St Andrew's Junior College

H2 Chemistry 2026

Lecture Notes 20

Solubility Equilibria

Assessment Objectives:

Candidates 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 reactions of halide ions with aqueous silver ions followed by aqueous ammonia (see also *an Introduction to the Chemistry of Transition Elements*)

Lecture Outline

1. Solubility and Solubility Product
2. Precipitation and Ionic Product
3. Factors affecting solubility

SLS Resources (req @students.edu.sg login)

Lesson 1: Solubility and Solubility Product	**Lesson 2: Precipitation of Sparingly Soluble Salts**	**Lesson 3: Common Ion Effect**
https://vle.learning.moe.edu.sg/moe-library/module/view/99023736-991d-4605-a652-df3a6f984c25	https://vle.learning.moe.edu.sg/moe-library/module/view/ed3826a7-ce8c-4140-97eb-fb189c6f077a	https://vle.learning.moe.edu.sg/moe-library/module/view/c29629d4-141c-4284-8f43-367950bf8405

1. SOLUBILITY AND SOLUBILITY PRODUCT

Salts can be classified as soluble or insoluble. But even "insoluble" salts dissolve to a very small extent in water.

A **saturated solution** is a solution in which the **maximum** amount of solute/salt has been dissolved. A saturated solution of an insoluble salt usually has a concentration of less than 0.001 mol dm^{-3}. Contrast this to a saturated solution of sodium chloride, which has a concentration of 6.15 mol dm^{-3}

For this chapter on solubility equilibrium, we will use the term "**sparingly soluble**" to describe insoluble salts.

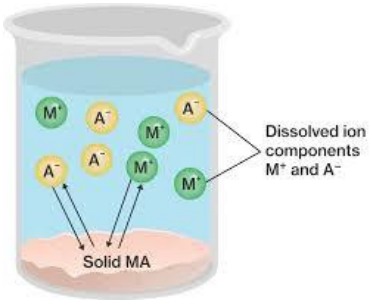
Soluble	**Sparingly soluble**
All nitrates	NIL
Most halides	Halides of Pb^{2+}, Ag^{+} and Cu^{+}
Most sulfates	Sulfates of Ba^{2+}, Pb^{2+} and Ca^{2+}
Oxides and hydroxides of Na^{+}, K^{+}, NH_4^{+} and the larger group 2 cations such as Ca^{2+}, Sr^{2+} and Ba^{2+}	Most oxides and hydroxides
Carbonates of Na^{+}, K^{+} and NH_4^{+}	Most carbonates
Chromates of Na^{+}, K^{+} and NH_4^{+}	Most chromates

Table 1: Soluble and sparingly soluble salts
(no need to memorise!!!!)

1.1 Solubility product

When a sparingly soluble salt e.g. AgC*l* solid is added slowly to pure water, it initially dissolves, but will eventually reach a point when no further solid dissolves and undissolved solid is seen. At this point, a **saturated solution** is formed.

The ions in the saturated solution are in **dynamic equilibrium** with the excess undissolved solid. This means that the ions move from the solid to the saturated solution at the same rate as they move from the solution to the solid.



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

We can write an equilibrium constant for this equilibrium. $K_c = [Ag^{+}(aq)][Cl^{-}(aq)]$
Recall from chemical equilibria that the **concentration of a pure solid and pure liquid is constant** and is omitted from the K_c expression.

The equilibrium constant for the dissolving of a sparingly soluble salt in water is known as its **solubility product, K_{sp}**. Hence,

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)] \quad \text{units: mol}^2\ \text{dm}^{-6}$$

(state symbols not req)

The solubility product of a sparingly soluble salt is the product of the concentrations of its constituent ions in a **saturated solution**, each raised to the power of its stoichiometric coefficient in the balanced equation.

Similar to K_c and K_p, the value of K_{sp} is **constant at a constant temperature**, and its units depends on the stoichiometric coefficients of the relevant ions.

For a sparingly soluble salt with general formula, A_xB_y

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

$$K_{sp} = [A^{y+}(aq)]^x[B^{x-}(aq)]^y \qquad \text{Units} = (\text{mol dm}^{-3})^{x+y}$$

Solute	K_{sp}
AgCl	1.8×10^{-10} mol^2 dm^{-6}
$BaSO_4$	1.3×10^{-10} mol^2 dm^{-6}
$CaCO_3$	4.8×10^{-9} mol^2 dm^{-6}
ZnS	1.6×10^{-23} mol^2 dm^{-6}

Solute	K_{sp}
$Zn(OH)_2$	2.0×10^{-17} mol^3 dm^{-9}
$Fe(OH)_2$	7.9×10^{-16} mol^3 dm^{-9}
$Mg(OH)_2$	1.1×10^{-11} mol^3 dm^{-9}
Fe_2S_3	1.0×10^{-88} mol^5 dm^{-15}

Table 2: Some solubility products of sparingly soluble salts in pure water at 25 °C

(no need to memorise!!!!)

Exercise 1

Write expressions for the K_{sp} and state its units:

(i) Ag_2CO_3

(ii) $Ca_3(PO_4)_2$

1.2 Solubility

The solubility of a sparingly soluble salt is the **maximum amount of solute** that can dissolve in **1 dm^3** of solution.

The solubility of a sparingly soluble salt indicates the concentration of its constituent ions in a saturated solution at a given temperature (assume 298K unless otherwise stated).

Solubility can be expressed in **g dm^{-3}**, or more commonly, in **mol dm^{-3}**.

E.g. The solubility of AgC*l* is 1.34 x 10^{-5} mol dm^{-3}

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

In 1 dm^3 of solution, 1.34 x 10^{-5} mol of AgC*l* dissolves, giving

- [Ag^+] = 1.34 x 10^{-5} mol dm^{-3}
- [Cl^-] = 1.34 x 10^{-5} mol dm^{-3}

Solubility is not the same as solubility product K_{sp}!

Solubility	**K_{sp} solubility product**
• **Maximum amount of salt** that can be **dissolved in 1 dm^3 of solution** • Value can **change** depending on solvent e.g. dissolve in H_2SO_4 vs H_2O • Units in g dm^{-3} or mol dm^{-3}	• An **equilibrium constant** • **Constant** at constant temperature • Units depends on formula of salt

1.3 Converting between solubility product and solubility, or vice versa

You may be asked to calculate the solubility product of a compound from its solubility, or vice versa.

Exercise 2

The **solubility** of $Fe(OH)_2$ is 5.8×10^{-6} mol dm^{-3}. Calculate its **solubility product, stating its units**.

$Fe(OH)_2(s) \rightleftharpoons$

In 1 dm^3 of solution, mol of $Fe(OH)_2$ dissolves, giving

- $[Fe^{2+}]$ =
- $[OH^-]$ =

***K_{sp}* =**

=

Exercise 3

The **solubility product** of silver chromate, Ag_2CrO_4, is 1.1×10^{-12} mol^3 dm^{-9} at 25°C.
Calculate the **solubility** of silver chromate at 25°C.

$Ag_2CrO_4(s) \rightleftharpoons$

Let solubility of Ag_2CrO_4 be *s* mol dm^{-3}

In 1 dm^3 of solution, mol of Ag_2CrO_4 dissolves, giving

- $[Ag^+]$ =
- $[CrO_4^{2-}]$ =

***K_{sp}* =**

☞ Self–Check: Q1 – 2

1.4 Relationship between Solubility and Solubility Product

Does a larger K_{sp} mean a higher solubility?

- We can directly relate K_{sp} to solubility **only if the salts have the same formula type**
  e.g. AgC*l*, $BaCO_3$ have the same formula type, with cation and anion in a 1:1 ratio
  e.g. CaF_2, $Zn(OH)_2$ have the same formula type, with cation and anion in a 1:2 ratio
- If the formula type of the salt is different, the K_{sp} values have different units, and we cannot directly relate K_{sp} to solubility! Instead, calculation of solubility from given K_{sp} is required.

Exercise 4

Calculate the solubilities of $BaCO_3$ and CaF_2. Which is the most and least soluble salt?

Solute	K_{sp}	Solubility
AgC*l*	1.8×10^{-10} mol^2 dm^{-6}	1.34×10^{-5} mol dm^{-3}
$BaCO_3$	5.0×10^{-9} mol^2 dm^{-6}	**mol dm^{-3}**
CaF_2	3.9×10^{-11} mol^3 dm^{-9}	**mol dm^{-3}**

$BaCO_3$	**CaF_2**
Let solubility of $BaCO_3$ be y mol dm^{-3}.	Let solubility of CaF_2 be z mol dm^{-3}.

We can directly relate K_{sp} value to solubility for $BaCO_3$ and AgC*l* as they have the same formula type. E.g. $BaCO_3$ has higher K_{sp} than AgC*l* → $BaCO_3$ is **more soluble** than AgC*l*.

We cannot directly relate K_{sp} value to solubility for CaF_2 and AgC*l* as they have different formula type. E.g. Although CaF_2 has smaller K_{sp} than AgC*l*, CaF_2 is **more soluble** than AgC*l*.

2. PRECIPITATION AND IONIC PRODUCT

2.1 Predicting precipitation of sparingly soluble salts

For a sparingly soluble salt with general formula, A_xB_y

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

Ionic Product = $[A^{y+}(aq)]^x[B^{x-}(aq)]^y$ Units = $(mol\ dm^{-3})^{x+y}$

The expression for ionic product (IP) is identical to that for solubility product (K_{sp}) – **but IP and K_{sp} are not the same.**

Solubility product K_{sp}	**Ionic product IP**
Product of the concentrations of the constituent ions of the salt **in a saturated solution**, each raised to the power of its stoichiometric coefficient in the balanced equation.	Product of the concentrations of the constituent ions of the salt in a solution **at the instant of mixing (before precipitation occurs)**, each raised to the power of its stoichiometric coefficient in the balanced equation.
Applicable to only saturated solutions of sparingly soluble salts.	Applicable to solutions of any concentration.
For the same sparingly soluble salt, its value is constant at a constant temperature	Its value is not constant – it depends on what solutions you mix!

Table 3: Difference between solubility product and ionic product

When a solution containing $A^{y+}(aq)$ and another containing $B^{x-}(aq)$ are mixed, $A_xB_y(s)$ may or may not be precipitated. We use **IP and K_{sp}** to predict whether precipitation will occur when solutions are mixed.

	Is the solution saturated?	**Is there precipitation?**
IP < K_{sp}	No	No. More salt can dissolve.
IP = K_{sp}	Yes	No. Rate of dissolving = Rate of precipitation.
IP > K_{sp}	Yes	Yes. Precipitation occurs to lower [ions].

Exercise 5

1.0 dm^3 of 1.0 x 10^{-3} mol dm^{-3} Ca^{2+} ions is mixed with an **equal volume** of 2.0 x 10^{-3} mol dm^{-3} SO_4^{2-} ions at 25 °C. Predict whether precipitation of $CaSO_4$ will occur.
[K_{sp} of $CaSO_4$ = 2.0 x 10^{-5} mol^2 dm^{-6} at 25 °C.]

Thinking process:
- What happens to the [ions] after mixing 2 solutions?
- What would be the new [ions] after mixing?
- What is IP compared to Ksp?

Learning point:
Dilution occurs during mixing.

When equal volumes of solutions are mixed, final concentration is

$[Ca^{2+}]$ after mixing =
$[SO_4^{2-}]$ after mixing =

$CaSO_4(s)$ ⇌

IP of $CaSO_4$ =

Exercise 6

Solutions of $Fe^{3+}(aq)$ ions have to be kept acidic to prevent the formation of iron(III) hydroxide precipitate. Calculate the maximum pH of a solution that contains 0.010 mol dm^{-3} $Fe^{3+}(aq)$ ions.
[K_{sp} of $Fe(OH)_3$ = 8.0 x 10^{-38} mol^4 dm^{-12} at 25 °C.]

$Fe(OH)_3(s)$ ⇌

At the point just before precipitation, IP = K_{sp}

Max pH = 2.3 → If the pH goes above **2.3**, ppt will occur

2.2 Selective Precipitation

A reagent can be added to a mixture of ions in a solution to separate one ion from the other. This is due to different solubilities and solubility products of their salts.

Exercise 7

A solution contains 0.1 mol dm^{-3} of $Ba^{2+}(aq)$ and 0.1 mol dm^{-3} of $Ca^{2+}(aq)$.
To separate $Ba^{2+}(aq)$ from $Ca^{2+}(aq)$, solid K_2CrO_4 is added.

K_{sp} of $BaCrO_4$ = 1.2 x 10^{-6} mol^2 dm^{-6}
K_{sp} of $CaCrO_4$ = 7.1 x 10^{-4} mol^2 dm^{-6}

- Will $BaCrO_4$ or $CaCrO_4$ precipitate first?

  It has a lower solubility. (Can compare Ksp directly as same formula type.)

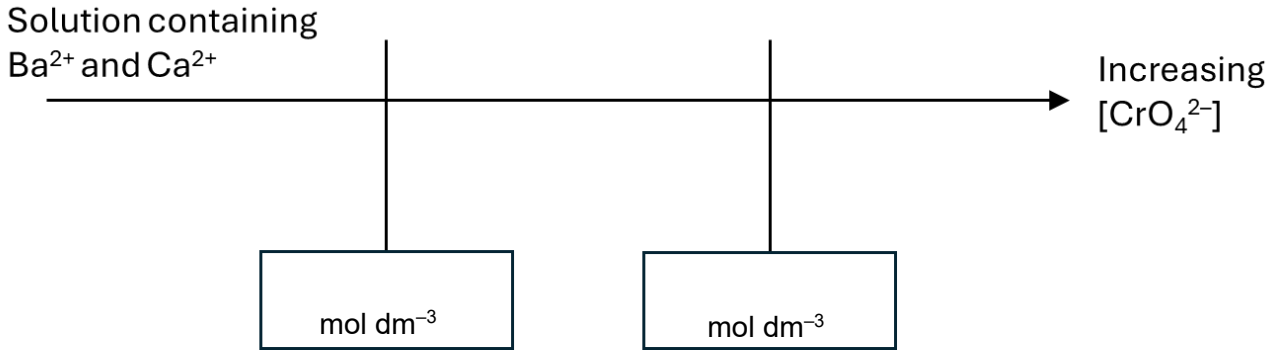
- Calculate the concentrations of CrO_4^{2-} required to begin precipitation of $BaCrO_4$ and $CaCrO_4$

<u>For ppt of $BaCrO_4$</u>
IP = K_{sp}

Any $[CrO_4^{2-}]$ higher than 1.2 x 10^{-5} mol dm^{-3} will result in ppt of $BaCrO_4$.

<u>For ppt of $CaCrO_4$</u>
IP = K_{sp}

Any $[CrO_4^{2-}]$ higher than 7.1 x 10^{-3} mol dm^{-3} will result in ppt of $CaCrO_4$.



- Hence, what concentration of CrO_4^{2-} is required for maximum separation of the ions?
  [Hint: This means majority of 1 ion is in ppt while the other is in solution, and we can filter to separate them]

- At that concentration of CrO_4^{2-}, the mixture is filtered. What is the concentration of Ba^{2+} remaining in the filtrate?

  When CrO_4^{2-} is 7.1 x 10^{-3} mol dm^{-3},

  When filtration takes place, $[Ba^{2+}]$ has decreased from 0.10 mol dm^{-3} to 1.69 x 10^{-4} mol dm^{-3}
  % of Ba^{2+} removed = [0.1 – (1.69 x 10^{-4}) / 0.1] x 100% = 99.8%
  Separation is effective.

☞ **Self–Check: Q3 – 4**

3. FACTORS AFFECTING SOLUBILITY

3.1 Common Ion Effect

The common ion effect refers to the lowering of the solubility of a sparingly soluble salt due to presence of a common ion.

Consider the equilibrium established in a saturated solution of silver chloride:

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

If more Cl^- ions (the common ion) are added to the solution e.g. by adding NaCl,

- $[Cl^-]$ **increases**
- By Le Chatelier's principle, **position of equilibrium** shifts to the **left to lower $[Cl^-]$**
- **More AgCl solid** is formed. **Solubility of AgCl decreases**.

Exercise 8

The K_{sp} of $Ca(OH)_2$ is 6.5 x 10^{-6} $mol^3\,dm^{-9}$ at 298K.
Calculate its solubility in (a) pure water (b) 0.1 mol dm^{-3} $Ca(NO_3)_2$

Recall:
Solubility is the maximum amount of solute that can dissolve in 1 dm^3 of solution

(a) In pure water
Let solubility of $Ca(OH)_2$ be *x* mol dm^{-3}

$Ca(OH)_2(s)$ ⇌

In 1 dm^3 of solution, **x** mol of $Ca(OH)_2$ dissolves, giving

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

(b) In 0.1 mol dm^{-3} $Ca(NO_3)_2$
Learning point: $[Ca^{2+}]$ from sparingly soluble $Ca(OH)_2$ is negligible as compared to $[Ca^{2+}]$ from soluble $Ca(NO_3)_2$.

The solubility of $Ca(OH)_2$ decreases in the presence of common ion Ca^{2+}.

☞ **Self–Check: Q5**

3.2 Formation of Complex Ions

The common ion effect (adding a common ion) lowers the solubility of a sparingly soluble salt. The opposite is also true – the solubility of a sparingly soluble salt can be increased by removal of a ion, e.g. via complex formation.

Silver halide, AgX, is precipitated when halide ions react with aqueous $AgNO_3$.

$$\mathbf{Ag^+(aq) + X^-(aq) \rightarrow AgX(s)} \qquad \mathbf{X = C\mathit{l}, Br, I}$$

The AgX formed can be differentiated by the:

- colour of the precipitate formed;
- reaction of the precipitate with NH_3(aq) (dilute and concentrated)

Precipitate	Colour	Solubility of AgX in dilute NH_3 (aq)	Solubility of AgX in conc. NH_3 (aq)	K_{sp} at 298K
AgC*l*	White	Ppt **soluble**	Ppt **soluble**	1.8×10^{-10}
AgBr	Cream	Ppt **insoluble**	Ppt **soluble**	5.0×10^{-13}
AgI	Yellow	Ppt **insoluble**	Ppt **insoluble**	7.9×10^{-17}

Do not need to memorise colours of ppt or solubility – in data booklet!
Do not need to memorize K_{sp} values, however, need to know that **K_{sp} of AgC*l* > AgBr > AgI**

In a saturated solution of AgX,

$$\mathbf{AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq)}$$ where X is C*l*, Br or I

When NH_3 is added, a silver(I) diamine complex forms.

$$\mathbf{Ag^+(aq) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq)}$$

- $[Ag^+]$ decreases due to the formation of $[Ag(NH_3)_2]^+$
- By LCP, POE shifts to the right to increase $[Ag^+]$
- Solubility of AgX increases

- AgC*l* is the most soluble (K_{sp} value is the largest) and requires only dilute ammonia to dissolve
- AgBr is less soluble than AgC*l* (K_{sp} value is smaller) and will require concentrated ammonia to dissolve
- AgI is the least soluble (K_{sp} value is the smallest) and does not dissolve even in concentrated ammonia

Appendix : Solubility 'issues' in daily life

- **Removal of Heavy Metals from wastewater by Chemical Precipitation:**

Heavy Metals Pollution: https://www.youtube.com/watch?v=ZMDi0U_HAaU

Chemical precipitation is the most common technology used in removing dissolved (ionic) metals from solutions, such as process wastewaters containing toxic metals. The ionic metals are converted to an insoluble form (particle) by the chemical reaction between the soluble metal compounds and the precipitating reagent. The particles formed by this reaction are removed from solution by settling and/or filtration. The unit operations typically required in this technology include neutralization, precipitation, coagulation/flocculation, solids/liquid separation, and dewatering.

The most widely used chemical precipitation process is hydroxide precipitation (also referred to as precipitation by pH), in which metal hydroxides are formed by using calcium hydroxide (lime) or sodium hydroxide (caustic) as the precipitant. Each dissolved metal has a distinct pH value at which the optimum hydroxide precipitation occurs—from 7.5 for chromium to 11.0 for cadmium. Metal hydroxides are amphoteric, which means that they are increasingly soluble at both low and high pH values. Therefore, the optimum pH for precipitation of one metal may cause another metal to solubilize or start to go back into solution. Most process wastewaters contain mixed metals and so precipitating these different metals as hydroxides can be a tricky process.

Source: http://www.appliedmechtech.com/wp-content/uploads/2016/08/Metal-Precip-Explained-University-of-Maryland.pdf

- **Acid Mine Drainage:**

Acid mine drainage (AMD) is the acidic water produced when rock containing sulfide minerals comes into contact with water and oxygen. The exposure often results in reactions that form sulfuric acid and dissolved iron.

Overall Reaction:
$4FeS_2(s) + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3(s) + 8SO_4^{2-} + 16H^+$

Some or all of this iron can precipitate to form the red, orange, or yellow sediments ($Fe(OH)_3$) on the streambed. The acid runoff further dissolves heavy metals such as aluminum, copper, lead and manganese. The rate and degree which acid can increase mine drainage proceeds by the action of certain bacteria. This is a common problem observed in abandoned mining sites.

Besides having a low pH, due to the high concentrations of dissolved solids in such water, it often poses a serious threat to groundwater quality which, in turn, can affect drinking water; it can also destroy aquatic life and the problems can be long term.

Source: https://edu.rsc.org/feature/acid-mine-drainage-a-legacy-of-an-industrial-past/2020087.article

Precipitation of calcium and magnesium ions in hard water causing build-up of white powdery substances on water pipes, kettles etc. Hard and Soft Water https://www.youtube.com/watch?v=2Fr0V9SZ6R8	Increased carbon dioxide in our atmosphere increases [carbonic acid] in oceans and affects marine life What Is Ocean Acidification? https://www.youtube.com/watch?v=daUQg-WHDIM