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 ≈ 10 mol.L^{-1}, highly soluble in water.
- **$Ca(OH)_2$ (Calcium Hydroxide)**: S ≈ 0.02 mol.L^{-1}, moderately soluble in water.
- **$Mg(OH)_2$ (Magnesium Hydroxide)**: S ≈ 10^{-4} mol.L^{-1}, slightly soluble in water.
- **NaCl(Sodium chloride)**: S ≈ 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 (Ks)

For a solid ionic compound AB dissolving in water

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

The equilibrium constant Ks is given by:

$$K_s = \frac{[A^+][B^-]}{[AB_{(solid)}]}$$

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):

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

General Case

For an anionic compound M_xA_y dissolving in water

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

The solubility product Ks is given by

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

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

Because solubility products are often extremely small, it is convenient to express them using:

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

So, $K_s = 10^{-pK_s}$

Note: A high Ks corresponds to a more soluble compound, whereas a low pKs indicates greater solubility.

Table 1. Solubility product constants (Ks) for some compounds in Water at 25°C, along with their corresponding pKs.

Compound	Formula	Ks	pKs
Silver bromide	$AgBr$	5.35×10^{-13}	12.27
Silver chloride	$AgCl$	1.77×10^{-10}	9.8
Calcium carbonate	$CaCO_3$	3.36×10^{-9}	8.47
Barium sulfate	$BaSO_4$	1.08×10^{-10}	9.97
Lead (II) sulfate	$PbSO_4$	2.53×10^{-8}	7.59
Magnesium hydroxide	$Mg(OH)_2$	1.0×10^{-11}	11.0
Lead (II) chloride	$PbCl_2$	1.70×10^{-5}	4.77
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}	5.30

4. Relation between molar solubility (S) and solubility product (Ks)

Case 1. *An ionic compound of type XY* (1:1)

An ionic compound XY is made up of a cation X^+ and an anion Y^-, each with a stoichiometric coefficient equal to 1

	$XY\ (s)$	$\rightleftharpoons$	$X^+\ (aq)+$	$Y^-(aq)$
T=0	S		0	0
T=eq	0		S	S

S: is the molar solubility (mol/L)

$$K_s = [X^+].[Y^-] = \boldsymbol{S.S} = \boldsymbol{S^2} \rightarrow S = \boldsymbol{K_s}^{1/2}$$

$$\rightarrow S = \sqrt{K_s}$$

Example

Consider the ionic compound Copper bromide (CuBr), dissolves in water according to the equilibrium. Given the solubility product $K_s(CuBr) = 5.3\times10^{-9}$, calculate the molar solubility.

Solution

Case 2. *An ionic compound of type* X_2Y (2:1)

In this case the dissolution equation gives cation $2X^+$ and an anion Y^-.

	$X_2Y\ (\boldsymbol{s})$	$\rightleftharpoons$	$2X^+\ (aq)+$	$Y^{2-}(\boldsymbol{aq})$
T=0	S		0	0
T=eq	0		2S	S

$$\boldsymbol{K_s} = [X^+]^2.[\boldsymbol{Y^{2-}}] = (\boldsymbol{2S^2}).\boldsymbol{S} = \boldsymbol{4S^3}$$

$$\rightarrow \boldsymbol{K_s} = \left(\frac{K_s}{4}\right)^{1/3} = \sqrt[3]{\frac{K_s}{4}}$$

Example

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})

Solution

Case 3. *An ionic compound of type* X_aY_b

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.

	$\boldsymbol{X_a Y_b}\ (\boldsymbol{s})$	$\rightleftharpoons$	$aX_b^+\ (aq)+$	$\boldsymbol{bY_a^-(aq)}$
T=0	S		0	0
T=eq	0		aS	bS

$$\boldsymbol{K_s} = [\boldsymbol{X_b^+}]^{\boldsymbol{a}}.[\boldsymbol{Y_a^-}]^{\boldsymbol{b}} = (\boldsymbol{aS})^{\boldsymbol{a}}.(\boldsymbol{bS})^{\boldsymbol{b}}$$

$$K_s = a^a . b^b . S^{a+b}$$

$$\frac{K_s}{a^a . b^b} = S^{a+b}$$

$$S = \left(\frac{K_s}{a^a . b^b}\right)^{\frac{1}{(a+b)}}$$

$$S = \sqrt[(a+b)]{\frac{K_s}{a^a . b^b}}$$

Example

We study the solubility of bismuth phosphate, $Bi_3(PO_4)_2$, a very sparingly soluble ionic solid. When it dissolves in water, it dissociates according to the following equation:

1. Write the expression of the solubility product Ks for this solid.
2. Deduce the relationship between Ks and the molar solubility S.
3. Calculate the solubility (S) if the given solubility product is Ks = 1.3 x 10^{-23}.

Solution

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

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

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

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

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 $Cu(OH)_2$ 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 $=2.2\times10^{-20}$.

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

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

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

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

???