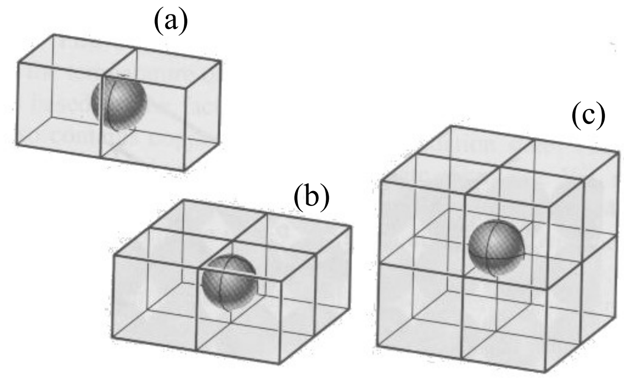
CHEM1902/4 Worksheet 11: The Solubility Product and Structures & Stoichiometry

Model 1: The Unit Cell

The smallest repeating unit that can be used to describe a crystal is called the *unit cell*. The structure of the solid can be built from the unit cell by stacking them together in three dimensions.The simplest unit cells are cubes. These are packed together, as shown opposite, like bricks to make up the infinite, three dimensional structure. Atoms on the corners, edges and faces of a unit cell are shared by more than one unit cell:

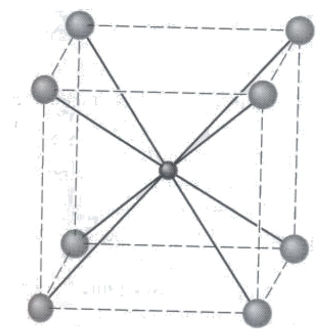


(a) an atom on a *face* is shared by *two* cells so only *half* belongs to each of the cells

(b) an atom on an *edge* is shared by four cells so only a *quarter* belongs to each of the cells

(c) an atom on a *corner* is shared by eight cells so only an *eighth* belongs to each of the cells

The unit cell opposite is of caesium chloride. It contains Cl^- at the corners of the cube and Cs^+ at the centre.



The caesium ion is completely in the cell:

- number of caesium ions in cell = 1

From Model 1, only an eighth of atoms on the corners belong to the cell. Hence:

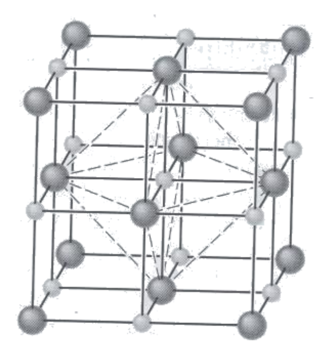
- number of chloride ions in cell = $8 \times \frac{1}{8} = 1$

The unit cell contains 1 caesium and 1 chloride and so the formula is CsCl.

Critical thinking questions

1. The picture opposite shows the structure of NaCl.

(a) The larger spheres represent Cl atoms. These are located on the *corners* and *faces* of the cube. How many Cl atoms are in the cell?

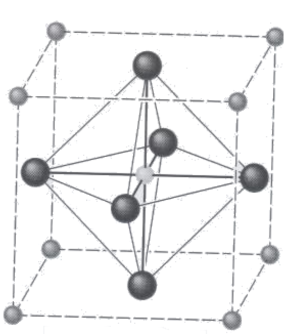


(b) The smaller spheres represent Na atoms. These are located on the *edges* and at the *centre* of the cube. How many Na atoms are in the cell?

(c) Is this cation : anion ratio consistent with the formula NaCl?

2. The picture opposite is the perovskite structure which is very important in minerals and in superconductors. It contains *three* different types of atoms.

(a) There is a Ti atom at the *centre* (light grey). How many Ti atoms in the cell?



(b) There are Ca atoms (dark grey) at each *corner*. How many Ca atoms are in the cell?

(c) There are O atoms (black) on each *face*. How many O atoms are in the cell?

(d) What is the formula of the mineral?

(e) What is the oxidation number of the titanium?

Model 2: The solubility product

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

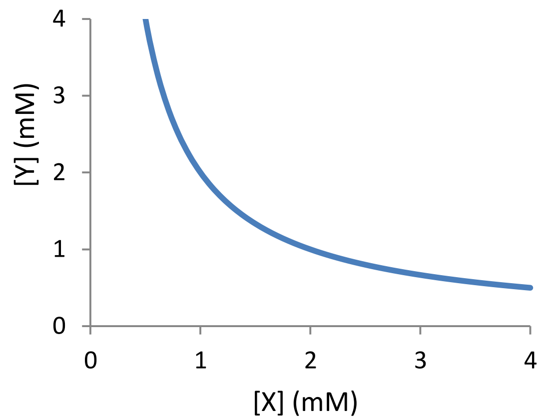
$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

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 K_{sp}. 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. 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

2. 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} =

3. $PbCl_2$ 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?

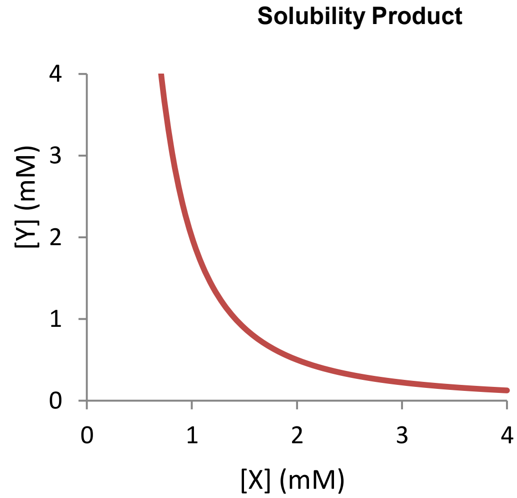
   (b) K_{sp} of $PbCl_2$ is 1.6×10^{-5}, using your answer to Q2(c) and Q3(a), work out $[Pb^{2+}(aq)]$ and $[Cl^-(aq)]$.

4. In terms of its K_{sp}, what is the molar solubility of $Fe(OH)_3$? (*Hint*: consider the procedure you followed in Q3 and think about the effect of the stoichiometry on the calculation.)

5 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 ($K_{sp} = 5 \times 10^{-15}$)

6. The figure opposite shows the solubility curve for a different salt to that in Q1.



(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) 2×10^{-3} (ii) 2×10^{-6} (iii) 2×10^{-9} (iv) 4×10^{-9}

Model 3: 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 1.8×10^{-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}.

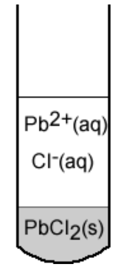
(c) Does a precipitate form?

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 4: 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 5: Solubility and pH

Metal hydroxides dissolve to give metal ions and hydroxide ions. The position of the equilibrium (i.e. the solubility) is very sensitive to pH since this controls $[OH^-(aq)]$. For example,

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

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 1×10^{-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.