As mentioned in the prior example the order of solubility is determined by looking at the sizes of the solubility products only when these have the same units. In the following example we shall look at a situation where the order of solubility for three species is to be determined.

Example 4- C:
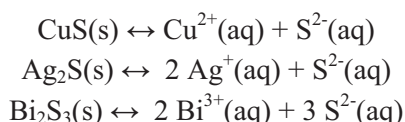*Relative solubility; second example*

We wish to determine the order of solubility for the following three solid species:

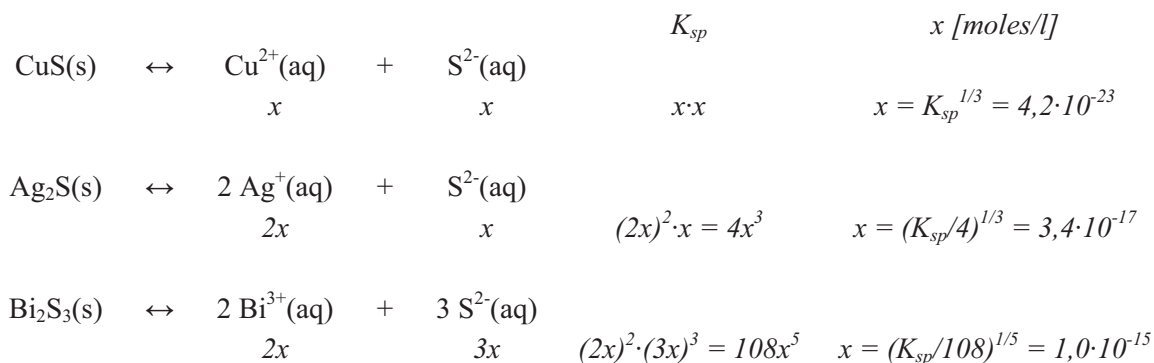$$CuS(s) \text{ having a } K_{sp}\text{-value of } K_{sp} = 8.5 \cdot 10^{-45} \, M^2$$
$$Ag_2S(s) \text{ having a } K_{sp}\text{-value of } K_{sp} = 1.6 \cdot 10^{-49} \, M^3$$
$$Bi_2S_3(s) \text{ having a } K_{sp}\text{-value of } K_{sp} = 1.1 \cdot 10^{-73} \, M^5$$

These three solid species give upon dissolution a different number of ions (which also may be seen from the different units for K_{sp}) following the reaction scheme:

$$CuS(s) \leftrightarrow Cu^{2+}(aq) + S^{2-}(aq)$$
$$Ag_2S(s) \leftrightarrow 2\,Ag^+(aq) + S^{2-}(aq)$$
$$Bi_2S_3(s) \leftrightarrow 2\,Bi^{3+}(aq) + 3\,S^{2-}(aq)$$

In order to determine the order of solubility a comparison of the K_{sp} values may not be used. On the contrary the solubility x for each of the species must be determined as sketched in a previous example:

					K_{sp}	x [moles/l]

$$CuS(s) \quad \leftrightarrow \quad Cu^{2+}(aq) \quad + \quad S^{2-}(aq)$$
$$\qquad\qquad\qquad\quad x \qquad\qquad\quad x \qquad\quad x \cdot x \qquad\quad x = K_{sp}^{1/3} = 4{,}2 \cdot 10^{-23}$$

$$Ag_2S(s) \quad \leftrightarrow \quad 2\,Ag^+(aq) \quad + \quad S^{2-}(aq)$$
$$\qquad\qquad\qquad\quad 2x \qquad\qquad\quad x \qquad (2x)^2 \cdot x = 4x^3 \qquad x = (K_{sp}/4)^{1/3} = 3{,}4 \cdot 10^{-17}$$

$$Bi_2S_3(s) \quad \leftrightarrow \quad 2\,Bi^{3+}(aq) \quad + \quad 3\,S^{2-}(aq)$$
$$\qquad\qquad\qquad\quad 2x \qquad\qquad\quad 3x \qquad (2x)^2 \cdot (3x)^3 = 108x^5 \quad x = (K_{sp}/108)^{1/5} = 1{,}0 \cdot 10^{-15}$$

Now the order of solubility may be determined by comparing the sizes of the solubility x. Therefore Bi_2S_3 is most soluble followed by Ag_2S. Least soluble is CuS and this has thereby been sketched that when the number of ions in the species are different the sizes of K_{sp} cannot be used to determine the order of solubility.

4.1.2 Ion effects on solubility

So far we have only paid attention to ionic species and their solubility in pure water. In this section we shall look at how solubility is influence by the presence of ions that one way of another also participates in the reaction of dissolution. This is something that we will look into in the following example:

Example 4- D:

Solubility and foreign ions

We wish to determine the solubility of silver chromate Ag_2CrO_4 in a 0.100 M aqueous solution of $AgNO_3$. Silver chromate has a solubility product of $K_{sp} = 9.0 \cdot 10^{-12} \, M^3$. before the solid silver chromate is dissolved there is already Ag^+ and NO_3^- ions present in the solution. As NO_3^- does not participate in the dissolution reaction for silver chromate, we may ignore this ion. The initial concentration of Ag^+ of 0.100 M has nevertheless an importance. We have the following initial concentrations:

$$[Ag^+]_0 = 0.100 \text{ M}$$
$$[CrO_4^{2-}]_0 = 0$$

The solubility concentration for silver chromate is as follows:

$$Ag_2CrO_4(s) \leftrightarrow 2Ag^+(aq) + CrO_4^{2-}(aq)$$

With corresponding equilibrium expression:

$$K_{sp} = [Ag^+]^2 \cdot [CrO_4^{2-}] = 9.0 \cdot 10^{-12} \, M^3$$

We assume as often that x moles/L of $Ag_2CrO_4(s)$ should be dissolved in order to reach equilibrium:

$$x \text{ moles/L } Ag_2CrO_4(s) \rightarrow 2x \text{ moles/L } Ag^+ (aq) + x \text{ moles/L } CrO_4^{2-}(aq)$$

Equilibrium concentrations may be specified as:

$$[Ag^+]_0 = [Ag^+]_0 + 2x = 0{,}100 \text{ M} + 2x \text{ M}$$
$$[CrO_4^{2-}] = [CrO_4^{2-}]_0 + x = 0 + x \text{ M}$$

By substitution into the equilibrium expression:

$$9.0 \cdot 10^{-12} \, M^3 = [Ag^+]^2 \cdot [CrO_4^{2-}] = (0{,}100 + 2x)^2 \cdot x \Leftrightarrow$$
$$x = 9.0 \cdot 10^{-10} \text{ M}$$

There may thereby by dissolved $9.0 \cdot 10^{-10}$ mol/L $Ag_2CrO_4(s)$ in 0.100 M $AgNO_3$. It is easy to realise that had we had a pure water solution, the solubility would have been found by the following equation:

$$9.0 \cdot 10^{-12} \, M^3 = [Ag^+]^2 \cdot [CrO_4^{2-}] = (2x)^2 \cdot x \Leftrightarrow$$
$$x = 1.3 \cdot 10^{-4} \text{ M}$$

Thus, there may be dissolved $1.3 \cdot 10^{-4}$ moles/L of $Ag_2CrO_4(s)$ in pure water. It may thereby been seen that by comparison of the aqueous solution with the 0.100 M $AgNO_3$ solution that there may be dissolved far more $Ag_2CrO_4(s)$ in pure water then in the solution containing Ag^+ ions already present. One may in an informal way say that the silver ions already present in the solution hinder the dissolution of silver chromate.

4.2 Precipitation

So far we have only looked at the dissolution of solid species in aqueous solutions with or without an initial concentration of ions. In this section we will look at the opposite process which is precipitation of solid material. We will look at the situation where two solutions are mixed by which a possibility arise for solid matter to precipitate. For this purpose we will use the so-called ion product which is defined in a similar manner as we defined the solubility product K_{sp} except that in the expression for the ion product the initial concentrations participate. For our example with CaF_2 the ion product is defined as:

$$Q = [Ca^{2+}]_0 \cdot [F^-]_0^2$$

If we pour a solution of Ca^{2+} ions into a solution containing F^- ions a possibility arise for the precipitation of solid CaF_2 depending on the respective concentrations. In order to be able to predict a possible precipitation we will look at the relation between K_{sp} and Q. The units for K_{sp} and Q are thereby identical which is why the two parameters may be compared readily. In general:

- Is the value of Q larger than K_{sp}, precipitation will take place and this precipitation will continue until the concentrations of remaining ions in the solution will fulfil the equation for K_{sp}, and then $Q=K_{sp}$.
- Is the value of Q less than K_{sp}; no precipitation will take place.

Often it is desired to determine more precisely whether or not a precipitation will take place because we want to determine the equilibrium concentration after precipitation. This is the topic for the next example.

Example 4- E:

Equilibrium concentration after precipitation of lead nitrate (PbNO₃)

We wish to determine the equilibrium concentrations of Pb^{2+} and I^- ions formed after precipitation of PbI_2 in a solution formed by mixing 100.0 mL of a 0.0500 M $Pb(NO_3)_2$ solution and 200.0 mL of a 0.100 M NaI solution.

Initially it must be determined whether or not solid PbI_2 is formed during the mixing of the solutions. The solubility product K_{sp} for PbI_2 is $1.4 \cdot 10^{-8}\,M^3$. The concentrations of Pb^{2+} and I^- after the mixing is easily achieved as:

$$\left[Pb^{2+}\right]_0 = \frac{0.100L \cdot 0.0500mol/L}{0.300L} = 1.67 \cdot 10^{-3}\,M \quad \text{and}$$

$$\left[I^-\right]_0 = \frac{0.200L \cdot 0.100mol/L}{0.300L} = 6.67 \cdot 10^{-2}\,M$$

Hereby the ion product for PbI_2 is determined as:

$$Q = [Pb^{2+}]_0 \cdot [I^-]_0^2 = 1.67 \cdot 10^{-3}\,M \cdot (6.67 \cdot 10^{-2}\,M)^2 = 7.43 \cdot 10^{-5}\,M^3$$

As in this case Q is larger than K_{sp} precipitation of $PbI_2(s)$ will happen. In order to determine the concentrations of Pb^{2+} and I^- ions after precipitations, we set up initially a *before* and an *after* scheme on the basis of moles following the principles below:

|	Pb^{2+}(aq)	+	2 I^-(aq)	→	PbI_2(s)
Before precipitation:	0.100 L · 0.0500 mol/L = $5.0 \cdot 10^{-3}$ mol		0.200 L · 0.100 mol/L = $2.0 \cdot 10^{-2}$ mol		The amount of precipitated matter will
After precipitation:	0 mol		$2.0 \cdot 10^{-2}$ mol – $5.0 \cdot 10^{-3}$ mol = $1.0 \cdot 10^{-2}$ mol		not affect the equilibrium

Now we let the equilibrium take place. At equilibrium the concentration of $[Pb^{2+}]$ is not zero as indicated above because the precipitation reaction does not proceed until all the lead ions are used. One may imagine that when PbI_2 precipitated a small amount of PbI_2 is simultaneously dissolved such that an equilibrium is set up. As there is an excess of I^- ions the small amount of re-dissolved PbI_2 is dissolved into a solution containing $1.0 \cdot 10^{-2}$ mol I^- in 300.0 mL solution. This gives a concentration of I^- of:

$$\left[I^-\right] = \frac{1.0 \cdot 10^{-2}mol/L}{0.300L} = 3.33 \cdot 10^{-2}\,M$$

Hereafter our problem may be formulated as: What is the solubility of solid PbI_2 in a $3.33 \cdot 10^{-2}$ M NaI solution? As earlier examples we start by writing the initial concentrations:

$$[Pb^{2+}]_0 = 0 \text{ M}$$
$$[I^-]_0 = 3.33 \cdot 10^{-2} \text{ M}$$

The end concentrations is found on the basis of the reaction scheme:

$$PbI_2(s) \leftrightarrow Pb^{2+}(aq) + 2\, I^-(aq)$$
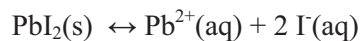
$$[Pb^{2+}] = x$$
$$[I^-] = 3.33 \cdot 10^{-2} \text{ M} + 2x$$

And by insertion into the expression for K_{sp} in the equation we achieve:

$$K_{sp} = 1.4 \cdot 10^{-8} \text{ M}^3 = [Pb^{2+}] \cdot [I^-] = x \cdot (3.33 \cdot 10^{-2} \text{ M} + 2x)^2 \Leftrightarrow$$
$$x = 1.3 \cdot 10^{-5} \text{ M}$$

Thus, the equilibrium concentrations become:

$$[Pb^{2+}]_{equilibrium} = 1.3 \cdot 10^{-5} \text{ M}$$
$$[I^-]_{equilibrium} = 3.33 \cdot 10^{-2} \text{ M} + 2x \approx 3.33 \cdot 10^{-2} \text{ M}$$

Thereby we have determined the equilibrium concentrations of lead and iodine ions in a solution that is prepared by mixing solutions of sodium iodine and lead.

4.2.1 Selective precipitation

Solutions of metal ions are often separated by selective precipitation which is precipitation with a reagent having an anion that forms a solid specie with only one of the metal ions in the solution. One example is a solution with Ba^{2+} ions as well as Ag^+ ions. Are NaCl added to the solution only AgCl precipitates whereas Ba^{2+} ions continues to be in the solution, as BaCl is easily soluble. This we will look further into in the following example.

Example 4- F:
Selective precipitation

A solution contains $1.0 \cdot 10^{-4}$ M Cu^+ ions and $2.0 \cdot 10^{-3}$ M Pb^{2+} ions. We now slowly add a aqueous solution containing I^- ions. Hereby, $PbI_2(s)$ precipitates following the reaction scheme below:

$$Pb^{2+} (aq) + I^-(aq) \rightarrow PbI_2(s)$$
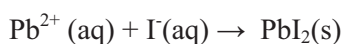
The K_{sp} values are $1.4 \cdot 10^{-8}$ M^3 for PbI_2 and $5.3 \cdot 10^{-12}$ M^2 for CuI respectively. We now wish to determine which one of the two solid species that precipitates first. Furthermore we wish to determine the concentration of I^- being necessary to precipitate each of the two solid species.

For PbI_2 the expression for K_{sp} is:

$$1.4 \cdot 10^{-8} M^3 = K_{sp} = [Pb^{2+}] \cdot [I^-]^2$$

As we know that the concentration of Pb^{2+} is $2,0 \cdot 10^{-3}$ M the largest possible concentration of I^- being able to exist without precipitation may be calculated from:

$$1.4 \cdot 10^{-8} M^3 = K_{sp} = [Pb^{2+}] \cdot [I^-]^2 = (2.0 \cdot 10^{-3}) \cdot [I^-]^2 \Leftrightarrow$$
$$[I^-] = 2.6 \cdot 10^{-3} M$$

A concentration of I^- ions above $2.6 \cdot 10^{-3}$ M will thereby lead to precipitation of $PbI_2(s)$. Similarly for CuI:

$$5.3 \cdot 10^{-12} M^2 = K_{sp} = [Cu^+] \cdot [I^-] = (1,0 \cdot 10^{-4}) \cdot [I^-] \Leftrightarrow$$
$$[I^-] = 5.3 \cdot 10^{-8} M$$

Thus, a concentration of I^- ions higher than $5.3 \cdot 10^{-8}$ M will lead to precipitation of CuI(s). On the basis of these calculations we can thereby settle which of the two solid species that will precipitate first. Are I^- ions added gradually CuI(s) will precipitate first whereby Cu^+ may be separated from Pb^{2+} using this principle.

4.3 Summing up on chapter 4

Central terms as solubility product and solubility equilibrium were introduced in this chapter. Through examples we saw how solubility may be calculated from information of solubility constants. Further we saw how the relative solubility of solid species may be determined on the basis of such constants.

> *An order of solubility of different solid species may be determined by looking at the solubility product K_{sp} ONLY when the numbers of ions are similar (meaning ONLY when the K_{sp} parameters have the same unit). When the number of ions in the solid species are different the order of solubility must be determined by calculating the solubility x in moles pr. litre as the solubility products K_{sp} do not have a similar unit and thereby may not be compared.*

As one of the more advanced examples we saw how the presence of foreign ions may influence the solubility of solid species but that it is still possible to calculate the solubility. Lastly, we looked at precipitation and here also introduced the ion product. We saw how the relation between the ion product and the solubility constant determined whether or not precipitation will take place or not. This was further illustrated through examples concerning selective precipitation.

5. Acids and bases

In this chapter we shall look at central parts of chemistry being acid and base chemistry. We will look at their interactions and further develop the theory of equilibrium introduced in the previous section. Large parts of the fundamental knowledge of acids and bases were thoroughly introduced in the high-school meaning that we will look at more advanced theory here. We start by mentioning that acid/base chemistry always takes place in aqueous solutions. Terms as *acid strength* and *base strength* have thereby only relevance in connection of aqueous solutions.

5.1 About acids and bases

Acid solutions are known from many types of foods. According to the famous Brønsted-Lowry definition an acid is a proton donor (in terms of H^+ ions), while a base is a proton receiver (water may act as an acid as well as act as a base).

In an acid-base reaction a H^+ ion is transferred from the acid to the base following the principle below where the acid is written in general as HA while the corresponding base is written as A^-:

$$\underbrace{HA(aq)}_{Syre} + \underbrace{H_2O(l)}_{Base} \leftrightarrow \underbrace{H_3O^+(aq)}_{Corresponderende\ acid} + \underbrace{A^-(aq)}_{Corresponderende\ base}$$

By transfer of the H^+ ion the acid HA is converted to its corresponding base A^-. Thus, HA and A^- is a corresponding acid/base pair.

5.1.1 Acid strength

The strength of an acid solution is defined on the basis of the position of the following equilibrium where the acid in general is written as HA while the corresponding base is written as A^-:

$$HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$$
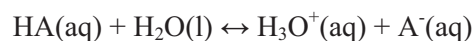
An acid is known to be strong when the equilibrium is strongly shifted to the right meaning that there is almost no HA left in the solution. On the contrary the acid is known to be weak when there is almost no corresponding base A^- in the solution. When the acid is strong the equilibrium arrow may be replaced by a right-pointing arrow but when the acid is weak the equilibrium arrow must be written.

An equilibrium expression for the general acid-base reaction may be expressed in a similar way as in chapter 3 and chapter 4:

$$K_a = \frac{[H_3O^+] \cdot [A^-]}{[HA]} = \frac{[H^+] \cdot [A^-]}{[HA]}$$

The equilibrium constant K_a, when we have an acid-base reaction, is known as the acids *dissociation-constant* or simply the strength-constant. Similarly is defined a dissociation-constant for bases K_b. We do not distinguish between H^+ and H_3O^+ ions in the following as long as one remembers that in aqueous solutions H^+ always exist as H_3O^+ ions. As the percent wise amounts of water molecules by far dominate the amount of acid-base components, the mole fraction of water is close to one. Water takes part of the equilibrium expressions with its mole fraction which is why it is often omitted in practice. Similarly corresponding to the considerations above it is clear that for strong acids the K_a values are large while K_a values are small for weak acids. As the K_a values vary a lot from acid to acid one has for the sake of convenience often chosen to express the acid constant in an acid *strength exponent* defined as:

$$pK_a = -\log[K_a] \qquad\qquad (5\text{-}1)$$

Based on this definition it is obvious that strong acids gets a very small or even negative pK_a value while strong acids have pK_a values from approximately 10 and up.

5.1.2 The pH-scale

Because the concentration of H^+ ions in solution generally is quite small one has for the sake of convenience chose to express a solutions acidness based on the decimal logarithm to the concentration of H^+ ions completely analogous to the principles that the acid constant K_a was expressed as an acid exponent pK_a. this is known as the pH scale and the pH values are defined as:

$$pH = -\log[H^+] = -\log[H_3O^+] \qquad\qquad (5\text{-}2)$$

This means that if a solution has a concentration of H^+ ions of e.g. $1.0 \cdot 10^{-7}$ M one would say that the pH value of the solution is 7. Figure 5-1 gives the pH-scale as well as pH-values for well-known aqueous solutions.
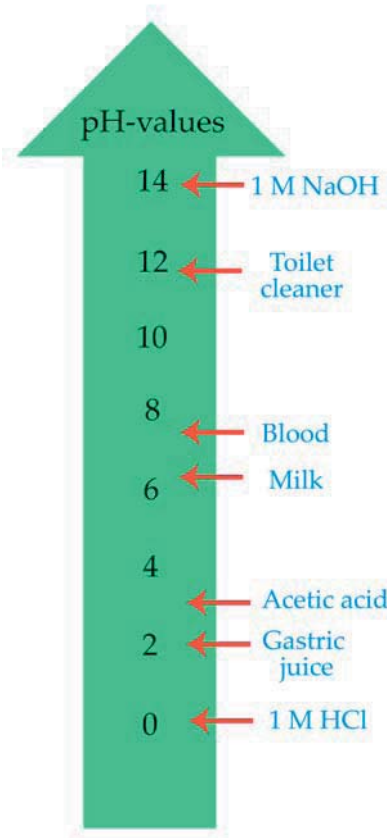
Figure 5- 1: The pH-scale

pH-values for well-known solutions.

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