

Dissolution and precipitation

I. Dissolution and precipitation phenomenon

1. Definition of solution:

The solution is any homogeneous mixture of pure compounds that do not react with each other.

Solution = solute + solvent (excess)

Solute (solid, liquid or gas)

Solvent (liquid)

Example :

- Aqueous solution of sodium chloride:

Solute: NaCl (solid) Solvent: H₂O (liquid)

- Solution of tetrachloride in benzene:

Solute: CCl₄ (liquid) Solvent: C₆H₆ (liquid)

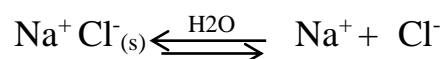
2. dissolution of solute in solvent

The present study focuses on crystallized salts as solute and water as solvent.

The dissolution of salt in solvent corresponds to two successive phenomena:

- Destruction of crystalline structure of the solid (salt).
- Electrostatic interactions between salt particles and the solvent leading to the solvation of the solute.

Example:



3. Saturation and supersaturation

When salt is dissolved in solvent, the dissolution phenomenon will take place gradually, starting by external faces of the solute.

Theoretically we should be able to achieve total dissolution of solute.

In fact, parallel to the phenomenon of dissolution another phenomenon of recombination of ions in solution occurs.

An equilibrium is reached when the amount of solute that is dissolved in solution is equal to the amount of solute that has recrystallized.

Solution is said to be saturated.

Example: An NaCl solution in water is saturated at 360g/l

4. Precipitation

Precipitation is the opposite phenomenon of dissolution. It takes place in 2 cases:

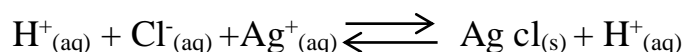
- As soon as the quantity of solute exceeds that which corresponds to saturation and we will have 2 phases:

o A liquid (solute dissolved in the solvent)

o A solid (undissolved solute)

- When, to solution containing ions, we add an ion capable of forming a salt.

Example



II. Solubility (S)

1. Definition:

Power of solute dissolution by solvents is limited.

We call solubility (denoted S), the maximum quantity of salt which can be dissolved per liter of solution.

S can be expressed in gram/liter: mass solubility or in mole/l: molar solubility. $S_{\text{mass}} = S_{\text{molar}} \cdot M_{\text{salt}}$

Example:

At ambient Temperature and in pure water $S_{\text{AgCl}} = 1,2 \cdot 10^{-5} \text{ mol/l}$.

Calculate the mass solubility of AgCl. ($M_{\text{AgCl}} = 143,5 \text{ g/mole}$)

Answer:

$$S(\text{AgCl})_{\text{g/l}} = S(\text{AgCl})_{\text{mole/l}} \cdot M_{\text{AgCl}} = 1,2 \cdot 10^{-5} \cdot 143,5 = 1,72 \cdot 10^{-3} \text{ g/l}$$

Remarks :

The concept of solubility is generally applied to poorly soluble salts.

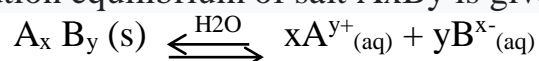
Salts are said to be very soluble when S is of the order 10^{-1} mole/l .

Salts are said to be poorly soluble when S is of the order 10^{-4} mole/l .

Several factors can influence the salt solubility : temperature, pressure, pH, nature of the solvent.....

2. Equilibrium of dissolution and law of mass action

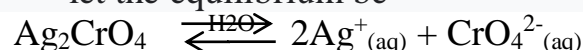
The dissolution equilibrium of salt $A_x B_y$ is given by the reaction:



The application of mass action law gives:

$$K = \frac{[A^{y+}]^x \cdot [B^{x-}]^y}{[A_x B_y]} : \text{ which is constant at equilibrium}$$

Example: let the equilibrium be

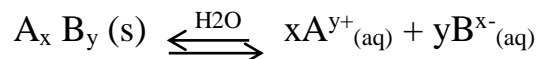


Establish the expression for the equilibrium constant.

Answer:
$$K = \frac{[Ag^+]^2 [CrO_4^{2-}]}{[Ag_2CrO_4]}$$

3.Solubility product (Ks)

a) **Definition:** Let be the salt dissociation reaction :



At equilibrium $K = \frac{[A^{y+}]^x \cdot [B^{x-}]^y}{[A_x B_y]} \dots\dots(1)$

From expression (1),we have : $K \cdot [A_x B_y] = [A^{y+}]^x \cdot [B^{x-}]^y$

As $A_x B_y$ studied salts are generally poorly soluble , $[A_x B_y]$ can be considered as constant, $K [A_x B_y]$ will be constant(denoted K_s) .

$K [A_x B_y] = [A^{y+}]^x \cdot [B^{x-}]^y = K_s$, K_s is called salt solubility product .

Example :

Establish the expression of the solubility product K_s for silver oxalate

Ag_2CrO_4 .

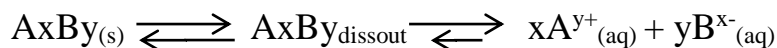


$$K_s = [Ag^+]^2 [CrO_4^{2-}]$$

b) Relationship between solubility and solubility product



Solubility S of $A_x B_y$ salt corresponds to $[A_x B_y]$ dissolves:



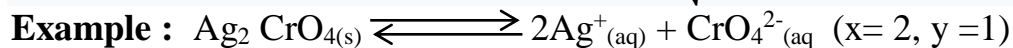
at $t=0$: C 0 0 0

at t_{eq} : C-S S x.s y.s

We have : $[A^{y+}] = x.s$ and $[B^{x-}] = y.s$

So : $K_s = [A^{y+}]^x [B^{x-}]^y = (x.s)^x \cdot (y.s)^y = x^x \cdot y^y \cdot s^{x+y}$

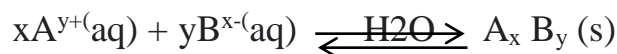
Then : $K_s = x^x \cdot y^y \cdot s^{x+y}$ $s = \sqrt[x+y]{\frac{K_s}{x^x y^y}}$



$$s = \sqrt[3]{\frac{K_s}{2^2 \cdot 1^1}} = \sqrt[3]{\frac{K_s}{4}} \approx 1,36 \cdot 10^{-4} \text{ mole/l (} K_{s\text{Ag}_2 \text{CrO}_4} = 10^{-11}\text{)}$$

c) Precipitation condition

For an A_xB_y salt, the precipitation reaction:



•If $[\text{A}^{y+}]^x [\text{B}^{x-}]^y < K_s$ _Solution is unsaturated: salt doesn't precipitate .

Example :

Let be an $\text{Ag}_2 \text{CrO}_4$ solution at 10^{-5} M , $K_s (\text{Ag}_2 \text{CrO}_4) = 10^{-11}$

The ionic product : $[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2 \cdot 10^{-5})^2 \times (1 \cdot 10^{-5})^1 = 4 \cdot 10^{-15}$

As : $[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 4 \cdot 10^{-15} < K_s (\text{Ag}_2 \text{CrO}_4) = 10^{-11}$ salt doesn't precipitate .

•If $[\text{A}^{y+}]^x [\text{B}^{x-}]^y = K_s$ _Solution is saturated: salt at border disso-precip .

Example :

Let be an $\text{Ag}_2 \text{CrO}_4$ solution at $1,36 \cdot 10^{-4} \text{ M}$, $K_s (\text{Ag}_2 \text{CrO}_4) = 10^{-11}$

As : $[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 10^{-11} = K_s (\text{Ag}_2 \text{CrO}_4)$ salt is at border.

•If $[\text{A}^{y+}]^x [\text{B}^{x-}]^y > K_s$ _Solution is supersaturated: salt precipitate

Example :

Let be an $\text{Ag}_2 \text{CrO}_4$ solution at $4 \cdot 10^{-4} \text{ M}$, $K_s (\text{Ag}_2 \text{CrO}_4) = 10^{-11}$

We have : $[Ag^+]^2[CrO_4^{2-}] = (2.4 \cdot 10^{-4})^2 \times (4 \cdot 10^{-4})^1 = 2,56 \cdot 10^{-10}$

As : $[Ag^+]^2[CrO_4^{2-}] = 2,56 \cdot 10^{-10} > K_s(Ag_2CrO_4) = 10^{-11}$ salt precipitate .

4. Parameters influencing the solubility of salt

a) Influence of solute and solvent nature

- An ionic or polar solute dissolves well in polar solvent (having a high dielectric constant).
- A non-polar solute dissolves well in non-polar solvent.

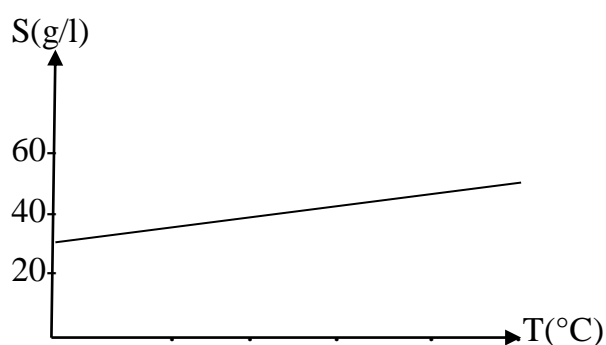
Remark :

Having higher dielectric constant, water is generally used as solvent .

b) Influence of temperature

In the majority of cases, solubility of salt increases with temperature.

Example:



Variation of S_{NaCl} as a function of T

c) Influence of the common ion

Let dissolves an A_xB_y salt in solvent containing B^{x-} ions coming from a very soluble C_xB_z salt.

The solubility product of A_xB_y salt is constant and is always written:

$K_s = [A^{y+}]^x [B^{x-}]^y$, but in this case $[B^{x-}] > y \cdot S$, where S represents the solubility of A_xB_y salt before introduction of the common ion.

The solubility of salt is then modified and S' .

If the B^{x-} ions coming from C_xB_z are at concentration C , we can write:

$$[A^{y+}] = [A^{y+}]_{AxBy} = x.s' \quad \text{and} \quad [B^{x-}] = [B^{x-}]_{AxBy} + [B^{x-}]_{C_xB_z} = y.s' + c$$

$$\text{So :} \quad K_s = (x.s')^x (y.s' + c)^y$$

As A_xB_y is poorly soluble, we can neglect $y.s'$ in front of C , so :

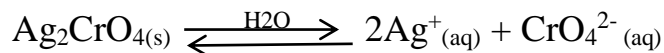
$$\text{For this reason :} \quad K_s = (x.s')^x \cdot c^y = x^x \cdot c^y \cdot s'^x \quad \text{which leads to :} \quad s' = \sqrt[x]{\frac{K_s}{x^x c^y}}$$

Example:

Solubility of silver chromate in pure water is $S_{Ag_2CrO_4} = 10^{-4}$ mole/l.

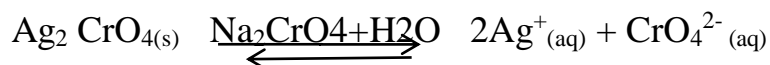
Calculate the solubility of Ag_2CrO_4 in solution of sodium chromate

Na_2CrO_4 at $C = 10^{-2}$ M. $K_s(Ag_2CrO_4) = 10^{-11}$



$$\text{at } t=0 \quad C_0 \quad 0 \quad 0$$

$$\text{at } t_{eq} \quad C_0 - s \quad 2s \quad s$$



$$\text{at } t=0 \quad C_0 \quad 0 \quad 0$$

$$\text{at } t_{eq} \quad C_0 - s' \quad 2s' \quad s' + C$$

$$K_s = [Ag^+]^2 [CrO_4^{2-}]_T = (2S')^2 (S' + C)$$

$$K_s = 4S'^2 C \longrightarrow S'^2 = \frac{K_s}{4C} \longrightarrow S' = \sqrt{\frac{K_s}{4C}}$$

$$\text{N.A : } S' = \sqrt{\frac{10^{-11}}{4 \cdot 10^{-2}}} = 0,5 \cdot 10^{-5} \text{ mole/l}$$

Ascertainment

The presence of common ion leads to the regression of solubility.

Deduction

The introduction of common ion causes a shift in the solubility in the direction which causes the common ions to disappear, thus promoting precipitation (Le Chatelier's law).

d) Influence of PH

The solubility of salt varies depending on the pH of the medium.

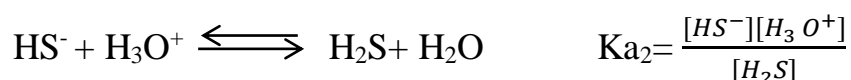
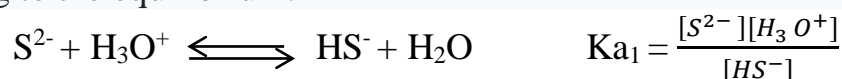
Let us study the case of divalent metal sulphides.

An MS sulphide solubilizes according to the equilibrium:

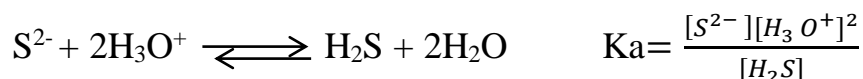


$$\text{at equilibrium } K_s = [M^{2+}][S^{2-}]$$

MS sulphides are salts of the weak diacid H_2S . S^{2-} ions are hydrolyzed according to the equilibrium:



And the global reaction :



$$K_a = K_{a1} \times K_{a2}$$

$$\text{So : } [S^{2-}] = K_{a1} \times K_{a2} \frac{[H_2S]}{[H_3O^+]^2} \quad (K_a = 10^{-22})$$

Furthermore, a solution saturated with H_2S corresponds to a concentration $10^{-1}M$ in H_2S .

$$\text{So : } [S^{2-}] = \frac{10^{-22} \cdot 10^{-1}}{[H_3O^+]^2} = \frac{10^{-23}}{[H_3O^+]^2}$$

And the expression for K_s becomes: $K_s = \frac{[M^{2+}] \cdot 10^{-23}}{[H_3O^+]^2}$

Also : : $[M^{2+}] = S$ Then $K_s = \frac{S}{[H_3O^+]^2} 10^{-23}$ so $S = K_s \cdot \frac{[H_3O^+]^2}{10^{-23}}$

And finally : **$\log S = \log \left(\frac{K_s}{10^{-23}} \right) - 2Ph$**

Example:

Calculate the solubility of Nickel sulfide NiS in a 0.1 M solution of H_2S at $Ph = 2.5$ we give : $K_s(NiS) = 3.10^{-19}$

Answer: We have $\log (s) = \log \left(\frac{K_s}{10^{-23}} \right) - 2pH$

$$\log (s) = \log \left(\frac{3.10^{-19}}{10^{-23}} \right) - 2 \times 2.5$$

$$= \log (3.10^4) - 5 = 4 + 0,47 - 5$$

$$\log (s) = -0.523 \longrightarrow S = 5,92.10^{-1} M$$