SOLUBILITY AND COMMON ION EFFECT

In the last post we have seen how salts are dissolved in water, how polar forces of water overcome the electrostatic attraction present between the ions and how water molecules hydrate ions to keep them separate. In this post we will study how an ionic solid dissolves in a solvent. What are the factors which govern the solubility of a solid and dissolving ability of a solvent?

In ionic solid, ions are bonded together by electrostatic force. A solvent must overcome this electrostatic attraction to split the ionic molecule. It is not so easy for a solvent to dissolve an ionic solute because it has to first break their lattice and weaken the electrostatic attraction present between the ions. Solvent also needs similar weapon to win this war. Usually solvents are covalent compounds but they may have some polar characters. If the solvent molecules are polar enough, they may weaken the electrostatic attraction between the ions of the ionic solid and then the molecules of solvent gather around the ions to solvate them, this process is called as solvation (when solvent is water we call it to hydrate the ions and the process is called Hydration). Solvation is very important because energy is released in this process and that’s how a solvent succeeds to overcome the lattice enthalpy of ionic solids.

Solvation enthalpy is a characteristic of solvent. It is lower for non polar solvents and higher for polar solvents. Lattice enthalpy must be overcome by solvation enthalpy for dissolution of a solid. That’s why non-polar substances dissolve in non-polar solvents and polar substances dissolve in polar solvents (like dissolves like). Water has higher solvation enthalpy and this is the reason why it is known as universal solvent.

On the basis of their solubility in water, solutes can be classified into three categories: insoluble, soluble and sparingly soluble. Insoluble solutes don’t dissolve in water and soluble solutes are completely soluble while the solutes which are partly dissolved fall under the category of sparingly soluble.

If you add sugar in water, it gets dissolved. If you continually add more sugar in this solution you will find that after a certain amount you won't be able to dissolve more sugar in it. That means sugar solution gets saturated and it won't dissolve any more sugar at this temperature and pressure. When we add more sugar in this saturated solution, an equilibrium develops between dissolved and undissolved sugar. If you want to know how you can dissolve more sugar in this saturated solution or how you can take out sugar from this solution, you will have to study this equilibrium.

Whenever a solute comes in contact with saturated solution, equilibrium is always developed between dissolved and undissolved solute. We will study this equilibrium with the example of Barium sulphate ($BaSO_4$):

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4{}^{2-}_{(aq)}$

Write the equation of equilibrium constant:

$K = \{[Ba^{2+}][\,SO_4{}^{2-}]\} / [\,BaSO_4]$
$K\,[BaSO_4] = [Ba^{2+}]\,[SO_4{}^{2-}]$

For a pure solid substance concentration remain constant, so we can write

$K_{sp} = [Ba^{2+}]\,[SO_4{}^{2-}]$

K_{sp} is the solubility product constant of solute which is the product of molar concentrations of ions. With the help of K_{sp} we can calculate maximum number of moles of solute which can be dissolved in 1 L of solvent; it is called as molar solubility of a solute and it is represented by "S". The molar concentration of ions will be equal to the molar solubility of solute. Let's see:

On dissolution $BaSO_4$ dissociates into one ion of Ba^{2+} and one ion of $SO_4{}^{2-}$. The molar concentration of ion is equal to the molar solubility of solute.

$[Ba^{2+}] = S$

$[SO_4^{2-}] = S$

So we can write the equation for K_{sp} as:

$K_{sp} = [S]\ [S]$
$K_{sp} = S^2$
$S = \sqrt{}K_{sp}$

Let’s take another example of zirconium phosphate (Zr_3PO_4). On dissolution in water it dissociates in to 3 ion of Zr^{4+} and 4 ion of PO_4^{3-}.

Zr3PO4 ⇌ 3 Zr4+ + 4 PO43-
$K = [Zr^{4+}]^3\ [PO_4^{3-}]^4\ /\ [Zr_3PO_4]$
$K\ [Zr_3PO_4] = [Zr^{4+}]^3\ [PO_4^{3-}]^4$
$K_{sp} = [Zr^{4+}]^3\ [PO_4^{3-}]^4$

Molar solubility of solute is equal to the molar concentration of ions. On dissolution of Zr_3PO_4 three ion of Zr^{4+} and four ion of PO_4^{3-} are produced.

So the molar concentration of one Zr^{4+} is equal to S and for three ions it will be 3S, similarly

$[Zr^{4+}] = 3S$
$[PO_4^{3-}] = 4S$

Now putting the values in the equation of K_{sp}

$K_{sp} = [3S]^3\ [4S]^4$
$K_{sp} = [27S]^3\ [256S]^4$
$K_{sp} = 6912\ S^{3+4}$
$S = (K_{sp}\ /\ 6912)^{1/7}$

We can derive the general equation for salt $M^{a+}_{p}X^{b-}_{q}$

$M^{a+}_{p}X^{b-}_{q} \rightleftharpoons p\ M^{a+} + q\ X^{b-}$

$K_{sp} = [M^{a+}]p\ [X^{b-}]q$

On dissolution of $M^{a+}_{p}X^{b-}_{q}$ salt p number of M^{a+} ions and q number of X^{b-} are produced. Solubility of salt is S, so the molar concentration of ions will be:

$[M^{a+}] = [pS]$

$[X^{b-}] = [qS]$

On putting the values in equation for K_{sp}

$K_{sp} = [pS]^{p}\ [qS]^{q}$

$K_{sp} = (p^{p} \times q^{q})\ S^{(p+q)}$

If the concentration of any ion is not the concentration at the time of equilibrium then K_{sp} is called as Q_{sp} as we have studied in the chemical equilibrium post.

The Le Chatelier’sprinciples are also applicable to the equilibrium between saturated solution and the solute. Let’s see how we can manipulate the solubility of a solute with the help of these laws.
If we increase the concentration of one ion then the equilibrium shifts in the backward direction till Q_{sp} becomes equal K_{sp}. And thus we can precipitate salt from the solution. Similarly if we remove any ion from the solution then the equilibrium shifts in the forward direction till $Q_{sp} = K_{sp}$ and we will be able to dissolve more solute in it. In both the situations we either add or remove one of the ions from the system.

Let’s take an example:

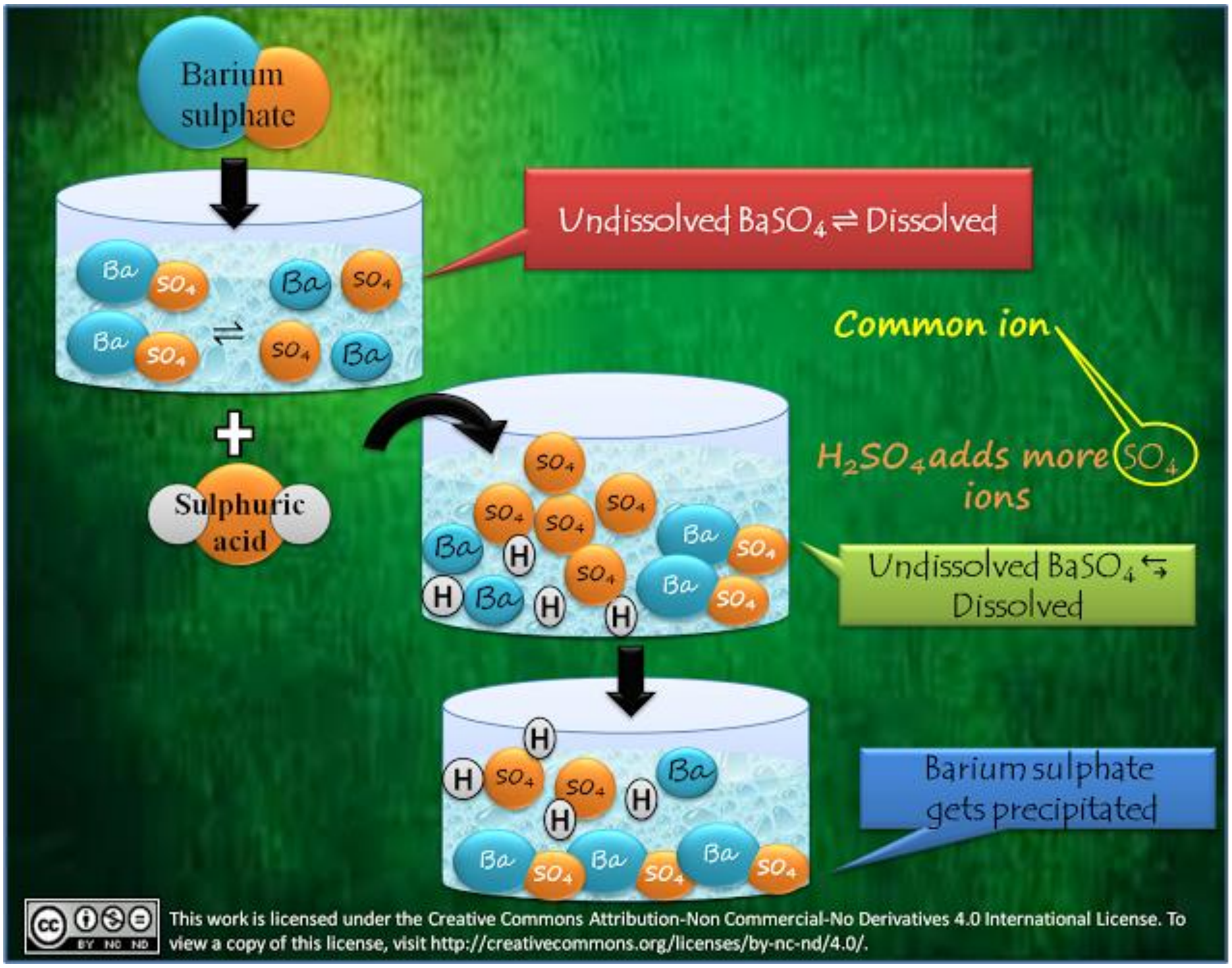
$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_{4}{}^{2-}_{(aq)}$

If we add H_2SO_4 to the solution, it increases concentration of SO_4^{2-} ions and shifts equilibrium to the left side of the reaction, as a result of which Barium gets precipitated as $BaSO_{4(s)}$.
H_2SO_4 is a strong acid and it dissociates completely:

$$H_2SO_{4(aq)} \longrightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

SO_4^{2-} ion is the common ion among these two reactions thus when its concentration increases due to dissociation of sulphuric acid it shifts equilibrium to the left side of the reaction resulting in the precipitation of Barium as $BaSO_{4(s)}$.

$$BaSO_{4(s)}\downarrow \leftrightarrows Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$



This phenomenon is known as “Common Ion Effect” and is widely used for the complete precipitation of soluble or sparingly soluble salts. We can get almost 99% pure salt by applying this phenomenon. Let’s take another example: If we want to get NaCl back from its saturated solution what will we do?

$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

If we pass HCl gas through it, concentration of Cl^{-} ions will be increased by dissociation of HCl and the equilibrium will be shifted in backward direction and NaCl will be precipitated.
“Common Ion Effect” is a very useful phenomenon; you will find its applications in your laboratory when you perform salt analysis

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