Raffles Institution
Year 6 H2 Chemistry 2023
Lecture Notes 20 – Solubility Equilibria

A Contents

(a) Solubility product
(b) Common ion effect
(c) Complex ion formation

C Lecture Outline

1. Solubility
2. Solubility product
3. Ionic product and precipitation
4. Common ion effect
5. Formation of complex ions
6. Effect of pH
7. Limitations to solubility product concept

B Learning Outcomes

At the end of the lectures, you 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:
  - common ion effect
  - formation of complex ions, as exemplified by the reactions of halide ions with aqueous silver ions followed by aqueous ammonia

D References

1. Chemistry in Context by Hill & Holman
2. A level Chemistry by Ramsden
3. Chemistry: The Molecular Nature of Matter and Change by Martin S. Silberberg

1 Solubility

1.1 Defining solubility

- The maximum amount of solute which can dissolve in a given amount of solvent at a particular temperature is called the **solubility** of the solute in that solvent.
- A solution containing the maximum amount of solute that can be dissolved in the given amount of solvent is called a **saturated solution**.
- The solubility of a salt at a stated temperature can be expressed in various units, e.g.

Solubility may be expressed as:	Units
number of moles of solute dissolved in 1 dm^3 of solution	mol dm^{-3}
mass of solute dissolved in 1 dm^3 of solution	g dm^{-3}
mass of solute dissolved in 100 g of solvent	g per 100 g solvent
mass of solute dissolved in 10^6 g of solution	ppm (parts per million)

Worked example 1

If the solubility of Ag_2CrO_4 is 6.05×10^{-5} mol dm^{-3}, what is the concentration of each of its constituent ions in a saturated solution?

■ Solution ■

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

In a saturated solution of Ag_2CrO_4, $[Ag^+] = (2)(6.05 \times 10^{-5}) = \underline{\mathbf{1.21 \times 10^{-4}\ mol\ dm^{-3}}}$

$[CrO_4^{2-}] = \underline{\mathbf{6.05 \times 10^{-5}\ mol\ dm^{-3}}}$

1.2 Dissolution as an Equilibrium Process

Soluble salts

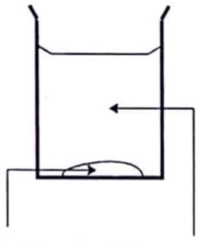
Soluble salts dissociate fully in solution into their constituent ions.

Example: $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$

Sparingly soluble salts

- When a small amount of a sparingly soluble ionic solid, MX, dissolves in water at a given temperature, an aqueous solution containing M^+ and X^- ions is formed.
- As more solid MX is added to the solution, the concentrations of the ions increase.
- Eventually, the solution becomes saturated, i.e. it contains the maximum amount of dissolved solute at that particular temperature in the presence of undissolved solute.
- At this point,
  - ⇒ The ions in the saturated solution are in **dynamic equilibrium** with the excess undissolved solid:

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



In a saturated solution, dissolution and precipitation occur at the **same rate**.

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

  - ⇒ The rate of the forward reaction equals rate of the backward reaction, and there is no net change in concentration of the ions.

2 Solubility Product

2.1 Defining the 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

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

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

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

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

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

- The solubility product, 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.
- Like other values of equilibrium constants, the value of K_{sp} varies only with temperature.

- The solubility products of some common compounds at 25 °C are shown below.

Compound	Solubility Product
$BaSO_4$	1.1×10^{-10} mol² dm⁻⁶
$BaCO_3$	2.6×10^{-9} mol² dm⁻⁶
$CaSO_4$	5.0×10^{-5} mol² dm⁻⁶
$CaCO_3$	3.4×10^{-9} mol² dm⁻⁶
$PbBr_2$	6.6×10^{-6} mol³ dm⁻⁹
$PbCl_2$	1.7×10^{-5} mol³ dm⁻⁹
PbI_2	9.8×10^{-9} mol³ dm⁻⁹

Compound	Solubility Product
AgCl	1.8×10^{-10} mol² dm⁻⁶
AgBr	5.4×10^{-13} mol² dm⁻⁶
AgI	8.5×10^{-17} mol² dm⁻⁶
NiS	4.0×10^{-21} mol² dm⁻⁶
ZnS	1.6×10^{-24} mol² dm⁻⁶
PbS	1.3×10^{-28} mol² dm⁻⁶
CuS	6.3×10^{-36} mol² dm⁻⁶

Worked example 2

Complete the table below.

Sparingly soluble salt	Equation for the solubility equilibrium	Expression for K_{sp}	Units for K_{sp}
$BaSO_4(s)$	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$	mol² dm⁻⁶
$Ag_2CrO_4(s)$	$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$	$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$	mol³ dm⁻⁹
$Ca_3(PO_4)_2(s)$	$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$	mol⁵ dm⁻¹⁵

2.2 Relationship between solubility and solubility product

- The solubility and solubility product of some compounds are shown below:

Compound	AgCl	AgBr	AgI	Ag_2CrO_4
K_{sp}	1.8×10^{-10} mol² dm⁻⁶	5.4×10^{-13} mol² dm⁻⁶	8.5×10^{-17} mol² dm⁻⁶	1.1×10^{-12} mol³ dm⁻⁹
Solubility / mol dm⁻³	1.34×10^{-5}	7.35×10^{-7}	9.22×10^{-9}	6.50×10^{-5}

- Note that:

Solubility product	Solubility
K_{sp} (AgCl) > K_{sp} (AgBr)	Solubility of AgCl > Solubility of AgBr
K_{sp} (AgBr) > K_{sp} (AgI)	Solubility of AgBr > Solubility of AgI
K_{sp} (AgCl) > K_{sp} (Ag_2CrO_4)	Solubility of AgCl < Solubility of Ag_2CrO_4

The information above illustrate the following points:

☑ Solubility products give a direct comparison of the solubility of two salts only if the total number of ions per unit formula of the compound produced in solution is the same in both cases, e.g. AgCl and AgBr (or AgBr and AgI).

⇒ In this 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 may not give a direct comparison of the solubility of the two salts. For such cases, the solubility of the two salts should be used for comparison.

2.3 Calculations of Solubility and Solubility Product

- The solubility of a sparingly soluble salt at a given temperature can be determined experimentally and the data obtained can be used to calculate the solubility product of the salt.

Worked Example 3 – *Calculating K_{sp} from solubility*

The solubility of silver sulfide, Ag_2S, is 2.48×10^{-15} mol dm^{-3} at 25 °C. Calculate its solubility product.

■ Solution ■

	$Ag_2S(s)$	$\rightleftharpoons$	$2Ag^+(aq)$	$+$	$S^{2-}(aq)$
eqm conc / mol dm^{-3}	–		$2(2.48 \times 10^{-15})$ $= 4.96 \times 10^{-15}$		2.48×10^{-15}

$$K_{sp} = [Ag^+]^2[S^{2-}] = (4.96 \times 10^{-15})^2(2.48 \times 10^{-15})$$

$$= \underline{\mathbf{6.10 \times 10^{-44}\ mol^3\ dm^{-9}}}$$

REMARKS

- Write down the eqm equation.
- $Ag_2S : Ag^+ : S^{2-}$
  $= 1 : 2 : 1$
- $[Ag^+] = 2[S^{2-}]$
- K_{sp} of a sparingly soluble compound is very small.

Worked Example 4 – *Calculating K_{sp} from solubility*

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

■ Solution ■

pOH = 14 – pH = 14 – 9.50 = 4.50

$[OH^-] = 10^{-4.50} = 3.16 \times 10^{-5}$ mol dm^{-3}

	$Fe(OH)_2(s)$	$\rightleftharpoons$	$Fe^{2+}(aq)$	$+$	$2OH^-(aq)$
eqm conc/ mol dm^{-3}	-		$(3.16 \times 10^{-5})/\ 2$ $= 1.58 \times 10^{-5}$		3.16×10^{-5}

$$K_{sp} = [Fe^{2+}][OH^-]^2 = (1.58 \times 10^{-5})\,(3.16 \times 10^{-5})^2$$

$$= \underline{\mathbf{1.58 \times 10^{-14}\ mol^3\ dm^{-9}}}$$

REMARKS

- Recall that
  pH + pOH = 14
  at 25 °C.
- Write down the eqm reaction.
- $Fe(OH)_2 : Fe^{2+} : OH^-$
  $= 1 : 1 : 2$
- $[Fe^{2+}] = ½\,[OH^-]$

Worked Example 5 – *Calculating solubility from K_{sp}*

Calculate the solubility of $Mg(OH)_2$ in water if the value of its K_{sp} at 25 °C is 6.3×10^{-10}.

■ Solution ■

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

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

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (s)(2s)^2$$

$$6.3 \times 10^{-10} = 4s^3$$

$$s = 5.40 \times 10^{-4}$$

Solubility of $Mg(OH)_2$ in water at 25 °C = $\underline{\mathbf{5.40 \times 10^{-4}\ mol\ dm^{-3}}}$

REMARKS

- When calculating solubility, "s" is usually used as the notation.
- Write down the eqm reaction.
- $[Mg^{2+}] = ½\,[OH^-]$

3 Ionic Product and Precipitation

3.1 Ionic Product

Consider a sparingly soluble ionic compound, $M_aX_b(s)$:

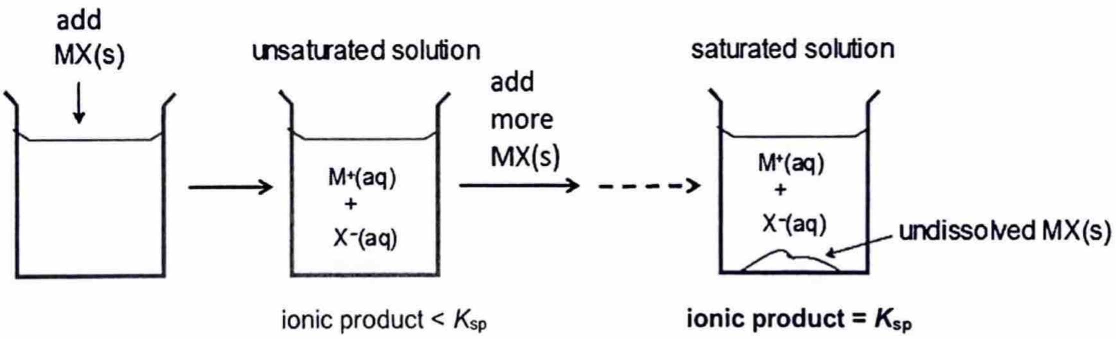
$$M_aX_b(s) \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$$

The ionic product is the product of the concentration of the constituent ions in the solution at that instant raised to the powers of the stoichiometric coefficients:

$$\boxed{\text{Ionic product} = [M^{b+}(aq)]^a[X^{a-}(aq)]^b}$$

Note:

- ☑ For K_{sp}, $[M^{b+}(aq)]$ and $[X^{a-}(aq)]$ are **equilibrium** concentrations of M^{b+} and X^{a-} in the presence of undissolved M_aX_b, i.e. a **saturated solution.**
- ☑ For ionic product, $[M^{b+}(aq)]$ and $[X^{a-}(aq)]$ are the **instantaneous** concentrations of M^{b+} and X^{a-}.
- ☑ In other words, the ionic product is a reaction quotient, Q, while K_{sp} is an equilibrium constant.
- ☑ **At equilibrium** (for a saturated solution with undissolved solid): $Q = K \Rightarrow$ **ionic product =** K_{sp}



- Consider the gradual addition of a sparingly soluble salt $M_aX_b(s)$ to water to form a solution. Before the solution becomes saturated with the salt, the added salt will dissolve and dissociate to form $M^{b+}(aq)$ and $X^{a-}(aq)$ ions.

- As more and more $M_aX_b(s)$ is added, the value of the ionic product for M_aX_b increases until it eventually reaches the value of the solubility product i.e. the solution becomes *just saturated* and further amount of $M_aX_b(s)$ added to the solution will no longer dissolve.

3.2 Predicting Precipitation using Ionic Product

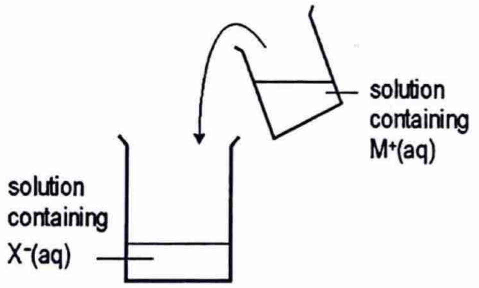
- When a known volume of a solution containing M^+ ions of known concentration is mixed with a known volume of a solution containing X^- ions of known concentration, we can predict whether precipitation will occur.

- This is done by calculating the value of the ionic product, $[M^+][X^-]$, and comparing it with the K_{sp} value of the salt. In this case, $[M^+]$ and $[X^-]$ in the ionic product expression refer to the initial concentrations of M^+ and X^- respectively in the resultant mixture upon mixing, assuming no precipitation occurs.

- The possible outcomes are summarised in the table below.

ionic product = $[M^+][X^-]$	Remarks	Precipitation?
ionic product < K_{sp}	Below saturation point. The solution is ***unsaturated***.	No
ionic product = K_{sp}	At saturation point The solution is ***just saturated***.	No
ionic product > K_{sp}	Beyond saturation point, precipitation of MX(s) occurs.	Yes Precipitation occurs until ionic product = K_{sp}.

- **Summary**



When mixing two solutions of known volumes and concentrations, e.g. M^+(aq) and X^-(aq),

1. Calculate the
   initial $[M^+]$ upon mixing
   initial $[X^-]$ upon mixing
   } use these values to calculate ionic product of the salt
   Note: total volume has increased
2. Precipitation will occur only if ionic product > K_{sp}

Worked Example 6 – *Predicting the formation of a precipitate given the K_{sp} value*

50 cm^3 of 0.010 mol dm^{-3} $AgNO_3$ solution is added to 50 cm^3 of 0.020 mol dm^{-3} HCl solution. Will precipitation occur? (K_{sp} of $AgCl$ = 1.8×10^{-10} mol^2 dm^{-6})

■ Solution ■

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

$[Ag^+] = (\tfrac{1}{2})(0.010) = 5.00 \times 10^{-3}$ mol dm^{-3}

$[Cl^-] = (\tfrac{1}{2})(0.020) = 1.00 \times 10^{-2}$ mol dm^{-3}

Ionic product $AgCl$ = $[Ag^+][Cl^-] = (5.00 \times 10^{-3})(1.00 \times 10^{-2})$

$= 5.00 \times 10^{-5}$ mol^2 dm^{-6}

Since ionic product > K_{sp} of $AgCl$, precipitation of $AgCl$ will occur.

REMARKS

- Calculate the concentrations of both ions after mixing, taking into account the total volume of solution.
- Use the initial concentrations to calculate ionic product.

Worked Example 7 – *Predicting the formation of a precipitate given the K_{sp} value*

10 cm^3 of 0.0020 mol dm^{-3} $AgNO_3$ solution is added to 600 cm^3 of 0.0005 mol dm^{-3} K_2CrO_4(aq). Will precipitation occur? (K_{sp} of Ag_2CrO_4 = 1.1 x 10^{-12} mol^3 dm^{-9})

■ Solution ■

Calculate ionic product of Ag_2CrO_4

$$[Ag^+] = \boxed{\frac{n_{Ag^+}}{V_{total}}} = \frac{(0.010)(0.0020)}{0.010 + 0.600} = 3.279 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[CrO_4^{2-}] = \boxed{\frac{n_{CrO_4^{2-}}}{V_{total}}} = \frac{(0.600)(0.0005)}{0.010 + 0.600} = 4.918 \times 10^{-4} \text{ mol dm}^{-3}$$

solution diluted after mixing

$$Ag_2CrO_4\text{ (s)} \rightleftharpoons 2Ag^+\text{(aq)} + CrO_4^{2-}\text{(aq)}$$

$$\begin{aligned}\text{ionic product of } Ag_2CrO_4 &= [Ag^+]^2[CrO_4^{2-}] \\ &= (3.279 \times 10^{-5})^2 (4.918 \times 10^{-4}) \\ &= 5.29 \times 10^{-13} \text{ mol}^3 \text{ dm}^{-9}\end{aligned}$$

Since ionic product < K_{sp} of Ag_2CrO_4, precipitation of Ag_2CrO_4 will not occur.

Worked Example 8 – *Minimum concentration of ions required for precipitate formation*

Wash water from a factory was suspected to contain Pb^{2+} ions. 1 cm^3 of 0.50 mol dm^{-3} KI(aq) was added to 10 cm^3 of the wash water. What is the concentration of Pb^{2+} ions in the wash water which when exceeded would cause yellow PbI_2(s) to be observed? (K_{sp} of PbI_2 = 9.8 x 10^{-9} mol^3 dm^{-9})

■ Solution ■

Let the minimum concentration of Pb^{2+}(aq) be s mol dm^{-3}.

$$[Pb^{2+}\text{(aq)}] = \frac{10 \times 10^{-3} \times s}{(1+10) \times 10^{-3}} = 0.9091s \text{ mol dm}^{-3}$$

$$[I^-\text{(aq)}] = \frac{1 \times 10^{-3} \times 0.5}{(1+10) \times 10^{-3}} = 0.04545 \text{ mol dm}^{-3}$$

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

$$\text{Ionic product} = [Pb^{2+}][I^-]^2 = (0.9091s)(0.04545)^2 = (1.878 \times 10^{-3})\text{ s mol}^3\text{ dm}^{-9}$$

For yellow PbI_2(s) to be observed

ionic product > K_{sp}

$$\begin{aligned}(1.878 \times 10^{-3})\text{ s} &> 9.8 \times 10^{-9} \\ \text{s} &> 5.22 \times 10^{-6}\end{aligned}$$

For yellow PbI_2(s) to be observed, the concentration of Pb^{2+}(aq) that has to be exceeded is **5.22 x 10^{-6} mol dm^{-3}**.

REMARKS

- Define unknown concentration.
- Remember to take into account the total volume of solution when calculating the initial concentrations upon mixing.
- Use the initial concentrations to calculate ionic product.

Worked Example 9 – *Given two ions which can form a precipitate on the addition of another ion, predict which ion will form a precipitate first.*

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

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

(b) Calculate the concentration of $Ag^+(aq)$ in the solution when PbI_2 starts to precipitate out.
(Given K_{sp} of AgI = 8.5×10^{-17} mol^2 dm^{-6} and K_{sp} of PbI_2 = 9.8×10^{-9} mol^3 dm^{-9})

■ Solution ■

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

K_{sp} of AgI = $[Ag^+(aq)][I^-(aq)]$

To precipitate AgI

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

K_{sp} of AgI = $[Ag^+][I^-]$

min $[I^-]$ = K_{sp} of AgI / $[Ag^+]$

= $(8.5 \times 10^{-17}) / (2.0 \times 10^{-4})$

= **4.25×10^{-13} mol dm^{-3}**

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

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

To precipitate PbI_2

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

K_{sp} of PbI_2 = $[Pb^{2+}][I^-]^2$

$$\text{min } [I^-] = \sqrt{\frac{K_{sp} \text{ of } PbI_2}{[Pb^{2+}]}} = \sqrt{\frac{9.8 \times 10^{-9}}{1.5 \times 10^{-3}}}$$

= **2.56×10^{-3} mol dm^{-3}**

Since the minimum $[I^-(aq)]$ required to ppt out AgI is less than that needed to ppt out PbI_2, **AgI will ppt out first**.

(b) From (a), **when $PbI_2(s)$ starts to ppt out,**

$[I^-(aq)]$ = 2.56×10^{-3} mol dm^{-3} (from part (a))

$$\text{At this } [I^-(aq)],\ [Ag^+] = \frac{K_{sp} \text{ of AgI}}{[I^-(aq)]} = \frac{8.5 \times 10^{-17}}{2.56 \times 10^{-3}}$$

= **3.32×10^{-14} mol dm^{-3}**

REMARKS

- Write down the eqm equations.
- Calculate the min. $[I^-(aq)]$ required for precipitation to occur and compare.
- Calculate the $[I^-(aq)]$ when PbI_2 starts to precipitate.
- Then determine $[Ag^+(aq)]$ using K_{sp} of AgI.

4 Common Ion Effect

- The common ion effect refers to the reduced solubility of a salt in a solution that already contains an ion common to that salt.
- Consider the dissolution of silver chloride, a sparingly soluble ionic compound, in water. The following equilibrium is established in a saturated solution of silver chloride.

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

① What happens when some NaCl(s), a soluble salt, is added to the saturated solution of AgCl?

- The added NaCl(s) dissolves in the solution and dissociates completely.
- Thus, the $[Cl^-]$ in the solution *increases momentarily*.
  (Note: In this case **Cl^- is the common ion**. It is common to both the AgCl and the NaCl.)
- This causes the equilibrium position of the above reaction to shift left in accordance to Le Chatelier's principle.
- This leads to the precipitation of some AgCl and a decrease in the $[Ag^+]$.
- Hence, the solubility of AgCl decreases in the presence of NaCl.

② What happens when some $AgNO_3(s)$, a soluble salt, is added to a saturated solution of AgCl?

- The added $AgNO_3(s)$ dissolves in the solution and dissociates completely.
- Thus, the $[Ag^+]$ in the solution *increases momentarily*.
  (Note: In this case **Ag^+ is a common ion** . It is common to both the AgCl and the $AgNO_3$.)
- This causes the equilibrium position of the above reaction to shift left in accordance to Le Chatelier's principle.
- This leads to the precipitation of some AgCl and a decrease in the $[Cl^-]$.
- Hence, the solubility of AgCl decreases in the presence of $AgNO_3$.

Worked Example 10 – *Calculation of solubility in the presence of a common ion*

Lead iodide, PbI_2, is a yellow precipitate and its K_{sp} value is 9.8×10^{-9} at 25 °C.

(a) Calculate the solubility of lead iodide in water at 25 °C.

(b) Calculate the solubility of lead iodide in 1.0 mol dm^{-3} NaI(aq).

■ **Solution** ■	**REMARKS**
(a) Let x mol dm^{-3} be the solubility of PbI_2 in water.	• Define unknown.
$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$	• Write down the eqm reaction.
$K_{sp} = [Pb^{2+}][I^-]^2 = x(2x)^2$	• $[Pb^{2+}] = ½\,[I^-]$
$9.8 \times 10^{-9} = 4x^3$	
x = **1.35×10^{-3} mol dm^{-3}**	

(b) Let y mol dm^{-3} be the solubility of PbI_2 in 1.0 mol dm^{-3} NaI(aq).

$$NaI(aq) \longrightarrow Na^+(aq) + \underset{1.0\ \text{mol dm}^{-3}}{I^-(aq)}$$

Let **y** mol dm^{-3} be the solubility of PbI_2 in the solution.

	$PbI_2(s)$	⇌	$Pb^{2+}(aq)$	+	$2I^-(aq)$
eqm conc/ mol dm^{-3}	-		**y**		**2y + 1.0**

$K_{sp} = [Pb^{2+}][I^-]^2 = (y)(2y + 1.0)^2$

*assumption

PbI_2 is sparingly soluble, **y** is small; hence $(2y + 1.0) \approx 1.0$

$K_{sp} = [Pb^{2+}][I^-]^2 = (y)(1.0)^2$

$K_{sp} = y = 9.8 \times 10^{-9}$

Solubility of PbI_2 in 1.0 mol dm^{-3} NaI(aq) = **9.8×10^{-9} mol dm^{-3}**

- NaI(aq) is a strong electrolyte and dissociates completely.
- I^-(aq) is the common ion.
- Use approximation since, from **(a)**, $1.35 \times 10^{-3} \ll 1.0$.

5 Formation of complex ions

5.1 Solubility Product and Complex ion formation

- 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 contains a central metal ion linked to one or more surrounding ions or molecules (called ligands) by dative covalent bonds. (Refer to the lectures notes on Transition Metals for more details.)

  Examples of some common complex ions:

$[Zn(OH)_4]^{2-}$	$[Ag(NH_3)_2]^+$	$[CuCl_4]^{2-}$
$[Al(OH)_4]^-$	$[Zn(NH_3)_4]^{2+}$	$[Cu(NH_3)_4]^{2+}$

Worked Example 11

Explain why the sparingly soluble salt AgC*l* is soluble in aqueous ammonia.
(*Refer to section 5.2 for comparison of solubility of silver halides in aqueous ammonia.)*

■ Solution ■

When AgC*l*(s) is added to water to form a saturated solution, the following equilibrium is established:

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

When aqueous ammonia is added, a complex ion, **$[Ag(NH_3)_2]^+$** is formed and the following equilibrium is established:

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ ....(2)
diamminesilver(I) ion

The formation of $[Ag(NH_3)_2]^+$ decrease the concentration of uncomplexed Ag^+ ions in the solution.

To counteract the decrease in $[Ag^+]$, the equilibrium position of reaction (1) shifts right, resulting in AgC*l* dissolving. With more aqueous ammonia added, the equilibrium position of reaction (2) shifts right. This in turn causes the equilibrium position of reaction (1) to shift right.

With sufficient NH_3(aq) added, the ionic product, $[Ag^+][Cl^-]$, will be less than K_{sp} and hence all the AgC*l* eventually dissolves.

Worked Example 12

When dilute hydrochloric acid was added to a saturated solution of lead(II) chloride containing undissolved solid lead(II) chloride, more $PbCl_2$ solid was formed. However, when concentrated hydrochloric acid was added until in excess to the same solution, all the $PbCl_2$ dissolved. Explain these observations.

■ Solution ■

In a saturated solution of $PbCl_2$ with undissolved $PbCl_2(s)$, the following equilibrium was established:

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

When dilute HCl was added, the Cl^- ions from HCl (a strong acid) exerts a **common ion effect** and caused the equilibrium position of reaction (1) to shift left. Hence, some $PbCl_2$ solid was formed, as the solubility of $PbCl_2$ is reduced.

However, when concentrated hydrochloric acid was added to the saturated solution, the high $[Cl^-]$ present led to the **formation of the complex ion, $[PbCl_4]^{2-}$**, and the following equilibrium was established:

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

The formation of $[PbCl_4]^{2-}$ decreased the concentration of uncomplexed $Pb^{2+}(aq)$ ions in the solution.

To counteract the decrease in $[Pb^{2+}]$, the equilibrium position of reaction (1) shifts right, resulting more $PbCl_2$ dissolving. With more hydrochloric acid added, the equilibrium position of reaction (2) shifts right. This in turn caused the equilibrium position of reaction (1) to shift right.

With sufficient HCl added, the ionic product, $[Pb^{2+}][Cl^-]^2$, will be less than K_{sp} and hence all the $PbCl_2$ eventually dissolved.

Worked Example 13

When aqueous ammonia is added gradually to a solution of Cu^{2+} ions, a blue precipitate of $Cu(OH)_2$ is first formed and this dissolves in excess aqueous ammonia to form a dark blue solution. Explain these observations.

■ Solution ■

$NH_3(aq)$ is a weak base which undergoes hydrolysis to produce OH^- ions.

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

When $NH_3(aq)$ is added to $Cu^{2+}(aq)$, the $[OH^-]$ in the Cu^{2+} solution is Increased and this makes the ionic product of $Cu(OH)_2$ Exceed the K_{sp} of $Cu(OH)_2$. Therefore, a blue precipitate of $Cu(OH)_2$ is formed and the following equilibrium is established:

$$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) \text{ ……….(1)}$$

When excess $NH_3(aq)$ is next added, the **complex ion, $[Cu(NH_3)_4]^{2+}$, is formed** and the following equilibrium is established:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{dark blue solution}}{[Cu(NH_3)_4]^{2+}(aq)} \text{ ……….(2)}$$

The formation of $[Cu(NH_3)_4]^{2+}$ Decreases the concentration of uncomplexed Cu^{2+} ions in the solution.

To counteract the decrease in $[Cu^{2+}]$, the equilibrium position of reaction (1) shifts Left, resulting in more $Cu(OH)_2$ dissolving, i.e. the blue precipitate dissolves.

With sufficient $NH_3(aq)$ added, the ionic product, $[Cu^{2+}][OH^-]^2$, will be Less than K_{sp} and hence, all the $Cu(OH)_2$ eventually dissolves to form the dark blue solution containing $[Cu(NH_3)_4]^{2+}$ ions.

Note: Refer to lecture notes on Transition Metals for more details of this example.

5.2 Solubility of Silver Halide Precipitates

- The behaviour of halide ions in $AgNO_3(aq)$ followed by $NH_3(aq)$ or conc. NH_3 is summarised here *(you can also refer to Section 9.2 of The Periodic Table II notes).*

		$Cl^-(aq)$	**$Br^-(aq)$**	**$I^-(aq)$**
Step 1	Add $AgNO_3(aq)$	white ppt of AgCl	pale cream ppt of AgBr	yellow ppt of AgI
Step 2	Add excess $NH_3(aq)$	ppt soluble	ppt partially soluble	ppt insoluble
	Add conc. NH_3	ppt soluble	ppt soluble	ppt insoluble

- In the qualititative analysis of halides (Cl^-, Br^- and I^-), $AgNO_3(aq)$ is added to the halide to form the silver halide ppt. NH_3 is subsequently added to test the solubility of the silver halide ppt in NH_3 (dilute or concentrated).

- Why do silver halides have different solubility in excess $NH_3(aq)$?

	K_{sp} values at 25°C / mol² dm⁻⁶
AgC*l*	1.8×10^{-10}
AgBr	5.4×10^{-13}
AgI	8.5×10^{-17}

Note:
AgF is very soluble in water.

$$AgX(s) \rightleftharpoons Ag^+(aq) + X^-(aq) \qquad K_{sp} \text{ of } AgX = [Ag^+(aq)][X^-(aq)]$$

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

- The K_{sp} value of AgI(s) is extremely **low** ⇒ easily exceeded.
- Even though $[Ag^+]$ is decreased (due to the formation of $[Ag(NH_3)_2]^+$) when $NH_3(aq)$ is being added, the added $NH_3(aq)$ cannot sufficiently lower $[Ag^+]$ to the extent where the ionic product is less than K_{sp}. As such, the **ionic product of AgI <u>will not fall</u> below its K_{sp}.**

  ⇒ Hence, AgI(s) remain insoluble even if excess $NH_3(aq)$ is added.

- The K_{sp} value of AgC*l*(s) is much higher than that of AgI(s). When excess $NH_3(aq)$ is added, $[Ag^+(aq)]$ decreases and the **ionic product of AgC*l* becomes smaller than its K_{sp}.**

  ⇒ Hence, AgC*l*(s) becomes soluble in excess $NH_3(aq)$.

- Since K_{sp} of AgBr is in between that of AgC*l* and AgI, AgBr is only partially soluble in excess $NH_3(aq)$.

6 Effect of pH

The solubility of sparingly soluble salts containing basic anions (i.e. conjugate bases of weak acids) are affected by the pH of the solution.

For a sparingly soluble salt containing the conjugate base of a weak acid, the solubility of the salt in an aqueous solution is often increased when a strong acid is added.

Worked Example 14

Calcium phosphate, a sparingly soluble salt, is soluble in dilute hydrochloric acid. Explain.

■ Solution ■

When calcium phosphate is added into water to form a saturated solution, the following equilibrium is established:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Since PO_4^{3-} is a conjugate base of a weak acid, it reacts with H^+ ions from HC*l* to establish the equilibria shown below, forming H_3PO_4, a weak acid.

$$PO_4^{3-}(aq) + H^+(aq) \rightleftharpoons HPO_4^{2-}(aq) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$
$$HPO_4^{2-}(aq) + H^+(aq) \rightleftharpoons H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) + H^+(aq) \rightleftharpoons H_3PO_4(aq)$$

This decreases the concentration of $PO_4^{3-}(aq)$ ions in the solution.

To counteract the decrease in $[PO_4^{3-}(aq)]$, the equilibrium position of reaction (1) shifts right, resulting in the dissolution of $Ca_3(PO_4)_2$. With more hydrochloric acid added, the equilibrium position of reaction (2) shifts right. This, in turn, causes the equilibrium position of reaction (1) to shift right.

With sufficient HC*l* added, the ionic product, $[Ca^{2+}]^3\,[PO_4^{3-}]^2$, will be less than K_{sp} and hence all the $Ca_3(PO_4)_2$ eventually dissolves.

7 Limitations to the Solubility Product Concept

- The solubility product concept is typically only used for "insoluble" compounds, i.e. the numerical value of solubility products is always very small, rarely exceeding 10^{-4}. It is not appropriate to use the solubility product concept for soluble compounds such as NaC*l*, $CuSO_4$ and $AgNO_3$.

- The solubility product of a sparingly soluble salt is essentially an equilibrium constant. Like other equilibrium constants, its value will change with temperature. Consequently, the temperature at which a solubility product is measured should always be specified unless it relates to the temperature 298 K under standard conditions.

- Note: Unlike solubility product, solubility is affected by temperature *and* concentrations of ions which are affected by common ions, complex formation and pH.

Summary – Solubility Equilibria

Solubility Equilibrium

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

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

e.g. $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{-}(aq)$

Solubility product (K_{sp})

For a saturated solution in equilibrium with undissolved solid, the solubility product, K_{sp}, is defined as

$$\mathbf{K_{sp} = [M^{b+}(aq)]^a\,[X^{a-}(aq)]^b}$$

e.g. $K_{sp} = [Zn^{2+}(aq)]\,[OH^{-}(aq)]^2$

The concentration used is the concentration of the constituent ions at equilibrium.

Ionic product (IP)

At any instant, we define the ionic product as

ionic product = $\mathbf{[M^{b+}(aq)]^a\,[X^{a-}(aq)]^b}$

e.g. ionic product = $[Zn^{2+}(aq)]\,[OH^{-}(aq)]^2$

The concentration used is the concentration of the constituent ions at that instant.

Solubility

Solubility of two salts cannot be compared by just comparing their K_{sp}, unless the total number of ions per unit formula of the compound produced in solution is the same.

If the salt has solubility *s* mol dm^{-3}, K_{sp} is related to *s* by:

$$\mathbf{K_{sp} = (as)^a \times (bs)^b}$$

e.g. If $Zn(OH)_2$ has solubility *s* mol dm^{-3},
$K_{sp} = (s) \times (2s)^2 = 4s^3$

Predicting precipitation

- If **ionic product < K_{sp}**, solution is *not saturated* and **no precipitation** occurs.
- If **ionic product = K_{sp}**, solution is *just saturated* but **no precipitation** occurs.
- If **ionic product > K_{sp}**, solution is *saturated* and **precipitation** occur **until ionic product = K_{sp}**.

Solubility of sparingly soluble salt

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

When $[M^{b+}]$ or $[X^{a-}]$ increases, position of equilibrium shifts left

Solubility decreases

Common ion effect

$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{-}(aq)$ (1)

When a common ion, i.e. Zn^{2+} or OH^{-}, is added, position of equilibrium (1) shifts left. Hence, more $Zn(OH)_2(s)$ is produced, i.e. solubility of $Zn(OH)_2$ decreases.

When $[M^{b+}]$ or $[X^{a-}]$ decreases, position of equilibrium shifts right

Solubility increases

Complex ion effect

$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{-}(aq)$ (1)

When excess $OH^{-}(aq)$ is added,
$Zn^{2+}(aq) + 4OH^{-}(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$

Formation of the complex ion decreases $[Zn^{2+}]$. Position of equilibrium (1) shifts right. Hence, more $Zn(OH)_2(s)$ can be dissolved, i.e. solubility of $Zn(OH)_2$ increases.

Acid-base reaction

$ZnCO_3(s) \rightleftharpoons Zn^{2+}(aq) + CO_3^{2-}(aq)$ (2)

When a strong acid is added,
$CO_3^{2-}(aq) + H^{+}(aq) \rightleftharpoons HCO_3^{-}(aq)$

CO_3^{2-} reacts with H^{+} and $[CO_3^{2-}]$ decreases. Position of equilibrium (2) shifts right. Hence, more $ZnCO_3(s)$ can be dissolved, i.e. solubility of $ZnCO_3$ increases.

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Year 6 H2 Chemistry 2023
Tutorial 20: Solubility Equilibria

Self–Check Questions

1 **(a)** *[IVY Solubility Equilibria Check Point 1 (Question 1)]*
The solubility of Ag_3PO_4 in pure water at 25 °C is 6.7 x 10^{-2} g dm^{-3}.
Calculate its K_{sp} at 25 °C.

(b) *[IVY Solubility Equilibria Check Point 1 (Question 2)]*
The K_{sp} of MgF_2 is 6.4 x 10^{-9} mol^3 dm^{-9}. Calculate its solubility in g dm^{-3}.

(c) The numerical value of K_{sp} for calcium phosphate is 1.0 x 10^{-26}.
Calculate the concentration of Ca^{2+} ions in a saturated solution of calcium phosphate.

2 *[IVY Solubility Equilibria Check Point 2]*
Predict whether precipitation will be observed when 0.5 dm^3 of 0.005 mol dm^{-3} $CaCl_2$(aq) and 0.25 dm^3 of 0.012 mol dm^{-3} Na_2SO_4(aq) are mixed. Explain your answer.
(K_{sp} of $CaSO_4$ = 2.4 x 10^{-5} mol^2 dm^{-6})

3 Given that the numerical value of the K_{sp} for $Ca(OH)_2$ is 6.5 x 10^{-6}, predict whether precipitation will be observed when each of the following solutions is added to separate test-tubes containing 2 cm^3 of 0.50 mol dm^{-3} $CaCl_2$(aq).

(a) 1 cm^3 of 2.0 mol dm^{-3} NaOH(aq),

(b) 1 cm^3 of 2.0 mol dm^{-3} NH_3(aq). (K_b of NH_3 = 1.74 x 10^{-5} mol dm^{-3})

Practice Questions

4 **(a)** The solubility product of lead(II) iodide at 298 K is 7.1 x 10^{-9} mol^3 dm^{-9}. At 298 K, calculate the solubility of lead(II) iodide in

(i) water,

(ii) 0.10 mol dm^{-3} BaI_2 solution,

(iii) 0.20 mol dm^{-3} $Pb(NO_3)_2$ solution.

(b) When solid lead(II) iodide was shaken with a solution of potassium iodide, its solubility was found to be 1.0 x 10^{-4} mol dm^{-3}.

(i) Calculate the concentration of the potassium iodide solution.

(ii) Suggest a reason for the increased solubility when lead(II) iodide was shaken with a large excess of potassium iodide as compared with water.

5 **N16/I/13 (Modified)**

Values of two solubility products are given.

$$K_{sp}\ (ZnF_2) = 3.2 \times 10^{-2}\ mol^3\ dm^{-9}$$
$$K_{sp}\ (BaF_2) = 1.6 \times 10^{-7}\ mol^3\ dm^{-9}$$

Solid zinc fluoride is shaken with water. The remaining solid is filtered off, leaving a saturated solution **X**. Drops of dilute aqueous barium nitrate are added to solution **X** until barium fluoride just precipitates.

(a) Calculate the concentration of $F^-(aq)$ in the saturated solution **X** before the addition of barium nitrate.

(b) Calculate the $[Ba^{2+}(aq)]$ in solution **X** when BaF_2 just precipitates.

6 The numerical values of the solubility products of some Group 2 fluorides, at 25 °C, are given in the table below.

	Numerical values of K_{sp}
BaF_2	1.84×10^{-7}
CaF_2	3.45×10^{-11}

A student accidentally mixed 25.0 cm^3 of 0.100 mol dm^{-3} $CaCl_2$ solution with 25.0 cm^3 of 0.100 mol dm^{-3} $BaCl_2$ solution in the laboratory. To separate the two metal ions, he added just enough solid KF to precipitate the maximum amount of CaF_2 from the mixture, without precipitating BaF_2.

(a) Determine the concentration of F^- in the solution at the end of the separation.

(b) Determine the concentration of Ca^{2+} remaining in the solution.

(c) Calculate the percentage of Ca^{2+} remaining in the solution and comment on the effectiveness of the separation.

7 Calcium hydroxide is a sparingly soluble ionic compound.

(a) Write an expression for the K_{sp} of calcium hydroxide.

(b) The K_{sp} of calcium hydroxide may be determined using a titrimetric method. In a particular experiment, an excess of solid calcium hydroxide was shaken with 0.010 mol dm^{-3} aqueous sodium hydroxide and allowed to reach equilibrium at 298 K. Then the mixture was filtered. 25.0 cm^3 of the filtrate was completely neutralised by 20.0 cm^3 of 0.050 mol dm^{-3} hydrochloric acid. Calculate, at 298 K,

(i) the concentration of OH^- in the filtrate.

(ii) the solubility product of calcium hydroxide.

(c) Equal volumes of NaOH(aq) and 0.010 mol dm^{-3} $Ca(OH)_2$(aq) were mixed at 298 K. Using your answer in **(b)(ii)**, determine the concentration of NaOH(aq) which, when exceeded, would bring about the precipitation of calcium hydroxide.

(d) Solid calcium nitrate is added to a saturated solution of calcium hydroxide at 25 °C. State and explain the effect (if any) on the K_{sp} value and solubility of calcium hydroxide.

(e) A saturated solution of calcium hydroxide is found to have a pH of 12.3 at 25 °C and a pH of 11.7 at 32 °C. [K_w (at 32 °C) = 1.70×10^{-14} mol^2 dm^{-6}]

(i) Calculate the concentrations of OH^- ions present in the saturated solution of calcium hydroxide at 25 °C and 32 °C respectively.

Explain whether the dissolution of calcium hydroxide in water is exothermic or endothermic.

(ii) Hence, state how the K_{sp} value of calcium hydroxide changes when temperature is increased.

(iii) A saturated solution of calcium hydroxide was diluted at 32 °C to a volume **V**. Sketch a graph to show how the pH of the solution varies with the volume of water added. Include any relevant pH values in your graph.

(f) State a use of calcium hydroxide which depends on its solubility in water.

8 Explain each of the following observations using the concept of equilibrium. Include relevant chemical equations in your answer.

(a) Explain why $BaCO_3$ is soluble in dilute hydrochloric acid but $BaSO_4$ is not.

(b) The addition of aqueous ammonia to aqueous magnesium chloride gives a white precipitate that is readily soluble in aqueous ammonium chloride.

(c) The gradual addition of aqueous ammonia to a solution of Zn^{2+} ions gives a white precipitate initially. When excess aqueous ammonia is added, the precipitate dissolves to form a colourless solution.

9 When aqueous silver nitrate is added to aqueous potassium chloride, a white precipitate is formed which dissolves in an excess of aqueous ammonia. The subsequent addition of aqueous sodium bromide causes the precipitation of a pale cream solid. The pale cream precipitate dissolves when aqueous sodium cyanide is added.

Explain the above observations and write balanced equations for the reactions that occur.

10 **N12/II/Q3(d)**

Selective precipitation of sulfides may be used to separate the cations present in a solution containing Cu^{2+}, Ni^{2+}, and Zn^{2+}.

The reagent used is hydrogen sulfide which behaves as a dibasic (diprotic) weak acid when in aqueous solution.

$$H_2S(g) + aq \rightleftharpoons H^+(aq) + HS^-(aq) \qquad K_a = 9.1 \times 10^{-8} \text{ mol dm}^{-3}$$

and

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \qquad K_a = 1.0 \times 10^{-15} \text{ mol dm}^{-3}$$

Metal sulfides are precipitated by the following reaction.

$$M^{2+}(aq) + S^{2-}(aq) \longrightarrow MS(s)$$

Relevant K_{sp} values are given in the table.

salt	K_{sp} / mol^2 dm^{-6}
CuS	6.3×10^{-36}
NiS	4.0×10^{-21}
ZnS	1.6×10^{-24}

The results of passing hydrogen sulfide through separate solutions of Cu^{2+}, Ni^{2+}, and Zn^{2+} are shown in the table below.

M^{2+} being tested	H_2S passed through an acidic solution of M^{2+}	H_2S passed through a neutral solution of M^{2+}	H_2S passed through an alkaline solution of M^{2+}
Cu^{2+}	black precipitate of CuS	black precipitate of CuS	black precipitate of CuS
Ni^{2+}	no precipitate	no precipitate	black precipitate of NiS
Zn^{2+}	no precipitate	white precipitate of ZnS	white precipitate of ZnS

Use the data above to give an explanation for each of the following questions.
You should give equations where appropriate. You are **not** expected to do any calculations in this part.

(a) Why is CuS the only sulfide of these three precipitated in acid solution? [2]

(b) Why is NiS precipitated in alkaline solution and not in neutral or acidic solution? [2]

(c) Why is ZnS precipitated in both neutral and alkaline solution? [2]