# CHEM1612 Worksheet 7: The Solubility Product

## Model 1: The solubility product

If as much solid has dissolved as is possible, the solution is saturated and equilibrium has been established.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)$$

The equilibrium constant is known as the '**solubility product**' and given the symbol $\boldsymbol{K_{sp}}$:

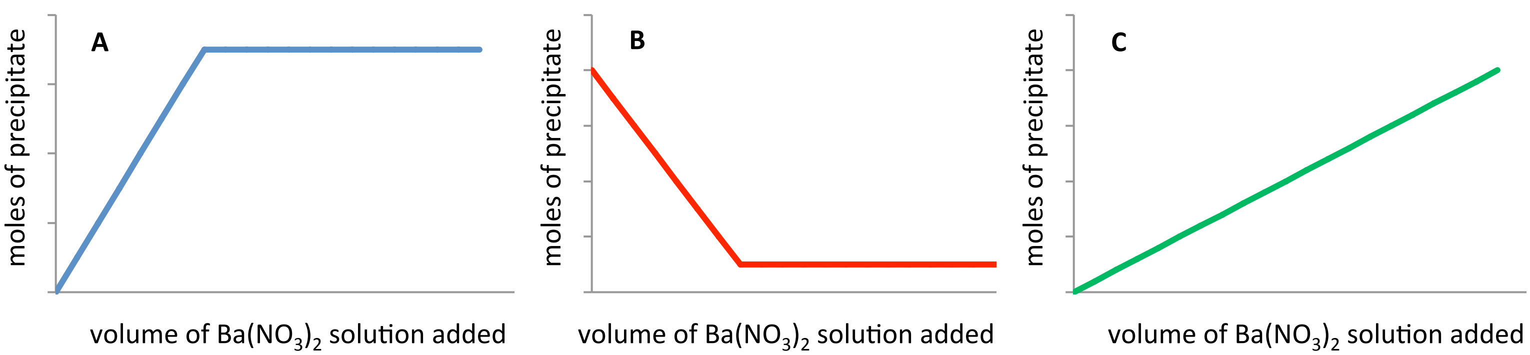
$$K_{sp} = [Mg^{2+}(aq)][OH^{-}(aq)]^2$$

It involves only the aqueous ions with the concentration of each raised to the power by which they appear in the dissolution reaction. The concentration of the solid is constant so does not appear in the expression. Clearly, this is only true if solid is present: if there is no solid present, the solution is *not* saturated and the reaction is *not* at equilibrium.

## Critical thinking questions

1. A solution of $Ba(NO_3)_2$ is added to a solution of $Na_2SO_4$ causing $BaSO_4$ to precipitate.

   Which graph below shows the amount of precipitate collected from a fixed amount of $Na_2SO_4$ solution as the $Ba(NO_3)_2$ is added indefinitely?

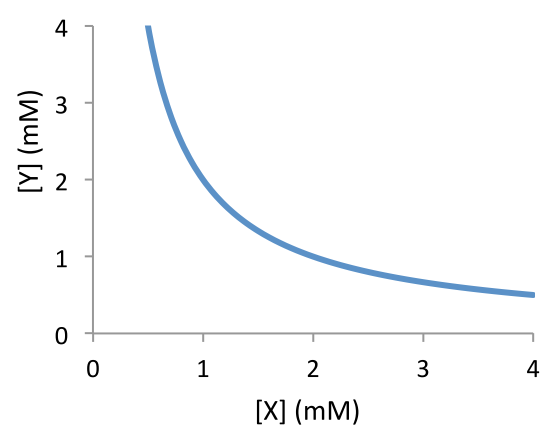



2. The figure opposite shows a solubility curve for a salt XY with $K_{sp} = 2 \times 10^{-6}$.

   Label the region(s) on the figure where:

   (a) the salt is completely dissolved

   (b) equilibrium has been established




3. Write down the solubility product for the following salts:

   (a) $AgCl(s)$: $K_{sp}$ =

   (b) $Ag_2SO_4(s)$ : $K_{sp}$ =

   (c) $PbCl_2(s)$ : $K_{sp}$ =

4. $PbCl_2$ is not very soluble in water with $K_{sp} = 1.6 \times 10^{-5}$. The number of moles of $PbCl_2$ that dissolve in a litre of water is called the *molar solubility*.

   (a) If $x$ moles of $PbCl_2$ dissolve in 1.00 L of water, what will be $[Pb^{2+}(aq)]$ and $[Cl^-(aq)]$ in terms of $x$?

   (b) $K_{sp}$ of $PbCl_2$ is $1.6 \times 10^{-5}$, using your answer to Q3(c) and Q4(a), work out $[Pb^{2+}(aq)]$ and $[Cl^-(aq)]$.

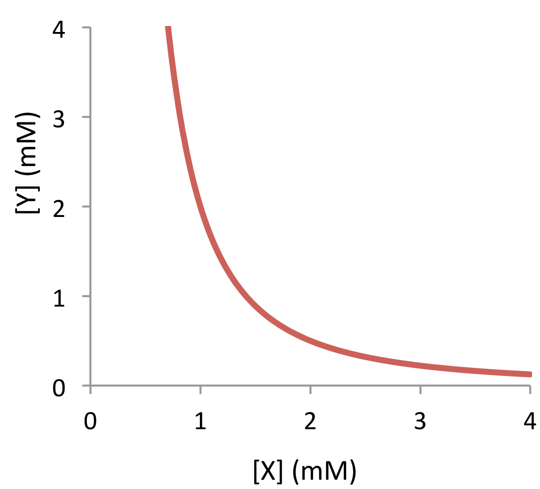
5. In terms of its $K_{sp}$, what is the molar solubility of $Fe(OH)_3$? (*Hint*: consider the procedure you followed in Q4 and think about the effect of the stoichiometry on the calculation.)

6. Order the following salts from lowest to highest solubility.

   (a) $SrSO_4$ ($K_{sp} = 2.8 \times 10^{-7}$)  (b) $Zn(OH)_2$ ($K_{sp} = 4.5 \times 10^{-17}$)
   (c) $PbI_2$ ($K_{sp} = 8.7 \times 10^{-9}$)  (d) MnS ($K_{sp} = 5 \times 10^{-15}$)

7. By considering your answer to Q6, explain if and when you can determine the relative solubility of salts simply by comparing their $K_{sp}$ values.

8. The figure opposite shows the solubility curve for a different salt to that in Q2.




   (a) Is the stoichiometry of the salt?

   (i) XY  (ii) $X_2Y$  (iii) $XY_2$?

   (b) What is the value of the solubility constant?

   (i) $2 \times 10^{-3}$  (ii) $2 \times 10^{-6}$

   (iii) $2 \times 10^{-9}$  (iv) $4 \times 10^{-9}$

## Model 2: To dissolve or not to dissolve?

The solubility product gives the *maximum* values of the ion concentrations that are allowed. If their concentrations are such that their product is *less* than $K_{sp}$, then more solid can dissolve.

**If $[Mg^{2+}(aq)][OH^{-}(aq)]^2 < K_{sp}$ then more solid can dissolve**

If their concentrations are such that their product is *more* than $K_{sp}$ then the concentrations must reduce: precipitation *must* occur.

**If $[Mg^{2+}(aq)][OH^{-}(aq)]^2 > K_{sp}$ then precipitation must occur**

The value of the product can thus be used to predict whether dissolution or precipitation can occur. Because of its importance, it is called the '**ionic product**' and given the symbol $Q_{sp}$:

$$Q_{sp} = [Mg^{2+}(aq)][OH^{-}(aq)]^2$$

**If $Q_{sp} < K_{sp}$ then dissolution will occur. If $Q_{sp} > K_{sp}$ then precipitation will occur.**

## Critical thinking questions

1. A solution is made by mixing 500.0 mL of 0.12 M NaOH solution with 500.0 mL of 0.10 M $Mg(NO_3)_2$. $K_{sp}$ is $1.8 \times 10^{-11}$

   (a) Assuming that no reaction occurs, what will $[Mg^{2+}(aq)]$ and $[OH^{-}(aq)]$ be after mixing?

   (b) Write down the value of the ionic product, $Q_{sp}$.

   (c) Does a precipitate form?

2. For each of the following experiments, predict whether or not a precipitate of $MgF_2$ will form. $K_{sp}$ $MgF_2(s) = 6.4 \times 10^{-9}$

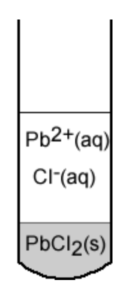
   (a) 500.0 mL of 0.050 M $Mg(NO_3)_2$ is mixed with 500.0 mL of 0.010 M NaF

   (b) 500.0 mL of 0.050 M $Mg(NO_3)_2$ is mixed with 500.0 mL of 0.0010 M NaF.

## Model 3: Le Châtelier's Principle and Solubility

If the concentration of a reactant is increased, the equilibrium responds by producing more products. If the concentration of a product is increased, the equilibrium responds by producing more reactant.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$




$PbCl_2$ is not very soluble in water. The picture shows a test tube containing a saturated solution of lead chloride in contact with a precipitate of solid.

The effect on this solubility of adding $Pb^{2+}(aq)$ or $Cl^{-}(aq)$ ions from another source is called the *common ion effect*.

### Critical thinking questions

1. Write down the solubility product expression, $K_{sp}$, for lead chloride.

2. Sodium chloride dissolves completely to give $Na^+$(aq) and $Cl^-$(aq) ions. If sodium chloride is added to the saturated solution, what would be the effect on the solubility of lead chloride? (*Hint:* consider how the equilibrium written above would shift, according to Le Châtelier's principle, when these ions are added).

3. If sodium chloride is added so that $[Cl^-(aq)] = 0.5$ M, rearrange your $K_{sp}$ expression to give $[Pb^{2+}(aq)]$.

4. What is the effect of adding extra $PbCl_2(s)$ to the test tube? (Be careful!)

## Model 4: Solubility and pH

Metal hydroxides dissolve to give metal ions and hydroxide ions. For example,

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

The position of the equilibrium (i.e. the solubility) is very sensitive to pH since this controls $[OH^-(aq)]$.

All forms of life depend on iron and the concentration of iron in the oceans and elsewhere is one of the primary factors limiting the growth rates of the most basic life forms. One reason for the low availability of iron(III) is the insolubility of $Fe(OH)_3$ which has a $K_{sp}$ of only $1 \times 10^{--39}$.

### Critical thinking questions

1. Write down the expression for the solubility product, $K_{sp}$, for $Fe(OH)_3$.

2. The pH of the oceans is currently 8.179. Use this to work out $[OH^-(aq)]$.

3. If $x$ moles of $Fe(OH)_3$ dissolve in 1.00 L of water, $[Fe^{3+}(aq)] = x$ mol $L^{-1}$. Use your answers to Q1 and Q2 to work out $x$ in the ocean.

4. If the amount of $CO_2$ in the atmospheres increases, the pH of the oceans will *decrease* due to the equilibrium below. What will happen to $[Fe^{3+}(aq)]$?

$$CO_2(g) + H_2O(l) \rightleftharpoons HCO_3^- + H_3O^+(aq)$$

5. The concentration of $Fe^{3+}$ in our blood is about $10^{-6}$ M. Assuming a typical blood pH of 7.4, calculate the concentration of free $Fe^{3+}$ in our blood and account for any difference with the actual concentration.