MOHAMED KHIDER UNIVERSITY OF BISKRA.

FACULTY OF EXACT SCIENCES AND NATURAL AND LIFE SCIENCES

DEPARTMENT OF BIOLOGY

Semester2: THERMODYNAMICS AND CHEMISTRY OF MINERAL SOLUTIONS

CHAPTER I
Part 3
Level: 1st year LMD

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4. Precipitation equilibrium: Solubility (S) and solubility product (Ks):

4.1. Definition:

a. Solubility (S): Solubility is the maximum amount of solid that can be dissolved in one liter of solution. We denote S, it is expressed in g/l (mass solubility) or in mol/l (molar solubility).
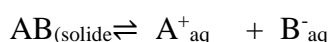
Salts are strong electrolytes with low solubility. They can be $AB_{(s)}$ or A_aB_b type.

$AB_{(salt)} \rightleftharpoons A^+_{aq} + B^-_{aq}$

We admit that as soon as solid AB is put into solution we have: $AB_{(solide)} \rightleftharpoons A^+_{aq} + B^-_{aq}$

b. Solubility product (Ks):

Consider the following reaction:

$AB_{(solide)} \rightleftharpoons A^+_{aq} + B^-_{aq}$

According to the law of mass action we obtain: $Kc = Ks = [A^+] [B^-]$

In the general case we have: $A_aB_{b\ (solid)} \rightleftharpoons aA^{+b}_{(aq)} + bB^{a-}_{(aq)}$

$Ks = [A^{+b}]^a . [B^{a-}]^b$

4.2. Relationship between solubility product and solubility:

Knowing that solubility depends on the temperature and the nature of the solid. There is a relationship between solubility (S) and solubility constant (Ks) (or solubility product).

$$A_aB_{b\ (solid)} \rightleftharpoons aA^{+b}_{(aq)} + bB^{a-}_{(aq)}$$
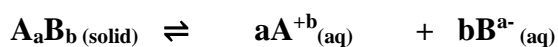
At   t=0 n_0 -   -

At   t=eq n_0-S aS   bS

$Ks = [A^{+b}]^a . [B^{a-}]^b = [aS]^a * [bS]^b$

Example 1: $AgCl_{(s)}$

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$

At   t=0 n_0 -   -

At   t=eq n_0-S S   S

$Ks = [Ag^+] [Cl^-] = S*S \Rightarrow Ks = S^2$

Example 2: $Ca_3(PO_4)_{2(s)}$

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+} + 2(PO_4)^{3-}$$

At   t=0 n_0 -   -

At   t=eq n_0-S 3S   2S

$Ks = [Ca^{2+}]^3 [(PO_4)^{3-}]^2 = (3S)^3 * (2S)^2 \Rightarrow Ks = 108\ S^5$
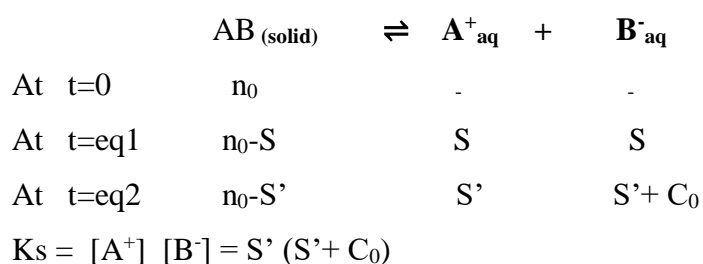
4.3. Factors that affect solubility:

a. Effect of the addition of an ion on solubility:

The solubility of a salt is also related to the initial presence of ions in the solution. If we modify the concentration of one of the ions, according to Le Chatelier's principle, the equilibrium will be shifted.
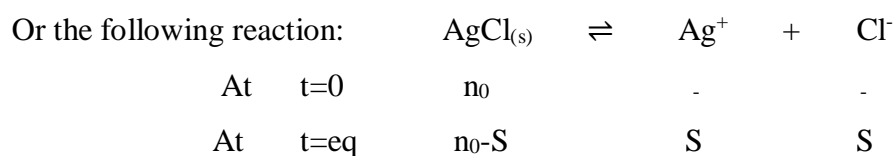
The solubility of an ionic salt is reduced when a common ion (anion or cation) is present in the solution (so that Ks keep its constant value).

In a general case:

Consider an AB salt with solubility in pure water. Let S' be the new solubility of AB in the presence of a second salt CB of concentration C_0, the common ion is B^-.
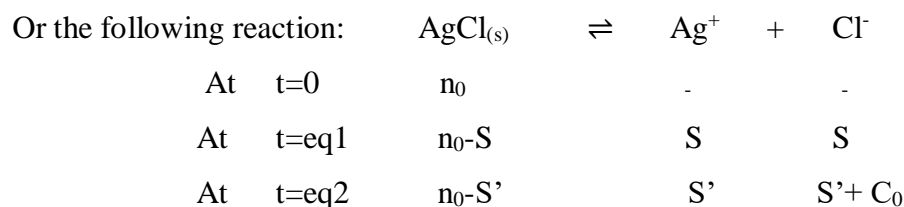
$$AB_{(solid)} \rightleftharpoons A^+_{aq} + B^-_{aq}$$

At t=0 n_0 -   -

At t=eq1 n_0-S S   S

At t=eq2 n_0-S' S' $S'+ C_0$

$Ks = [A^+] [B^-] = S' (S'+ C_0)$

Example: For example AgCl in the presence of KCl.

Or the following reaction: $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

At   t=0 n_0 -   -

At   t=eq n_0-S S   S

$Ks = [Ag^+] [Cl^-] = S*S \Rightarrow Ks= S^2$

To this solution we add Cl^- ions and form KCl (with a concentration C_0) to the salt AgCl(s), according to LeChatelier's principle, the equilibrium will be shifted towards the opposite direction (-1) $\Rightarrow$ the formation of AgCl(s) $\Rightarrow$ the solubility of AgCl(s) in the presence of KCl will decrease (S'). $\Rightarrow$ S' < S

Or the following reaction: $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

At   t=0 n_0 -   -

At   t=eq1 n_0-S S   S

At   t=eq2 n_0-S' S' $S'+ C_0$

$Ks = [Ag^+]_N [Cl^-]_N = S' (S'+ C_0)$

To find we have two cases:

1-If the difference between S and $C_0 \Rightarrow (S - C_0)$ belongs to the interval: $[10^{-1} -10^{-3}]$.

$\Rightarrow$ You have to solve an equation: **Ks** $=$ S' (S'+ C$_0$) $\Rightarrow$ Ks $=$ S'^{2} + S'C$_0$

Δ$=$ b^2- 4ac (cas : Δ<0, Δ=0, Δ>0).

2- If the difference between S and C$_0$ $\Rightarrow$ (S - C$_0$) belongs to the interval: [10^4- 10^7]

$\Rightarrow$ We must simplify the equation: **Ks** $=$ S' ($\cancel{S'^2}$+ C$_0$) $\Rightarrow$ **Ks** $=$ S'C$_0$.

b. Influence of pH on solubility:

These are the compounds of which one of the ions has an acidic or basic character, that is to say releasing one of the following ions

Anion: OH$^-$ hydroxide; ethanoate CH$_3$COO$^-$; Nitrite NO$_2^-$; carbonates CO$_3^{2-}$; hydrogencarbonate HCO$_3^-$.

Cations: NH$_4^+$; ethylamonium C$_2$H$_5$NH$_3$.

It is necessary to add the acid-base equilibrium(s) of constant ka. <u>The solubility increases if the pH decreases in this case.</u>

Example: the solubility of Zn(OH)$_2$; or NH$_4$Cl; or Pb(CH$_3$COO)$_2$ will depend on the pH.

c. Effect of temperature and agitation:

As the temperature increases the solubility increases, in addition agitation accelerates the dissolution of salt.

4.4. Precipitation condition:

Consider the following dissolution reaction: A$_a$B$_{b \text{ (solid)}}$ $\rightleftharpoons$ aA$^{b+}_{aq}$ + bB$^{a-}_{aq}$

Consider the following precipitation reaction: aA$^{b+}_{aq}$ + bB$^{a-}_{aq}$ $\rightleftharpoons$ A$_a$B$_{b \text{ (solid)}}$

We define the ionic product as follows: Pi $=$ [A^{b+}]^a [B^{a-}]^b

Case 1: If we have: Ks > Pi $=$ [A^{b+}]^a [B^{a-}]^b $\Rightarrow$ the solution is not saturated (unsaturated).

Case 2: If we have: Ks $=$ Pi $=$ [A^{b+}]^a [B^{a-}]^b $\Rightarrow$ the solution is saturated.

Case 3: If we have: Ks < Pi $=$ [A^{b+}]^a [B^{a-}]^b $\Rightarrow$ the solution is supersaturated (precipitation).