CHEM1102 Worksheet 11: The Solubility Product and Structures & Stoichiometry

Model 1: The Unit Cell

In metals and ionic solids, the atoms are arranged in very ordered arrangements. The number of atoms in such a solid is enormous: if you were sitting on one, you would see atoms in every direction as far as you can see. The best way to describe the structure is to look for the smallest repeating unit. This 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

Critical thinking questions
1. The picture opposite shows the simple cubic unit cell, which only has atoms on the corners of the cube. What is the net number of atoms belonging to the unit cell? (Hint: how many atoms are on the corners and how much of each one belongs to the cell)
2. The picture opposite shows the body centred unit cell, which has an atom at the centre as well as atoms on the corners of the cube. What is the net number of atoms in the unit cell?
3. The picture opposite shows the face centred unit cell, which has atoms on the faces and on the corners of the cube. What is the net number of atoms in the unit cell?

Model 2: The Unit Cell and Stoichiometry

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 overleaf 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?
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?

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

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

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

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

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

What is the formula of the mineral?

What is the oxidation number of the titanium?

**Model 3: The solubility product**

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

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \]

The equilibrium constant is known as the ‘solubility product’ and given the symbol \( K_{sp} \):

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

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. Write down the solubility product for the following salts:
   (a) \( \text{AgCl}(s) : K_{sp} = \)
   (b) \( \text{Ag}_2\text{SO}_4(s) : K_{sp} = \)
   (c) \( \text{PbCl}_2(s) : K_{sp} = \)

2. \( \text{PbCl}_2 \) is not very soluble in water with \( K_{sp} = 1.6 \times 10^{-5} \). The number of moles of \( \text{PbCl}_2 \) that dissolve in a litre of water is called the molar solubility.
   (a) If \( x \) moles of \( \text{PbCl}_2 \) dissolve in 1.00 L of water, what will be \([\text{Pb}^{2+}(aq)]\) and \([\text{Cl}^-(aq)]\) in terms of \( x \)?
   (b) \( K_{sp} \) of \( \text{PbCl}_2 \) is \( 1.6 \times 10^{-5} \), using your answer to Q1(c) and Q2(a), work out \([\text{Pb}^{2+}(aq)]\) and \([\text{Cl}^-(aq)]\).
3. In terms of its $K_{sp}$, what is the molar solubility of Fe(OH)$_3$? (*Hint:* consider the procedure you followed in Q2 and think about the effect of the stoichiometry on the calculation.)

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

**Model 4: 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 $[\text{Mg}^{2+}(aq)][\text{OH}^{-}(aq)]^2 < K_{sp}$ 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 $[\text{Mg}^{2+}(aq)][\text{OH}^{-}(aq)]^2 > K_{sp}$ 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 $Q_{sp}$:

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

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 $[\text{Mg}^{2+}(aq)]$ and $[\text{OH}^{-}(aq)]$ 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 5: 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.

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

PbCl₂ 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 Pb²⁺(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 [Pb²⁺(aq)].
4. What is the effect of adding extra PbCl₂(s) to the test tube? (Be careful!)

Model 6: 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 \(1 \times 10^{-39}\).

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, [Fe³⁺(aq)] = \(x\) mol L⁻¹. Use your answers to Q1 and Q2 to work out \(x\) in the ocean.
4. If the amount of CO₂ in the atmospheres increases, the pH of the oceans will decrease due to the equilibrium below. What will happen to [Fe³⁺(aq)]?

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

5. The concentration of Fe³⁺ in our blood is about \(10^{-6}\) M. Assuming a typical blood pH of 7.4, calculate the concentration of free Fe³⁺ in our blood and account for any difference with the actual concentration.