Anderson Serangoon Junior College

2024 JC1 H2 Chemistry

Solubility Equilibria

Content	Resources
1 Introduction **2** Salts and saturated solutions 2.1 Types of salts 2.2 Difference between a soluble salts and a sparingly soluble salt 2.3 Saturated solution **3** Solubility and solubility product (K_{sp}) 3.1 Solubility of solute (in water) 3.2 Solubility product (K_{sp}) 3.3 Relationship between solubility and solubility product 3.4 Calculations 3.5 Calculations (continued) **4** Effect on solubility of ionic salts when equilibrium is disturbed 4.1 Common ion effect	**Lecture 1** • Lecture notes: Pg 1 to 10 • SLS quiz: Qn 1 and 2
4.2 Effect on solubility of ionic salts by chemical reactions **5** Ionic Product and Precipitation 5.1 Ionic product 5.2 When and why does precipitation occurs? 5.3 Calculations **6** Further Applications of K_{sp} on solubility of silver halides	**Lecture 2** • Lecture notes: Pg 11 to 18 • SLS quiz: Qn 3 and 4

Learning Outcomes

Students should be able to:

(a) show understanding of, and apply, the concept of solubility product, K_{sp}

(b) calculate K_{sp} from concentrations and *vice versa*

(c) discuss the effects on the solubility of ionic salts by the following:

(i) common ion effect

(ii) formation of complex ion as exemplified by the reaction of halide ions with aqueous silver ions followed by aqueous ammonia (See also – An Introduction to the Chemistry of Transition Elements)

References

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2. Chemistry, The Molecular Nature of Matter and Change (Fourth Edition), Silberberg, McGraw Hill
3. Chemistry & Chemical Reactivity (Sixth Edition), Kotz, Treichel and Weaver, Thomson
4. Chemistry The Central Science (Ninth Edition), Brown, LeMay, Bursten, Prentice Hall
5. Chemistry (Sixth Edition), Zumdahl and Zumdahl, Houghton Mifflin
6. Understanding Advanced Physical Inorganic Chemistry, The Learner's Approach, Jeanne Tan, Kim Seng Chan, WS Education

1. INTRODUCTION

Solubility is a very important phenomenon that impacts our daily life, environment and health.

Water with high content of calcium or magnesium ions (known as hard water) are present in some regions of the world. Mineral deposits can be found on cooking dishes or in bathtubs. Sometimes, you may also have felt like there was a film of residue left on your hands after washing your hands with soap.

Hard water can leave a film on glasses coming out of the dishwasher.
(http://water.usgs.gov/edu/hardness.html)

Mineral deposits are formed due to the formation of insoluble precipitates by calcium or magnesium ions in the hard water. These deposits can make hard water unsuitable for many uses. They can reduce the lifespan of equipment, raise the costs of heating the water, lower the efficiency of electric water heaters, or clog pipes.

A variety of methods can be used to minimise the hardness of water. For example, mineral deposits in pots can sometimes be removed by running vinegar (an acid) through the pot. At the end of this topic, try to make sense of why precipitation occurs, and why the above method works in removing the mineral deposits.

In this topic, we will find out the answer to the following questions:

- What is a saturated solution?
- What is solubility and solubility product? How are they related?
- When and why does precipitation take place?
- What are the effects on the solubility of ionic salts when its equilibrium is disturbed?

2. SALTS AND SATURATED SOLUTIONS

2.1 Types of salts

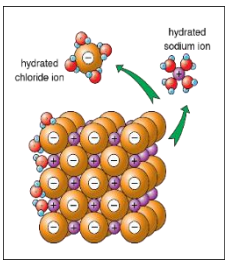
Ionic compounds can be classified as soluble or sparingly soluble salts. We often use the term "insoluble salt" to describe ionic compounds that have low solubility in water. However, these are more appropriately described as **sparingly soluble** salts.

Recall from 'O' levels that **all ionic compounds containing Na^+, K^+ and NH_4^+ are soluble**. The table below shows a general classification of salts as either soluble or sparingly soluble.

Solubility in water	
Soluble Salts	**Sparingly Soluble Salts**
All nitrates (NO_3^-)	–
Nitrites (NO_2^-)	Only $AgNO_2$
Halides (Cl^-, Br^-, I^-)	Only halides of Ag^+, Pb^{2+}, Cu^+. $PbCl_2$, $PbBr_2$, PbI_2 are soluble in hot water
Sulfates (SO_4^{2-})	Only sulfates of Ba^{2+}, Ca^{2+} and Pb^{2+}
Only sulfides of **Na^+, K^+ and NH_4^+**	Sulfides (S^{2-})
Only carbonates of **Na^+, K^+ and NH_4^+**	Carbonates (CO_3^{2-})
Only oxides of **Na^+, K^+, NH_4^+** and larger Group 2 cations (e.g. Ca^{2+}, Sr^{2+}, Ba^{2+})	Oxides (O^{2-})
Only hydroxides of **Na^+, K^+, NH_4^+** and larger Group 2 cations (e.g. Ca^{2+}, Sr^{2+}, Ba^{2+})	Hydroxides (OH^-)

When you add a sparingly soluble salt (or "insoluble salt") into water at a fixed temperature, it will dissolve in water until a point when, to the naked eye, no more solute can dissolve. This is when a **saturated solution** is obtained (See section 2.3 – page 4).

2.2 Difference between a soluble salt and a sparingly soluble salt



Source: https://manoa.hawaii.edu/exploringourfluidearth/chemical/properties-water/comparison-water-other-liquids

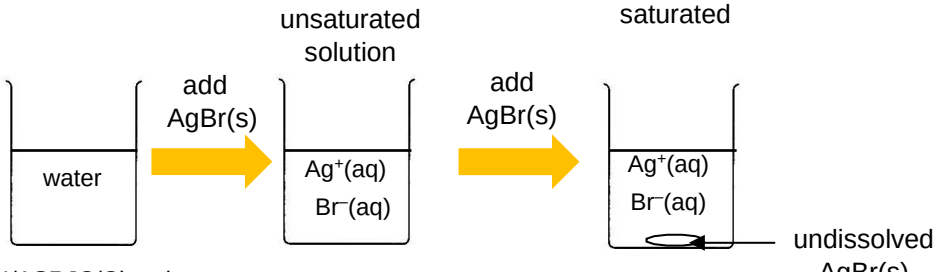
- When a **soluble salt** is added to water, it **dissociates completely** to give separate hydrated ions in the solution.

  e.g. $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$

- When a **sparingly soluble salt** is added to water gradually, it **dissolves slightly** and produces a mixture consisting of a very dilute solution of the ions in **equilibrium** with the undissolved solid.

  e.g. $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

  The solution is said to have become **saturated** and any excess solid would remain **undissolved** and settle to the bottom.

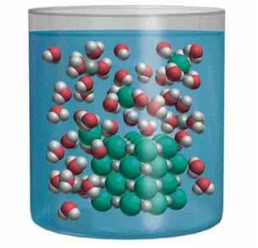


2.3 Saturated solution

A saturated solution is one that contains the **maximum amount of solute in a given amount of solvent** such that the **ions are in equilibrium with the solid**.

$$M_xA_y(s) \underset{\text{crystallise / precipitate}}{\overset{\text{dissolve}}{\rightleftharpoons}} x\ M^{m+}(aq) + y\ A^{a-}(aq)$$

At equilibrium in a saturated solution, the rate of dissolution (from solid to hydrated ions) is equal to the rate of crystallisation or precipitation (from the hydrated ions to the solid).



Source: http://wps.prenhall.com/wps/media/objects/3312/3391718/blb1302.html

3. SOLUBILITY AND SOLUBILITY PRODUCT (K_{sp})

3.1 Solubility of a solute (in water)

The solubility of a substance (salt) is the **maximum amount of solute that dissolves in 1 dm^3 of water to form a saturated solution** at a stated temperature.

- The units for solubility of a salt is either in **g dm^{-3}** or **mol dm^{-3}**.

- **Example**
  - If the solubility of $PbCl_2$ is 44.1 g dm^{-3} at 25^{o}C, it means that a maximum mass of 44.1 g (0.1585 mol) of $PbCl_2$ can dissolve in 1 dm^3 of water forming a saturated solution at 25^{o}C.
  - At saturation, $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$
  - This implies that 0.1585 mol $Pb^{2+}(aq)$ and 0.3170 mol $Cl^-(aq)$ are formed in 1 dm^3 of the saturated solution.

- The value of the solubility of a sparingly soluble salt, at **a stated temperature**, is
  - determined experimentally and
  - used to calculate the solubility product, K_{sp}, of the salt.

- *To determine the solubility of a sparingly soluble salt (at a given temperature).*
  1. Prepare the saturated solution – by dissolving the salt until no more solid can dissolve, and **undissolved solid remains** in the solution.
  2. Filter to remove the undissolved solid.
  3. Perform a titration to determine the concentration of the salt that dissolved in the solution.

3.2 Solubility product, K_{sp}

In a **saturated solution** of **sparingly soluble** salt, M_xA_y, the following equilibrium exists:

$$M_xA_y(s) \rightleftharpoons x\ M^{m+}(aq) + y\ A^{a-}(aq)$$ *This is a heterogeneous equilibrium.*

The equilibrium constant, K_c, would then be:

$$K_c = \frac{[M^{m+}]^x[A^{a-}]^y}{[M_xA_y]}$$

Since M_xA_y is a solid, the $[M_xA_y]$ term is a constant and hence we can rewrite the equilibrium constant as:

$$K_c\ [M_xA_y] = [M^{m+}]^x\ [A^{a-}]^y$$

and define a new equilibrium constant, K_{sp}:

$$\boldsymbol{K_{sp} = [M^{m+}]^x\ [A^{a-}]^y} \qquad \text{units: } \textbf{mol}^{(x+y)}\ \textbf{dm}^{-3(x+y)}$$

Hence, K_{sp} is the product of the concentrations of the ions of the sparingly soluble salt in a saturated solution, raised to the powers of their stoichiometric coefficients in a balanced chemical equation.

The units of K_{sp} are dependent on the formula of the ionic salt.

- like any other equilibrium constants, **K_{sp} is a constant at constant temperature.**
- the concept of solubility product is only valid for **saturated solutions of sparingly soluble salts**; it does not apply to soluble salts such as NaC*l* and $CuSO_4$.

Let's Practise!

For the following sparingly soluble salts, write:

- the equation that represents the equilibrium between the sparingly soluble salt and its dissolved ions in a saturated solution.
- an expression for the solubility product, stating its units.

	equation	K_{sp}
(a) silver chloride	$AgCl\ (s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	$K_{sp} = [Ag^+]\ [Cl^-]$ mol^2 dm^{-6}
(b) silver sulfide	$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$	$K_{sp} = [Ag^+]^2\ [S^{2-}]$ mol^3 dm^{-9}
(c) zinc hydroxide	$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$	$K_{sp} = [Zn^{2+}]\ [OH^-]^2$ mol^3 dm^{-9}
(d) calcium phosphate	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$	$K_{sp} = [Ca^{2+}]^3\ [PO_4^{3-}]^2$ mol^5 dm^{-15}

3.3 Relationship between solubility and solubility product, K_{sp}

The magnitude of K_{sp} gives a measure of the solubility of the salt at a stated temperature.
For salts of the **same formula type**, the **smaller** the K_{sp} value, the **less soluble** is the salt.

Formula of salt	K_{sp} value	Remarks
$CaSO_4$ $PbSO_4$ AgCl AgI	6.1×10^{-5} 1.3×10^{-8} 1.6×10^{-10} 1.5×10^{-16}	Since the salts have the same type of formula (i.e. MA), the K_{sp} trend is indicative of solubility trend $\Rightarrow$ solubility of $CaSO_4$ > $PbSO_4$ > AgCl > AgI
CaF_2 $Cu(OH)_2$	4.0×10^{-11} 1.6×10^{-19}	Since the salts have the same type of formula (i.e. MA_2), the K_{sp} trend is indicative of solubility trend $\Rightarrow$ $Cu(OH)_2$ is less soluble than CaF_2

Quick Check:
Can we always compare solubility of salts just by comparing their K_{sp} values and why?

Yes. If the formula type e.g. $BaSO_4$ and $CaCO_3$ are the same i.e. total number of ions in the formula unit is the same.

How do we compare solubility of salts with different formula type (e.g. $PbSO_4$ and CaF_2)? Can we still compare based on their K_{sp} values?
Refer to Exercise 2.

3.4 Calculations

3.4.1 Calculate K_{sp} given the solubility

Suggested approach for the calculation:
1. *Write the equation that represents the equilibrium between the sparingly soluble salt & its dissolved ions.*
2. *Calculate the concentration of the respective ions (in mol dm^{-3}), from the solubility of salt.*
3. *Write the K_{sp} expression of the salt.*
4. *Substitute and solve for K_{sp}.*

Exercise 1

(a) The solubility of silver chloride, at 25 °C, is 1.26×10^{-5} mol dm^{-3}. Calculate its solubility product at 25 °C.

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

Since solubility of AgCl = 1.26×10^{-5} mol dm^{-3},
$[Ag^+] = 1.26 \times 10^{-5}$ mol dm^{-3}
$[Cl^-] = 1.26 \times 10^{-5}$ mol dm^{-3}

$K_{sp} = [Ag^+][Cl^-]$
$= (1.26 \times 10^{-5})(1.26 \times 10^{-5})$
$= \mathbf{1.59 \times 10^{-10}\ mol^2\ dm^{-6}}$

Note

A solubility of 1.26×10^{-5} mol dm^{-3} indicates that a maximum of 1.26×10^{-5} mol of AgCl is dissolved in 1 dm^3 of solution.

1 mol of AgCl dissolves to give 1 mol of Ag^+ ions and 1 mol of Cl^- ions.

(b) The solubility of lead(II) chloride, at 25 °C, is 44.1 g dm^{-3}. Calculate its solubility product at 25 °C.

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

Solubility in mol dm^{-3} = $\frac{44.1}{207.2+2(35.5)}$

= 0.1585 mol dm^{-3}

$[Pb^{2+}]$ = 0.1585 mol dm^{-3}

$[Cl^-]$ = 2 x 0.1586 = 0.3170 mol dm^{-3}

$K_{sp} = [Pb^{2+}] [Cl^-]^2$

$= (0.1585)(0.3170)^2$

$= \mathbf{1.59 \times 10^{-2}\ mol^3\ dm^{-9}}$

Note

Convert the units of solubility to mol dm^{-3} first.

A solubility of 0.1586 mol dm^{-3} indicates that a maximum of 0.1586 mol of $PbCl_2$ is dissolved in 1 dm^3 of solution.

1 mole of $PbCl_2$ dissolves to give 1 mole of Pb^{2+} ions and 2 moles of Cl^- ions.

Checkpoint 1

	True or False?
1. Temperature has no effect on solubility and the value of K_{sp}	False
2. When writing K_{sp} equations, compounds in solid form should be included.	False
3. Large K_{sp} implies fast dissolution.	False

3.4.2 Calculate solubility given the K_{sp}

Suggested approach for the calculation:
1. *Let the solubility of the salt be s mol dm^{-3}.*
2. *Write the equation that represents the equilibrium between the sparingly soluble salt & its dissolved ions.*
3. *State the concentration of the respective ions in terms of s.*
4. *Write the K_{sp} expression of the salt.*
5. *Substitute and solve for s.*

Exercise 2

(a) Lead(II) sulfate has a solubility product of 1.3 x 10^{-8} mol^2 dm^{-6}. Calculate its solubility in mol dm^{-3}.

Let the solubility of $PbSO_4$ be *s* mol dm^{-3}.

	$PbSO_4(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$SO_4^{2-}(aq)$
Eqm conc / mol dm^{-3}			*s*		*s*

K_{sp} of $PbSO_4 = [Pb^{2+}] [SO_4^{2-}]$

$1.3 \times 10^{-8} = (s)(s)$

$s = \sqrt{1.3 \times 10^{-8}}$

$= \mathbf{1.14 \times 10^{-4}\ mol\ dm^{-3}}$

Note

For a saturated solution of $PbSO_4$:
If solubility of $PbSO_4$ = *s* mol dm^{-3}

Then,
$[Pb^{2+}]$ = *s* mol dm^{-3}
$[SO_4^{2-}]$ = *s* mol dm^{-3}

Since 1 mol of $PbSO_4$ dissolves to give 1 mol of Pb^{2+} ions and 1 mol of SO_4^{2-} ions.

(b) Calcium fluoride, CaF_2 has a solubility product of 4.0×10^{-11} mol^3 dm^{-9}. Calculate its solubility in mol dm^{-3}.

Let the solubility of CaF_2 be s mol dm^{-3}.

	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$2F^-(aq)$
Eqm conc / mol dm^{-3}			s		$2s$

K_{sp} of $CaF_2 = [Ca^{2+}] [F^-]^2$

$4.0 \times 10^{-11} = (s)(2s)^2$

$$s = \sqrt[3]{\frac{4.0 \times 10^{-11}}{4}}$$

$= \underline{\mathbf{2.15 \times 10^{-4}\ mol\ dm^{-3}}}$

Note

For a saturated solution of CaF_2:
If solubility of CaF_2 = s mol dm^{-3}

Then,
$[Ca^{2+}] = s$ mol dm^{-3}
$[F^-] = 2s$ mol dm^{-3}

Since 1 mol of CaF_2 dissolves to give 1 mol of Ca^{2+} ions and 2 mol of F^- ions.

Formula of salt	K_{sp} value	Solubility/ mol dm^{-3}	Which salt is more soluble?
$PbSO_4$	1.3×10^{-8}	1.14×10^{-4}	
CaF_2	4.0×10^{-11}	2.15×10^{-4}	√

Observe that the solubility of CaF_2 is > solubility of $PbSO_4$, although the K_{sp} of CaF_2 is < K_{sp} of $PbSO_4$. Therefore, when comparing the solubility of salts with **different formula type** (especially when their K_{sp} values are close), you need to **calculate the solubility values** from their respective K_{sp} for comparison.

4. EFFECT ON SOLUBILITY OF IONIC SALTS WHEN EQUILIBRIUM IS DISTURBED

In this section, we will consider the changes in solubility of a sparingly soluble salt due to the addition or removal of ions in these cases:

- **Common Ion Effect**
- **Chemical reactions (complex ion formation, acid–base reaction)**

In each of the above scenario, we will discuss qualitatively how the solubility changes by applying the ***Le Chatelier's Principle*** to determine how the position of equilibrium shifts. We will also determine quantitatively how the solubility changes.

Note that in these cases, the value of $\boldsymbol{K_{sp}}$ **does not change** since the temperature remains unchanged.

4.1 Common Ion Effect

4.1.1 Effect on the solubility of ionic salts by the common ion effect

The phenomenon of **reduced solubility** with the **addition of a common cation or anion** to a sparingly soluble salt is called the **common ion effect**.

For example, we can decrease the solubility of silver chloride in a saturated solution of the salt by adding a soluble salt with a common anion (e.g. NaC*l*).

$$\begin{aligned} &NaCl(s) \longrightarrow Na^+(aq) + \mathbf{Cl^-}(aq) \\ &AgCl(s) \rightleftharpoons Ag^+(aq) + \mathbf{Cl^-}(aq) \end{aligned} \qquad (1)$$

The **increase in [C*l*$^-$]** due to the added NaC*l* will **shift the position of equilibrium (1) to the left**. This will result in the precipitation of silver chloride, i.e. the **solubility of silver chloride decreases.**

Checkpoint 2

For a saturated solution of a sparingly soluble salt	True or False?
1. Concentration of ions will remain constant although common ions are added at equilibrium.	False

4.1.2 Calculations involving common ion effect

Suggested approach for the calculation:
1. *Let the solubility of the **sparingly soluble** salt be y mol dm^{-3}.*
2. *Write the equation that represents the equilibrium between the sparingly soluble salt & its dissolved ions.*
3. *State the concentration of the respective ions in terms of y.*
4. *Write the K_{sp} expression of the salt.*
5. *Substitute and solve for y.*

Exercise 3: Calculation of (reduced) solubility in the presence of a common ion.

(a) Given that the K_{sp} of AgC*l* is 1.6 x 10^{-10} mol^2 dm^{-6}, calculate the solubility of silver chloride in 0.10 mol dm^{-3} NaC*l*.

Let the solubility of AgC*l* be y mol dm^{-3}

$$\begin{aligned} &NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq) \\ &AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \end{aligned}$$

Eqm conc / mol dm^{-3}		y		y **+ 0.10**

$K_{sp} = [Ag^+]\,[Cl^-]$

$1.6 \times 10^{-10} = y\,(y + 0.10)$

$$y = \frac{1.6 \times 10^{-10}}{y + 0.10} \approx \frac{1.6 \times 10^{-10}}{0.10} \quad \text{(since y << 0.10)}$$

y = **1.60 x 10^{-9} mol dm^{-3}**

Note: Assumption is valid since 1.60 x 10^{-9} << 0.10

Note
- *The concentration of Cl$^-$ is contributed by both AgCl and NaCl.*
- *Since the contribution of Cl$^-$ from the complete dissociation of NaCl exerts a common ion effect and suppresses the dissociation of AgCl, it can be assumed that y << 0.10 such that (y + 0.10) ≈ 0.10.*

(b) The value of the solubility product, K_{sp}, for $Ca(OH)_2$ is 8.0×10^{-6} mol^3 dm^{-9} at 25 °C. Calculate the solubility of $Ca(OH)_2$ at 25 °C in a solution with $[OH^-] = 0.158$ $moldm^{-3}$.

Let the solubility of $Ca(OH)_2$ be y mol dm^{-3}

	$Ca(OH)_2$ (s)	$\rightleftharpoons$	Ca^{2+}(aq)	+	$2OH^-$(aq)
Eqm conc / mol dm^{-3}			y		(2y + 0.158) ≈ 0.158

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

$$8.0 \times 10^{-6} = y\,(0.158)^2$$

$$y = \frac{8 \times 10^{-6}}{(0.158)^2}$$

$$= \mathbf{3.20 \times 10^{-4}\ mol\ dm^{-3}}$$

Note

- *The concentration of OH^- is contributed by both $Ca(OH)_2$ and OH^- in solution.*
- *Since the contribution of OH^- in the solution exerts a common ion effect and suppresses the dissociation of $Ca(OH)_2$, it can be assumed that $2y << 0.158$ such that $(2y + 0.158) \approx 0.158$.*

Checkpoint

For a saturated solution of a sparingly soluble salt	True or False?
The value of K_{sp} changes with the amount of solid or ions added at a given temperature.	False

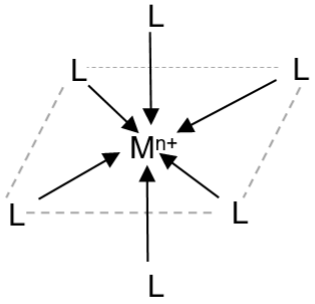
4.2 Effect on solubility of ionic salts by chemical reactions

The solubility of a sparingly soluble salt may be enhanced with the addition of a reagent that consumes either the cation or the anion of the salt.

4.2.1 Effect of Complex ion formation on solubility

A complex ion consists of a central metal ion (cation) that is surrounded by anions or molecules called ligands. The ligand has at least a lone pair of electrons that can form a co–ordinate (dative covalent) bond with the central cation. (You will learn more in 'An Introduction to the Chemistry of Transition Elements')

Examples of ligands:
Cl^-, OH^-, CN^-, SCN^- (thiocyanate ion), H_2O, NH_3, CO (carbon monoxide)



List of common complex ions (*To be covered in 'An Introduction to the Chemistry of Transition Elements'*)

1. Halide ligand
   - $[PbX_4]^{2-}$ (X = Cl, Br, I)
   - $[CuCl_4]^{2-}$
2. Hydroxide ligand
   - $[Al(OH)_4]^-$
   - $[Pb(OH)_4]^{2-}$
   - $[Zn(OH)_4]^{2-}$
   - $[Cr(OH)_6]^{3-}$
3. Ammonia ligand
   - $[Ag(NH_3)_2]^+$
   - $[Zn(NH_3)_4]^{2+}$
   - $[Cu(NH_3)_4]^{2+}$

- The solubility of $PbCl_2$ increases with the addition of concentrated HCl

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq) \quad \textbf{(1)}$$

$$Pb^{2+}\,(aq) + 4Cl^-\,(aq) \rightleftharpoons PbCl_4^{2-}(aq) \quad \textbf{(2)}$$

Reason

- When concentrated HCl is added, Cl^- will react with Pb^{2+} to form a complex ion $[PbCl_4]^{2-}$(aq). $[Pb^{2+}]$ decreases, causing position of equilibrium (1) to shift right to increase the $[Pb^{2+}]$. Hence, solubility of $PbCl_2$ increases.

4.2.2 Effect of acid-base reaction on solubility

Acid–base reactions may result in changes in the concentration of the ions and hence the solubility of the salts.

Example: Barium chromate is soluble in a dilute acid but precipitates in the presence of a base

$$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq) \quad \textbf{(1)}$$
$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l) \quad \textbf{(2)}$$

(i) In the presence of a dilute acid

CrO_4^{2-} ion undergoes acid–base reaction in the presence of acid to form $Cr_2O_7^{2-}$ ion (see equilibrium 2). $[CrO_4^{2-}]$ decreases and the position of equilibrium (1) shifts to the right and it is observed that $BaCrO_4(s)$ dissolves.

(ii) In the presence of a base

When a base is added to the resulting solution, $[H^+]$ decreases and the position of equilibrium (2) shifts to the left. This causes $[CrO_4^{2-}]$ to increase and the position of equilibrium (1) shifts to the left. Hence, $BaCrO_4(s)$ precipitates.

5. IONIC PRODUCT AND PRECIPITATION

5.1 Ionic Product

Ionic product is the product of the concentration of the constituent ions in the solution at that instant raised to the powers of the stoichiometric coefficient.

For any sparingly soluble salt (M_xA_y) dissolved in the solvent,

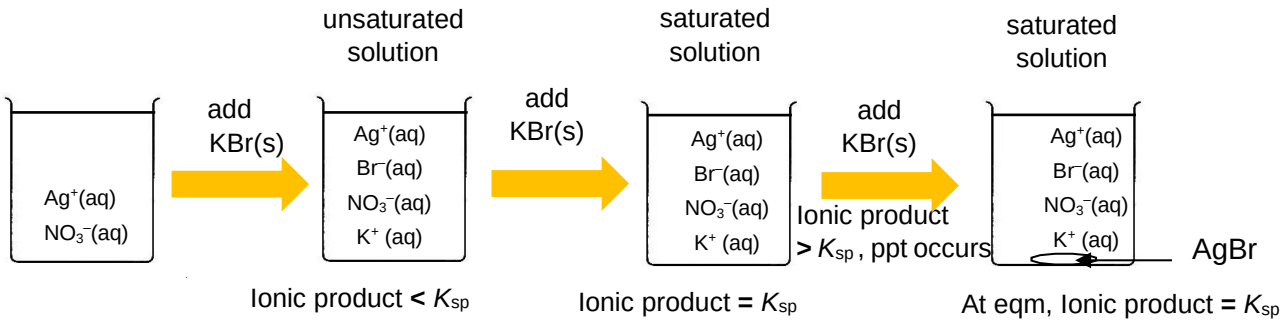
$$M_xA_y(s) \rightleftharpoons x\,M^{m+}(aq) + y\,A^{a-}(aq)$$

Ionic Product (I.P.)	Solubility Product
Ionic Product = $[M^{m+}]^x\,[A^{a-}]^y$	$K_{sp} = [M^{m+}]^x\,[A^{a-}]^y$
$[M^{m+}]$ and $[A^{a-}]$ refer to the concentrations of M^{m+} and A^{a-} in **the solution at that instant**.	$[M^{m+}]$ and $[A^{a-}]$ refer to the concentrations of M^{m+} and A^{a-} in a **saturated** solution **at equilibrium**.

5.2 When and why does precipitation occur?

We can make use of the ***ionic product***, which has the same expression as that for K_{sp}, to predict whether precipitation of a sparingly soluble salt occurs when known quantities of two salts are mixed.

Consider an aqueous solution of $AgNO_3$,



- KBr(s) is gradually added to it, the concentration of the bromide ions in the solution increases. This leads to an increase in the numerical value of the ionic product of AgBr.
- As more KBr(s) is added, the value of the ionic product will eventually be equivalent to that of K_{sp}. This is when a saturated solution of the sparingly soluble salt (AgBr) is formed.
- On adding more KBr(s), the value of the ionic product will be greater than that of K_{sp}. This is when precipitation of AgBr will occur.

Thus, with the K_{sp} and ionic product, we can predict whether precipitation of a sparingly soluble salt occurs when known quantities of two salts are mixed.

In summary, for a solution that contains a sparingly soluble salt, if:

ionic product **<** K_{sp}	no precipitation is observed since the solution is still unsaturated
ionic product **=** K_{sp}	the solution is saturated and the system is in equilibrium
ionic product **>** K_{sp}	precipitation occurs until ionic product (in the solution) = K_{sp} *At the point when ionic product > K_{sp}, the rate of precipitation is greater than the rate of dissolution. So the net outcome is that you have precipitate being formed continuously (⇒ value of the ionic product decreases as concentration of each of the ions in the solution decreases). When ionic product = K_{sp}, the rate of precipitation equals the rate of dissolution, and thus there is no further precipitation.*

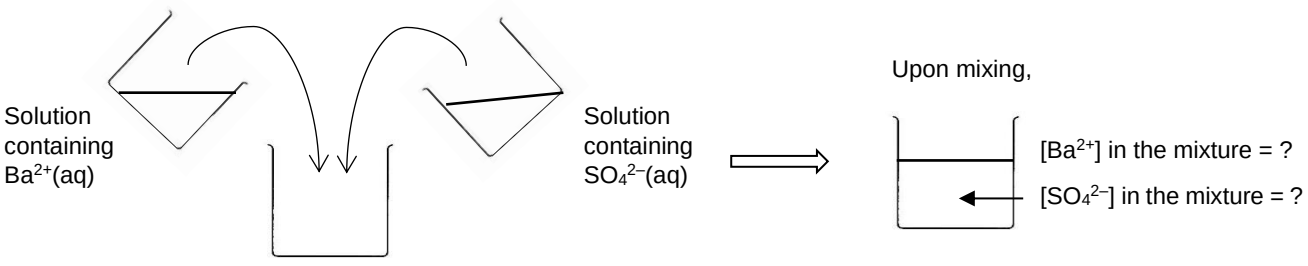
5.3 Calculations

Exercise 3: Predict if precipitation will occur when two solutions of known quantities are mixed

Suggested approach for the calculation:

1. *Identify the ppt and write the equation that represents the equilibrium between the sparingly soluble salt & its dissolved ions.*
2. *Calculate ionic product.*
   - *Calculate the concentration of both ions in the mixture upon mixing.*
   - *Write the ionic product expression of the salt.*
   - *Substitute and calculate the ionic product.*
3. *Compare ionic product against given K_{sp}.*

(a) Predict if precipitation will occur when equal volumes of 0.01 mol dm^{-3} $BaCl_2$ and 0.10 mol dm^{-3} Na_2SO_4 are mixed. (K_{sp} of $BaSO_4$ = 1.1 x 10^{-10} mol^2 dm^{-6})



Will $BaSO_4$(s) be formed upon mixing the solutions?

Approach:
The precipitate in question is $BaSO_4$(s). To determine if precipitation will occur, we need to compare the value of the ionic product against the value of K_{sp} given.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$$[Ba^{2+}] = \frac{0.01}{2} = 0.005\ \text{mol dm}^{-3}$$

$$[SO_4^{2-}] = \frac{0.10}{2} = 0.05\ \text{mol dm}^{-3}$$

ionic product = [Ba^{2+}] [SO_4^{2-}]
= (0.005)(0.05)
= 2.50 x 10^{-4} mol^2 dm^{-6}
> K_{sp} of $BaSO_4$
$\Rightarrow$ precipitation occurs

Note:

- *The concentrations for both solutions are halved due to dilution (equal volumes of solution are mixed together).*
- *Concentration of ion in the resultant mixture*

$$= \frac{\text{no of moles of ion}}{\text{New total volume/ dm}^3}$$

(the new volume = total volume in the resultant mixture)

(b) 60 cm^3 of 0.002 mol dm^{-3} potassium iodide solution is added to 40 cm^3 of 0.001 mol dm^{-3} lead(II) nitrate solution. Given that the solubility product of lead iodide is 7.1 x 10^{-9} mol^3 dm^{-9}, will there be precipitation of lead iodide?

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

$$[Pb^{2+}] = \frac{40(0.001)}{40+60} = 4.00\times10^{-4}\ \text{mol dm}^{-3}$$

$$[I^-] = \frac{60(0.002)}{40+60} = 1.20\times10^{-3}\ \text{mol dm}^{-3}$$

ionic product = [Pb^{2+}] [I^-]^2
= (4.00 x 10^{-4})(1.20 x 10^{-3})^2
= 5.76 x 10^{-10} mol^3 dm^{-9}
< K_{sp} of PbI_2
$\Rightarrow$ precipitate of PbI_2 is not observed

Note:
Concentration of ion in the resultant mixture

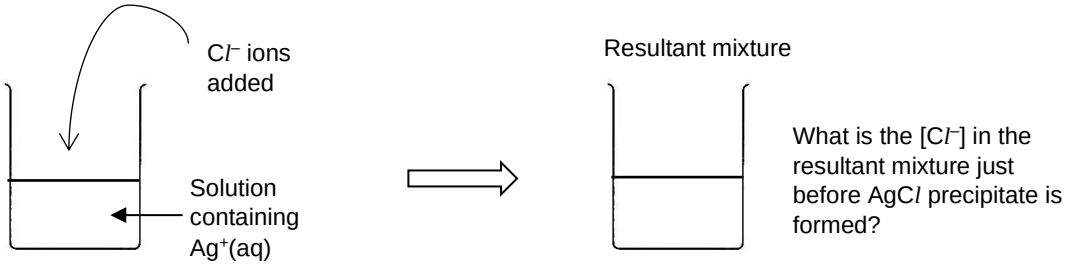
$$= \frac{\text{no of moles of ion}}{\text{New total volume/ dm}^3}$$

(the new volume = total volume in the resultant mixture)

Exercise 4: Calculate minimum concentration of ions needed for precipitation (without volume change)

Suggested approach for the calculation:
1. *Identify the ppt and write the equation that represents the equilibrium between the sparingly soluble salt & its dissolved ions.*
2. *Ionic product = K_{sp}*
   - *Calculate the concentration of ions in the mixture upon mixing.*
   - *Write the ionic product expression of the salt*
3. *Substitute and solve for the unknown concentration*

(a) The solubility product of silver chloride is 1.8×10^{-10} mol^2 dm^{-6}.
Calculate the maximum concentration of chloride ions that could dissolve in a solution containing 5.0×10^{-3} mol dm^{-3} silver nitrate without the formation of any precipitate.



$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$[Ag^+] = [AgNO_3] = 5.0 \times 10^{-3}$ mol dm^{-3}

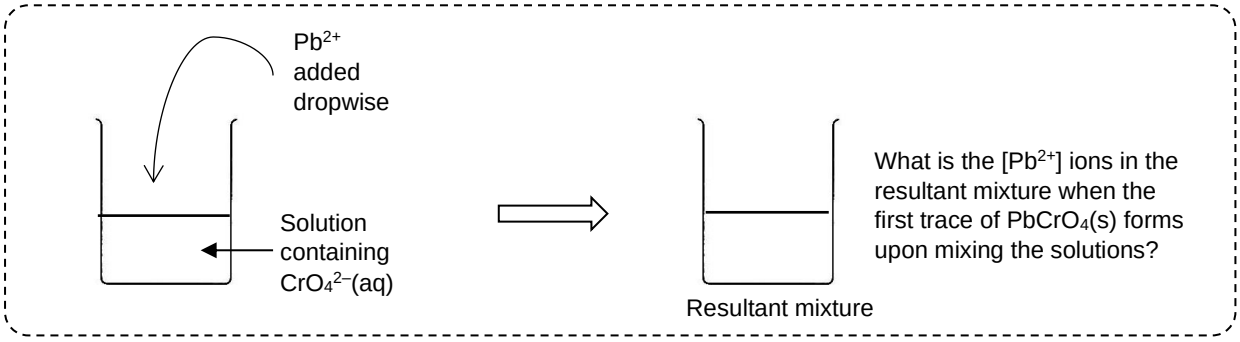
$[Cl^-]_{max}$ occurs when ionic product = K_{sp} of AgCl
$(5 \times 10^{-3})\ [Cl^-]_{max} = 1.8 \times 10^{-10}$
$[Cl^-]_{max}$ = **3.6×10^{-8} mol dm^{-3}**

Note:
*A saturated solution contains the **maximum amt of solute in a given amt of solvent** such that the **ions are in equilibrium with the solid**.*

Thus, maximum $[Cl^-]$ without ppt forming occurs when the Ionic product = K_{sp} of AgCl

Since there is no mention of dilution, we can assume that there is no change in volume when chloride ions are added.

(b) The solubility product of $PbCrO_4$ at 15 ^oC is 1.69 x 10^{-14} mol^2 dm^{-6}. Concentrated $Pb(NO_3)_2$ is added dropwise to 0.0100 mol dm^{-3} K_2CrO_4. What is the concentration, in mol dm^{-3}, of Pb^{2+} ions when the first trace of precipitate of $PbCrO_4$ appears?



$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$

$[CrO_4^{2-}] = 0.0100$ mol dm^{-3}

When first trace of ppt forms,
ionic product = K_{sp} of $PbCrO_4$

$[Pb^{2+}] (0.0100) = 1.69 \times 10^{-14}$

$[Pb^{2+}] =$ **1.69 x 10^{-12} mol dm^{-3}**

Note:
*We can **assume** that volume of solution containing K_2CrO_4 (aq) = total volume in the resultant mixture.*
Thus, $[CrO_4^{2-}]$ before mixing = $[CrO_4^{2-}]$ in the resultant mixture.

Why?
Since concentrated $Pb(NO_3)_2$(aq) is added to the solution of K_2CrO_4, only a small volume of it is needed to cause the solution to become saturated.

Calculate minimum concentration of ions needed for precipitation (with volume change)

(c) The solubility product of $PbCrO_4$ at 15 °C is 1.69 x 10^{-14} mol^2 dm^{-6}. Equal volumes of x mol dm^{-3} of $Pb(NO_3)_2$ and 0.0100 $moldm^{-3}$ of K_2CrO_4 were mixed together.
What is the minimum concentration, x, in mol dm^{-3}, of Pb^{2+} ions in order to see the first trace of $PbCrO_4$ precipitate?

At first trace of $PbCrO_4$ ppt., ionic product = K_{sp} of $PbCrO_4$

$$\left(\frac{x}{2}\right)\left(\frac{0.0100}{2}\right) = 1.69 \times 10^{-14}$$

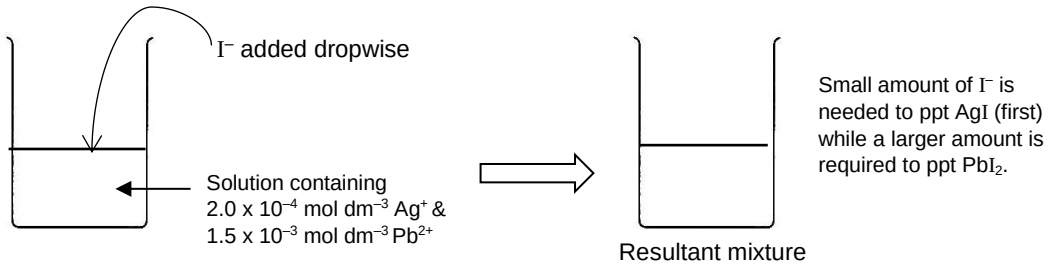
$[Pb^{2+}]$ = **6.76 x 10^{-12} mol dm^{-3}**

Exercise 5: Selective Precipitation – To predict which precipitate will be formed first.

A solution contains 2.0 x 10^{-4} mol dm^{-3} of Ag^+ and 1.5 x 10^{-3} mol dm^{-3} of Pb^{2+} ions.

(a) If a small amount of solid sodium iodide is carefully added, show that AgI precipitates before PbI_2 precipitates out.

(b) Calculate the concentration of Ag^+ in the solution when PbI_2 starts to precipitate out.
(Given K_{sp} of AgI = 8.3 x 10^{-17} mol^2 dm^{-6} and PbI_2 = 7.1 x 10^{-9} mol^3 dm^{-9})



(a) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

K_{sp} of AgI = $[Ag^+][I^-]$ = 8.3 x 10^{-17}
To ppt out AgI,

$$\text{Minimum } [I^-] = \frac{K_{sp}\,(AgI)}{[Ag^+(aq)]} = \frac{(8.3 \times 10^{-17})}{(2.0 \times 10^{-4})} = 4.15 \times 10^{-13} \text{ mol dm}^{-3}$$

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$
K_{sp} of PbI_2 = $[Pb^{2+}][I^-]^2$ = 7.1 x 10^{-9}
To ppt out PbI_2,

$$\text{Minimum } [I^-] = \sqrt{\frac{K_{sp}\,(PbI_2)}{[Pb^{2+}(aq)]}} = \sqrt{\frac{(7.1\times10^{-9})}{(1.5\times10^{-3})}} = \textbf{2.18 x } \mathbf{10^{-3}} \textbf{ mol dm}^{-3}$$

AgI precipitates out first as less $[I^-]$ is needed.

(b) When PbI_2 first precipitates out, minimum $[I^-(aq)]$ = 2.18 x 10^{-3} mol dm^{-3}.

At this $[I^-(aq)]$, $[Ag^+(aq)] = \frac{K_{sp}\,(AgI)}{[I^-(aq)]} = \frac{(8.3 \times 10^{-17})}{(2.18 \times 10^{-3})}$

= **3.81 x 10^{-14} mol dm^{-3}**

6. Further Applications of K_{sp} on solubility of silver halides

Reagent added	F^-	Cl^-	Br^-	I^-
$AgNO_3$ (aq)	no ppt	white ppt of AgC*l*	cream ppt of AgBr	yellow ppt of AgI
Solubility of AgX in: (i) dilute NH_3 (aq) (ii) conc. NH_3 (aq)	–	 soluble soluble	 insoluble soluble	 insoluble insoluble
K_{sp}		10^{-10}	10^{-13}	10^{-17}

Let's consider a **saturated solution** of **sparingly soluble** salt, AgC*l*, the following equilibrium (1) exists:

$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ **(1)**

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ **(2)**

In the presence of dilute NH_3(aq), $[Ag^+]$ **<u>decreases</u>** as a soluble $[Ag(NH_3)_2]^+$ **complex** is formed (see equilibrium 2). $[Ag^+]$ is being decreased to the extent that the ionic product of AgC*l* < K_{sp} of AgC*l.* The **position of equilibrium (1) shifts to the <u>right</u>** to replace some of the Ag^+. Thus, AgC*l* <u>dissolves</u>. That explains why of AgC*l*(s) is soluble in aqueous NH_3.

Why is AgBr insoluble in dilute NH_3 but soluble in concentrated NH_3?

We learn that in order for AgBr to be soluble, I.P (AgBr) < K_{sp} (AgBr). The low K_{sp} value of AgBr suggests that there will only be a very low concentration of Ag^+ in a saturated solution of AgBr.

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ (2)

Thus, only in the presence of **concentrated** NH_3,

- $[Ag^+]$ is being decreased to a great extent such that the ionic product of AgBr < K_{sp} of AgBr.
- Position of equilibrium (1) shifts to the right till AgBr(s) dissolves.

Why is AgI insoluble even in concentrated NH_3?

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ (2)

Although the higher concentration of NH_3 will cause position of equilibrium (1) to shift to the right, the I.P (AgI) is still greater than the very low K_{sp} of AgI. Therefore, AgI remains as insoluble.

Summary

A saturated solution of the salt contains the **maximum amount of solute in a given amount of solvent** such that the **ions are in equilibrium with the solid**.

Its **solubility in water** is the **maximum amount of solute that dissolves in 1 dm^3 of water to form a saturated solution** at a given temperature
(units: mol dm^{-3} or g dm^{-3})

$M_xA_y(s) \rightleftharpoons x\ M^{m+}(aq) + y\ A^{a-}(aq)$

***Solubility product*, $K_{sp} = [M^{m+}]^x\ [A^{a-}]^y$**
(units: **$mol^{(x+y)}\ dm^{-3(x+y)}$**)
K_{sp} is an equilibrium constant that is constant at a given temperature.

The concentration terms in the K_{sp} expression correspond to the instantaneous concentration of each of the ions in the solution at equilibrium.

***Ionic product* = $[M^{m+}]^x\ [A^{a-}]^y$**

The concentration terms in the **ionic product** expression correspond to the instantaneous concentration of each of the ions in the solution at any specific point of time.

How will I know if precipitation occurs?

Ionic Product < K_{sp} ➔ no ppt forms (solution is unsaturated)
Ionic Product > K_{sp} ➔ ppt forms until ionic product = K_{sp}
Ionic product = K_{sp} ➔ the solution is saturated and the system is in equilibrium (first trace of ppt)

When comparing solubility of different sparingly soluble salts:
For same formula type: the lower the K_{sp} value, the less soluble the salt
For different formula type: calculate the solubility values from their respective K_{sp} for comparison.

For a sparingly soluble salt (M_xA_y)

Use LCP to discuss the effects of addition or removal of ions have on the solubility of a sparingly soluble salt:
$M_xA_y(s) \rightleftharpoons x\ M^{m+}(aq) + y\ A^{a-}(aq)$ – (1)

Common ion effect (either M^{m+} or A^{a-})
Due to the common ion, P.O.E (1) shifts **left**, solubility **decreases**

When one of the ions (e.g. A^{a-}) undergo acid–base reaction
If $[A^{a-}]$ increase, P.O.E (1) shifts **left**, solubility **decreases.**
If $[A^{a-}]$ decrease, P.O.E (1) shifts **right**, solubility **increases.**

When one of the ions (e.g. M^{m+}) forms a complex ion
$[M^{m+}]$ decrease as complex ion is formed, P.O.E (1) shifts **right**, solubility **increase.**

If more than one cation or anion is present in a mixture, **selective precipitation** can be done to separate the ions from their sparingly soluble salts of different solubility.

General Strategies for solving calculation questions:
(A) Given K_{sp} find solubility in a solvent (or vice versa)
Step 1: Write equation that represents equilibrium between sparingly soluble salt & its ions
Step 2: Find the concentration of ions in the solution
Step 3: Write K_{sp} expression
Step 4: Substitute conc. in step 3 and solve for solubility (or K_{sp})

(B) Predict if ppt forms (or determine conc. of ions for ppt formation):
Step 1 & step 2: Same as above
Step 3: Write ionic product expression
Step 4: Substitute concentrations of ions and comparing ionic product with K_{sp}
(or compare ionic product with K_{sp} and solve for unknown concentration)