

5. Solubility product

Salt dissolution consist in solubilization of the solid body in the solvent. It is possible that after evaporating the solvent, the solid body will be recovered in the form of crystallites. In case of the solubility product the most common considered solvent is water. Solubility of solid bodies in liquids (solvents) is expressed as a mass (of salt) per 100g of water (mass/100g_{H2O}) (see subchapter about crystallization).

a) Salts of AB type (e.g. AgCl, NaBr, NaCl, CaSO₄, etc.) are dissolving according to the equation:

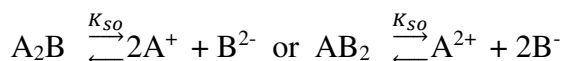
$AB \xrightleftharpoons{K_{so}} A^{n+} + B^{n-}$ Hence, it is possible to write down the expression for K_{so} (which stands for solubility product)

$$K_{so} = [A^{n+}] \cdot [B^{n-}]$$

Theoretically, when the above expression is formed, one should take into account the left side of the equation - AB. However, as AB is a solid body, its activity is equal to 1. Thus, we can omit this in the above expression as it is division by one – which is not changing any value. When such salt is dissolving in pure water (without any previously dissolved ions), then amount of both types of ions (A and B) in the solution is the same.

b) Salts of A₂B or AB₂ type:

Both cases can be considered in the same way:



$$K_{so} = [A^+]^2 \cdot [B^{2-}] \quad \text{or} \quad K_{so} = [A^{2+}] \cdot [B^-]^2$$

It is important to remember about exponents that occur in the expressions for K_{so} . Exponents other than one always accompany those expression components that have stoichiometric coefficient (other than one, which is always omitted) in the in the reaction equation.

In such cases it is easy to observe that dissolving A₂B or AB₂ salt results in forming ions at the ratio, respectively (A:B), 2:1 or 1:2.

Constants K_{so} can be compared to each other, but only if stoichiometry (constitution) of the salts in question is the same. One cannot compare directly solubility products of salts with stoichiometries AB and A₂B, as this could bring to the wrong conclusions. In such situations salt solubility in each case should be calculated separately and only then direct comparison of solubilities or individual ions' concentrations is possible.

What are the concentrations of the individual ions? Depending on the type a) or type b)

a) If we know that dissolving AB salt (e.g. AgCl) results in the formation of equal amounts of Ag⁺ and Cl⁻, then from the given constant $K_{soAgCl} = 1.7 \cdot 10^{-10}$ we can calculate what will be the concentration of those ions in the solution above the precipitate, in the saturated solution. $K_{so} = [Ag^+][Cl^-]$ – if we consider, that solubility r in this case is equal to the ions' concentration $[Ag^+] = [Cl^-] = r$, then solubility product expression can be transformed into the following form: $K_{so} = r \cdot r$ Thus, in order to determine r value the following expression has to be computed: $\sqrt{K_{so}} = r$ it is important to remember that r here is expressed in the same units as the concentration.

b) In case of salts of A₂B type, e.g. Ag₂CrO₄, the calculation procedure is analogical.

$[Ag^+] = 2r$ and $[CrO_4^{2-}] = r$ thus $K_{so} = [Ag^+]^2[CrO_4^{2-}] \Rightarrow K_{so} = (2r)^2 \cdot r = 4r^3$

If constant is given $K_{soAg_2CrO_4} = 1 \cdot 10^{-12}$ one can calculate r .

$$r = \sqrt[3]{\frac{K_{so}}{4}}$$

It is worth remembering that silver ions concentration $[Ag^+]$ value is equal to $2r$.

The above examples should be enough to calculate r for the following salts: $AlCl_3$, $Fe_2(SO_4)_3$.

Salt effect occurs in the systems in which solution already contains some amount of any of the ions that are a part of the salt which we want to dissolve in this solution. Then the equilibrium of the dissolution process will be shifted. For instance, for the $AgCl$ salt it would be as follows:

$AgCl \rightleftharpoons Ag^+ + Cl^-$ - if in the solution there is already extent (from the solubility product of the $AgCl$ point of view) of the Ag^+ or Cl^- ions, then the equilibrium will be shifted towards left, in order to remove extent of the ions from the system. When the solubility product of the given salt is surpassed, precipitation of this salt forms. More detailed explanation is given in the following Example 1.

Example 1.

We would like to dissolve $AgCl$ salt in the 0.01M solution of $AgNO_3$. What would be the maximum concentration of Cl^- ions in the resulting solution? In other words – how much of the $AgCl$ salt can be dissolved at most?

$$K_{soAgCl} = 1.7 \cdot 10^{-10} \Rightarrow K_{soAgCl} = [Ag^+][Cl^-]$$

As we have an extent of the $[Ag^+]$ ions which is 0.01 M, we can put that value into the K_{so} expression.

$$\text{After substitution: } 1.7 \cdot 10^{-10} / 0.01 = [Cl^-] \Rightarrow [Cl^-] = 1.7 \cdot 10^{-8} \text{ M}$$

Thus, only such amount of $AgCl$ salt is possible to dissolve in this solution. It is much less than $AgCl$ salt solubility in pure water: $\sqrt{K_{so}} = r$, where $r = 1.3 \cdot 10^{-5} \text{ M}$.

Salt effect can also occur in the system in which foreign ions are present (other than those comprising considered salt). Due to the changes of ionic strength a higher solubility of the poorly soluble salt takes place, compared to the pure water. It is the result of significant changes of ionic strength of the solution (see -> ionic strength, ionic activity). More detailed explanation is given in the following Example 2.

Example 2.

0.01M solution of $NaNO_3$ is given and certain amount of poorly soluble AgI salt is given.

$$K_{soAgI} = 8.5 \cdot 10^{-17} \Rightarrow [Ag^+] = [I^-] = 9.2 \cdot 10^{-9} \text{ M}$$

In such a case concentrations of Ag^+ and I^- salts are so small, that we can omit them in the ionic strength calculation.

$$\text{Calculation of the solution ionic strength: } I = 0.5 \cdot (0.01 \cdot (+1^2) + 0.01 \cdot (-1^2)) = 0.5 \cdot 0.02 = 0.01$$

Subsequently we calculate activity coefficients for Ag^+ and I^- ions: $f_{Ag^+} = f_{I^-}$. We can use the following equation for that:

$$-\log(f_i) = \frac{0.5 \cdot (z_i^2) \cdot \sqrt{I}}{1 + \sqrt{I}}$$

$$-\log(f_{Ag+}) = \frac{0.5 \cdot (1^2) \cdot \sqrt{0.01}}{1 + \sqrt{0.01}}$$

$$f_{Ag+} = 0.9 \Rightarrow a_{Ag+} = [Ag^+] \cdot f_{Ag+} = 9.2 \cdot 10^{-9} \cdot 0.9 = 8.3 \cdot 10^{-9}$$

If we will consider solubility product as a product of activities (not concentrations, which is a simplification), we can observe that maximum possible activity of Ag^+ ions is exactly $9.2 \cdot 10^{-9}$. If so, we can compare $8.3 \cdot 10^{-9}$ and $9.2 \cdot 10^{-9}$. $9.2 \cdot 10^{-9}$ value is higher of those two. It appears that activity coefficient f of Ag^+ ions due to the increase of ionic strength (caused by foreign ions presence) becomes lower than 1.¹ If the theoretical activity of Ag^+ ions calculated based on the given data is lower than Ag^+ ions activity resulting from the solubility product, it can be concluded that the AgI salt would be more soluble in the presence of foreign ions than in the pure water. In order to obtain ionic activity value of $9.2 \cdot 10^{-9}$ one has to dissolve salt in the following amount:

$9.2 \cdot 10^{-9} / 0.9 = 10.2 \cdot 10^{-9}$, which is the value higher than $9.2 \cdot 10^{-9}$ and is the final proof of higher solubility of AgI salt in the presence of foreign ions.

The most common well soluble salts are all those in which the anion is NO_3^- ion or cation is any of the two ions: Na^+ or K^+ .

Sometimes in the calculations so called ionic product I_j becomes handy. For the given salt ionic product I_j expression is the same as the expression for the solubility product K_{so} , with a notable distinction that in I_j expression the real values of $[A^+]$ and $[B^-]$ are substituted. It allows for direct comparison of the obtained value with K_{so} . As a result one can conclude if the precipitation in the considered case will occur or not:

If $I_j > K_{so}$ it means that ionic product has exceeds solubility product, thus ionic concentration in the system is too high compared to the limit given by solubility product. As a result, system will strive towards equilibrium and **precipitate will form**.

If $I_j = K_{so}$ it means it is a saturated solution. **No precipitate** will form, but also **no more salt can be dissolved** in such solution.

If $I_j < K_{so}$ it means that ions concentration in the solution is too low and **precipitate will not form**. It is still **possible to dissolve more salt**.

Task 5.1

Calculate the solubility of the chromium hydroxide in pure water.

$$K_{soCr(OH)_3} = 6.31 \cdot 10^{-31} \quad M_{Cr(OH)_3} = 103 \text{ g/mol}$$

$$\text{Hint: } K_{so} = 27r^4$$

Answer: $r = 1.24 \cdot 10^{-8} \text{ M}$, which can be transformed into $1.28 \cdot 10^{-7} \text{ g per } 100 \text{ gH}_2\text{O}$

¹ $f = 1$ value can be assigned to systems that are not diluted too much. This way there is certainty that the ion is surrounded with an appropriate number of water molecules.

Task 5.2

Calculate what would be the pH of the saturated $\text{Mg}(\text{OH})_2$ solution. $K_{\text{soMg}(\text{OH})_2} = 1.26 \cdot 10^{-11}$

Answer: pH = 10.47

Task 5.3

Calculate the maximum solubility of the PbCl_2 in the solution with $[\text{Pb}^{2+}] = 0.05\text{M}$ content.

$$K_{\text{soPbCl}_2} = 1.7 \cdot 10^{-5}$$

Answer: It is possible to dissolve at most 0.018 moles of the PbCl_2 per 1 dm³ of such solution.

Task 5.4

Compare the solubility of PbCO_3 and PbCl_2 salts. Calculate, in which of saturated solution of each of these salts there is a higher Pb^{2+} ions concentration. $K_{\text{soPbCl}_2} = 1.7 \cdot 10^{-5}$

$$K_{\text{soPbCO}_3} = 3.31 \cdot 10^{-14}$$

Answer: $[\text{Pb}^{2+}]$ in PbCl_2 saturated solution is 0.016M, and in PbCO_3 saturated solution is $1.82 \cdot 10^{-7}$ M. Thus, PbCl_2 is dissolving in water to the higher extent than PbCO_3 .

Task 5.5

Equal volumes of 0.001 M AgNO_3 and of 0.05 M Na_2CrO_4 solutions have been mixed together. Calculate, whether in this system it is possible to obtain precipitate of Ag_2CrO_4 ?

$$K_{\text{soAg}_2\text{CrO}_4} = 2 \cdot 10^{-12}$$

Answer: Yes, precipitate will form, as ionic product is $6.25 \cdot 10^{-9}$ M, so the solubility product will be exceeded.

Task 5.6

200 ml of 0.01 M CaNO_3 solution and 50 ml of 0.02 M Na_2CO_3 solution have been mixed together. Calculate, whether precipitate will form? $\text{p}K_{\text{soCaNO}_3} = 7.92$

Answer: Yes, precipitate will form, as ionic product is equal to $3.2 \cdot 10^{-5}$, thus, its value is larger than value of K_{so} .

Task 5.7

We have saturated solution of PbCrO_4 and 0.1 M solution of NaCl . Is it possible by mixing those two solution to obtain PbCl_2 precipitate? $K_{\text{soPbCrO}_4} = 1.59 \cdot 10^{-14}$ $K_{\text{soPbCl}_2} = 1.7 \cdot 10^{-5}$

Answer: No, it is not possible, as ionic product will be not exceeded.