ mol/L

The solubility of AgCl in a 0.1 M hydrochloric acid is **S′** $=1.8\times10^{-9}$ mol/L

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

Solubility (**S**↘) 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

$$\mathrm{Fe(OH)_3}(s) \leftrightarrow \mathrm{Fe^{3+}}(aq) + 3\mathrm{OH^-}(aq)$$

The solubility product Ks is

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

The autoionization of water is given by

$$K_e = [\mathrm{OH^-}][\mathrm{H_3O^+}] \qquad [\mathrm{OH^-}] = \frac{K_e}{[\mathrm{H_3O^+}]}$$

$$K_s = [\mathrm{Fe^{3+}}]\left(\frac{K_e}{[\mathrm{H_3O^+}]}\right)^3$$

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

$$K_s = S\left(\frac{K_e}{[\mathrm{H_3O^+}]}\right)^3 \qquad S = \frac{K_s \times [\mathrm{H_3O^+}]^3}{K_e^3}$$

Solubility (S↗) typically increases with the addition of H_3O^+ ions, which means the pH decreases (pH↘).

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 $Cu(OH)_2$ in pure water is given by the reaction:

$$\mathrm{Cu(OH)_2}(s) \leftrightarrow \mathrm{Cu^{2+}}(aq) + 2\mathrm{OH^-}(aq).$$

The solubility product : Ks =2.2×10^{-20}.

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

$$\mathrm{Cu^{2+}}(aq) + 4\mathrm{NH_3}(aq) \leftrightarrow [\mathrm{Cu(NH_3)_4}]^{2+}(aq).$$

The formation constant of this complex is : $K_f = 1.0\times10^{13}$.

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

Solution

???