CHAPTER IV :

DISSOLUTION-PRECIPITATION REACTIONS

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CHAPTER IV :

DISSOLUTION-PRECIPITATION REACTIONS

This chapter explores the concept of solubility, the principles behind precipitation reactions, and the solubility product constant (Ksp), which quantifies the equilibrium between dissolved and undissolved species. Additionally, it examines various factors influencing solubility, such as temperature, common ion effect, and pH. Understanding these processes is essential for applications in analytical chemistry.

1-Solubility

The solubility **S** of a solid compound is the maximum number of moles of this solid that can dissolve in one liter of solvent at a given temperature.

Example :

- NaCl: S ≈ 6 mole/L, NaCl is a very water-soluble compound.

- AgCl: S ≈ 10-5 mole/L. AgCl is a compound with very low solubility in water.

When the concentration of a compound AB is greater than the solubility value, the solution is said to be saturated with AB and precipitation occurs.

2-Precipitation reaction.

When two solutions containing the two ions (Ba^{2+} and SO^{-2}_4) of a poorly soluble compound $BaSO_4$ are mixed separately, the latter precipitates during mixing (provided that saturation with $BaSO_4$ is reached).

$BaCl_2$ Solution $BaCl_2$--->Ba^{+2}+2Cl^-	+	$NaSO_4$ Solution $NaSO_4$--->Na^++ SO^{-2}_4	=	$BaSO_4$ Precipitate Ba^{+2}+ SO^{-2}_4---> $BaSO_4$

3-Solubility product.

3-1-Definition

When a compound ($BaSO_4$) precipitates during a precipitation reaction, traces of its ions (Ba^{2+}(aq) and SO_4^{2-}(aq)) always remain in solution, even if the solubility is very low.

An equilibrium is therefore established between the solid formed ($BaSO_4$) and the ions remaining in solution (Ba^{2+}(aq) and SO_4^{2-}(aq)): heterogeneous equilibrium:

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

L.A.M: $K_C = [Ba^{2+}][SO_4^{2-}]/[BaSO_4]$; $[BaSO_4]=1$

$$K_C = K_s = [Ba^{2+}][SO_4^{2-}] \ mol^2.l^{-2}$$

Ks is the solubility product of **$BaSO_4$.**

We also define **pKs = -log Ks**, which is a characteristic of **$BaSO_4$**. The more soluble the compound, the greater Ks, the smaller the **pKs.**

To compare two compounds, it is more accurate to compare their solubility. For a solid of general formula , **AxBy**:

$$A_xB_y \Longleftrightarrow xA^{+y} + yB^{-x}$$

$$xS \qquad yS$$

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

$$\Rightarrow \quad K_s = (XS)^x(yS)^y$$

$$S = (k_s / X^xY^y)^{1/x+y}$$

Example :

$CaCO_3 \Longleftrightarrow Ca^{2+} + CO_3^{2-}$	$K_s = [Ca^{2+}][CO_3^{2-}]$ $= S \times S = S^2$	$S = (K_s)^{1/2}$
$BaF_2 \Longleftrightarrow Ba^{2+} + 2F^-$	$K_s = [Ba^{2+}][F^-]^2$ $= S \times (2S)^2 = 4S^3$	$S = (K_s/4)^{1/3}$
$Ca_3(PO_4)_2 \Longleftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	$K_s = (3S)^3(2S)^2 = 108\ S^5$	$S = (K_s/108)^{1/5}$

3-2-Precipitation conditions :

$A^+ + B^- \Longleftrightarrow AB$ $\quad$ $Ks = [A+]_{eq}\,[B^-]_{eq}$ at equilibrium

If we mix **[A+]** and **[B⁻]** we find three cases:

$[A+]\,[B^-] < K_s$: case of under-saturation: no precipitation of **AB**.

$[A+]\,[B^-] = K_s$: saturation, so precipitation of **AB**

$[A+]\,[B^-] > K_s$: saturation, so precipitation of **AB** with return to equilibrium conditions

Exercice : A mixture containing :

-50 ml of $BaCl_2 = 10^{-5}M$

- 50 ml of $NaSO_4 = 2.10^{-2}M$

-100 ml of $AgNO_3 = 10^{-5}M$

total volume = 200 ml

Is there any precipitation of $BaSO_4$ and **AgCl** during mixing?

Given that at 25°C : $K_s(BaSO_4) = 1{,}1\times10^{-10}$ et $K_s(AgCl) = 1{,}6\times10^{-10}$.

Solution :

$[Ba^{2+}] = 2{,}5\times10^{-6}$ M and $[SO_4^{2-}] = 5\times10^{-3}$ M

-$[Ba^{2+}][SO_4\ ] = 1{,}25\times10^{-8}\ mol^2.l^{-2} > 1{,}1\times10^{-10}\ mol^2.l^{-2}$

-So there is a precipitation of **$BaSO_4$** with a return to equilibrium conditions:

$[Ba^{2+}]\,[SO_4^{-2}\ ] = 1{,}1\times10^{-10}\ mol^2.l^{-2}$.

-$[Cl^-] = 5\times10^{-6}$ M et $[Ag+] = 5\times10^{-6}$ M

- $[Ag+][Cl^-] = 2{,}5\times10^{-11}\ mol^2l^{-2} < 1{,}6\times10^{-10}\ mol^2.l^{-2}$ - Therefore, no precipitation of AgCl.

4-Factors influencing solubility.

4-1-Influence of temperature.

$$AxBy \underset{2}{\overset{1}{\Longleftrightarrow}} xA^{y+} + yB^{x-}$$ $\quad$ $\Delta Hr°$= enthalpy of dissolution.

Direction 1 --> : dissolution

Direction 2 <-- : precipitation

According to the vanthoff equation; $(d\ln Ks)/dT = \Delta H°r(dissolution) / RT^2$
Note that;

-If $\Delta H > 0$:

- Temperature increases: system evolves in the direction of the **endothermic reaction direction (1): dissolution ↑: Ks ↑ (solubility ↑).**

-If $\Delta H < 0$:

-the temperature decreases: evolution of the system in the direction of the **exothermic reaction direction (2): dissolution↓ Ks ↓ (solubility ↓)**

Example :

$$MgF_2 \Longleftrightarrow Mg^{2+} + 2F^- \qquad \Delta H < 0 \text{ (exothermic)}$$

The reaction is exothermic in direction 2, if we increase the temperature, the reaction will move towards direction 1, so we obtain an endothermic system => **the solubility decreases.**

4-2-Effect of common ions :

We are looking for the solubility of (AB) in a strong electrolyte solution (AC). Let

A+: common ion.

$$AB \Longleftrightarrow A^+ + B^- \quad ; \quad AC \Longrightarrow A^+ + C^-$$

$$\mathbf{S+[A^+] \quad S}$$

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

So; $$\mathbf{Ks} = (\mathbf{S} + [\mathbf{AC}]) \times \mathbf{S}$$

If the solubility is negligible compared to the concentration of **AC**, we can write that :

$$\mathbf{K_s} = \mathbf{S} \times [\mathbf{AC}]$$

So ; $$\mathbf{S} = \mathbf{K_s} / [\mathbf{AC}]$$

4-3- Influence of pH.

Example 1 :

$$Fe(OH)_3 \Longleftrightarrow Fe^{+3} + 3OH^- \quad ; \quad K_s = [Fe^{+3}][OH^-]^3$$

$$K_e = [OH^-]\,[H_3O^+] \implies [OH^-] = K_e / [H_3O^+]$$

$$K_s = [Fe^{+3}]\,(K_e / [H_3O^+])^3$$

Or;

$$S = [Fe^{+3}] \implies Ks = S \times (K_e / [H_3O^+])^3$$

$$S = K_s \times ([H_3O^+] / K_e)^3$$

- If **$[H_3O^+]$** : increases ==> **pH:** decreases ==> **S:** increases.

- If **$[H_3O^+]$** : decreases ==> **pH:** increases ==> **S:** decreases.