NOT IN H1 Chemistry Syllabus

2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC
SOLUBILITY EQUILIBRIA

Name: ____ Civics Group: _________

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 reactions of halide ions with aqueous silver ions followed by aqueous ammonia

LECTURE CONTENT

REFERENCES

- Peter Cann and Peter Hughes, Chemistry (2015)
- Martin S. Silberberg, *Chemistry: The molecular nature of Matter and Change*. 3rd Edition, McGraw Hill
- Chang / Goldsby Chemistry 12th edition
- Kotz,J.C., Treichel, P.M. & Townsend, J. (2011). Principles of Chemical Reactivity.

1 Introduction

In Chemical Equilibrium, we learnt the concept of dynamic equilibrium and the Le Chatelier's principle. In this topic, we will apply this knowledge to the dynamic equilibrium that exists between an undissolved solute and its dissolved ions in solution, and use the Le Chatelier's principle to explain the factors that affect the solubility of a salt. In other words, we will explore the **solubility equilibria of sparingly soluble ionic compounds**.

1.1 Soluble and Sparingly Soluble Compounds

Ionic compounds such as $NaCl$ are classified as **soluble salts** because they dissolve readily in water to form solutions. When a soluble ionic compound dissolves in water, it **dissociates completely** into its constituent ions e.g. $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$.

There are other ionic compounds such as $AgCl$ which do not dissolve readily in water. While these compounds are often classified as **insoluble salts**, it does not mean that the salt does not dissolve at all. It simply means that the amount that dissolves is so small that we cannot, with our eyes, observe if any solid has dissolved when we put it in water. Such compounds are said to be '**sparingly soluble**'.

The table shows the solubility of some ionic compounds in water.

soluble compounds	**sparingly soluble compounds**
all nitrates (NO_3^-)	–
most halides (Cl^-, Br^-, I^-)	halides of Ag^+, Pb^{2+}, Cu^+
most sulfates (SO_4^{2-})	sulfates of Pb^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}
oxides (O^{2-}) of Group 1 cations, *e.g.* Na^+, K^+ and some Group 2 cations, e.g. Ca^{2+}, Sr^{2+}, Ba^{2+}	most oxides
hydroxides (OH^-) of Group 1 cations, *e.g.* Na^+, K^+ and some Group 2 cations, e.g. Ca^{2+}, Sr^{2+}, Ba^{2+}	most hydroxides
carbonates (CO_3^{2-}) of Na^+, K^+ and NH_4^+	most carbonates

1.2 Solubility and Saturated Solutions

As a solute dissolves in a solvent, the concentration of the solute particles in the solution increases. But this cannot occur infinitely. There is a maximum amount of solute that can dissolve in a particular solvent at a particular temperature. When this upper limit is reached, the solution is said to be **saturated** at that temperature, and no more solute will dissolve in the saturated solution.

For example, the **maximum** mass of $NaCl$ that can be dissolved in 1 dm^3 of water is 357 g at 25 °C. We characterise this as the **solubility** of $NaCl$.

Solubility of a salt, s, is the amount (or mass) of solute (salt) that can be dissolved in **1 dm^3 of a given solvent (e.g. water)** to form a **saturated solution** at a given temperature.
Units of solubility: mol dm^{-3} (molar solubility) or g dm^{-3}

Note:
Solubility is most often expressed in terms of **number of moles** of solute dissolved in 1 dm^3 of solvent. Hence, when calculating solubility, give your answer in **mol dm^{-3}** unless otherwise stated.

2 Solubility Equilibria and Solubility Product, K_{sp}

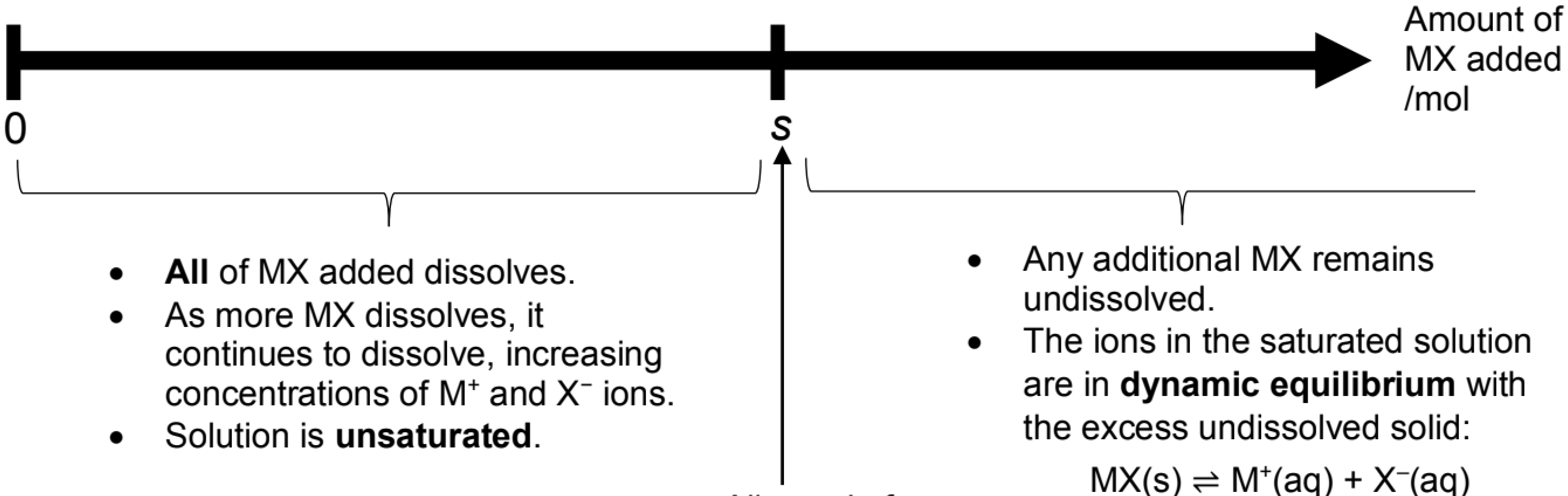
Learning Outcome:

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

2.1 Solubility Equilibria

Consider a sparingly soluble ionic solid, MX, with solubility, s mol dm^{-3}.

When increasing quantities of MX is added to 1 dm^3 of water:



- **All** of MX added dissolves.
- As more MX dissolves, it continues to dissolve, increasing concentrations of M^+ and X^- ions.
- Solution is **unsaturated**.

- All s mol of MX added dissolves.
- Solution is **saturated**.

- Any additional MX remains undissolved.
- The ions in the saturated solution are in **dynamic equilibrium** with the excess undissolved solid:

  $$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

- The **rate of the forward reaction** (dissolution) is **equal** to the **rate of the backward reaction** (precipitation).
- There is **no net change** in concentration of M^+ and X^- ions.

2.2 Solubility Product

The equilibrium established in a **saturated** solution of a **sparingly soluble** salt with the general formula M_aX_b is:

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

By applying the equilibrium law, the equilibrium constant, K_c ,is given by

$$K_c = \frac{\left[M^{b+}(aq)\right]^a\left[X^{a-}(aq)\right]^b}{\left[M_aX_b(s)\right]}$$

The **concentration of a pure solid**, which is proportional to its density, is **constant at a particular temperature**. Since $\left[M_aX_b(s)\right]$ is constant at a given temperature,

$$K_c\left[M_aX_b(s)\right] = \left[M^{b+}(aq)\right]^a\left[X^{a-}(aq)\right]^b = \text{constant}$$

Hence, we may define a new equilibrium constant called **solubility product**, $\boldsymbol{K_{sp}}$.

K_{sp} of $M_aX_b(s)$ = $\left[M^{b+}(aq)\right]^a\left[X^{a-}(aq)\right]^b$ units: $(\text{mol dm}^{-3})^{a+b}$

Solubility product, $\boldsymbol{K_{sp}}$, is the product of the molar concentrations of the constituent ions in a **saturated solution of a sparingly soluble salt**, raised to the powers as indicated by the stoichiometric coefficients in the balanced equation for the equilibrium, **at a given temperature**.

The **solubility product, $\boldsymbol{K_{sp}}$**, for the sparingly soluble salt M_aX_b is the **equilibrium constant** for the equilibrium established between the undissolved salt and its constituent ions in a **saturated** solution. If a solution at a particular temperature is unsaturated, the equilibrium between the excess undissolved solute and the dissolved ions does not exist, which means that K_{sp}, is not defined.

Like other equilibrium constants, the value of K_{sp} **changes only with temperature**.

For the discussion of the solubility product, we are only concerned with salts that are **sparingly soluble**. For sparingly soluble salts, the numerical value of K_{sp} is always very small, rarely exceeding 10^{-4} and can be as low as 10^{-40}.

Example 2A

Write an expression for the solubility product of each of the sparingly soluble salt and state its units.

	salt	equation	solubility product and units
(a)	$AgCl$	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	
(b)	PbI_2		
(c)	Ag_2CO_3		
(d)	$Ca_3(PO_4)_2$		

Checkpoint 1

- A **saturated solution** is one in which no more of the solute will dissolve. It contains the maximum quantity of solute that is normally possible at the given temperature.
- **Solubility of a salt, *s***, refers to the amount (or mass) of solute (salt) that can be dissolved in **1 dm^3 of a given solvent** (e.g. water) to form a **saturated solution** at a given temperature.
- Let M_aX_b be the formula of a sparingly soluble salt,

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

$$\boxed{K_{sp} = [M^{b+}]^a[X^{a-}]^b}$$

Units of K_{sp}: $(\text{mol dm}^{-3})^{a+b}$

where $[M^{b+}]$ and $[X^{a-}]$ are concentrations of ions (in mol dm^{-3}) in a **saturated** solution.

- Like other equilibrium constants (i.e. K_c), the value of K_{sp} **varies with temperature only**.

2.3 Calculations Involving Solubility and Solubility Product

Learning Outcome:
(b) calculate K_{sp} from concentrations and vice versa

2.3.1 Calculating solubility product, K_{sp}, from solubility of a sparingly soluble salt

Example 2B

The solubility of silver chloride is 1.46×10^{-3} g dm^{-3} at 18 °C. Calculate the solubility product of silver chloride at this temperature. (Molar mass of $AgCl$: 143.5 g mol^{-1})

$$\text{solubility of } AgCl = \frac{1.46 \times 10^{-3}\ \text{g dm}^{-3}}{143.5\ \text{g mol}^{-1}} = 1.02 \times 10^{-5}\ \text{mol dm}^{-3}$$

	$AgCl(s)$	$\rightleftharpoons$	$Ag^+(aq)$	+	$Cl^-(aq)$
eqm concentration/mol dm^{-3}			1.02×10^{-5}		1.02×10^{-5}

$K_{sp} = [Ag^+(aq)][Cl^-(aq)]$
$= (1.02 \times 10^{-5})^2$
$=$ **1.04×10^{-10} mol^2 dm^{-6}**

Example 2C

The pH of a saturated solution of $Fe(OH)_2$ is found to be 9.50 at 25 ºC.
Calculate the solubility product of $Fe(OH)_2$ at 25 ºC.

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

	$Fe(OH)_2(s)$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+	$2OH^-(aq)$
eqm concentration /mol dm^{-3}					

Take note of the mole ratio of the ions!

pOH = 14 – pH =

$[OH^-]$ =

$[Fe^{2+}]$ =

K_{sp} of $Fe(OH)_2$ =

Check: K_{sp} of a sparingly soluble salt should be very small.

2.3.2 Calculating solubility from solubility product, K_{sp}, of a sparingly soluble salt

Example 2D

The numerical value of K_{sp} of $BaCO_3$ is 5.1×10^{-9} at 25 °C.
Find the solubility of $BaCO_3$ in mol dm^{-3}.

Let the solubility of $BaCO_3$ be *s* mol dm^{-3}

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$

eqm concentration/mol dm^{-3} s s

$$K_{sp} = [Ba^{2+}][CO_3^{2-}]$$
$$5.1 \times 10^{-9} = s^2$$
$$s = \underline{\mathbf{7.14 \times 10^{-5}\ mol\ dm^{-3}}}$$

Example 2E

Find the solubility of $Mg(OH)_2$ in mol dm^{-3} and in g dm^{-3}, given the numerical value of K_{sp} of $Mg(OH)_2$ is 6.30×10^{-10}. (Molar mass of $Mg(OH)_2$: 58.3 g mol^{-1})

Let the solubility of $Mg(OH)_2$ be *s* mol dm^{-3}

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

eqm concentration/mol dm^{-3}

K_{sp} =

solubility of $Mg(OH)_2$ =

Self Check 2A

1. Calculate the K_{sp} of Ag_2SO_4 given that its solubility is 4.47 g dm^{-3}.[1.18×10^{-5} $mol^3\ dm^{-9}$]

2. Find the solubility of cobalt(II) hydroxide in mol dm^{-3}, and hence, deduce the concentration of OH^- at equilibrium given that the solubility product of cobalt(II) hydroxide is 1.6×10^{-15} $mol^3\ dm^{-9}$. [1.47×10^{-5} mol dm^{-3}]

2.4 Solubility and Solubility Product

The table shows the solubility and solubility product of some salts.

salt	K_{sp}	solubility / mol dm^{-3}
$\mathrm{AgC}l$	1.8×10^{-10} mol^2 dm^{-6}	1.33×10^{-5}
AgBr	5.4×10^{-13} mol^2 dm^{-6}	7.31×10^{-7}
AgI	8.5×10^{-17} mol^2 dm^{-6}	9.23×10^{-9}
$\mathrm{PbI_2}$	7.1×10^{-9} mol^3 dm^{-9}	1.21×10^{-3}
$\mathrm{Ag_2CrO_4}$	1.1×10^{-12} mol^3 dm^{-9}	6.50×10^{-5}

From the table, it is observed that:

- solubility of AgBr > solubility of AgI and K_{sp} of AgBr > K_{sp} of AgI
- solubility of $\mathrm{PbI_2}$ > solubility of $\mathrm{Ag_2CrO_4}$ and K_{sp} of $\mathrm{PbI_2}$ > K_{sp} of $\mathrm{Ag_2CrO_4}$
- solubility of $\mathrm{Ag_2CrO_4}$ > solubility of $\mathrm{AgC}l$ **BUT** K_{sp} of $\mathrm{Ag_2CrO_4}$ < K_{sp} of $\mathrm{AgC}l$

The solubility product (K_{sp}) of two salts can only give a direct comparison of two salts only if the salts give the **same total number of ions** in solution *e.g.* AgBr and AgI, $\mathrm{PbI_2}$ and $\mathrm{Ag_2CrO_4}$.
The **larger the K_{sp} value**, the **higher the solubility** of the salt.

When the total number of ions produced in solution is different (*e.g.* $\mathrm{AgC}l$ and $\mathrm{Ag_2CrO_4}$), the solubility product cannot be used directly to conclude about the solubilities of the salts.

The relationship between solubility product and solubility, *s*, differs depending on the number of ions produced in solution, as summarised in the table below.

no. of ions	formula Type	example	K_{sp}	*s*, solubility
2 ions	XY	$\mathrm{PbSO_4}$; $\mathrm{MgCO_3}$	s^2 mol^2 dm^{-6}	$s = \sqrt{K_{sp}}$
3 ions	$\mathrm{XY_2}$, $\mathrm{X_2Y}$	$\mathrm{PbI_2}$; $\mathrm{Ag_2CrO_4}$	$4s^3$ mol^3 dm^{-9}	$s = \sqrt[3]{\frac{K_{sp}}{4}}$
4 ions	$\mathrm{XY_3}$, $\mathrm{X_3Y}$	$\mathrm{Fe(OH)_3}$; $\mathrm{Ag_3PO_4}$	$27s^4$ mol^4 dm^{-12}	$s = \sqrt[4]{\frac{K_{sp}}{27}}$
5 ions	$\mathrm{X_2Y_3}$, $\mathrm{X_3Y_2}$	$\mathrm{A}l_2\mathrm{S_3}$; $\mathrm{Ca_3(PO_4)_2}$	$108s^5$ mol^5 dm^{-15}	$s = \sqrt[5]{\frac{K_{sp}}{108}}$

Checkpoint 2

- For a sparingly soluble salt M_aX_b, the following equilibrium is established in an aqueous medium:

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

If the salt has solubility *s* mol dm^{-3}, $K_{sp} = (as)^a \times (bs)^b \ (\text{mol dm}^{-3})^{a+b}$

- Solubility products give a direct comparison of the solubility of two salts only if the **total number of ions** produced in solution is the **same** in both cases, *e.g.* $AgCl$ and $BaCO_3$ (or Ag_2CrO_4 and CaF_2). In that case, the **higher the K_{sp} value, the higher the solubility of the ionic compound**.

- If the **total number of ions** produced is **different**, as in the case of $AgCl$ and Ag_2CrO_4, then the solubility products do not give a comparison of solubilities, and a calculation must be performed.

3 Ionic Product

When solutions of salts are mixed, we can predict if **precipitation** occurs by calculating its ionic product and comparing it with the K_{sp} value of a sparingly soluble salt.

The **ionic product (IP)** of a **sparingly soluble** salt is the product of the molar concentrations of the constituent ions in the solution, raised to the appropriate powers.
i.e. ionic product for $M_aX_b = [M^{b+}]^a[X^{a-}]^b$

The expressions for solubility product and ionic product may look the same but the concentration terms in the two expressions are different.

e.g. For a sparingly soluble salt, $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

solubility product, K_{sp}	**ionic product**
K_{sp} of $AgCl = [Ag^+]_{eqm}[Cl^-]_{eqm}$	ionic product of $AgCl = [Ag^+][Cl^-]$
$[Ag^+]$ and $[Cl^-]$ are respectively the **equilibrium concentrations** of Ag^+ and Cl^- in a **saturated solution**.	$[Ag^+]$ and $[Cl^-]$ are respectively the **instantaneous concentrations** of Ag^+ and Cl^- in **the solution at any point in time** (i.e. may or may not be saturated).

3.1 Predicting Precipitation Using Ionic Product

Consider a sparingly soluble salt, M_aX_b. When a known volume of a solution containing M^{b+} ions of known concentration is mixed with a known volume of a solution containing X^{a-} ions of known concentration, we can predict whether precipitation will occur prior to mixing.

This is achieved by **calculating the ionic product, $[M^{b+}]^a[X^{a-}]^b$**, and **comparing it with the K_{sp} value**. In this case, $[M^{b+}]$ and $[X^{a-}]$ in the ionic product expression refer to the concentrations of M^{b+} and X^{a-} respectively in the resultant mixture **after mixing, before reaction** (if any) **occurs**.

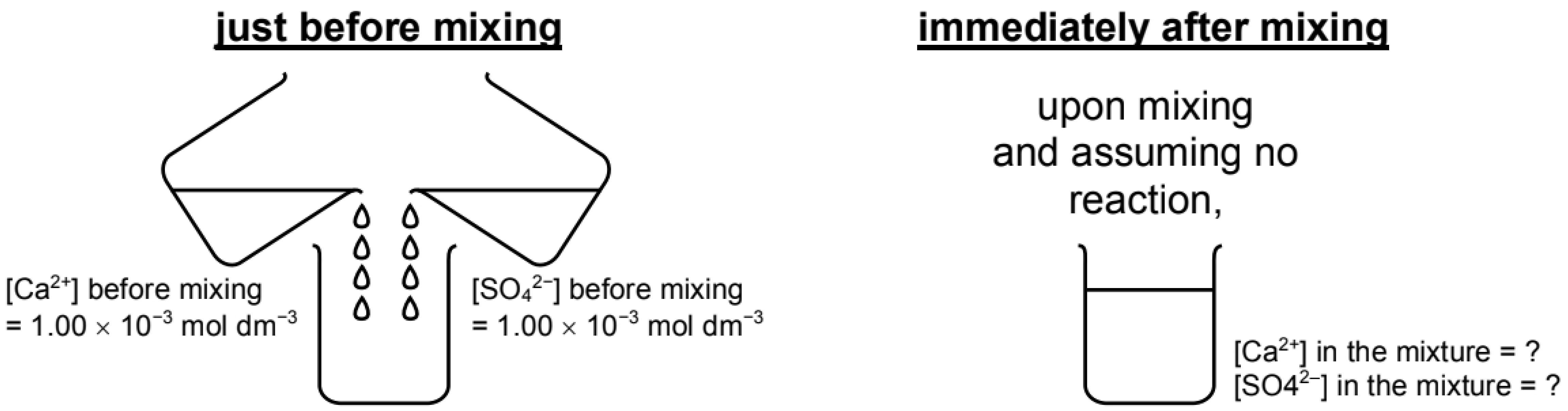
The possible outcomes are shown in the table below.

outcome	**implication**	**precipitation?**
ionic product < K_{sp}	the solution is **unsaturated**	no
ionic product = K_{sp}	the solution is **saturated**	no
ionic product > K_{sp}	the solution is **saturated** and MX(s) can be observed	yes precipitation occurs until ionic product = K_{sp}.

In summary, when an aqueous solution containing M^{b+} ions is mixed with an aqueous solution containing X^{a-} ions, **precipitation** of the sparingly soluble ionic compound, M_aX_b, only occurs if **ionic product > K_{sp}**.

Example 3A

1.00×10^{-3} mol dm^{-3} solution of Ca^{2+} is mixed with an equal volume of 1.00×10^{-3} mol dm^{-3} solution of SO_4^{2-} at 25.0 ºC. Will precipitation occur? (K_{sp} of $CaSO_4$ = 2.40×10^{-5} mol^2 dm^{-6})



In the resultant solution immediately after mixing and assuming no reaction,

$$\left[Ca^{2+}\right] = \left[SO_4^{2-}\right] = \frac{1.00 \times 10^{-3}}{2} = 5.00 \times 10^{-4} \text{ mol dm}^{-3}$$

The initial concentration of each ion is halved since final volume has doubled.

$$IP = \left[Ca^{2+}\right]\left[SO_4^{2-}\right] = \left(5.00 \times 10^{-4}\right)^2$$
$$= 2.50 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6} < 2.40 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

Since **IP < K_{sp}** of $CaSO_4$, precipitation of $CaSO_4$ **will not** occur.

Example 3B

Will a precipitate form when 0.100 dm^3 of 3.00×10^{-3} mol dm^{-3} $Pb(NO_3)_2$(aq) is added to 0.400 dm^3 of 5.00×10^{-3} mol dm^{-3} Na_2SO_4(aq)? (K_{sp} of $PbSO_4$ = 1.60×10^{-8} mol^2 dm^{-6})

After mixing,

$\left[Pb^{2+}\right] =$

Concentrations of the ions will change due to mixing, which changes the total volume the ions are in.

$\left[SO_4^{2-}\right] =$

Use the concentrations at the instance of mixing to calculate IP.

$IP = \left[Pb^{2+}\right]\left[SO_4^{2-}\right] =$

Since IP _____ K_{sp}, precipitation ____.

Example 3C

$Ca(NO_3)_2(s)$ is added to a 2.00×10^{-4} mol dm^{-3} solution of $MgSO_4$. What is the minimum $[Ca^{2+}]$ before a precipitate of $CaSO_4$ can be formed? (K_{sp} of $CaSO_4$ = 2.40×10^{-5} mol^2 dm^{-6})

To precipitate $CaSO_4$, IP > K_{sp}

$[Ca^{2+}][SO_4^{2-}] > 2.40 \times 10^{-5}$ mol^2 dm^{-6}

$MgSO_4(aq) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$

$[SO_4^{2-}]$ =

$[Ca^{2+}]$ >

$[Ca^{2+}]_{min}$ =

Self Check 3A

1. 0.100 dm^3 of 2.0×10^{-3} mol dm^{-3} $Ba(NO_3)_2$ solution is added to 0.300 dm^3 of 4.0×10^{-3} mol dm^{-3} Na_2SO_4 solution. Precipitation of $BaSO_4$ occurs as a result. Calculate the ionic product of $BaSO_4$ in the solution before precipitation starts.
[1.5×10^{-6} mol^2 dm^{-6}]

2. Will a precipitate form when 25 cm^3 of 5.0×10^{-4} mol dm^{-3} of $SrCl_2(aq)$ is added to 25 cm^3 of 2.0×10^{-3} mol dm^{-3} Na_2SO_4 ? (K_{sp} of $SrSO_4$ = 8.1×10^{-7} mol^2 dm^{-6})
[No precipitation]

3.2 Selective Precipitation of Ions

Selective precipitation is the separation of ions in an aqueous solution by using a reagent that forms a precipitate with **one or a few of the other ions but not all**. Ions (cations or anions) can be separated from each other based on the different solubility of their salts.

Example 3D

In a solution, $[Ag^+] = 1.00 \times 10^{-2}$ mol dm^{-3} and $[Pb^{2+}] = 2.00 \times 10^{-2}$ mol dm^{-3}. $NaCl(s)$ is added to this solution.
Given: K_{sp} of $AgCl = 1.80 \times 10^{-10}$ mol^2 dm^{-6}, K_{sp} of $PbCl_2 = 1.60 \times 10^{-5}$ mol^3 dm^{-9}

(a) What is the minimum concentration of Cl^- necessary for each salt to be precipitated?

To precipitate a salt from the solution, IP > K_{sp}.
For $AgCl$,

$$[Ag^+][Cl^-] > 1.80 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

For $PbCl_2$,

$$[Pb^{2+}][Cl^-]^2 > 1.60 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

(b) What salt precipitates first?

________ is precipitated first since the minimum concentration of chloride needed to precipitate it is ______________.

(c) What percentage of the first cation is left in the solution when the second cation starts to precipitate? Is the separation effective?

To separate the two ions, we want to add $NaCl(s)$ such that $[Cl^-]$ is **high enough to precipitate $AgCl$** (i.e. IP > K_{sp} of $AgCl$), up to the point when **$PbCl_2$ is just about to precipitate out** (i.e. IP = K_{sp} of $PbCl$).

$[Cl^-]$ when $PbCl_2$ is just about to precipitate out =

% of Ag^+ left in solution =

Almost all Ag^+ is precipitated out when Pb^{2+} is just about to precipitate out.

Hence, separation is very ___________.

Checkpoint 3

- For a sparingly soluble salt M_aX_b, the following equilibrium is established in an aqueous medium:

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

☑ For K_{sp}, $\left[M^{b+}(aq)\right]$ and $\left[X^{a-}(aq)\right]$ refers to the **equilibrium** concentrations of M^{b+} and X^{a-} in the presence of undissolved M_aX_b, *i.e.* a **saturated** solution.

☑ For ionic product, $\left[M^{b+}(aq)\right]$ and $\left[X^{a-}(aq)\right]$ refers to the **instantaneous** concentrations of M^{b+} and X^{a-}.

☑ In other words, the ionic product is a **reaction quotient** (refer to Chemical Equilibrium lecture notes) while K_{sp} is an **equilibrium constant**.

☑ At equilibrium, ionic product = K_{sp}.

- In general, the **precipitation** of a sparingly soluble ionic compound, M_aX_b, by mixing a solution containing M^{b+}(aq) with a solution containing X^{a-}(aq), will only occur if **ionic product > K_{sp}**.

scenarios	**remarks**	**will ppt be formed?**
ionic product < K_{sp}	below saturation point. the solution is unsaturated.	no
ionic product = K_{sp}	at saturation point. the solution is saturated.	no
ionic product > K_{sp}	beyond saturation point. saturated solution is formed with undissolved solid.	yes

4 Factors affecting Solubility

Learning Outcome:

(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

4.1 Common Ion Effect

The **common ion effect** (in solubility equilibrium) refers to the **reduced solubility of a salt** in a solution that already contains an ion that is common to that salt.

Consider an equilibrium mixture of solid calcium fluoride and its aqueous ions in solution:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

What happens when some $CaCl_2(s)$ is added to the saturated solution of CaF_2?

- The $CaCl_2(s)$ added dissolves in the solution and **dissociates completely**.
- $[Ca^{2+}]$ in the solution **increases**.
- By Le Chatelier's Principle, the position of equilibrium of the above reaction will **shift to the left** to decrease $[Ca^{2+}]$.
- As the ionic product exceeds the solubility product, K_{sp}, of CaF_2, this leads to the **precipitation of some CaF_2**, until the ionic product equals K_{sp} again.
- Hence **solubility of CaF_2 decreases** in the presence of dissolved $CaCl_2$.

Note:

1. When a common ion such as Ca^{2+} is added and the $[Ca^{2+}]$ in the solution increases, the **ionic product** of CaF_2 **increases** and **exceeds** the solubility product, K_{sp} of CaF_2 (i.e. IP > K_{sp}). Thus the precipitation of CaF_2 takes place.
2. Due to the common ion effect, the **solubility** of a sparingly soluble salt in an aqueous solution containing a common ion is **less** than its solubility in water. However, the **solubility product** of the salt **does not change** as **K_{sp} only changes when temperature changes.**

Example 4A

Given the numerical value of K_{sp} of AgC*l* is 2.00 × 10^{-10} at 25 °C, calculate the solubility of AgC*l* in

(a) pure water

Let *s* be the solubility of AgC*l* in mol dm^{-3}.

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

Eqm concentration/mol dm^{-3} $\qquad s \qquad s$

$$K_{sp} = [Ag^+][Cl^-] = \mathbf{s}^2 = 2.00 \times 10^{-10}\ mol^2\ dm^{-6}$$
$$s = \underline{\mathbf{1.40 \times 10^{-5}\ mol\ dm^{-3}}}$$

(b) 0.100 mol dm^{-3} NaC*l*.

Let *s′* be the solubility of AgC*l* in 0.100 mol dm^{-3} NaC*l*

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

eqm concentration/mol dm^{-3} $\qquad s' \qquad s' + 0.100$

Cl^- (aq) is the common ion.

Total concentration of Cl^- = $s' + 0.100$

$K_{sp} = [Ag^+][Cl^-] = (s')(s' + 0.100)$

Assume $s' \ll 0.100$, thus $(s' + 0.100) \approx 0.100$

$$(s')(0.100) = 2.00 \times 10^{-10}\ mol^2\ dm^{-6}$$
$$s' = \underline{\mathbf{2.00 \times 10^{-9}\ mol\ dm^{-3}}}$$

Can use approximation since, from **(a)**, the solubility of AgC*l* = 1.40 × $10^{-5} \ll 0.1$.

<u>Comparing answers from (a) and (b)</u>

Solubility of AgC*l* decreases in the presence of Cl^-, the common ion.
(2.00 × 10^{-9} mol dm^{-3} in (b) **<** 1.40 × 10^{-5} mol dm^{-3} in **(a)**).

This is known as the **common ion effect**. In other words, the solubility of a sparingly soluble salt **decreases** in the presence of a second solute that contains a common ion.

Self Check 4A

A saturated solution of $Mg(OH)_2$ has a pH of 10.52. Given that the numerical value of K_{sp} of $Mg(OH)_2$ is 1.80 × 10^{-11},

(a) Calculate the solubility of $Mg(OH)_2$ in this solution. [1.64 × 10^{-4} mol dm^{-3}]

(b) Calculate the solubility of $Mg(OH)_2$ if the saturated solution in **(a)** is mixed with a solution maintained (*i.e.* buffered) at pH 9.00. [0.180 mol dm^{-3}]

4.2 Formation of Complex Ion

In some instances, the solubility of a sparingly soluble salt in aqueous solution is increased if a reagent added reacts with one of its constituent ions to form a **complex ion**.

A complex ion has a metal ion at its centre with a number of other molecules or anions (called **ligands**) surrounding it. The metal ions accept electron pairs by co-ordinate (dative covalent) bond from neutral molecules or anions to form complex ions

Examples of some common complex ions:

$[Zn(OH)_4]^{2-}$	$\underline{\mathbf{[Ag(NH_3)_2]^{+}}}$	$[PbC\ell_4]^{2-}$
$\underline{\mathbf{[A\ell(OH)_4]^{-}}}$	$[Zn(NH_3)_4]^{2+}$	$\underline{\mathbf{[CuC\ell_4]^{2-}}}$
$[Pb(OH)_4]^{2-}$	$\underline{\mathbf{[Cu(NH_3)_4(H_2O)_2]^{2+}}}$	$[CoC\ell_4]^{2-}$

Note: Some of the complex ions that you need to know the formula of are the ones that are in **bold** and <u>underlined</u>.

<u>Case 1:</u>

When NaOH(aq) is added to a solution containing $A\ell^{3+}$, a white precipitate of $A\ell(OH)_3$ is formed. This precipitate dissolves in excess NaOH to form the complex ion $[A\ell(OH)_4]^-$. Such complex ions are soluble in water.

Explanation:
Initially, when NaOH(aq) is added to a solution containing $A\ell^{3+}$, since K_{sp} of $A\ell(OH)_3$ is very low, IP easily exceeds K_{sp}.

Precipitation of $A\ell(OH)_3$ occurs until IP = K_{sp} and equilibrium exists between the $A\ell(OH)_3$ precipitate and its ions.

$$A\ell(OH)_3(s) \rightleftharpoons A\ell^{3+}(aq) + 3OH^-(aq) \text{------------------------------------} (1)$$

In excess NaOH, the complex ions $[A\ell(OH)_4]^-$ are formed.

$$A\ell^{3+}(aq) + 4OH^-(aq) \rightleftharpoons [A\ell(OH)_4]^-(aq) \text{ ----------------------------------} (2)$$

- Formation of the complex ions causes $[A\ell^{3+}]$ to **decrease**.
- This shifts the position of equilibrium in (1) to the **right** to produce more $A\ell^{3+}$.
- This also results in decrease in the ionic product of $A\ell(OH)_3$. When **the ionic product decreases below the K_{sp}**, the white precipitate of $A\ell(OH)_3$ **dissolves.**
- Complex ion formation **increases** the solubility of a sparingly soluble salt.

Case 2:

When $AgNO_3$(aq) is added to a solution containing halide ions, (X^-), silver halide (other than silver fluoride), is precipitated. When this reaction is followed with the addition of NH_3(aq), AgC*l* dissolves in both dilute and concentrated NH_3, AgBr dissolves only in dilute aqueous NH_3, while AgI does not dissolve in both dilute and concentrated NH_3.

The table below summarises the reactions of the halide ions with aqueous silver nitrate and the subsequent solubility of the silver halides in dilute and concentrated ammonia.

halide ion		F^- (aq)	Cl^- (aq)	Br^- (aq)	I^- (aq)
K_{sp} of AgX / $mol^2\ dm^{-6}$		–	1.80×10^{-10}	5.40×10^{-13}	8.50×10^{-17}
solubility of AgX(s) in water		–	AgC*l* most soluble	→	AgI is least soluble
(A) Addition of $AgNO_3$(aq) to X^-(aq)					
Observations		no ppt	white ppt	cream ppt	yellow ppt
(B) Addition of NH_3(aq) to resulting mixture from (A)					
Observations	**(i) add dilute NH_3**	–	<u>soluble</u>	insoluble	insoluble
	(ii) add conc. NH_3	–	<u>soluble</u>	<u>soluble</u>	insoluble

Explanation:

(A) <u>Addition of $AgNO_3$(aq) to X^-(aq)</u>

When $AgNO_3$(aq) is added to a solution containing halide ion (X^-), since the numerical values of the K_{sp} of AgX are very low, IP easily exceeds K_{sp}, hence precipitation occurs and a dynamic equilibrium exists between the AgX precipitate and its ions.

$$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq) \text{ -- (1)}$$

(B) <u>Addition of NH_3(aq) to resulting solution from (A)</u>

The subsequent addition of ammonia results in the formation of the stable diamminesilver(I) complex, $[Ag(NH_3)_2]^+$.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \text{---------------------------------- (2)}$$

Addition of NH_3 shifts the position of equilibrium (2) to the **right**, causing a **decrease** in **$[Ag^+(aq)]$**. The decrease in $[Ag^+(aq)]$ causes the position of equilibrium (1) to shift to the **right** and **ionic product of AgX** to **decrease**, hence **increasing** the **solubility** of AgX.

<u>Comparing between addition of dilute and concentrated NH_3</u>

For AgC*l*, the addition of dilute NH_3 is sufficient to lower $[Ag^+(aq)]$ such that the ionic product becomes **smaller** than K_{sp} of AgC*l*. Hence, the AgC*l* precipitate **dissolves completely** in dilute NH_3.

For AgBr, the K_{sp} is lower than that of AgC*l*. The addition of **dilute** NH_3 is **not** sufficient to lower $[Ag^+(aq)]$ to the point where the ionic product becomes smaller than its K_{sp}. Hence, the AgBr precipitate **does not dissolve** in dilute NH_3. However, when **concentrated** NH_3 is added, it will **sufficiently** lower $[Ag^+(aq)]$ such that the ionic product becomes **smaller** than its K_{sp} and the AgBr precipitate **dissolves**.

For AgI, the value of K_{sp} is extremely low. Thus, regardless of the concentration of NH_3 added, the ionic product of AgI remains **greater** than its K_{sp}. Hence, the AgI precipitate remains whether dilute or concentrated NH_3 is added.

Example 4B

The addition of **concentrated** hydrochloric acid to a saturated solution of lead(II) chloride containing some undissolved solid lead(II) chloride causes the solid to dissolve, whereas the addition of **dilute** hydrochloric acid to the same mixture does not have the same effect. Explain.

In a saturated solution of $PbCl_2$, the following equilibrium is established:

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

- When **dilute** hydrochloric acid is added, the **addition of Cl^-(aq)**, a common ion, shifts the position of equilibrium **(1)** to the **left**, causing lead(II) chloride to be **less soluble**.
- However, when **concentrated** hydrochloric acid is added, the high concentration of Cl^- present leads to the formation of the **complex anion**, $[PbCl_4]^{2-}$:

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

- This **decreases the concentration of Pb^{2+}(aq) ions**, shifting the position of equilibrium (1) to the **right** to counteract the decrease in $[Pb^{2+}(aq)]$.
- This also **decreases the ionic product** of $PbCl_2$. When the ionic product of $PbCl_2$ decreases to **below** its K_{sp}, the $PbCl_2$ precipitate will dissolve.

Example 4C

When aqueous ammonia is added gradually to a solution of Cu^{2+} ions, a blue precipitate is first formed. When excess aqueous ammonia is added, the blue precipitate dissolves to form a deep blue solution. Explain.

- NH_3 is a weak base which **produces OH^-(aq)** in water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- When aqueous ammonia is **first** added, Cu^{2+}(aq) forms **$Cu(OH)_2(s)$**:

$$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons \underset{\text{(pale blue precipitate)}}{Cu(OH)_2(s)} \text{----------------------------------} \textbf{(1)}$$

- When **excess** aqueous ammonia is added, the **complex ion $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq)** is formed:

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{(dark blue solution)}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 4H_2O(l) \text{ ---------------} \textbf{(2)}$$

- This **decreases the concentration of Cu^{2+}(aq) ions**, shifting the position of equilibrium (1) to the **left** to counteract the decrease in $[Cu^{2+}(aq)]$.
- This also **decreases the ionic product** of $Cu(OH)_2$. When the ionic product of $Cu(OH)_2$ decreases to **below** its K_{sp}, blue $Cu(OH)_2$ precipitate will dissolve.

4.3 Effects of pH

Changes to the pH of a solution may affect the solubility of a sparingly soluble salt containing either Brønsted acids or bases.

For example, a sparingly soluble salt, magnesium hydroxide, $Mg(OH)_2$, dissolves in water according to the following equation: $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$----------------- **(1)**

When an acid like HC*l*(aq) is added:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

the acid will **neutralise** the OH^-(aq) to form water, thus **lowering** [OH^-(aq)]. According to Le Chatelier's Principle, the position of equilibrium (1) will shift to the **right** to offset the decreased [OH^-]. Thus, **ionic product** of $Mg(OH)_2$ **decreases** causing its **solubility** to **increase** when the pH of the solution decreases.

Therefore, the solubility of a sparingly soluble salt containing **basic** anions **increases** as [H^+] **increases** (*i.e.* pH **decreases**).

Example 4D

Explain why the solubility of the sparingly soluble CH_3CO_2Ag salt increases when a strong acid is added.

$$CH_3CO_2Ag(s) \rightleftharpoons Ag^+(aq) + CH_3CO_2^-(aq) \text{ -------------------------------------(1)}$$

When a strong acid is added, the H^+ ions will combine with **$\underline{CH_3CO_2^-}$**, a **relatively strong conjugate base** to form the weak acid, **$\underline{CH_3CO_2H}$** as shown in equilibrium (2).

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3CO_2H(aq) \text{ -------------------------------------(2)}$$

The reaction of H^+(aq) with $CH_3CO_2^-$(aq) ions to form CH_3CO_2H causes the **$\underline{[CH_3CO_2^-(aq)]}$** to **<u>decrease</u>**. The position of equilibrium (1) will shift to the **<u>right</u>** to offset the decreased [$CH_3CO_2^-$(aq)]. **Ionic product also decreases** as **<u>more</u>** CH_3CO_2Ag dissolves. Thus, the solubility of CH_3CO_2Ag increases when a strong acid is added.

Checkpoint 5

For a sparingly soluble salt M_aX_b, the following equilibrium is established in an aqueous medium:

$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq) \text{ ---------------------------------- (1)}$$

- If a common ion, *i.e.* M^{b+} or X^{a-} is added, position of equilibrium **(1)** shifts <u>left</u>. This means that more solid salt is produced, *i.e.* the salt becomes **less soluble**.
  The **common ion effect** refers to the **<u>reduced solubility</u>** of a salt in a solution that already contains **<u>an ion common to that salt</u>**.
- The **solubility of a sparingly soluble salt is increased** upon the addition of a reagent that consumes either the cation (M^{b+}) or the anion (X^{a-}) of the salt to form **a complex ion**. When the concentration of the cation or anion is decreased, according to Le Chatelier's Principle, the position of equilibrium (1) would shift to the **right** and cause **ionic product to decrease** and **<u>more salt to dissolve</u>**.
- Changes to the pH of a solution may affect the solubility of a sparingly soluble salt containing either Brønsted acids or bases. *E.g.*: the solubility of a sparingly soluble salt containing **basic** anions such as OH^-, CO_3^{2-}, $CH_3CO_2^-$ **increases** as $[H^+]$ **increases** (*i.e.* pH **decreases**).

Some interesting videos to check out…

World's Saltiest Water
(Periodic Videos)

Envisioning Chemistry: Precipitation in Super Slow Motion
(Beauty of Science)