

Solubility and complex ions.

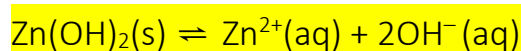
The following information will be provided in the Resource Booklet from 2020

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

$[\text{Ag}(\text{CN})_2]^-$	$[\text{Ag}(\text{NH}_3)_2]^+$
$[\text{Al}(\text{OH})_4]^-$	$[\text{Cu}(\text{NH}_3)_4]^{2+}$
$[\text{Pb}(\text{OH})_4]^{2-}$	$[\text{Zn}(\text{OH})_4]^{2-}$
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$
$[\text{Ni}(\text{CN})_4]^{2-}$	

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

- Identify type as AB,  $A_2B$  or  $AB_2$
- Think about the charges on the ions
- Write the equation – do NOT write  $\text{Zn}(\text{OH})_2 + \text{H}_2\text{O} \rightleftharpoons$
- Use the correct  $\rightleftharpoons$  arrow
- State symbols not essential (based on evidence from schedule)



Write the expression for  $K_s$  ( $\text{Zn}(\text{OH})_2$ ).

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

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

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

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

Let solubility be 's':

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

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

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

$$K_s = 4s^3$$

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

$$s = \sqrt[3]{\frac{3.80 \times 10^{-17}}{4}}$$

$$s = 2.12 \times 10^{-6} \text{ mol L}^{-1}$$

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

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

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  $Zn(OH)_2$  and  $NaOH$
- 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.

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

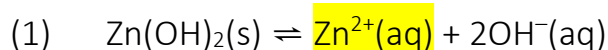
$$3.80 \times 10^{-17} / 0.105 = [OH^-]^2$$

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

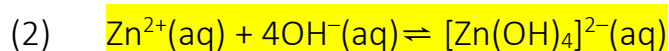
$$[OH^-] = 1.90 \times 10^{-8} \text{ mol L}^{-1}$$

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

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



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



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

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

Determine whether a precipitate of  $\text{Zn(OH)}_2$  will form when 30.0 mL of sodium hydroxide solution,  $\text{NaOH}$ , at pH 13.1 is added to 20.0 mL of 0.0242 mol  $\text{L}^{-1}$  zinc nitrate,  $\text{Zn(NO}_3)_2$ .

- 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 total 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  $[\text{OH}^-]$  concentration. Here  $K_w / [\text{H}_3\text{O}^+] = [\text{OH}^-]$  is used.
  - $K_w / [\text{H}_3\text{O}^+]$  which equals  $1 \times 10^{-14} / 10^{-13.1}$  is used to calculate  $[\text{OH}^-]$ .
  - Alternatively use  $\text{pOH} = 14 - \text{pH}$  and then  $[\text{OH}^-] = 10^{-\text{pOH}}$ .  $[\text{OH}^-] = 10^{-0.9}$ .

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

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

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

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

Since IP or Q >  $K_s$ , a precipitate of  $\text{Zn(OH)}_2$  will form.