





Pioneer Junior College
Higher 2 Chemistry (9647)
Ionic Equilibria II: Solubility Product (Tutor's Copy)

References

- 1 Chemistry for Advanced Level, Peter Cann and Peter Hughes
- 2 Chemistry in Context (5th Edition) by Hill and Holman

Web-based Resources

No.	Description	QR Code	No.	Description	QR Code
1	Introduction to Solubility Product. http://www.chemguide.co.uk/physical/kspmenu.html#top		2	An online tutorial on K_{sp} . http://www.youtube.com/watch?v=FsU8Ss6jiKs	
3	A video on Common Ion Effect. http://www.youtube.com/watch?v=pskvC5ROCdc		4	A video of an experiment which illustrates the Common Ion Effect. http://www.youtube.com/watch?v=2nzshkd0d78	

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- 1 Introduction
- 2 Solubility
- 3 Solubility Product
- 4 Ionic Product
- 5 Applications of Solubility Product
- 6 Limitation to Solubility Product Concept
- 7 Summary

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) show understanding of the common ion effect.

1 INTRODUCTION

Ionic compounds can be classified as soluble or insoluble in water.

Soluble	Insoluble
All Group I (eg. Na^+ , K^+) and ammonium (NH_4^+) compounds	Carbonates (CO_3^{2-}) except those of Group I (eg. Na_2CO_3 , K_2CO_3) and $(\text{NH}_4)_2\text{CO}_3$
All Nitrates (NO_3^-)	Hydroxides (OH^-) except those of Group I (eg. NaOH , KOH), $\text{NH}_3(\text{aq})$ and $\text{Ba}(\text{OH})_2$
Nitrites (NO_2^-) except AgNO_2	Sulfites (SO_3^{2-}) except those of Group I (eg. Na_2SO_3 , K_2SO_3) and $(\text{NH}_4)_2\text{SO}_3$
Halides (Cl^- , Br^- , I^-) except those of Ag^+ (eg. AgBr) and Pb^{2+} (eg. AgI). Lead(II) halides (eg. PbI_2) are soluble in hot water	Phosphates (PO_4^{3-}) except those of Group I (eg. Na_3PO_4 , K_3PO_4) and $(\text{NH}_4)_3\text{PO}_4$
Sulfates (SO_4^{2-}) except Ag_2SO_4 , BaSO_4 and PbSO_4 CaSO_4 is sparingly soluble	Sulfides (S^{2-}) except those of Group I (eg. Na_2S , K_2S) and $(\text{NH}_4)_2\text{S}$
Chromates (CrO_4^{2-}) except Ag_2CrO_4 , BaCrO_4 , PbCrO_4	

Diagram 1: Table showing solubilities of some common salts

2 SOLUBILITY

- As a solute begins to dissolve in a solvent, the concentration of the solute particles in the solution increases.
- When a **sparingly soluble** ionic salt is first added to water, a little solid dissolves.
- As increasing quantities of this salt is added to water, a **saturated** solution will eventually be formed.
- For most solutes, they have a limited solubility in a particular solvent.

Definitions:

A **saturated solution** is a solution that contains the **maximum amount of solute** that can be dissolved in a solvent.

Solubility of a salt is the **maximum number of moles** of **solute** (OR mass of solute) that can be **dissolved** in 1 dm^3 to form a **saturated solution** at a fixed temperature.

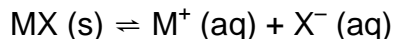
E.g. the solubility of AgCl in water at 25°C is 1.4×10^{-5} mol per 1 dm^3 .

This is the maximum amount of AgCl that can be dissolved in water to give a saturated solution at that temperature.

- Units of solubility are usually mol dm^{-3} (molar solubility) or g dm^{-3} .
- It is often expressed in mol dm^{-3} when comparing solubilities between two compounds due to difference in their relative formula masses.
- Solubility can be affected by (See section 5)
 - (i) **temperature** (salts generally dissolve better in hot water than cold water)
 - (ii) **common ion effect** (e.g. presence of NaCl in a saturated solution of AgCl will decrease solubility of AgCl in that solution)
 - (iii) pH (eg. metal hydroxides)
 - (iv) complex formation

3 SOLUBILITY PRODUCT, K_{sp}

- In a saturated solution, ions are in equilibrium with the excess undissolved solute:



- The solid particles continuously dissolve and solute particles are continuously precipitated.



When the above equilibrium is established, the solution is said to be **saturated**.

At this point, the equilibrium constant is:

$$K_c = \frac{[Ag^+][BrO_3^-]}{[AgBrO_3]}$$

However, $[AgBrO_3]$ represents the concentration of a pure solid, and is therefore a constant. Thus,

$$K_c [AgBrO_3] = [Ag^+][BrO_3^-]$$

$$K_{sp} = [Ag^+][BrO_3^-] \text{ and is a constant, at a given temperature.}$$

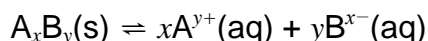
- The new constant, K_{sp} , is called the **solubility product** of $AgBrO_3$.
- Units of K_{sp} of $AgBrO_3$: $mol^2 dm^{-6}$

DEFINITION

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

In general, for a sparingly soluble ionic salt A_xB_y dissolving in water:

- Using the general formula A_xB_y for a sparingly soluble salt,



the general expression for the solubility product is given by

$$K_{sp} = [A^{y+}(aq)]_{eqm}^x [B^{x-}(aq)]_{eqm}^y$$

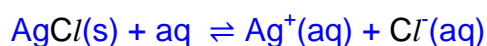
- The solubility product concept is only valid for **sparingly soluble** salts.
- For soluble salts such as $NaCl$, $CuSO_4$ and $AgNO_3$, the use of the K_{sp} concept is inappropriate.

- 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} **is a constant at constant temperature** (and its value changes only if temperature changes).
- Units of K_{sp} are not fixed, refer to diagram 2 remarks

QUICK CHECK 1

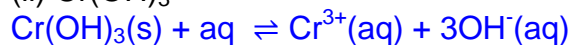
Write an expression for the solubility product for each of the following compounds and state the units of the solubility product.

(i) AgCl



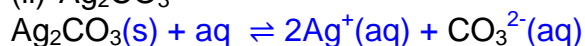
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \text{ mol}^2 \text{ dm}^{-6}$$

(ii) Cr(OH)_3



$$K_{sp} = [\text{Cr}^{3+}]_{\text{eqm}} [\text{OH}^-]_{\text{eqm}}^3 \text{ mol}^4 \text{ dm}^{-12}$$

(ii) Ag_2CO_3



$$K_{sp} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] \text{ mol}^3 \text{ dm}^{-9}$$

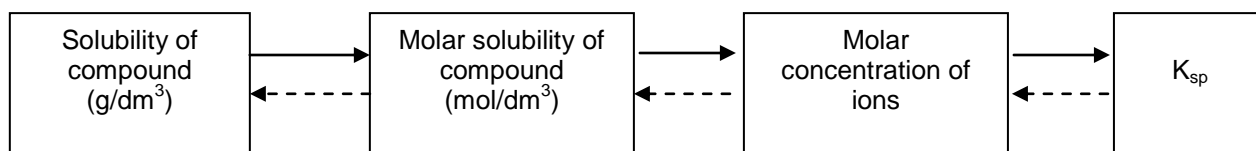
Relationship between Solubility and Solubility Product

Salt	Formula	Formula type	K_{sp}	Remarks
calcium sulfate lead(II) sulfate silver chloride barium sulfate silver bromide silver iodide	CaSO_4 PbSO_4 AgCl BaSO_4 AgBr AgI	AB	2.0×10^{-5} 1.6×10^{-8} 2.0×10^{-10} 1.0×10^{-10} 5.0×10^{-13} 8.0×10^{-17}	Units of $K_{sp} = \text{mol}^2 \text{dm}^{-6}$ Solutes have the <u>same type of formula</u> (i.e. AB). The <u>greater</u> the numerical value of the K_{sp} , the <u>higher</u> the solubility.
lead(II) iodide copper(II) hydroxide silver sulfide	PbI_2 Cu(OH)_2 Ag_2S	AB_2	1.4×10^{-8} 2.2×10^{-20} 6.0×10^{-51}	Units of $K_{sp} = \text{mol}^3 \text{dm}^{-9}$ Solutes have the <u>same type of formula</u> (i.e. AB₂). The <u>greater</u> numerical value of K_{sp} , the <u>higher</u> the solubility.
chromium(III) hydroxide iron(II) hydroxide copper(I) iodide	Cr(OH)_3 Fe(OH)_2 CuI	- (salts of different formula given here)	2.0×10^{-29} 1.6×10^{-14} 5.1×10^{-12}	Units of $K_{sp} = (\text{mol dm}^{-3})^n$ where, n = total number of ions in a formula unit Solutes have <u>different types of formulae</u> . We compare their <u>solubilities</u> instead of K_{sp} . (see example 4)

Diagram 2: Table showing some K_{sp} values and comparison of solubilities of some salts

- The numerical value of K_{sp} is an indication of the solubility of a solute in water at a given temperature.
- For solutes of the **SAME formula type**, the lower the K_{sp} , the lower its solubility i.e. the less soluble is the solid (or the greater numerical value of K_{sp} , the higher the solubility, the more soluble it is).
- For solutes with **DIFFERENT formula type**, we CANNOT compare their K_{sp} to check which compound is more soluble. We compare their solubilities in terms of mol dm^{-3} instead. (see example 4)

Diagram 3: SOLUBILITY VS SOLUBILITY PRODUCT

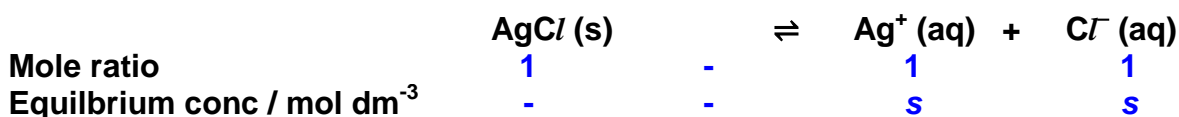


- K_{sp} can be calculated from the solubility of the salt and vice versa.

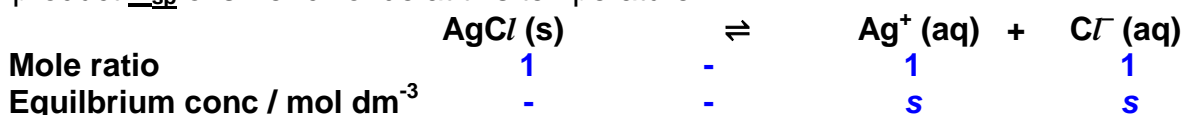
3.1 Calculation of solubility product K_{sp} from solubility

Worked example 1

- Consider the dissolving of solid silver chloride, $AgCl$.
- Solubility** of $AgCl$ is $s \text{ mol dm}^{-3}$, meaning that **s moles of $AgCl$ dissolve in 1 dm^3 water to form a saturated solution at equilibrium.**
- From the equation, to produce a saturated solution, **s moles of $AgCl$ is dissolved in 1 dm^3 of water, forming s moles of Ag^+ and s moles of Cl^- .**



If the solubility of $AgCl$ at 18°C is given as $1.0 \times 10^{-5} \text{ mol dm}^{-3}$, what is the solubility product K_{sp} of silver chloride at this temperature?

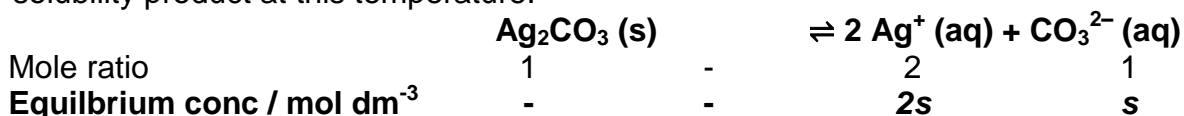


$$s = [Ag^+_{(aq)}]_{eqm} = [Cl^-_{(aq)}]_{eqm} = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\begin{aligned}
 K_{sp} &= [Ag^+_{(aq)}]_{eqm} [Cl^-_{(aq)}]_{eqm} \\
 &= s^2 \\
 &= (1.0 \times 10^{-5})^2 = 1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}
 \end{aligned}$$

Example 2

Given that the solubility of Ag_2CO_3 at 20°C is $1.25 \times 10^{-4} \text{ mol dm}^{-3}$, find its solubility product at this temperature.

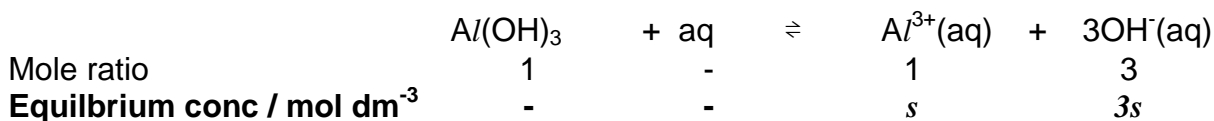


$$\begin{aligned}
 K_{sp} &= [Ag^+]^2 [CO_3^{2-}] \\
 &= (2s)^2 \times (s)^1 = 4s^3 \\
 &= (2 \times 1.25 \times 10^{-4})^2 (1.25 \times 10^{-4}) \\
 &= 7.81 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}
 \end{aligned}$$

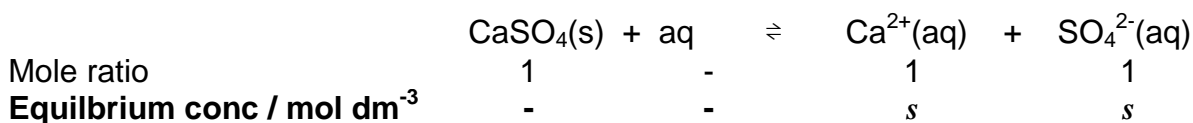
Quick-check 2

Given that the solubility of aluminium hydroxide, $\text{Al}(\text{OH})_3$, is $1.42 \times 10^{-7} \text{ g dm}^{-3}$, calculate its solubility product. Given that M_r of $\text{Al}(\text{OH})_3 = 78.0$

$$\begin{aligned} \text{Molar solubility, } s &= (1.42 \times 10^{-7}) / 78.0 \\ &= 1.82 \times 10^{-9} \text{ mol dm}^{-3} \end{aligned}$$



$$\begin{aligned} K_{sp} &= [\text{Al}^{3+}(\text{aq})]_{\text{eqm}} [\text{OH}^{-}(\text{aq})]_{\text{eqm}}^3 \\ &= (1.82 \times 10^{-9}) (3 \times 1.82 \times 10^{-9})^3 \\ &= 2.97 \times 10^{-34} \text{ mol}^4 \text{ dm}^{-12} \end{aligned}$$

3.2 Calculation of solubility from solubility product, K_{sp}
Example 3


$$[\text{CaSO}_4(\text{aq})]_{\text{eqm}} = [\text{Ca}^{2+}(\text{aq})]_{\text{eqm}} = [\text{SO}_4^{2-}(\text{aq})]_{\text{eqm}} = s$$

$$\begin{aligned} \text{Therefore, } K_{sp} &= [\text{Ca}^{2+}]_{\text{eqm}} [\text{SO}_4^{2-}]_{\text{eqm}} \\ &= s \times s = s^2 \\ \sqrt{K_{sp}} &= s \end{aligned}$$

$$\text{solubility, } s = \sqrt{K_{sp}}$$

From *Diagram 2*, K_{sp} of $\text{CaSO}_4 = 2.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$.

Thus, the solubility of CaSO_4 in water, $s = \sqrt{2.0 \times 10^{-5}} = 4.47 \times 10^{-3} \text{ mol dm}^{-3}$ (or 0.609 g dm^{-3}).

Example 4

Given that the solubility product of lead(II) iodide is $1.4 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$, calculate the solubility of lead(II) iodide and hence determine if it is more soluble than calcium sulfate.

	$\text{PbI}_2(\text{s}) + \text{aq}$	\rightleftharpoons	$\text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$	
Mole ratio	1	-	1	2
Solubility / mol dm^{-3}	s	-	-	-
Equilibrium conc / mol dm^{-3}	-	-	s	$2s$

$$K_{\text{sp}} = [\text{Pb}^{2+}(\text{aq})]_{\text{eqm}} [\text{I}^{-}(\text{aq})]_{\text{eqm}}^2$$

$$= 4s^3$$

$$\sqrt[3]{\frac{K_{\text{sp}}}{4}} = s$$

$$\text{Solubility, } s = \sqrt[3]{\frac{1.4 \times 10^{-8}}{4}}$$

$$= 1.52 \times 10^{-3} \text{ mol dm}^{-3}$$

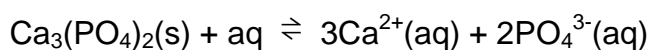
Compare solubilities:

Solubility of $\text{PbI}_2 <$ solubility of CaSO_4 ($4.47 \times 10^{-3} \text{ mol dm}^{-3}$)

PbI_2 is less soluble than CaSO_4 .

Example 5

Express the solubility, $s \text{ mol dm}^{-3}$, of calcium phosphate, in terms of its solubility product, when it is dissolved in water to form a saturated solution.



$$s \text{ mol of } \text{Ca}_3(\text{PO}_4)_2 \equiv 3s \text{ mol of } \text{Ca}^{2+} \equiv 2s \text{ mol of } \text{PO}_4^{3-}.$$

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})]_{\text{eqm}}^3 [\text{PO}_4^{3-}(\text{aq})]_{\text{eqm}}^2 = (3s)^3 (2s)^2 = 108s^5$$

$$s = \sqrt[5]{\frac{K_{\text{sp}}}{108}}$$

4 IONIC PRODUCT

The **ionic product (IP)** of a **solution** is the product of the molar concentrations of the constituent ions in the solution, raised to the appropriate powers.

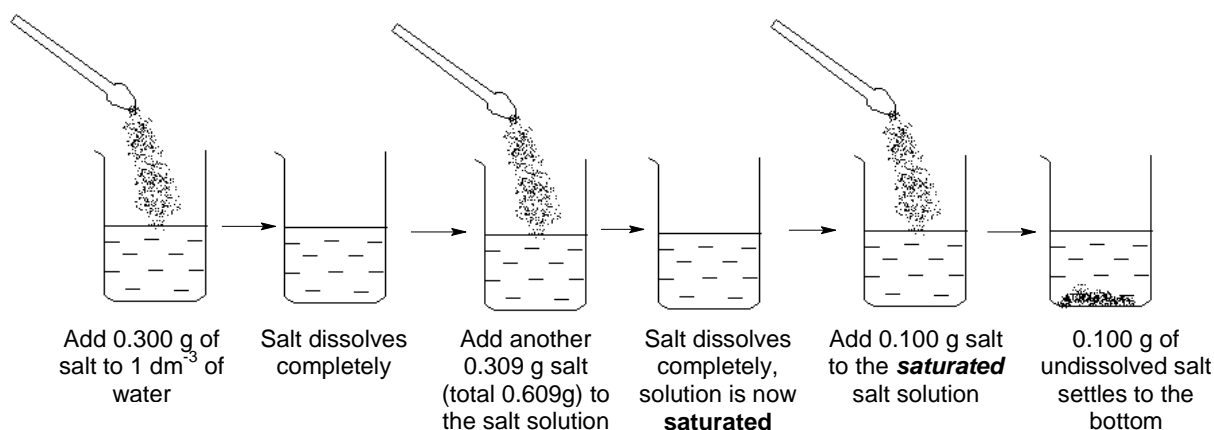
- In general, for an ionic compound, A_xB_y :

$$\text{Ionic product} = [A^{y+}]^x[B^{x-}]^y$$

- The ionic product of a compound is calculated **at the point of mixing** 2 or more solutions or when dissolving the compound in a solution.
 - The point of mixing can be thought of as the moment **immediately after mixing**, at $t=0$, before any precipitation occurs.
- Ionic product does **NOT** have a constant value. It depends on what is present in the solution **at the point of mixing**.
- Comparing ionic product against K_{sp} allows us to predict whether precipitation will occur or not.
- Eg. in a solution of $CaSO_4$, $IP = [Ca^{2+}][SO_4^{2-}]$

Relationship between Ionic Product and Solubility Product, K_{sp}

- Consider the dissolution of calcium sulfate ($s = 4.47 \times 10^{-3} \text{ mol dm}^{-3}$)



Solution 1

Solution 2

Solution 3

Diagram 3: Dissolving $CaSO_4$ to eventually result in a saturated solution

In **solution 1**, **ionic product** $< K_{sp}$, hence all solid will dissolve.
The solution is **unsaturated**.

In **solution 2**, **ionic product** $= K_{sp}$, all solid will dissolve.
The solution is **saturated**.

In **solution 3**, **ionic product** $> K_{sp}$, excess solid is precipitated.
The solution is **saturated**.

- When an aqueous solution containing cation A^+ , is mixed with another aqueous solution containing Y^- anion, precipitation may or may not occur depending on the concentrations of the ions present.
- Consider the mixing of $AX(aq)$ and $BY(aq)$,

$$AX(aq) + BY(aq) \rightleftharpoons AY(s) + BX(aq)$$

In order to predict precipitation of $AY(s)$ upon mixing, it is necessary to calculate the ionic product of AY at the point of mixing, then compare its value with K_{sp} .

Note: must consider mutual dilution on mixing 2 solutions

A summary table of the 3 possible scenarios of IP compared to K_{sp} :

Ionic Product	Is the solution saturated?	Is there precipitation?
$IP < K_{sp}$	<ul style="list-style-type: none"> The solution is not saturated. More ionic salt (eg. $CaSO_4$) can dissolve in the solution until $IP = K_{sp}$. 	<ul style="list-style-type: none"> No precipitation can occur yet.
$IP = K_{sp}$	<ul style="list-style-type: none"> The solution is just saturated. Concentration of ions $[Ca^{2+}]$ or $[SO_4^{2-}]$ at that temperature = solubility of $CaSO_4$. 	<ul style="list-style-type: none"> This is the point where: <ul style="list-style-type: none"> the ppt just dissolves or the first trace of ppt just appears
$IP > K_{sp}$	<ul style="list-style-type: none"> The solution is saturated. 	<ul style="list-style-type: none"> Precipitation of $CaSO_4$ occurs. $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$ Equilibrium shifts to the left to form the ppt thus IP drops, until $IP = K_{sp}$.

4.1 Predicting Precipitation

Example 6 (Mixing two solutions of equal volumes)

Suppose we mix a $10^{-3} \text{ mol dm}^{-3}$ solution of Ca^{2+} ions with an equal volume of a $10^{-3} \text{ mol dm}^{-3}$ solution of SO_4^{2-} at 25°C . Will a precipitate of CaSO_4 form?

[Given that the K_{sp} of $\text{CaSO}_4 = 2.4 \times 10^{-5} \text{ mol dm}^{-3}$.]

Immediately after mixing equal volumes of the two solutions and before any precipitation has occurred,

$$\begin{aligned} [\text{Ca}^{2+}] \text{ at point of mixing} &= \text{no. of moles of } \text{Ca}^{2+} \text{ before mixing} \div \text{total volume} \\ &= 10^{-3} \div 2 = 5 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{SO}_4^{2-}] \text{ at point of mixing} &= \text{no. of moles of } \text{SO}_4^{2-} \text{ before mixing} \div \text{total volume} \\ &= 10^{-3} \div 2 = 5 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

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

$$\text{IP} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (5 \times 10^{-4})^2 = 2.5 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6} < K_{\text{sp}}$$

Since $\text{IP} < K_{\text{sp}}$, no precipitation occurs.

Quick-check

Predict if there will be precipitation of Ag_2CO_3 when equal volumes of $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ AgNO_3 and $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ Na_2CO_3 are mixed.

(Given: K_{sp} of $\text{Ag}_2\text{CO}_3 = 8.2 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$)

The ppt is Ag_2CO_3 .

$$\begin{aligned} [\text{Ag}^+] \text{ at point of mixing} &= \text{no. of moles of } \text{Ag}^+ \text{ before mixing} \div \text{total volume} \\ &= (2.0 \times 10^{-5}) / 2 \\ &= 1.0 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

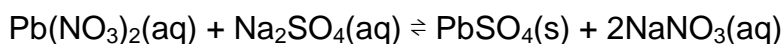
$$\begin{aligned} [\text{CO}_3^{2-}] \text{ at point of mixing} &= \text{no. of moles of } \text{CO}_3^{2-} \text{ before mixing} \div \text{total volume} \\ &= (2.0 \times 10^{-5}) / 2 \\ &= 1.0 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{Ionic product of } \text{Ag}_2\text{CO}_3 &= [\text{Ag}^+]^2[\text{CO}_3^{2-}] \\ &= (1.0 \times 10^{-5})^2(1.0 \times 10^{-5}) \\ &= 1 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9} < K_{\text{sp}} \end{aligned}$$

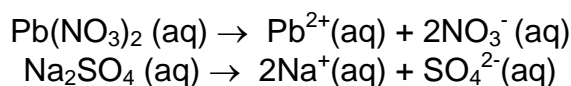
Since ionic product $< K_{\text{sp}}$, Ag_2CO_3 will not be precipitated.

Example 7 (Mixing two solutions of different volumes)

Deduce whether or not a precipitate will form when 300 cm³ of 1.0 × 10⁻³ mol dm⁻³ Pb(NO₃)₂ and 200 cm³ of 1.0 × 10⁻² mol dm⁻³ Na₂SO₄ are mixed.
(Given: K_{sp} of PbSO₄ = 1.6 × 10⁻⁸ mol² dm⁻⁶)



Total volume of mixture = 500 cm³



$$\begin{aligned}[\text{Pb}^{2+}] \text{ at the point of mixing} &= \text{no. of moles of Pb}^{2+} \text{ before mixing} \div \text{total volume} \\ &= \left(\frac{300}{1000} \times 1.0 \times 10^{-3} \right) / (500 / 1000) \\ &= 6.0 \times 10^{-4} \text{ mol dm}^{-3}\end{aligned}$$

$$\begin{aligned}[\text{SO}_4^{2-}] \text{ at the point of mixing} &= \text{no. of moles of SO}_4^{2-} \text{ before mixing} \div \text{total volume} \\ &= \left(\frac{200}{1000} \times 1.0 \times 10^{-2} \right) / (500 / 1000) \\ &= 4.0 \times 10^{-3} \text{ mol dm}^{-3}\end{aligned}$$

$$\begin{aligned}\text{Ionic product of PbSO}_4 &= [\text{Pb}^{2+}] [\text{SO}_4^{2-}] \\ &= 6.0 \times 10^{-4} \times 4.0 \times 10^{-3} \\ &= 2.4 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6} > K_{sp}\end{aligned}$$

Since ionic product > K_{sp} , PbSO₄ will be precipitated.

Example 8 (Dissolving a solid into a solution)

Deduce if precipitation of lead(II) chloride occurs when 0.500 g of sodium chloride is dissolved in 100 cm³ of 0.100 mol dm⁻³ lead(II) nitrate.
(Given: K_{sp} of PbCl₂ = 1.7 × 10⁻⁵ mol³ dm⁻⁹)

$$\begin{aligned}\text{Amount of NaCl} &= 0.500 / (23.0 + 35.5) \\ &= 8.55 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}[\text{Cl}^-] &= (8.55 \times 10^{-3}) / (100/1000) \\ &= 0.0855 \text{ mol dm}^{-3}\end{aligned}$$

$$\begin{aligned}\text{Ionic product} &= [\text{Pb}^{2+}] [\text{Cl}^-]^2 \\ &= 0.100 \times 0.0855^2 \\ &= 7.31 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9} > K_{sp}\end{aligned}$$

Since ionic product > K_{sp} , PbCl₂ will be precipitated.

Note: For this case, it is not required to calculate the concentration of the ions at the point of mixing as solids are assumed to have negligible volumes compared to aqueous solutions.

5. Factors affecting solubility

5.1 ***Common Ion Effect

- Consider the sparingly soluble ionic salt, BaSO_4 ,

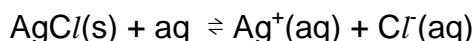
$$\text{BaSO}_4(\text{s}) + \text{aq} \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$$

In the presence of either $\text{Ba}^{2+}(\text{aq})$ or $\text{SO}_4^{2-}(\text{aq})$ from a secondary source (eg. addition of $\text{Ba}(\text{OH})_2(\text{aq})$), the **position of the above equilibrium will shift to the left** as predicted by Le Chatelier's Principle, i.e. more $\text{BaSO}_4(\text{s})$ will be precipitated.

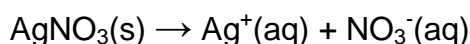
- Hence, the **presence of a common ion** will **decrease the solubility of a sparingly soluble salt**. This is known as the **common ion effect**.

Example 9 (Common ion effect)

When some solid silver nitrate is added to a saturated solution of silver chloride, more white precipitate is formed. Explain.



When $\text{AgNO}_3(\text{s})$ is added (recall that all nitrate salts are soluble),



$[\text{Ag}^+(\text{aq})]$ increases.

By Le Chatelier's Principle, position of equilibrium shifts to the left, i.e. more $\text{AgCl}(\text{s})$ will be formed.

Example 10 (Common ion effect)

Given the solubility product of BaSO_4 is $1.00 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$, calculate the solubility of BaSO_4 in:

(a) water

Let the solubility of BaSO_4 in water be $s \text{ mol dm}^{-3}$.

	$\text{BaSO}_4(\text{s}) + \text{aq} \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$			
Mole ratio	1	-	1	1
Equilibrium conc / mol dm^{-3}	-	-	s	s

$$\begin{aligned}
 K_{\text{sp}} &= [\text{Ba}^{2+}]_{\text{eqm}} [\text{SO}_4^{2-}]_{\text{eqm}} = s^2 \\
 s^2 &= 1.00 \times 10^{-10} \\
 s &= 1.00 \times 10^{-5} \text{ mol dm}^{-3}
 \end{aligned}$$

(b) $0.100 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$

Let the solubility of BaSO_4 in $0.100 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ be $y \text{ mol dm}^{-3}$.

	$\text{BaSO}_4(\text{s}) + \text{aq} \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$			
Mole ratio	1	-	1	1
Equilibrium conc / mol dm^{-3}	-	-	y	y

	$\text{Na}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{Na}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$		
Mole ratio	1	2	1
Concentration / mol dm^{-3}	0.100	0.200	0.100

$$\begin{aligned} [\text{Ba}^{2+}] &= y \text{ (from } \text{BaSO}_4\text{)} \\ [\text{SO}_4^{2-}] &= y + 0.100 \text{ (from } \text{BaSO}_4 \text{ and } \text{Na}_2\text{SO}_4\text{)} \end{aligned}$$

$$\begin{aligned} K_{\text{sp}} &= [\text{Ba}^{2+}]_{\text{eqm}} [\text{SO}_4^{2-}]_{\text{eqm}} \\ &= (y)(y + 0.100) = 1.00 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

Since $0.100 \gg y$ (solubility of BaSO_4 in $\text{Na}_2\text{SO}_4(\text{aq})$ is very low and y is negligible)
 $(y + 0.100) \approx 0.100$.

$$\begin{aligned} 0.100y &= 1.00 \times 10^{-10} \\ y &= 1.00 \times 10^{-9} \text{ mol dm}^{-3} \end{aligned}$$

Comparing the 2 values obtained in **9(a)** and **9(b)**, there is a significant decrease in solubility due to common ion effect.

Note:

- **Solubility** of a solute can be changed by temperature and other factors such as common ion effect, pH etc.
- **Solubility product**, K_{sp} , depends only on **temperature**.

5.2 Complex formation

Complex ion formation tends to **increase** the solubility of a salt. See Applications of solubility product, 6.2, Qualitative analysis.

5.3 Effects of pH

pH can affect the solubility of salts such as metal hydroxides See Applications of solubility product, 6.1, Selective precipitation (using pH).

6 APPLICATIONS OF SOLUBILITY PRODUCT

6.1 Selective Precipitation (using pH)

- Ions of the same charge that form compounds **differing greatly in solubility** can be separated when reacted with oppositely charged ion.

Example: An aqueous solution containing both $\text{Ca}^{2+}(\text{aq})$ and $\text{Pb}^{2+}(\text{aq})$ can be separated by adding $\text{OH}^{-}(\text{aq})$ to precipitate $\text{Pb}(\text{OH})_2(\text{s})$, and filtering off the solid, leaving $\text{Ca}^{2+}(\text{aq})$ in the solution.

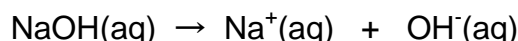
- Separation can also be made even if both salts are sparingly soluble, provided that the **K_{sp} values are sufficiently different**.

Example: Precipitation in wastewater treatment

An aqueous solution containing Cu^{2+} , Pb^{2+} and Hg^{2+} can be separated by adding aqueous solution of NaOH.

$$\begin{array}{lll} \text{Given:} & K_{\text{sp}} (\text{Cu}(\text{OH})_2) & = 2 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9} \\ & K_{\text{sp}} (\text{Pb}(\text{OH})_2) & = 1.43 \times 10^{-20} \text{ mol}^3 \text{ dm}^{-9} \\ & K_{\text{sp}} (\text{Hg}(\text{OH})_2) & = 3.6 \times 10^{-26} \text{ mol}^3 \text{ dm}^{-9} \end{array}$$

If a solution of NaOH is added to an acidic mixture of the 3 ions.

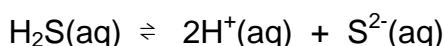


As the pH of the solution increases, $[\text{OH}^{-}]$ increases. Precipitation occurs with the least soluble metal hydroxide (lowest K_{sp} value). Hence, $\text{Hg}(\text{OH})_2$ will be precipitated first, followed by $\text{Pb}(\text{OH})_2$, and finally $\text{Cu}(\text{OH})_2$.

Controlled addition of sodium hydroxide results in the selective precipitation of all 3 ions and to prevent formation of soluble metal complexes.

Selective precipitation is often used in waste disposal facilities to separate out toxic metal cations (eg Hg^{2+} , Cd^{2+}), from less toxic ones (eg Cu^{2+} , Fe^{2+}), so that they can be safely disposed.

For highly toxic ions, hydrogen sulfide (H_2S) can also be used in a similar manner for precipitation. First, H_2S is added to the solution. As H_2S is a weak acid,



Addition of NaOH shifts the dissociation of H_2S to the right, increasing $[\text{S}^{2-}(\text{aq})]$. When $[\text{S}^{2-}(\text{aq})]$ is high enough, the least soluble metal sulfide will be precipitated.

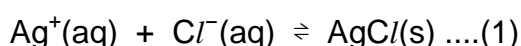
6.2 Qualitative Analysis

- Solubility product is often used in qualitative analysis in the identification of metal cations through **complex ion formation**.
- Typical reagents used in Q.A. include **aqueous sodium hydroxide** or **aqueous ammonia**.
- Precipitation, dissolution and colour of precipitate, in limited and excess reagent, can give the identity of the metal cation.
- A complex ion is defined as a central metal cation / atom that is dative bonded to anions or molecules called ligands. The ligand has at least **one** lone pair of electrons that can form a dative covalent bond with the central metal ion / atom.

<i>Halides</i>	<i>Cl⁻(aq)</i>	<i>Br⁻(aq)</i>	<i>I⁻(aq)</i>
Add AgNO₃(aq)	<i>white AgCl ppt</i>	<i>cream AgBr ppt</i>	<i>yellow AgI ppt</i>
Solubility of AgX in:			
(i) excess dilute NH₃(aq)	<i>soluble to give colourless solution</i>	<i>insoluble</i>	<i>insoluble</i>
(ii) excess concentrated NH₃(aq)	<i>soluble to give colourless solution</i>	<i>soluble to give colourless solution</i>	<i>insoluble</i>

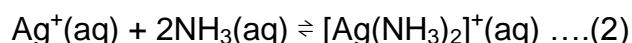
Diagram 4: Qualitative analysis of halides using aqueous AgNO₃ and aqueous NH₃

- (a) When aqueous sodium chloride is added to aqueous silver nitrate, a white precipitate of silver chloride is formed:



The position of equilibrium (1) lies far to the right as **ionic product > K_{sp}(AgCl)**.

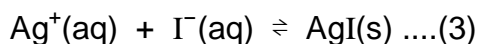
When aqueous ammonia is added, the white precipitate dissolves to form a colourless solution (due to complex ion of Ag(NH₃)₂⁺ being formed):



When excess NH₃ is added (high [NH₃]), the position of equilibrium (2) shifts to the **right** and [Ag⁺] decreases, resulting in a **decrease** in ionic product.

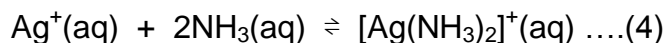
The decrease in ionic product causes it to be **smaller than** K_{sp}(AgCl) and the position of equilibrium (1) to shift to the **left** and AgCl dissolves completely.

- (b) When aqueous potassium iodide is added to aqueous silver nitrate, a yellow precipitate of silver iodide is formed:



The position of equilibrium (3) lies even further to the right as $K_{\text{sp}}(\text{AgCl}) > K_{\text{sp}}(\text{AgI})$. Precipitation of AgI occurs as ionic product $\gg K_{\text{sp}}(\text{AgI})$.

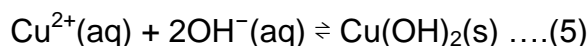
Unlike AgCl, the AgI precipitate **does not** dissolve in excess aqueous ammonia.



When excess NH_3 is added, the position of equilibrium (4) shifts to the **right** and $[\text{Ag}^+]$ decreases. This causes a **decrease** in the ionic product. While the ionic product decreases, it is **still higher** than $K_{\text{sp}}(\text{AgI})$ (as $K_{\text{sp}}(\text{AgI})$ is very small) and thus there is no dissolution of AgI in excess aqueous ammonia.

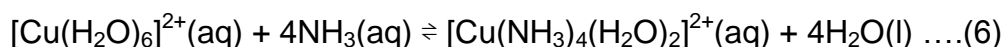
Since $K_{\text{sp}}(\text{AgCl}) > K_{\text{sp}}(\text{AgBr}) > K_{\text{sp}}(\text{AgI})$, AgI remains insoluble in dilute or concentrated NH_3 due to its extremely low K_{sp} . Even with low $[\text{Ag}^+]$, its ionic product still exceeds its K_{sp} .

- (c) When aqueous ammonia is added to aqueous copper(II) sulphate, a blue precipitate of copper(II) hydroxide is formed:



OH^- comes from the partial dissociation of NH_3 in water ($\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$). The position of equilibrium (5) lies far to the right. **Ionic product $> K_{\text{sp}}(\text{Cu}(\text{OH})_2)$** hence precipitation occurs

When **excess** aqueous ammonia is added, the precipitate dissolves to form a deep blue solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

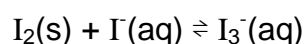


Increasing $[\text{NH}_3]$ by adding an excess causes the position of equilibrium (6) to shift to the **right**. This causes the **$[\text{Cu}^{2+}]$** or $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to **decrease**. The **ionic product $< K_{\text{sp}}(\text{Cu}(\text{OH})_2)$** and position of equilibrium (5) shifts to the **left** and $\text{Cu}(\text{OH})_2$ precipitate dissolves.

- (d) It is not always necessary that complex ions must involve metal cations.

The 'iodine solution' used in redox titrations is not exactly a solution of iodine in water since iodine is not very soluble in water.

An 'iodine solution' is made by dissolving iodine crystals in potassium iodide solution. The brown colour of the 'iodine solution' is due to the complex I_3^- .



I_2 is a covalent molecule, where the predominant intermolecular forces present is the weak van der Waals' forces and thus it is not very soluble in polar solvents such as water.

By reacting I_2 with I^- to form I_3^- , it converts I_2 into an ionic form which increases solubility in polar solvent greatly.

7 LIMITATION TO SOLUBILITY PRODUCT CONCEPT

The K_{sp} concept is valid only for saturated solution of sparingly soluble salts in which the total concentration of ions is no more than $0.0100 \text{ mol dm}^{-3}$.

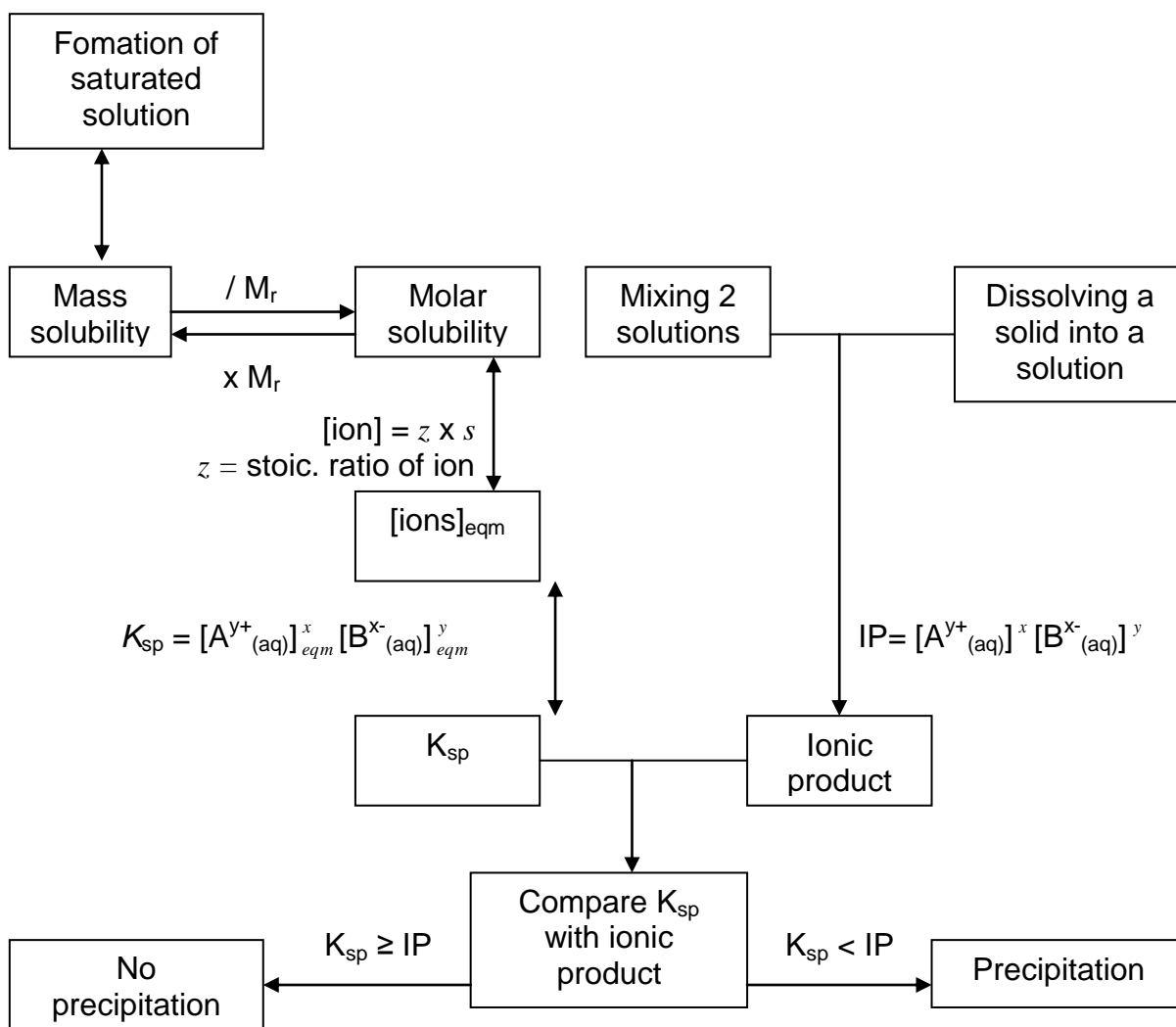
For higher concentration, inter-ionic attractions occur and K_{sp} is no longer constant (such solutions are no longer ideal).

8 SUMMARY

Comparing ionic product to K_{sp} ,

	Solution	Precipitation	Remarks
Ionic product $< K_{sp}$	Unsaturated	No	Further dissolution is possible
Ionic product $= K_{sp}$	Saturated	No	No further dissolution
Ionic product $> K_{sp}$	Saturated	Yes	No further dissolution

Flowchart



Solubility of Silver Halides in Ammonia

Halide	$Cl^-(aq)$	$Br^-(aq)$	$I^-(aq)$
Colour of halide	white	cream	yellow
solubility in excess dilute $NH_3(aq)$	soluble	insoluble	insoluble
solubility in excess concentrated $NH_3(aq)$	soluble	soluble	insoluble