14 Chemistry of the Aqueous Solution: Solubility Equilibria

GUIDING QUESTIONS

- What is a saturated solution?
- What is solubility and solubility product? How are they related?
- What and why does precipitation take place?

LEARNING OUTCOMES

Students should be able to:

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

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

10.2(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

REFERENCES

1. Martin S. Silberberg, *Chemistry: The molecular nature of Matter and Change*. 3rd Edition, McGraw Hill, Chapter 18
2. Graham C. Hill and John S. Holman, *Chemistry in Context*, second Edition, ELBS, Chapter 22

1 INTRODUCTION

LOOKING BACK

In Topic 7 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, when the rate of precipitation and dissolution is equal, and use the Le Chatelier's principle to explain the factors that affect the solubility of a salt.

Equilibria involving ions in aqueous solution are important in industrial, analytical and biological processes. The dissolving and precipitating of ionic compounds in aqueous solution are phenomena that occur both within us and around us. For example, the dissolving of enamel on teeth in acidic solutions causes tooth decay; the precipitation of certain salts in our kidneys produces kidney stones; the precipitation of calcium carbonate from underground water forms stalactites and stalagmites inside caves. The principles and characteristics of these heterogeneous equilibria in aqueous solutions are very similar to those in other systems in chemical equilibria.

In this extension topic, we will explore the **solubility equilibria** of sparingly soluble ionic compounds.

2 SOLUBILITY AND SATURATED SOLUTIONS

DEFINITION

Solubility of a salt is the number of moles (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.

For example, the solubility of $NaCl$ in water at 25 °C is 357 g dm^{-3} or 6.102 mol dm^{-3}.
This is the maximum amount of $NaCl$ that can be dissolved in water to give a saturated solution at that temperature.

- **Units of solubility:** mol dm^{-3} (molar solubility) or g dm^{-3}

Ionic compounds with low solubility are said to be **sparingly soluble**. The table below summarises some ionic compounds with very high solubility ('soluble') and very low solubility ('insoluble').

Ions	Solubility
NO_3^-	All nitrates are soluble
Cl^-, Br^-, I^-	All halides are soluble except Ag^+ and Pb^{2+}
SO_4^{2-}	All sulfates are soluble except Pb^{2+}, Ba^{2+} and Ca^{2+}
CO_3^{2-}	All carbonates are insoluble except Na^+, K^+ and NH_4^+
O^{2-}	All oxides are insoluble except Na^+ and K^+
OH^-	All hydroxides are insoluble except Na^+ and K^+

As a solute begins to dissolve in a solvent, the concentration of the solute particles in the solution increases. But this cannot occur infinitely, most solutes have a finite (limited) solubility in a particular solvent at a particular temperature. For the sparingly soluble salts, they reach equilibrium with relatively little solute dissolved.

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.

3 SOLUBILITY EQUILIBRIA AND SOLUBILITY PRODUCT, K_{sp}

When increasing quantities of a sparingly soluble ionic salt are added to water, a saturated solution will eventually be formed. Upon addition of excess solute, a dynamic **equilibrium** is set up, in which there is simultaneous dissolution of the excess undissolved solute and precipitation of the solute from the ions in the solution. These two processes take place at the same rate. Ions in the saturated solution are at equilibrium with the excess undissolved solute:

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

Now, consider a mixture containing a saturated aqueous solution of silver chloride and some undissolved silver chloride. The system is at **equilibrium**:

$$\mathrm{AgC}l\mathrm{(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{C}l^-\mathrm{(aq)}$$

We can write:

$$K_c = \frac{[\mathrm{Ag^+}][\mathrm{C}l^-]}{[\mathrm{AgC}l]}$$

However, [AgC*l*] represents the 'concentration' of a pure solid, and is therefore a constant.

Therefore,

$$K_c \times [\mathrm{AgC}l] = [\mathrm{Ag^+}][\mathrm{C}l^-]$$
$$\Rightarrow K_{sp} = [\mathrm{Ag^+}][\mathrm{C}l^-]$$

The new constant, K_{sp}, is called the **solubility product** of AgC*l*.

Units of K_{sp} of AgC*l*: $\mathrm{mol^2\ dm^{-6}}$

DEFINITION

Solubility product, K_{sp}, of a sparingly soluble salt is the product of the molar concentrations of the constituent ions in a **saturated solution**, raised to the appropriate powers **at a given temperature**.

Note: Appropriate power refers to the stoichiometric coefficient of the substance in the balanced equation for the reaction.

- The concept of solubility product is valid only for sparingly soluble salts. For soluble salts such as $NaCl$, $CuSO_4$ and $AgNO_3$, the use of the K_{sp} concept is inappropriate.

- As such, 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}.

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

- Using the general formula A_xB_y for a sparingly soluble salt, the solubility equilibrium is:

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

and the general expression for solubility product is given by:

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$$

where $[A^{y+}]$ and $[B^{x-}]$ are concentrations of ions(in mol dm^{-3}) in a saturated solution.

Lecture Exercise 3.1

Write an expression for the solubility product of each of the following salts and state its units:

Ans:

(a) PbI_2

(b) Ag_2CO_3

(c) $Ca_3(PO_4)_2$

Self-Practice 3.1

Write an expression for the solubility product of each of the following salts and state its units:

(a) $FeCO_3$ (b) SrF_2 (c) Hg_2SO_4

(a) (b) (c)

An experimental investigation on the solubility product of $AgBrO_3$ at 16 °C

$$AgBrO_3(s) \rightleftharpoons Ag^+(aq) + BrO_3^-(aq)$$

Different initial volumes of $AgNO_3$(aq) and $KBrO_3$(aq), both of initial concentrations of 0.10 mol dm^{-3}, were added to 200 cm^3 of distilled water at 16 °C. The $[Ag^+]$ and $[BrO_3^-]$ at equilibrium were determined and shown in the table below:

Initial vol. of 0.10 mol dm^{-3} $AgNO_3$ / cm^3	Initial vol. of 0.10 mol dm^{-3} $KBrO_3$ / cm^3	$[Ag^+]$ at equilibrium / mol dm^{-3}	$[BrO_3^-]$ at equilibrium / mol dm^{-3}	$[Ag^+]_{eqm} \times [BrO_3^-]_{eqm}$ / $mol^2\,dm^{-6}$
40	10	0.0144	0.0024	3.45×10^{-5}
30	20	0.0081	0.0041	3.32×10^{-5}
25	25	0.0058	0.0058	3.36×10^{-5}
20	30	0.0042	0.0082	3.44×10^{-5}
10	40	0.0033	0.0102	3.37×10^{-5}

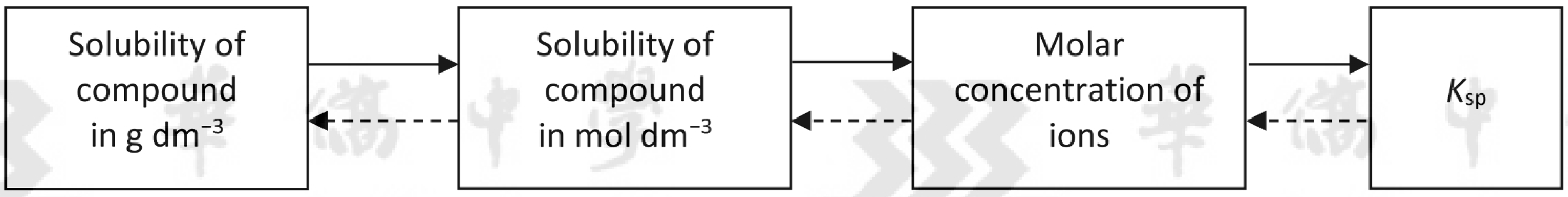
It is important to note that the product of the equilibrium concentrations of Ag^+(aq) and BrO_3^-(aq) in all 5 sets of experiments were almost constant.

$[Ag^+][BrO_3^-]$ = constant at a given temperature = 3.39×10^{-5} $mol^2\,dm^{-6}$ at 16 °C

This value of $[Ag^+][BrO_3^-]$ is the solubility product of $AgBrO_3$ at 16 °C.

In other words, this value of K_{sp} of $AgBrO_3$ at 16 °C is independent of the amount of Ag^+ and BrO_3^- added to the solution, provided that a saturated solution is obtained. (i.e. some undissolved $AgBrO_3$ is in contact with the solution.)

4 SOLUBILITY VS SOLUBILITY PRODUCT



- Solubility and solubility product are different.
- K_{sp} can be calculated from the solubility of the salt and vice versa.

4.1 Calculation of K_{sp} from solubility

Lecture Exercise 4.1

The solubility of silver chloride is 1.46×10^{-3} g dm^{-3} at 18 °C. What is the solubility product of silver chloride at this temperature? (M_r of AgC*l* is 143.5)

Self-practice 4.1

Calculate the K_{sp} of Ag_2SO_4 given that its solubility is 4.47 g dm^{-3}. (M_r of Ag_2SO_4 is 312.1)

(1.18×10^{-5} mol^3 dm^{-9})

4.2 Calculation of solubility from K_{sp}

Lecture Exercise 4.2

A suspension of solid $Mg(OH)_2$ in water is sold as "milk of magnesia" to alleviate minor stomach disorders by neutralising stomach acid. The $[OH^-]$ is too low to harm the mouth and throat, but the suspension dissolves in the acidic stomach juices.

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}. (M_r of $Mg(OH)_2$ is 58.3)

Self-practice 4.2

A sparingly soluble salt, cobalt(II) hydroxide, dissociates in aqueous solution according to the equation below.

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

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} $mol^3\ dm^{-9}$?

(7.37×10^{-6}; 1.47×10^{-5})

Determining the solubility product of a sparingly soluble compound

Scenario:

To plan an experiment to determine a value of the solubility product K_{sp} of a sparingly soluble salt, and to investigate how the solubility will be affected by the presence of a common ion (see section 6.1).

Approach:

This experiment is in two parts: part 1, preparing the saturated solution(s), and part 2, determining the amount of dissolved solid (usually by titration).

Part 1: To prepare a saturated solution of the sparingly soluble compound, take into consideration the following characteristics of heterogeneous equilibria:

$$MX\,(s) \rightleftharpoons M^{+}\,(aq) + X^{-}\,(aq).$$

- To establish an equilibrium, the saturated solution must also contain excess (undissolved) solid. If you are not required to determine the mass of the dissolved solid gravimetrically, there is no need to weigh the amount of solid added accurately, so long as there is undissolved solid in the saturated solution. At this stage, this is called a suspension because it contains undissolved solid.

- Like all reversible reactions, it takes time to reach equilibrium. Therefore the suspension is shaken in stoppered bottles / conical flasks, or stirred in beakers with a glass rod, and then allowed to stand for a while (about 5 – 10 min), at the end of which, the excess solid settles to the bottom.

- Solubility and K_{sp} values are dependent on temperature, so the temperature of the suspension must be maintained (usually by a water bath or thermostat), and be recorded.

- To investigate the effect of a common ion (see section 6.1), you may be required to set up several (usually five) different saturated solutions with different starting concentrations of the common ion.

Part 2: To determine the amount of dissolved solid, a titration procedure is often carried out. For example, standard hydrochloric acid will be used to titrate the saturated solution if X^{-} is OH^{-}. However, before this titration is carried out, the suspension must be filtered to remove the undissolved solid. To prevent the introduction of water which will dilute the saturated solution, it is critical that the filtration is carried out using dry filter funnel, dry filter paper, and the filtrate is collected in a dry conical flask.

Generic procedure for determining solubility

1. Measure (volume) of (solvent) into a conical flask, using a measuring cylinder.
2. Add (solid) to the conical flask and swirl. Continue adding (solid) until no more can dissolve.
3. Stopper the flask and shake.
4. Leave the flask to stand in a water bath maintained at 25 °C for (a suitable time) .
5. Filter the suspension into a dry conical flask, using dry filter funnel and dry filter paper.
6. Pipette 25 cm^3 of the filtrate (saturated solution) into another conical flask.
7. (titration procedure).

5 IONIC PRODUCT

DEFINITION

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.

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

The ionic product of AgC*l* is therefore given by: IP of $AgCl = [Ag^+][Cl^-]$

- IP has the same mathematical expression as K_{sp}.
- IP can take on any value and is only numerically equal to K_{sp} in saturated solutions.
- Unlike K_{sp} which applies only in saturated solutions and at equilibrium, IP is applicable in unsaturated solutions as well as in theoretical terms at the instant of mixing (or the instant before precipitation occurs). Refer to the following exercises.

Lecture Exercise 5.1

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 °C. No precipitation of $CaSO_4$ occurs. Calculate the ionic product of $CaSO_4$ in the resulting solution.

Self-practice 5.1

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 (assume the point in time just after the solutions are mixed but before precipitate appears). (1.5×10^{-6})

5.1 Using K_{sp} and IP to predict the occurrence of precipitation

- The value of IP indicates the direction in which the solubility reaction will occur. The idea of IP and K_{sp} is analogous to that of Q_c and K_c.

- When IP < K_{sp}, the forward reaction (dissolution of the salt) occurs. When IP > K_{sp}, the backward reaction (precipitation of the salt) occurs. Relate this to what you learnt in Topic 7 Chemical Equilibria about Q_c and K_c.

- Hence, the value of IP allows us to predict if precipitation would occur when two solutions are mixed.

- When two solutions are mixed, precipitation may or may not occur depending on:
  (a) concentration of ions after mixing
  (b) K_{sp} of the salt present

Consider the sparingly soluble salt $BaSO_4$, $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$$IP = [Ba^{2+}][SO_4^{2-}]$$

Context	Adding solid $BaSO_4$ in small amounts into pure water.	Mixing a solution of $Ba^{2+}(aq)$ and a solution of $SO_4^{2-}(aq)$
IP vs K_{sp}	When does the solution become saturated?	Will there be precipitation?
IP < K_{sp} Forward reaction occurs.	The solution is **not** saturated. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ More $BaSO_4$ can dissolve in the solution until IP = K_{sp}.	**No** precipitation occurs.
IP = K_{sp} At equilibrium	The solution is saturated. No more $BaSO_4$ can dissolve. The solution contains the **maximum** amount of Ba^{2+} and SO_4^{2-}. Upon further addition of solid, IP remains equal to K_{sp}. Undissolved solid is present in equilibrium with the saturated solution.	The **first trace** of precipitate just **appears**. (or is just about to appear)
IP > K_{sp} Backward reaction occurs.		Precipitation of $BaSO_4$ **occurs.** $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ Equilibrium shifts to the left, forming the precipitate until IP = K_{sp}.

Lecture Exercise 5.2

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} $Na_2SO_4(aq)$? (numerical value of K_{sp} of $PbSO_4$ is 1.60×10^{-8})

Lecture Exercise 5.3

$Ca(NO_3)_2(s)$ 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? (numerical value of K_{sp} of $CaSO_4$ is 2.40×10^{-5})

Self-practice 5.2

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 ? (Numerical value of K_{sp} of $SrSO_4$ is 8.1×10^{-7} mol^2 dm^{-6}).

5.2 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 can be separated from each other based on the different solubilities of their salts.

Lecture Exercise 5.4

In a solution, $[Ag^+] = 1.00 \times 10^{-2}$ mol dm^{-3} and $[Pb^{2+}] = 2.00 \times 10^{-2}$ mol dm^{-3}. NaC*l*(s) is added to this solution.
(numerical value of K_{sp} of AgC*l* is 1.80×10^{-10}, numerical value of K_{sp} of PbC*l*$_2$ is 1.60×10^{-5})

(i) What is the minimum concentration of C*l*$^-$ necessary for each salt to be precipitated?

(ii) Which salt precipitates first?

(iii) How can Ag^+ be separated from Pb^{2+}? Find the % of Ag^+ left in the solution. Is the separation effective?

6 FACTORS AFFECTING SOLUBILITY

6.1 Common Ion Effect

Consider a mixture of solid calcium fluoride and its aqueous ions in a saturated solution:

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

If a water-soluble solute containing the **common ion** Ca^{2+} or F^{-} is added, e.g. adding $CaCl_2$(aq) or NaF(aq), by Le Chatelier's Principle, the position of equilibrium will shift to the left to decrease $[Ca^{2+}]$ or $[F^{-}]$. Less CaF_2 will dissolve, reducing the solubility of CaF_2.

Lecture Exercise 6.1

The numerical value of K_{sp} of Ag*Cl* is 2.00×10^{-10} at 25 °C.

(i) What is the solubility of Ag*Cl*?

(ii) Calculate the solubility of Ag*Cl* in 0.100 mol dm^{3} Na*Cl* (aq).

Comments on the data:

- When a saturated solution is obtained by dissolving the pure salt in water, the concentrations of the ions are in the ratio determined by the stoichiometry of the salt.

- Solubility of $AgCl$ decreases in the presence of Cl^-, the common ion (2.00×10^{-9} mol dm^{-3} in (ii) < 1.40×10^{-5} mol dm^{-3} in (i)). 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.

6.2 Formation of complex ion:

Some metal ions can accept electron pairs from neutral molecules or anions to form **complex ions**.

Example 1:
When NaOH(aq) is added to a solution containing Al^{3+}, a white precipitate of $Al(OH)_3$ is formed. This precipitate dissolves in excess NaOH to form the complex ion $[Al(OH)_4]^-$. Such complex ions are soluble in water.

Explanation:

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

Precipitate starts forming when IP = K_{sp} and equilibrium exists between some $Al(OH)_3(s)$ and its ions.

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

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

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

- Formation of the complex ions removes Al^{3+} from the solution, hence $[Al^{3+}]$ decreases.

- This shifts the position of equilibrium in (1) to the right to produce more Al^{3+}, and the white precipitate of $Al(OH)_3$ dissolves.

- Complex ion formation **increases** the solubility of a sparingly soluble salt.

Example 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 up by adding $NH_3(aq)$, $AgCl$ dissolves in both dilute and concentrated NH_3, AgBr does not dissolve in dilute aqueous NH_3, but dissolves in concentrated NH_3, while AgI does not dissolve in both dilute and concentrated NH_3.

The table below summarises the reaction 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)
Reaction with $AgNO_3$ (aq)		No ppt	White ppt	Cream ppt	Yellow ppt
Solubility of AgX	**(i) in dilute NH_3**	–	Soluble	Insoluble	Insoluble
	(ii) in conc. NH_3	–	Soluble	Soluble	Insoluble
K_{sp} of AgX/ $mol^2\,dm^{-6}$		–	1.80×10^{-10}	5.40×10^{-13}	8.50×10^{-17}

Explanation:

Initially, 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 AgX is formed.

Precipitates starts forming and equilibrium exists between the AgX and its ions.

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

The subsequent addition of ammonia results in the formation of the stable diammine silver(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 $[Ag^+]$ to decrease (and the value of ionic product, $[Ag^+][X^-]$, to decrease). The decrease in $[Ag^+]$ causes the position of equilibrium (1) to shift to the right, hence **increasing** the solubility of AgX. The solubility of the silver halides in ammonia depends on the K_{sp} of the silver halides. For the AgX solid to dissolve completely in ammonia, the ionic product must decrease to $\leq K_{sp}$.

The K_{sp} values of silver halides decrease in the order: $AgCl > AgBr > AgI$.

For $AgCl$, when dilute NH_3 is added, the precipitate **dissolves completely** because the addition of dilute NH_3 is sufficient to lower $[Ag^+]$ such that the ionic product becomes **smaller** than K_{sp} of $AgCl$.

For AgBr, K_{sp} is lower, so the ionic product is still **greater** than K_{sp} when **dilute** NH_3 is added. Hence, the precipitate **does not dissolve completely** in dilute NH_3. However, when **concentrated** NH_3 is added, it will sufficiently lower $[Ag^+]$ such that the ionic product becomes **smaller** than K_{sp} and the precipitate **dissolves completely**.

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

Lecture Exercise 6.2

Explain why the solubility of $PbCl_2$ decreases in dilute HC*l* but increases in concentrated HC*l*.

6.3 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**. A Brønsted acid is a proton donor whereas a Brønsted base is a proton acceptor. The Brønsted acid-base theory was introduced briefly in Topic 4 Reactions & Stoichiometry.

DEFINITIONS

The pH of a solution is the negative logarithm to base ten of the molar concentration of hydrogen ion, i.e. $\text{pH} = -\lg[\text{H}^+]$

The pOH of a solution is the negative logarithm to base ten of the molar concentration of hydroxide ion, i.e. $\text{pOH} = -\lg[\text{OH}^-]$

i.e. $[\text{H}^+] = 10^{-\text{pH}}$ and $[\text{OH}^-] = 10^{-\text{pOH}}$

Also, at 25 °C, pH + pOH = 14 (refer to Topic 15 Acid-base Equilibria).

For example, a sparingly soluble salt, magnesium hydroxide, $Mg(OH)_2$, dissolves in aqueous solution according to the equation below.

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

Addition of a strong Brønsted acid like HC*l* (which will decrease pH) will neutralise the OH^- to form water. The removal of OH^- lowers $[OH^-]$. According to the Le Chatelier's Principle, the position of the above equilibrium will shift to the right to offset the decreased $[OH^-]$, more $Mg(OH)_2$ dissolves.

Thus, the solubility of $Mg(OH)_2$ increases 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**).

Self-practice 6.1

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

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

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

7 APPLICATION AND RELEVANCE TO REAL-LIFE CONTEXTS

The following examples illustrate the relevance of the K_{sp} concept to a range of phenomena and contexts.

- Daily life
  In regions with hard water (that contains calcium and magnesium ions), mineral deposits can sometimes be seen on cooking dishes or in bathtubs. These deposits are caused by the precipitates of calcium/magnesium ions in the hard water. These deposits can make hard water unsuitable for many uses. Thus, variety of ways can be used to reduce the hardness of water, for example, by the addition of sodium carbonate.

- Health
  Kidney stones are a biological example of how the concept of solubility is experienced in our lives. A kidney stone is usually made up of a salt of calcium, commonly ethanedioate or phosphate. Thus people who are prone to kidney stones have to limit or avoid eating foods with high ethanedioate content (e.g. spinach, peanuts and sweet potatoes). A possible approach to treating kidney stones is to drink a large amount of water so as to flush out the kidney stones from the urinary tract.

Looking ahead:
The concepts learnt about the dynamic equilibrium of a saturated solution will be useful when we explore the chemistry of inorganic compounds in further topics (such as in Inorganic Qualitative Analysis experiments and Topic 22 Chemistry of the Transition Elements). For example, the Le Chatelier's principle, common ion effect and the formation of metal complex ions will be applied to explain the precipitation and dissolution of metal salts in inorganic reactions.