

CHAPTER IV :

DISSOLUTION-PRECIPIATION REACTIONS

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CHAPTER IV :

DISSOLUTION-PRECIPIATION REACTIONS

This chapter explores the concept of solubility, the principles behind precipitation reactions, and the solubility product constant (K_{sp}), 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.

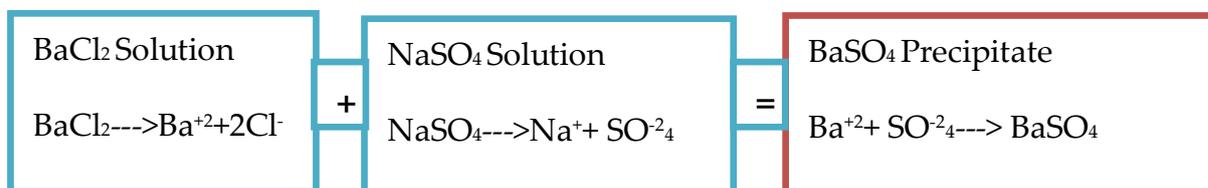
Example :

- NaCl: $S \approx 6$ mole/L, NaCl is a very water-soluble compound.
- AgCl: $S \approx 10^{-5}$ 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.

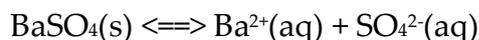
2-Precipitation reaction.

When two solutions containing the two ions (Ba^{2+} and SO_4^{2-}) of a poorly soluble compound $BaSO_4$ are mixed separately, the latter precipitates during mixing (provided that saturation with $BaSO_4$ is reached).

**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 ($\text{Ba}^{2+}(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$): heterogeneous equilibrium:



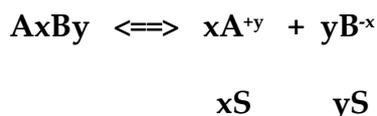
L.A.M: $K_c = [\text{Ba}^{2+}][\text{SO}_4^{2-}]/[\text{BaSO}_4] ; [\text{BaSO}_4]=1$

$$K_c=K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \text{ mol}^2.\text{l}^{-2}$$

K_s is the solubility product of BaSO_4 .

We also define $\text{p}K_s = -\log K_s$, which is a characteristic of BaSO_4 .
The more soluble the compound, the greater K_s , the smaller the $\text{p}K_s$.

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



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

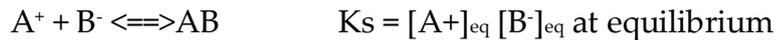
$$\Rightarrow K_s = (\text{xS})^x(\text{yS})^y$$

$$S = (k_s / \text{X}^x\text{Y}^y)^{1/x+y}$$

Example :

$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	$K_s = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$ $= S \times S = S^2$	$S = (K_s)^{1/2}$
$\text{BaF}_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{F}^-$	$K_s = [\text{Ba}^{2+}] [\text{F}^-]^2$ $= S \times (2S)^2 = 4S^3$	$S = (K_s/4)^{1/3}$
$\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	$K_s = (3S)^3(2S)^2 = 108 S^5$	$S = (K_s/108)^{1/5}$

3-2-Precipitation conditions :



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

Exercise : A mixture containing :

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

- 50 ml of $Na_2SO_4 = 2 \cdot 10^{-2}M$

-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 $25^\circ C$: $K_s(BaSO_4) = 1,1 \times 10^{-10}$ et $K_s(AgCl) = 1,6 \times 10^{-10}$.

Solution :

$[Ba^{2+}] = 2,5 \times 10^{-6} M$ and $[SO_4^{2-}] = 5 \times 10^{-3} M$

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

-So there is a precipitation of **BaSO₄** with a return to equilibrium conditions:

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

$-[Cl^-] = 5 \times 10^{-6} M$ et $[Ag^+] = 5 \times 10^{-6} M$

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

4-Factors influencing solubility.

4-1-Influence of temperature.



Direction 1 --> : dissolution

Direction 2 <-- : precipitation

According to the vanthoff equation; $(\ln K_s) / dT = \Delta H^{\circ}(\text{dissolution}) / RT^2$
 Note that;

-If $\Delta H > 0$:

- Temperature increases: system evolves in the direction of the **endothermic reaction direction (1): dissolution \uparrow : $K_s \uparrow$ (solubility \uparrow).**

-If $\Delta H < 0$:

-the temperature decreases: evolution of the system in the direction of the **exothermic reaction direction (2): dissolution \downarrow $K_s \downarrow$ (solubility \downarrow)**

Example :



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.



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

$$K_s = [\text{A}^+][\text{B}^-]$$

So;
$$K_s = (S + [\text{AC}]) \times S$$

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

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

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

4-3- Influence of pH.

Example 1 :



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

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

Or;

$$S = [\text{Fe}^{+3}] \implies K_s = S \times (K_e / [\text{H}_3\text{O}^+])^3$$

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

- If $[\text{H}_3\text{O}^+]$: increases \implies **pH**: decreases \implies **S**: increases.

- If $[\text{H}_3\text{O}^+]$: decreases \implies **pH**: increases \implies **S**: decreases.