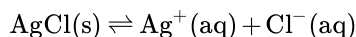


## 1.2: Solubility equilibria

### Solubility product constant ( $K_{sp}$ )

All ionic compounds dissolve in water to some extent. Ionic compounds are **strong electrolytes**, i.e., dissociating completely into ions upon dissolution. When the amount of ionic compound added to the mixture exceeds the solubility limit, the excess undissolved solute (solid) exists in equilibrium with its dissolved aqueous ions. For example, the following equation represents the equilibrium between solid  $\text{AgCl(s)}$  and its dissolved  $\text{Ag}^+(\text{aq})$  and  $\text{Cl}^-(\text{aq})$  ions, where the subscript (s) means solid, i.e., the undissolved fraction of the compound, and (aq) means aqueous or dissolved in water.



Like any other chemical equilibrium, this equilibrium has an equilibrium constant ( $K_{eq}$ ) :

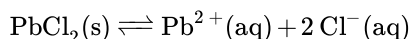
$$K_{eq} = [\text{Ag}^+][\text{Cl}^-]$$

Note that solid or pure liquid species do not appear in the equilibrium constant expression as the concentration in the solid or pure liquid remains constant. This equilibrium constant has a separate name, **Solubility Product Constant** ( $K_{sp}$ ), based on the fact that it is a product of the molar concentration of dissolved ions, raised to the power equal to their respective coefficients in the chemical equation, e.g.,

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

The solubility product constant ( $K_{sp}$ ) is the equilibrium constant for an ionic compound dissolving in an aqueous solution.

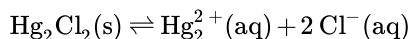
Similarly, the dissolution equilibrium for  $\text{PbCl}_2$  can be shown as:



with

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.6 \times 10^{-5}$$

And the dissolution equilibrium for  $\text{Hg}_2\text{Cl}_2$  is similar:



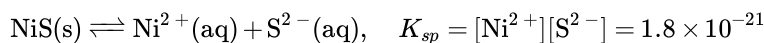
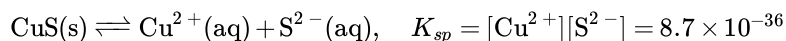
with

$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = 1.3 \times 10^{-18}$$

### Selective precipitation

**Selective precipitation** involves adding a reagent that precipitates one of the dissolved cations or a particular group of dissolved cations but not the others.

According to solubility rule# 5, both  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  form insoluble salts with  $\text{S}^{2-}$ . However, the solubility of  $\text{CuS}$  and  $\text{NiS}$  differ enough that if an appropriate concentration of  $\text{S}^{2-}$  is maintained,  $\text{CuS}$  can be precipitated leaving  $\text{Ni}^{2+}$  dissolved. The following calculations based on the  $K_{sp}$  values prove it.



The molar concentration of sulfide ions  $[\text{S}^{2-}]$ , in moles/liter in a saturated solution of the ionic compound can be calculated by rearranging their respective  $K_{sp}$  expression, e.g., for  $\text{CuS}$  solution,  $K_{sp} = [\text{Cu}^{2+}][\text{S}^{2-}]$  rearranges to:

$$[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Cu}^{2+}]}$$

Assume  $\text{Cu}^{2+}$  is 0.1 M; plugging in the values in the above equation allows calculating the molar concentration of  $\text{S}^{2-}$  in the saturated solution of CuS:

$$[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Cu}^{2+}]} = \frac{8.7 \times 10^{-36}}{0.1} = 8.7 \times 10^{-35} \text{ M}$$

Similar calculations show that the molar concentration of  $\text{S}^{2-}$  in the saturated solution of 0.1M NiS is  $1.8 \times 10^{-20}$  M. If  $\text{S}^{2-}$  concentration is kept more than  $8.7 \times 10^{-35}$  M but less than  $1.8 \times 10^{-20}$  M, CuS will selectively precipitate leaving  $\text{Ni}^{2+}$  dissolved in the solution.

Another example is the selective precipitation of Lead, silver, and mercury by adding HCl to the solution. According to rule# 3 of solubility of ionic compounds, chloride  $\text{Cl}^-$  forms soluble salt with the cations except with Lead ( $\text{Pb}^{2+}$ ), Mercury ( $\text{Hg}_2^{2+}$ ), or Silver ( $\text{Ag}^+$ ). Adding HCl as a source of  $\text{Cl}^-$  in the solution will selectively precipitate lead ( $\text{Pb}^{2+}$ ), mercury ( $\text{Hg}_2^{2+}$ ), and silver ( $\text{Ag}^+$ ), leaving other cations dissolved in the solution.

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