Solubility and complex ions.

The following information will be provided in the Resource Booklet from 2020

Complex ions for 91392: *Demonstrate understanding of equilibrium principles in aqueous systems*

$[Ag(CN)_2]^-$	$[Ag(NH_3)_2]^+$
$[Al(OH)_4]^-$	$[Cu(NH_3)_4]^{2+}$
$[Pb(OH)_4]^{2-}$	$[Zn(OH)_4]^{2-}$
$[Zn(NH_3)_4]^{2+}$	$[Ni(NH_3)_6]^{2+}$
$[Ni(CN)_4]^{2-}$	

Write the equation for the equilibrium occurring in a saturated solution of zinc hydroxide, $Zn(OH)_2$.

- *Identify type as AB, A_2B or AB_2*
- *Think about the charges on the ions*
- *Write the equation – do NOT write $Zn(OH)_2$ + H_2O ⇌*
- *Use the correct ⇌ arrow*
- *State symbols not essential (based on evidence from schedule)*

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

Write the expression for K_s $(Zn(OH)_2)$.

- *Identify type as AB, A_2B or AB_2*
- *It is AB_2, cation : anion ratio is 1:2*

$$K_s = [Zn^{2+}][OH^-]^2$$

Calculate the solubility of $Zn(OH)_2$ in water at 25°C, and give the $[Zn^{2+}]$ and $[OH^-]$ in the solution.

K_s $(Zn(OH)_2) = 3.80 \times 10^{-17}$.

Let solubility be ‘s’:

$[Zn^{2+}]$ = s and $[OH^-]$ = 2s

Since $K_s = [Zn^{2+}][OH^-]^2$, $K_s = s \times (2s)^2 = 4s^3$

Or

- *Recognising AB_2 type solid, and using the formula sheet, $K_S = 4s^3$*
- *Rearranging so $s = \sqrt[3]{\frac{K_S}{4}}$*
- *Realising that concentration of OH^- ions is double that of Zn^{2+} ions because every $Zn(OH)_2$ that dissolves forms 1 x Zn^{2+} ion and 2 x OH^- ions*
- *Remember the units of solubility are mol L^{-1}, when s is found here*

$K_S = 4s^3$

$3.80 \times 10^{-17} = 4s^3$

$$s = \sqrt[3]{\frac{3 \cdot 80 \times 10^{-17}}{4}}$$

s = 2.12×10^{-6} mol L^{-1}

$[Zn^{2+}] = 2.12 \times 10^{-6}$ mol L^{-1}

$[OH^-] = 4.24 \times 10^{-6}$ mol L^{-1}

The presence of a common ion decreases the solubility of a sparingly soluble solid, such as $Zn(OH)_2$.

Calculate the concentration of the hydroxide ions, OH^-, in solution after 25.0 mL of 0.210 mol L^{-1} zinc chloride, $ZnCl_2$, solution was added to 25.0 mL of a saturated $Zn(OH)_2$ solution

- *Identify that the common ion here (ion in common) is OH^- as it is in Zn(<u>OH</u>)$_2$ and Na<u>OH</u>*
- *Realise that the $[Zn^{2+}]$ from the 0.210 mol L^{-1} zinc chloride, $ZnCl_2$, solution is far greater than the $[Zn^{2+}]$ from $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$, so the small amount from the $Zn(OH)_2$ dissolving can be ignored*
- *Recall that the numerical value of K_s is a constant (@ 25°C)*

$K_S = [Zn^{2+}][OH^-]^2$

$3.80 \times 10^{-17} = 0.210/2 \times [OH^-]^2$

Note: divide by 2 due to dilution factor from adding two solutions together of equal volumes.

$3.80 \times 10^{-17} = 0.105 \times [OH^-]^2$

$3.80 \times 10^{-17} / 0.105 = [OH^-]^2$

Calculate $[OH^-]^2$ and then $[OH^-]$

$[OH^-] = 1.90 \times 10^{-8}$ mol L^{-1}

Use equilibrium principles to explain why the solubility of $Zn(OH)_2$ increases when an excess of dilute sodium hydroxide, NaOH, is added. Include relevant equation(s) in your answer.

- *Recall that $Zn(OH)_2$ is a sparingly soluble salt*
- *Start again with the equation for the equilibrium*
- *Addition of a small amount of NaOH would favour the back reaction and solubility would decrease BUT addition of excess NaOH causes the complex ion to form*
- ***Find the relevant complex ion formula from the resource sheet,** $[Zn(OH)_4]^{2-}$*
- *Do NOT confuse [ ] for concentration with [ ] around the complex ion formula!*
- *The excess OH^- from NaOH reacts with and removes some $Zn^{2+}(aq)$ ions*
- *Use equilibrium principles – removing Zn^{2+} ions will favour the reaction that counteracts that change – the forward reaction $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$ until K_s is restored. $Zn(OH)_2(s)$ dissolves – the solubility of $Zn(OH)_2$ increases......... The precipitate dissolves.*

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

When the OH^- ions are in excess, the $Zn^{2+}(aq)$ ions can form a (soluble) complex ion:

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

A decrease in $[Zn^{2+}(aq)]$ will result in the forward reaction (1) being favoured, to restore equilibrium / minimise or counteract the change.

This causes more solid $Zn(OH)_2$ to dissolve / the solubility of $Zn(OH)_2$ increases / so that $[Zn^{2+}][OH^-]^2$ will again equal K_s

Determine whether a precipitate of $Zn(OH)_2$ will form when 30.0 mL of sodium hydroxide solution, NaOH, at pH 13.1 is added to 20.0 mL of 0.0242 mol L^{-1} zinc nitrate, $Zn(NO_3)_2$.

- *Realise that predicting whether precipitation occurs (or not) involves calculating IP or Q (ionic product)*
- *Know that if volumes being mixed are EQUAL then concentrations can simply be halved BUT if not you need to work out the <u>total</u> volume and calculate the new concentrations made on the moment of mixing*
- *Compare Q to K_S: If IP or Q > K_S a precipitate forms, if IP or Q < K_S no precipitate forms.*
- *Realise that a pH value can be used to calculate $[OH^-]$ concentration. Here $K_w / [H_3O^+] = [OH^-]$ is used.*
  - *$K_w / [H_3O^+]$ which equals $1 \times 10^{-14}/10^{-13.1}$ is used to calculate $[OH^-]$.*
  - *Alternatively use pOH = 14 – pH and then $[OH^-] = 10^{-pOH}$. $[OH^-] = 10^{-0.9}$.*

$[OH^-]$ at pH 13.1 = $1 \times 10^{-14}/10^{-13.1}$ = 0.1259 mol L^{-1}

$[Zn^{2+}]$ = 20/50 x 0.0242 = 9.68×10^{-3} mol L^{-1}

$[OH^-]$ = 30/50 x 0.1259 = 0.0755 mol L^{-1}

IP or Q = $[Zn^{2+}][OH^-]^2$ = $9.68 \times 10^{-3} \times (0.0755)^2$ = 5.52×10^{-5} (5.53×10^{-5})

Since IP or Q > K_S, a precipitate of $Zn(OH)_2$ will form.