### Demonstrate understanding of equilibrium principles in aqueous systems

### **Collated Questions 2013 – 2021**

Solubility Product calculations and Predicting Precipitation.

Solubility of solids in water and in solutions already containing one of the ions A or B (a common ion) or due to the formation of a complex ion, or the reaction of a basic anion with added acid.

### (2021:1)

- (a) (i) Write the equation for the equilibrium occurring in a saturated solution of magnesium hydroxide, Mg(OH)<sub>2</sub>.
  - (ii) Write the expression for  $K_s(Mg(OH)_2)$ .
  - (iii) Calculate the solubility of Mg(OH)<sub>2</sub> in water at 25 °C, and give [Mg<sup>2+</sup>] and [OH<sup>-</sup>].  $K_s(Mg(OH)_2) = 7.10 \times 10^{-12}$
- (b) When dilute sodium hydroxide, NaOH, is added to a saturated solution of Mg(OH)<sub>2</sub>, the concentration of Mg<sup>2+</sup> ions in the saturated solution decreases.
  - (i) Explain, using equilibrium principles, why the concentration of Mg<sup>2+</sup> ions in the saturated solution decreases upon the addition of NaOH.
  - (ii) Calculate the concentration of  $Mg^{2+}$  ions in a solution after 30.0 mL of 0.120 mol  $L^{-1}$  NaOH is added to 20.0 mL of a saturated  $Mg(OH)_2$  solution. Assume the concentration of  $OH^-$  ions in the original saturated solution of  $Mg(OH)_2$  is insignificant.
- (c) Determine whether a precipitate of  $Mg(OH)_2$  will form when 65.0 mL of 0.240 mol L<sup>-1</sup> magnesium nitrate,  $Mg(NO_3)_2$ , is added to 40.0 mL of NaOH solution of pH 12.8.

#### (2020:2)

- (a) (i) Write the equation for the equilibrium occurring in a saturated solution of lead bromide, PbBr<sub>2</sub>.
  - (ii) Write the expression for K<sub>s</sub>(PbBr<sub>2</sub>).
  - (iii) Calculate the solubility of PbBr<sub>2</sub> in water at 25 °C.  $K_s(PbBr_2) = 2.10 \times 10^{-6}$
- (b) Determine whether a precipitate of lead bromide, PbBr<sub>2</sub>, will form when 125 mL of  $0.0365 \text{ mol L}^{-1}$  lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, is added to 175 mL of  $0.00262 \text{ mol L}^{-1}$  magnesium bromide, MgBr<sub>2</sub>

- (c) (i) Explain the effect of the following on the solubility of nickel hydroxide, Ni(OH)<sub>2</sub>, in water. Include relevant equation(s) in your answer. No calculations are necessary.
  - Ammonia solution, NH₃(aq), is added:
  - The pH is decreased below 4:
  - (ii) Calculate the solubility of a saturated solution of nickel hydroxide at pH 8.25.  $K_s(Ni(OH)_2) = 6.00 \times 10^{-16}$

### (2019:1)

- (a) (i) Write the equation for the equilibrium occurring in a saturated solution of zinc hydroxide, Zn(OH)<sub>2</sub>.
  - (ii) Write the expression for  $K_s(Zn(OH)_2)$ .
  - (iii) Calculate the solubility of Zn(OH)<sub>2</sub> in water at 25°C, and give the [Zn<sup>2+</sup>] and [OH<sup>-</sup>] in the solution.  $K_s(Zn(OH)_2) = 3.80 \times 10^{-17}$
  - (iv) The presence of a common ion decreases the solubility of a sparingly soluble solid, such as Zn(OH)<sub>2</sub>. Calculate the concentration of the hydroxide ions, OH<sup>-</sup>, in solution after 25.0 mL of 0.210 mol L<sup>-1</sup> zinc chloride, ZnCl<sub>2</sub>, solution was added to 25.0 mL of a saturated Zn(OH)<sub>2</sub> solution.
- (b) Use equilibrium principles to explain why the solubility of Zn(OH)<sub>2</sub> increases when an excess of dilute sodium hydroxide, NaOH, is added. Include relevant equation(s) in your answer.
- (c) 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<sup>-1</sup> zinc nitrate,  $Zn(NO_3)_2$ .

# (2018:1)

- (b) (i) Write the equation for the equilibrium occurring in a saturated solution of calcium fluoride, CaF<sub>2</sub>.
  - (ii) Calculate the solubility of CaF<sub>2</sub> in water at 25°C.  $K_s$  (CaF<sub>2</sub>) = 3.20 × 10<sup>-11</sup>
- (c) Explain the effect of the following on the solubility of iron(III) hydroxide, Fe(OH)<sub>3</sub>, in water. Include relevant equation(s) in your answer. No calculations are necessary.
  - (i) pH lowered below 4
  - (ii) Potassium thiocyanate, KSCN, solution added

### (2018:3)

- (a) (i) Write the solubility product expression, K<sub>s</sub>, for silver chloride, AgCl.
  - (ii) Why does the solubility of AgCl decrease when a small volume of silver nitrate, AgNO<sub>3</sub>, solution is added to a saturated solution of AgCl? Explain your answer.
  - (iii) Show by calculation whether a precipitate of AgCl will form when 70.0 mL of 0.0220 mol  $L^{-1}$  AgNO<sub>3</sub> is added to 50.0 mL of 0.0550 mol  $L^{-1}$  sodium chloride, NaCl.  $K_s(AgCl) = 1.80 \times 10^{-10}$

### (2017:1)

- (b) 40.0 mL of  $0.150 \text{ mol L}^{-1}$  HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution.
  - (i) Write an equation for the equilibrium occurring in a saturated solution of AgBr.
  - (ii) Explain the changes that occur to the concentrations of the species in the saturated solution of AgBr on the addition of the HBr solution.
  - (iii) Calculate the concentration of the silver ions,  $Ag^+$ , after the HBr solution has been added.  $K_s(AgBr) = 5.00 \times 10^{-13}$ . Assume the concentration of  $Br^-$  in the original saturated solution of AgBr is insignificant.

# (2017:2)

- (b) (i) Write the equation for the equilibrium occurring in a saturated solution of copper(II) hydroxide, Cu(OH)<sub>2</sub>.
  - (ii) Write the expression for  $K_s(Cu(OH)_2)$
  - (iii) Calculate the solubility of Cu(OH)<sub>2</sub> in water at 25°C.  $K_s(Cu(OH)_2) = 4.80 \times 10^{-20}$
- (c) Explain why the solubility of Cu(OH)<sub>2</sub> increases when dilute hydrochloric acid is added.

# (2016:1)

Silver carbonate,  $Ag_2CO_3$ , is a sparingly soluble salt. Ks  $(Ag_2CO_3) = 8.10 \times 10^{-12}$  at 25°C  $M(Ag_2CO_3) = 276$  g mol<sup>-1</sup>

- (a) Write the solubility product expression, Ks, for silver carbonate (Ag<sub>2</sub>CO<sub>3</sub>).
- (b) Calculate the mass of Ag<sub>2</sub>CO<sub>3</sub> that will dissolve in 50 mL of water to make a saturated solution at 25°C.
- (c) Explain how the solubility of  $Ag_2CO_3$  will change if added to 50 mL of a 1.00 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, solution. Support your answer with balanced equations. *No calculations are necessary.*

(d) Show by calculation whether a precipitate of  $Ag_2CO_3$  will form when 20.0 mL of 0.105 mol  $L^{-1}$  silver nitrate,  $AgNO_3$ , solution is added to 35.0 mL of a 0.221 mol  $L^{-1}$  sodium carbonate,  $Na_2CO_3$ , solution. Ks  $(Ag_2CO_3) = 8.10 \times 10^{-12}$  at 25°C

### (2015:2)

Sufficient calcium carbonate, CaCO<sub>3</sub>(s), is dissolved in water to make a saturated solution.

- (a) (i) Write the equation for the equilibrium occurring in a saturated solution of CaCO<sub>3</sub>.
  - (ii) Write the expression for K<sub>s</sub> (CaCO<sub>3</sub>).
  - (iii) Calculate the solubility product of CaCO<sub>3</sub>,  $K_s$ (CaCO<sub>3</sub>). The solubility of CaCO<sub>3</sub> is 5.74  $\times$  10<sup>-5</sup> mol L<sup>-1</sup>.
- (b) Some marine animals use calcium carbonate to form their shells. Increased acidification of the oceans poses a problem for the survival of these marine animals. Explain why the solubility of CaCO₃ is higher in an acidic solution. Use an equation to support your explanation.
- (c) Show, by calculation, that a precipitate of lead(II) hydroxide,  $Pb(OH)_2$ , will form when 25.0 mL of a sodium hydroxide solution, NaOH, at pH 12.6 is added to 25.0 mL of a 0.00421 mol L<sup>-1</sup> lead(II) nitrate,  $Pb(NO_3)_2$ , solution.

$$K_s (Pb(OH)_2) = 8.00 \times 10^{-17} \text{ at } 25^{\circ}C$$

### (2014:2)

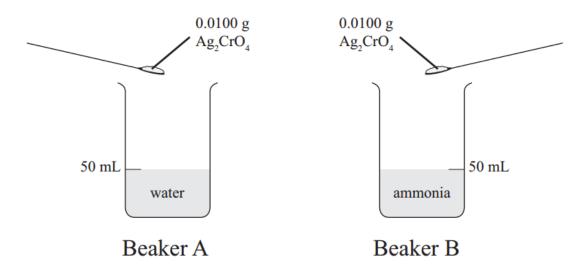
A flask contains a saturated solution of PbCl<sub>2</sub> in the presence of undissolved PbCl<sub>2</sub>.

- (a) (i) Write the equation for the dissolving equilibrium in a saturated solution of PbCl<sub>2</sub>.
  - (ii) Write the expression for  $K_s$  (PbCl<sub>2</sub>).
  - (iii) Calculate the solubility (in mol  $L^{-1}$ ) of lead(II) chloride in water at 25°C, and give the [Pb<sup>2+</sup>] and [Cl<sup>-</sup>] in the solution.  $K_s$  (PbCl<sub>2</sub>) = 1.70 × 10<sup>-5</sup> at 25°C
- (b) A sample of seawater has a chloride ion concentration of 0.440 mol L<sup>-1</sup>. Determine whether a precipitate of lead(II) chloride will form when a 2.00 g sample of lead(II) nitrate is added to 500 mL of the seawater.  $K_s$  (PbCl<sub>2</sub>) = 1.70 × 10<sup>-5</sup>. M(Pb(NO<sub>3</sub>)<sub>2</sub>) = 331 g mol<sup>-1</sup>.
- (c) The solubility of zinc hydroxide, Zn(OH)<sub>2</sub>, can be altered by changes in pH. Some changes in pH may lead to the formation of complex ions, such as the zincate ion, [Zn(OH)<sub>4</sub>]<sup>2-</sup>. Use equilibrium principles to explain why the solubility of zinc hydroxide increases when the pH is less than 4 or greater than 10. *No calculations are necessary*.

### (2013)

In an experiment, a saturated solution was made by dissolving  $1.44 \times 10^{-3}$  g of Ag<sub>2</sub>CrO<sub>4</sub> in water and making it up to a volume of 50.0 mL. M (Ag<sub>2</sub>CrO<sub>4</sub>) = 332 g mol<sup>-1.</sup>

- (a) Write the K<sub>s</sub> expression for Ag<sub>2</sub>CrO<sub>4</sub>(s).
- (b) (i) Calculate the solubility of  $Ag_2CrO_4(s)$ , and hence give the  $[Ag^+]$  and  $[CrO_4^{2-}]$  in the solution.
  - (ii) Determine the K<sub>s</sub> (Ag<sub>2</sub>CrO<sub>4</sub>).
- (c) In another experiment,  $0.0100 \, \text{g}$  of  $Ag_2CrO_4$  in beaker A was made up to a volume of 50.0 mL with water. In beaker B,  $0.0100 \, \text{g}$  of  $Ag_2CrO_4$  was made up to a volume of 50.0 mL with  $0.100 \, \text{mol} \, \text{L}^{-1}$  ammonia solution.



Compare and contrast the solubility of Ag<sub>2</sub>CrO<sub>4</sub> in beaker A and beaker B. No calculations are necessary.

### From expired AS 90700

### (2012)

Iron(II) hydroxide, Fe(OH)<sub>2</sub>, has a K<sub>s</sub> of  $4.10 \times 10^{-15}$  at 25°C.

- (a) (i) Write the equation for Fe(OH)<sub>2</sub> dissolving in water.
  - (ii) Write the expression for  $K_s$  (Fe(OH)<sub>2</sub>).
- (b) Calculate the solubility (in mol  $L^{-1}$ ) of iron(II) hydroxide in water at 25°C.
- (c) (i) Determine whether a precipitate of iron(III) hydroxide, Fe(OH)<sub>3</sub>, will form when Fe(NO<sub>3</sub>)<sub>3</sub> is dissolved in water. [Fe(NO<sub>3</sub>)<sub>3</sub>] =  $1.05 \times 10^{-4}$  mol L<sup>-1</sup>. Assume the pH of the water is 7.

$$K_s$$
 (Fe(OH)<sub>3</sub>) = 2.00 × 10<sup>-39</sup>.

## (2011)

Zinc hydroxide, Zn(OH)<sub>2</sub>, has a K<sub>s</sub> of  $3.00 \times 10^{-17}$  at 25°C.

- (a) (i) Write an equation for zinc hydroxide dissolving in water.
  - (ii) Write the K<sub>s</sub> expression for zinc hydroxide.
- (b) Calculate the solubility (in mol  $L^{-1}$ ) of zinc hydroxide at 25°C.
- (c) A saturated solution of zinc hydroxide, Zn(OH)<sub>2</sub>, contains a small amount of solid Zn(OH)<sub>2</sub> at the bottom of the container. The pH of the solution is increased. Discuss the effect of increasing the pH on the amount of solid present, and also on the nature and concentration of the species present in the solution.

No calculations are necessary.

# (2010)

- (a) Sufficient Ag<sub>2</sub>CrO<sub>4</sub> is dissolved in water to form a saturated solution.
  - (i) Write the equation for the equilibrium present in a saturated solution of Ag<sub>2</sub>CrO<sub>4</sub>.
  - (ii) Write the expression for  $K_s$  (Ag<sub>2</sub>CrO<sub>4</sub>).
- (d) Calculate the solubility of  $Ag_2CrO_4$  in a saturated solution in mol  $L^{-1}$ .  $K_s$  ( $Ag_2CrO_4$ ) = 3.00 × 10<sup>-12</sup>
- (c) Discuss how the solubility of Ag<sub>2</sub>CrO<sub>4</sub> will change if it is dissolved in the following solutions. *No calculations are necessary.* 
  - (i)  $0.1 \text{ mol } L^{-1} \text{ K}_2 \text{CrO}_4$
  - (ii)  $0.1 \text{ mol } L^{-1} \text{ NH}_3$

### (2009)

Addition of chloride ions to a solution of silver nitrate often results in the formation of a white precipitate of silver chloride (AgCl).

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) K_{s}(AgCl) = 1.56 \times 10^{-10}$$

- (a) Calculate the concentration, in mol  $L^{-1}$ , of silver ions in a saturated solution of silver chloride at 25°C.
- (b) Solid sodium chloride is added to 5.00 L of 0.100 mol L<sup>-1</sup> silver nitrate solution. Calculate the minimum mass of sodium chloride that would be needed to produce a saturated solution of AgCl. Assume that there is no change in volume when the sodium chloride is added.  $M(NaCl) = 58.5 \text{ g mol}^{-1}$
- (c) Discuss reasons for the fact that a precipitate of silver chloride dissolves on the addition of excess aqueous ammonia.

## (2008,3)

- (a) (i) Write an equation for the sparingly soluble salt lead(II) chloride (PbCl<sub>2</sub>) dissolving in water.
  - (ii) Write the solubility product expression for lead(II) chloride.
- (b) Calculate the solubility, in mol L<sup>-1</sup>, of PbCl<sub>2</sub> in water at 25°C.  $K_s$  (PbCl<sub>2</sub>) = 1.60 × 10<sup>-5</sup> at 25°C
- (c) Sea water contains many dissolved salts. The chloride ion concentration in a sample of sea water is 0.440 mol L<sup>-1</sup>. Determine whether a precipitate of lead(II) chloride will form when a 1.00 g sample of lead(II) nitrate is added to 500 mL of the sea water. Your answer must be clearly justified.  $M(Pb(NO_3)_2) = 331$  g mol<sup>-1</sup>.

### (2008,4)

The  $K_s$  of aluminium hydroxide, Al(OH)<sub>3</sub>, at 25°C, is  $3 \times 10^{-34}$ , indicating that it has very low solubility. The solubility may be altered by changes in pH (due to acidic or basic properties) and formation of complex ions such as the aluminate ion,  $[Al(OH)_4]^-$ . Discuss why aluminium hydroxide becomes more soluble in aqueous solutions that have a pH less than 4, or a pH greater than 10. In your answer include:

- the equation for the reaction that relates to Ks  $(Al(OH)_3)$
- equations for the reactions that relate to changes in the solubility of aluminium hydroxide at pH less than 4 or greater than 10
- a discussion of the equilibrium principles involved.

### (2007)

Magnesium hydroxide (known as milk of magnesia) is another substance that the patient consumed to control the acidity of the solution in the stomach.  $K_s$  (Mg(OH)<sub>2</sub>) =  $1.25 \times 10^{-11}$ 

(b) (i) Calculate the solubility of magnesium hydroxide in water in mol  $L^{-1}$ .

## (2006)

Sea-water contains appreciable amounts of ions other than Na<sup>+</sup> and Cl<sup>-</sup>. One substance that is less soluble than sodium chloride is calcium sulfate. This is precipitated in the first stage of the purification process used to produce table salt (sodium chloride).

$$K_s$$
 (CaSO<sub>4</sub>) = 2.45 × 10<sup>-5</sup>.

- (a) (i) Write the equation for the equilibrium reaction in a saturated solution of calcium sulfate.
  - (ii) Calculate the solubility of CaSO<sub>4</sub> in water.

Evaporating the sea-water to dryness would produce a mixture of salts including NaCl. However, precipitation of NaCl occurs if concentrated hydrochloric acid is added to a saturated NaCl solution.

(b) Explain why this precipitation occurs.

As part of the process for extracting table salt from sea-water, sodium hydroxide is added to the seawater to precipitate the magnesium ions as magnesium hydroxide. The concentration of  $Mg^{2+}$  ions at this stage is 0.555 mol  $L^{-1}$ .

(c) Calculate the minimum hydroxide ion concentration and hence the pH of the solution needed for precipitation to occur.  $K_s(Mg(OH)_2) = 7.10 \times 10^{-12}$ .

# (2005)

- (a) Describe what is meant by the term 'solubility'.
- (b) The solubility product,  $K_s$ , of AgCl has a value of  $1.56 \times 10^{-10}$  at 25°C and this value increases to  $2.15 \times 10^{-8}$  at 100°C. Explain why  $K_s$  is higher at 100°C. Include reference to the relevant equilibrium equation in your answer.

The chloride ion concentration in sea water can be determined by titrating a sample with aqueous silver nitrate (AgNO<sub>3</sub>) using potassium chromate ( $K_2CrO_4$ ) as the indicator. As the silver nitrate is added, a precipitate of silver chloride, (AgCl) forms. When most of the AgCl has precipitated, the Ag<sup>+</sup>(aq) concentration becomes high enough for a red precipitate of Ag<sub>2</sub>CrO<sub>4</sub> to form.

- (c) Show that the solubility of  $Ag_2CrO_4$  in pure water at 25°C is higher than that of AgCl.  $K_s(AgCl) = 1.56 \times 10^{-10} K_s (Ag_2CrO_4) = 1.30 \times 10^{-12}$
- (d) If the concentration of chromate ions is  $6.30 \times 10^{-3}$  mol L<sup>-1</sup> at the point when the Ag<sub>2</sub>CrO<sub>4</sub> starts to precipitate, calculate the concentration of Ag<sup>+</sup> ions in the solution.

#### **Answers**

(2021:1)

(a) (i) 
$$Mg(OH)_2 \Rightarrow Mg^{2+} + 2OH^{-}$$

- (ii)  $K_s = [Mg^{2+}][OH^{-}]^2$
- (iii) Let solubility be s:  $[Mg^{2+}] = s \ [OH^-] = 2s \ 4s^3 = 7.10 \times 10^{-12} \ s = 1.21 \times 10^{-4} \text{ mol L}^{-1}$   $[Mg^{2+}] = 1.21 \times 10^{-4} \text{ mol L}^{-1}$   $[OH^-] = 2 \times 1.21 \times 10^{-4} \text{ mol L}^{-1}$
- (b) (i)  $Mg(OH)_2 \Rightarrow Mg^{2+} + 2OH^{-}$

Addition of dilute NaOH causes an increase in  $[OH^-]$  (OH $^-$  is a common ion). As a result, the equilibrium favours the reverse reaction / speeds up the rate of the reverse reaction to consume some of the OH $^-$ . This causes more solid Mg(OH)<sub>2</sub> to be produced, so  $[Mg^{2+}]$  in solution decreases.

- (ii)  $K_s = [Mg^{2+}][OH^{-}]^2$  7.10 x  $10^{-12} = [Mg^{2+}]$  x  $(30/50 \times 0.120)^2$   $[Mg^{2+}] = 1.37 \times 10^{-9} \text{ mol } L^{-1}$
- (c)  $[Mg^{2+}] = 65/105 \times 0.240 = 0.149 \text{ mol L}^{-1}$   $[OH^{-}] = 40/105 \times (1 \times 10^{-14}/10^{-12.8}) = 0.0240 \text{ mol L}^{-1}$  $IP = [Mg^{2+}][OH^{-}]^2 = 0.149 \times (0.0240)^2 = 8.58 \times 10^{-5}$ . Since IP > Ks, a precipitate of  $Mg(OH)_2$  will form.

(2020:2)

(a) (i) 
$$PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^{-}$$

(ii) 
$$K_s = [Pb^{2+}] [Br^{-}]^2$$

(iii) Let solubility be s: 
$$K_s = 4s^3$$
  $S = \sqrt[3]{\frac{2.10 \times 10^{-6}}{4}}$   $s = 8.07 \times 10^{-3} \text{ mol L}^{-1}$ 

(b) 
$$[Pb^{2+}] = 125/300 \times 0.0365 = 1.52 \times 10^{-2} \text{ mol L}^{-1}.$$

$$[Br^{-}] = 175/300 \times 2 \times 0.00262 = 3.06 \times 10^{-3} \text{ mol } L^{-1}.$$

 $IP = [Pb^{2+}][Br^{-}]^2 = 1.42 \times 10^{-7}$ . Since IP < Ks, no  $PbBr_2$  precipitate will form.

(c) (i) Ni(OH)<sub>2</sub> ⇒ Ni<sup>2+</sup> + 2OH<sup>-</sup> When ammonia solution is added, the Ni<sup>2+</sup> ions are removed from the saturated solution to form a complex ion, as shown below:

 $Ni^{2+} + 6NH_3 \Rightarrow [Ni(NH_3)_6]^{2+}$  To restore the equilibrium, more solid  $Ni(OH)_2$  dissolves to replace some of the  $Ni^{2+}$  / increase  $[Ni^{2+}]$ . Therefore the solubility of  $Ni(OH)^2$  increases.

When the pH is decreased below pH 4, [H<sub>3</sub>O<sup>+</sup>] increases. The H<sub>3</sub>O<sup>+</sup> remove the OH<sup>-</sup> from the equilibrium according to the neutralisation equation below:

 $H_3O^+ + OH^- \rightarrow 2H_2O$  To restore the equilibrium, more solid Ni(OH)<sub>2</sub>dissolves to replace some of the OH<sup>-</sup> / increase [OH<sup>-</sup>]. Therefore the solubility of Ni(OH)<sub>2</sub> increases.

(ii) 
$$Ni(OH)_2 \Rightarrow Ni^{2+} + 2OH^- K_s = [Ni^{2+}][OH^-]^2$$
  
 $Ks = [Ni^{2+}][OH^-]^2 [OH^-] = 1 \times 10^{-14} / 10^{-8.25} = 1.78 \times 10^{-6} \text{ mol L}^{-1}$   
 $6.00 \times 10^{-16} = [Ni^{2+}] \times (1.78 \times 10^{-6})^2 [Ni^{2+}] = 1.90 \times 10^{-4} \text{ mol L}^{-1}$ 

### (2019:1)

- (a) (i)  $Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^{-}$ 
  - (ii)  $K_s = [Zn^{2+}][OH^-]^2$
  - (iii) Let solubility be 's':  $[Zn^{2+}] = s$ ,  $[OH^{-}] = 2s$ ,  $K_s = 4s^3$   $4s^3 = 3.80 \times 10^{-17} \quad s = 2.12 \times 10^{-6} \text{ mol L}^{-1}$  $[Zn^{2+}] = 2.12 \times 10^{-6} \text{ mol L}^{-1}$ ,  $[OH^{-}] = 4.24 \times 10^{-6} \text{ mol L}^{-1}$
  - (iv)  $K_s = [Zn^{2+}][OH^-]^2$  $3.80 \times 10^{-17} = (0.210/2) \times [OH^-]^2 \quad [OH^-] = 1.90 \times 10^{-8} \text{ mol } L^{-1}$

Note: 0.210/2 due to dilution factor from adding two solutions together.

- (b)  $Zn(OH)_2 \Rightarrow Zn^{2+} + 2OH^-$  When the OH<sup>-</sup> ions are in excess, the  $Zn^{2+}$  ions can form a complex ion:  $Zn^{2+} + 4OH^- \rightarrow [Zn(OH)_4]^{2-}$  A decrease in  $[Zn^{2+}]$  will result in the forward reaction being favoured, to restore equilibrium / minimise 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  $K_s$ .
- (c)  $[Zn^{2+}] = 20/50 \times 0.0242 = 9.68 \times 10^{-3} \text{ mol L}^{-1}$   $[OH^{-}] = 30/50 \times 1 \times 10^{-14}/10^{-13.1} = 0.0755 \text{ mol L}^{-1}$  $IP = [Zn^{2+}][OH^{-}]^2 = 9.68 \times 10^{-3} \times (0.0755)^2 = 5.52 \times 10^{-5} \text{ (5.53 x 10}^{-5} \text{. Since IP} > K_s, a precipitate of Zn(OH)<sub>2</sub> will form.$

### (2018:1)

- (b) (i)  $CaF_2 \rightleftharpoons Ca2^+ + 2F^-$ 
  - (ii)  $K_s = [Ca^{2+}][F^-]^2$

Let solubility be 's':  $[Ca^{2+}] = s$ ,  $[F^{-}] = 2s$ ,  $K_s = 4s^3$   $s = 2.00 \times 10^{-4} \text{ mol } L^{-1}$ 

- (c) (i) In a saturated solution: Fe(OH)<sub>3</sub> 

  Fe<sup>3+</sup> + 3OH<sup>-</sup>. As the pH is lowered, [H<sub>3</sub>O<sup>+</sup>] increases. The H<sub>3</sub>O<sup>+</sup> will remove and neutralise OH<sup>-</sup> / H<sub>3</sub>O<sup>+</sup> + OH<sup>-</sup> → 2H<sub>2</sub>O. A decrease in [OH<sup>-</sup>] will result in the forward reaction being favoured, to restore equilibrium / minimise the change. This causes more solid Fe(OH)<sub>3</sub> to dissolve, i.e. the solubility of Fe(OH)<sub>3</sub> increases / so that [Fe<sup>3+</sup>][OH<sup>-</sup>] will again equal Ks.
  - (ii) The SCN<sup>-</sup> ions can form a complex ion with Fe<sup>3+</sup> ions: Fe<sup>3+</sup> + SCN<sup>-</sup>  $\rightarrow$  [FeSCN]<sup>2+</sup> Since the Fe<sup>3+</sup> are removed from the equilibrium, more Fe(OH)<sup>3</sup> dissolves to replace some of the Fe<sup>3+</sup>, i.e. equilibrium will shift towards the products / speed up the forward reaction. As a result, the solubility of Fe(OH)<sup>3</sup> increases.

### (2018:3)

- (a) (i)  $K_s = [Ag^+][Cl^-]$ 
  - (ii) The Ag<sup>+</sup> is a common ion. By increasing [Ag<sup>+</sup>], the equilibrium will shift towards the reactants to use up some of the extra Ag<sup>+</sup>, so more solid AgCl will form, i.e. the solubility of AgCl will decrease.
  - (iii) Final [Ag<sup>+</sup>] =  $70/120 \times 0.0220 = 0.0128 \text{ mol L}^{-1}$ . Final [Cl<sup>-</sup>] =  $50/120 \times 0.0550 = 0.0229 \text{ mol L}^{-1}$ . Q = [Ag<sup>+</sup>][Cl<sup>-</sup>] =  $0.0128 \times 0.0229 = 2.94 \times 10^{-4}$ . Since Q > Ks, AgCl will form a precipitate.

# (2017)

- (b) 40.0 mL of  $0.150 \text{ mol L}^{-1}$  HBr solution was added to 25.0 mL of a saturated silver bromide, AgBr, solution.
  - (i) Write an equation for the equilibrium occurring in a saturated solution of AgBr.  $AgBr \rightleftharpoons Ag^+ + Br^-$
  - (ii) Explain the changes that occur to the concentrations of the species in the saturated solution of AgBr on the addition of the HBr solution.

Br<sup>-</sup> is a common ion / added to solution

An increase in [Br<sup>-</sup>] will result in the reverse reaction being favoured, to restore equilibrium / minimise the change.

This results in a decrease in [Ag<sup>+</sup>] (since Ag<sup>+</sup> reacts with some of the added Br<sup>-</sup> to help use it up) / AgBr becomes less soluble, (until [Ag<sup>+</sup>][Br<sup>-</sup>] is again equal to Ks.)

(iii) Calculate the concentration of the silver ions,  $Ag^+$ , after the HBr solution has been added.  $K_s$  (AgBr) =  $5.00 \times 10^{-13}$ . Assume the concentration of Br<sup>-</sup> in the original saturated solution of AgBr is insignificant.

AgBr 
$$\rightleftharpoons$$
 Ag<sup>+</sup> + Br<sup>-</sup> K<sub>s</sub>(AgBr) = [Ag<sup>+</sup>] [Br<sup>-</sup>]  
 $5 \times 10^{-13} = [Ag^+] \times \frac{0.150 \times 40}{65}$  [Ag<sup>+</sup>] = 5.42 ×10<sup>-12</sup> mol L<sup>-1</sup>

### (2017:2)

(b) (i) Write the equation for the equilibrium occurring in a saturated solution of copper(II) hydroxide, Cu(OH)<sub>2</sub>.

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$$

(ii) Write the expression for  $K_s$  (Cu(OH)<sub>2</sub>)

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

(iii) Calculate the solubility of Cu(OH)<sub>2</sub> in water at 25°C. K<sub>s</sub> (Cu(OH)<sub>2</sub>) =  $4.80 \times 10^{-20}$ Let s = solubility [Cu<sup>2+</sup>] = s

$$[OH^{-}]^{2} = (2s)^{2}$$

$$K_{s} = 4s^{3}$$

$$4s^3 = 4.80 \times 10^{-20} \text{ So; } s = 2.29 \times 10^{-7} \text{ mol } L^{-1}$$

(c) Explain why the solubility of Cu(OH)<sub>2</sub> increases when dilute hydrochloric acid is added.

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$$

When copper(II) hydroxide is dissolved in an acidic solution, the  $H_3O^+$  ions neutralise the  $OH^-$  ions /  $H_3O^+ + OH^- \rightarrow 2H_2O$ 

A decrease in  $[OH^-]$  will result in the forward reaction being favoured, to restore equilibrium / minimise the change. This causes more solid  $Cu(OH)_2$  to dissolve, i.e. the solubility of  $Cu(OH)_2$  increases / so that  $[Cu^{2+}][OH^-]$  will again equal  $K_s$ .

# (2016)

Silver carbonate,  $Ag_2CO_3$ , is a sparingly soluble salt. Ks  $(Ag_2CO_3) = 8.10 \times 10^{-12}$  at 25°C  $M(Ag_2CO_3) = 276$  g mol<sup>-1</sup>

(a) Write the solubility product expression, Ks , for silver carbonate (Ag $_2CO_3$ ).

$$K_s = [Ag^+]^2[CO_3^{2-}]$$

(b) Calculate the mass of Ag<sub>2</sub>CO<sub>3</sub> that will dissolve in 50 mL of water to make a saturated solution at 25°C.

```
Let s = \text{solubility}

[Ag^+] = 2s \quad [CO_3^{2-}] = s \quad K_s = 4s^3

s = 1.27 \times 10^{-4} \text{ mol L}^{-1}

n = c \times v = 6.33 \times 10^{-6} \text{ mol}

m = n \times M = 1.75 \times 10^{-3} \text{ g}

OR \quad g \quad L^{-1} = c \times M = 0.0349 \text{ g L}^{-1}

so mass in 50 mL = (0.0349 \times 50) / 1000 = 1.75 \times 10^{-3} \text{ g}
```

(c) Explain how the solubility of  $Ag_2CO_3$  will change if added to 50 mL of a 1.00 mol L<sup>-1</sup> ammonia, NH<sub>3</sub>, solution. Support your answer with balanced equations. No calculations are necessary.

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

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

The equilibrium responds by favouring the forward reaction and thus more dissolves.

(d) Show by calculation whether a precipitate of  $Ag_2CO_3$  will form when 20.0 mL of 0.105 mol L<sup>-1</sup> silver nitrate,  $AgNO_3$ , solution is added to 35.0 mL of a 0.221 mol L<sup>-1</sup> sodium carbonate,  $Na_2CO_3$ , solution. Ks  $(Ag_2CO_3) = 8.10 \times 10^{-12}$  at 25°C

```
AgNO<sub>3</sub> dilution: (20/55) x 0.105= 0.0382
Na<sub>2</sub>CO<sub>3</sub> dilution: (35/55) x 0.221 = 0.141
Q/I.P. = [0.03818]^2[0.1406] = 2.06 \times 10^{-4}
As Q/I.P. > K_s, a precipitate will form.
```

### (2015)

Sufficient calcium carbonate, CaCO₃(s), is dissolved in water to make a saturated solution.

- (a) (i) Write the equation for the equilibrium occurring in a saturated solution of CaCO<sub>3</sub>.  $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ 
  - (ii) Write the expression for  $K_s$  (CaCO<sub>3</sub>).

$$K_s = [Ca^{2+}][CO_3^{2-}]$$

(iii) Calculate the solubility product of CaCO<sub>3</sub>,  $K_s$ (CaCO<sub>3</sub>). The solubility of CaCO<sub>3</sub> is 5.74  $\times$  10<sup>-5</sup> mol L<sup>-1</sup>.

$$K_s(CaCO_3) = (5.74 \times 10^{-5})^2 = 3.29 \times 10^{-9}$$

(b) Some marine animals use calcium carbonate to form their shells. Increased acidification of the oceans poses a problem for the survival of these marine animals. Explain why the solubility of CaCO<sub>3</sub> is higher in an acidic solution. Use an equation to support your explanation.

The  $H_3O^+$  from the acidic solution reacts with the  $CO_3^{2-}$ . This reduces  $[CO_3^{2-}]$ , causing the equilibrium to shift towards the products / RHS to replace some of the lost  $CO_3^{2-}$ . Therefore more solid  $CaCO_3$  will dissolve.

 $2H_3O^+ + CO_3^{2-} \rightarrow 3H_2O + CO_2$  (or other correct alternative e.g.  $2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$ )

(c) Show, by calculation, that a precipitate of lead(II) hydroxide, Pb(OH)<sub>2</sub>, will form when 25.0 mL of a sodium hydroxide solution, NaOH, at pH 12.6 is added to 25.0 mL of a  $0.00421 \text{ mol L}^{-1} \text{ lead(II)}$  nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, solution.

$$K_s (Pb(OH)_2) = 8.00 \times 10^{-17} \text{ at } 25^{\circ}\text{C}$$

```
pH =12.6, pOH = 1.4 and so [OH–] = 0.0398

Pb(OH)<sub>2</sub> \rightleftharpoons Pb<sup>2+</sup> + 2OH<sup>-</sup>

Q = [Pb^{2+}][OH^-]^2

[Pb^{2+}] = 0.5 \times 0.00421 = 2.105 \times 10^{-3} \quad [OH^-] = 0.5 \times 0.0398 = 1.99 \times 10^{-2}

Q = (2.105 \times 10^{-3}) \times (1.99 \times 10^{-2})^2 \quad Q = 8.34 \times 10^{-7}

Since Q > K_s, a precipitate of Pb(OH)<sub>2</sub> will form.
```

### (2014)

- (a) (i)  $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$ 
  - (ii)  $K_s = [Pb^{2+}][Cl^{-}]^2$
  - (iii)  $[Pb^{2+}] = x$   $[Cl^{-}] = 2x$   $K_s = 4x^3$   $x = \sqrt[3]{Ks}/4$   $x = \sqrt[3]{\frac{1.70 \times 10^{-5}}{4}} = 1.62 \times 10^{-2}$  mol L<sup>-1</sup>  $[Pb^{2+}] = 1.62 \times 10^{-2}$  mol L<sup>-1</sup>  $[Cl^{-}] = 3.24 \times 10^{-2}$  mol L<sup>-1</sup>
- (b)  $n(Pb(NO3)2) = 2.00 / 331 = 6.04 \times 10^{-3} \text{ mol}$   $\therefore [Pb^{2+}] = 6.04 \times 10^{-3} \text{ mol} / 0.500 \text{ L} = 1.21 \times 10^{-2} \text{ mol L}^{-1}$   $Q = (1.21 \times 10^{-2}) \times (0.440)^2 = 2.34 \times 10^{-3}$ As Q > Ks, a precipitate will form.

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

When pH is less than 4 / low,  $[OH^-]$  is decreased due to the reaction with  $H_3O^+$  to form water,

$$H_3O^+ + OH^- \rightarrow H_2O$$

So equilibrium shifts to the right to produce more [OH<sup>-</sup>], therefore more Zn(OH)<sub>2</sub> will dissolve.

When pH is greater than 10 / high, then more OH<sup>-</sup> is available and the complex ion (zincate ion) will form.

$$Zn(OH)_2(s) + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$$

OR 
$$Zn^{2+} + 4OH^{-} \rightarrow [Zn(OH)_{4}]^{2-}$$

This decrease in  $[Zn^{2+}]$  causes the position of equilibrium to shift further to the right, therefore more  $Zn(OH)_2$  dissolves.

## (2013)

- (a) Ks =  $[Ag^+]^2[CrO_4^{2-}]$
- (b) (i)  $n(Ag_2CrO_4) = m/M = 1.44 \times 10^{-3} / 332 = 4.33 \times 10^{-6} \text{ mol on } 50 \text{ mL}$   $[Ag_2CrO_4] = 4.33 \times 10^{-6} / 50 \times 10^{-3} = 8.67 \times 10^{-5} \text{ mol } L^{-1}.$   $[Ag^+] = 8.67 \times 10^{-5} \times 2 = 1.73 \times 10^{-4} \text{ mol } L^{-1}$   $[CrO_4^{2-}] = 8.67 \times 10^{-5} \text{ mol } L^{-1}$ 
  - (ii)  $K_s = (1.73 \times 10^{-4})^2 \times 8.67 \times 10^{-5} = 2.61 \times 10^{-12}$
- (c) Dissolving 0.0100g of silver chromate in 50 mL water will result in solid being present, as the required amount to make a saturated solution is  $1.44 \times 10^{-3}$  g in 50 mL, so any more than this will form a solid.

If the same mass is added to 50 mL of ammonia, more will dissolve and less solid will be present due to the formation of a complex ion.

The Ag<sub>2</sub>CrO<sub>4</sub> will dissociate completely and form an equilibrium.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

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

The silver ion will then react further with NH<sub>3</sub>, removing it from the above equilibrium. Thus, more Ag<sub>2</sub>CrO<sub>4</sub> will dissolve to re-establish equilibrium.

# (2012)

Iron(II) hydroxide, Fe(OH)<sub>2</sub>, has a K<sub>s</sub> of  $4.10 \times 10^{-15}$  at 25°C.

(a) (i) Write the equation for  $Fe(OH)_2$  dissolving in water.

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

- (ii) Write the expression for  $K_s$  (Fe(OH)<sub>2</sub>).  $Ks = [Fe^{2+}][OH^-]^2$
- (b) Calculate the solubility (in mol L<sup>-1</sup>) of iron(II) hydroxide in water at 25°C. Let s be the solubility:  $[Fe^{2+}] = s$   $[OH^-] = 2s$   $Ks = s \times (2s)^2$   $4.10 \times 10^{-15} = 4s^3$   $s = 1.01 \times 10^{-5}$  mol L<sup>-1</sup> Solubility of  $Fe(OH)_2(s) = 1.01 \times 10^{-5}$  mol L<sup>-1</sup>
- (c) (i) Determine whether a precipitate of iron(III) hydroxide, Fe(OH)<sub>3</sub>, will form when Fe(NO<sub>3</sub>)<sub>3</sub> is dissolved in water. [Fe(NO<sub>3</sub>)<sub>3</sub>] =  $1.05 \times 10^{-4}$  mol L<sup>-1</sup>. Assume the pH of the water is 7.

```
K_s (Fe(OH)<sub>3</sub>) = 2.00 × 10<sup>-39</sup>. Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq) IP = [Fe^{3+}] [OH^-]^3 At P = [OH^-] = 1 \times 10^{-7} \text{ mol } L^{-1} P = [1.05 \times 10^{-4}] [1 \times 10^{-7}]^3 = 1.05 \times 10^{-25} \text{ Since } IP > 1.05 \times 10^{-10} Will form a precipitate
```

## (2011)

Zinc hydroxide, Zn(OH)<sub>2</sub>, has a  $K_s$  of  $3.00 \times 10^{-17}$  at  $25^{\circ}$ C.

(a) (i) Write an equation for zinc hydroxide dissolving in water.

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

- (ii) Write the  $K_s$  expression for zinc hydroxide.  $K_s = [Zn^{2+}][OH^-]^2$
- (b) Calculate the solubility (in mol L<sup>-1</sup>) of zinc hydroxide at 25°C. Let s be solubility  $Ks = 4^3$   $s = 1.96 \times 10^{-6} \text{ mol L}^{-1}$
- (c) A saturated solution of zinc hydroxide,  $Zn(OH)_2$ , contains a small amount of solid  $Zn(OH)_2$  at the bottom of the container. The pH of the solution is increased.

Discuss the effect of increasing the pH on the amount of solid present, and also on the nature and concentration of the species present in the solution.

No calculations are necessary. Raising the pH will increase the concentration of  $OH^-$  ions. This will initially cause additional precipitate to form. Once the pH has been increased sufficiently (enough  $OH^-$  has been added) the formation of a complex ion with  $Zn^{2+}$  will occur, lowering  $OH^-$  ion concentration in solution. Thus the precipitate will redissolve as a complex ion and less precipitate will be at the bottom of the test tube.

### (2010)

- (a) Sufficient Ag<sub>2</sub>CrO<sub>4</sub> is dissolved in water to form a saturated solution.
  - (i) Write the equation for the equilibrium present in a saturated solution of Ag<sub>2</sub>CrO<sub>4</sub>.  $Ag_2CrO_4(s) = 2Ag^+(aq) + CrO_4^{2-}(aq)$
  - (ii) Write the expression for  $K_s$  (Ag<sub>2</sub>CrO<sub>4</sub>).  $K_s = [Ag^+]^2$  [CrO<sub>4</sub><sup>2-</sup>]
- (d) Calculate the solubility of  $Ag_2CrO_4$  in a saturated solution in mol L<sup>-1</sup>.  $K_s$  ( $Ag_2CrO_4$ ) = 3.00 × 10<sup>-12</sup> Let Solubility = s Ks = 4s <sup>3</sup> s = 9.09 × 10<sup>-5</sup> mol L<sup>-1</sup>
- (c) Discuss how the solubility of Ag<sub>2</sub>CrO<sub>4</sub> will change if it is dissolved in the following solutions. *No calculations are necessary.* 
  - (i) 0.1 mol L<sup>-1</sup> K<sub>2</sub>CrO<sub>4</sub>  $Ag_2CrO_4(s) = 2Ag^+(aq) + CrO_4^{2-}(aq)$  Less silver chromate dissolves. Silver chromate is in equilibrium. More chromate ions shift this to the left.
  - (ii)  $0.1 \text{ mol L}^{-1} \text{ NH}_3$  Ammonia complexes with silver ions.  $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$  This removes silver ions from the equilibrium mixture. The silver chromate equilibrium will shift to the RHS.

### (2009)

Addition of chloride ions to a solution of silver nitrate often results in the formation of a white precipitate of silver chloride (AgCl).

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) K_s (AgCl) = 1.56 \times 10^{-10}$$

- (a) Calculate the concentration, in mol L<sup>-1</sup>, of silver ions in a saturated solution of silver chloride at 25°C.  $K_s = [Ag^+][Cl^-]$  Let  $s = solubility = 1.56 \times 10^{-10} = s^2$   $s = 1.25 \times 10^{-5}$   $[Ag^+] = 1.25 \times 10^{-5}$  (mol L<sup>-1</sup>)
- (b) Solid sodium chloride is added to 5.00 L of 0.100 mol L<sup>-1</sup> silver nitrate solution. Calculate the minimum mass of sodium chloride that would be needed to produce a saturated solution of AgCl. Assume that there is no change in volume when the sodium chloride is added.  $M(NaCl) = 58.5 \text{ g mol}^{-1}$ .  $K_s = [Ag^+][Cl^-] 1.56 \times 10^{-10} = [0.100][Cl^-] [Cl^-] = 1.56 \times 10^{-9} \text{ n} = c \times V = 1.56 \times 10^{-9} \times 5.00 \text{ mol} = 7.80 \times 10^{-9} \text{ mol } m = n \times M = 7.80 \times 10^{-9} \text{ mol} \times 58.5 \text{ g mol}^{-1} = 4.56 \times 10^{-7} \text{ g}$
- (c) Discuss reasons for the fact that a precipitate of silver chloride dissolves on the addition of excess aqueous ammonia. Dilute  $NH_3$  will react with  $Ag^+$  to produce the complex ion  $[Ag(NH_3)_2]^+$ .  $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$  This decreases  $[Ag^+]$ . This moves the solubility equilibrium below to the right  $AgCl(s) = Ag^+(aq) + Cl^-(aq)$  increasing the solubility of AgCl / causing more AgCl to dissolve, therefore the precipitate disappears.

### (2008:3)

- (a) (i) Write an equation for the sparingly soluble salt lead(II) chloride (PbCl<sub>2</sub>) dissolving in water.  $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ 
  - (ii) Write the solubility product expression for lead(II) chloride.  $Ks(PbCl_2) = [Pb^{2+}][Cl^{-}]^2$
- (b) Calculate the solubility, in mol L<sup>-1</sup>, of PbCl<sub>2</sub> in water at 25°C.  $K_s$  (PbCl<sub>2</sub>) = 1.60 × 10<sup>-5</sup> at 25°C Let s be the solubility  $K_s = s$  (2s)<sup>2</sup> 1.60 × 10<sup>-5</sup> = 4s<sup>3</sup> s = 0.0159 mol L<sup>-1</sup> solubility of PbCl<sub>2</sub>(s) = 0.0159 mol L<sup>-1</sup> (allow 0.0160 or 0.016)
- (c) Sea water contains many dissolved salts. The chloride ion concentration in a sample of sea water is 0.440 mol L<sup>-1</sup>. Determine whether a precipitate of lead(II) chloride will form when a 1.00 g sample of lead(II) nitrate is added to 500 mL of the sea water. Your answer must be clearly justified. M(Pb(NO<sub>3</sub>)<sub>2</sub>) = 331 g mol<sup>-1</sup>.  $n(Pb(NO_3)_2) = 1.00 \text{ g / } 331 \text{ g mol}^{-1} = 3.02 \times 10^{-3} \text{ mol. If the lead nitrate is dissolved in the 500 mL, then } [Pb^{2+}] = 6.04 \times 10^{-3} \text{ mol L}^{-1} \text{ Q} = [Pb^{2+}] [Cl^-]^2 = 6.04 \times 10^{-3} \times (0.440)^2 = 1.17 \times 10^{-3}$ . As Q (1.17 × 10<sup>-3</sup>) exceeds Ks (1.60 × 10<sup>-5</sup>), a precipitate will form.

### (2008:4)

The  $K_s$  of aluminium hydroxide,  $AI(OH)_3$ , at 25°C, is  $3 \times 10^{-34}$ , indicating that it has very low solubility. The solubility may be altered by changes in pH (due to acidic or basic properties) and formation of complex ions such as the aluminate ion,  $[AI(OH)_4]^-$ . Discuss why aluminium hydroxide becomes more soluble in aqueous solutions that have a pH less than 4, or a pH greater than 10. In your answer include:

- the equation for the reaction that relates to Ks (Al(OH)₃)
- equations for the reactions that relate to changes in the solubility of aluminium hydroxide at pH less than 4 or greater than 10
- a discussion of the equilibrium principles involved.

```
AI(OH)_3(s) \rightleftharpoons AI^{3+}(aq) + 3OH^-(aq)
```

Acidic conditions When the pH is less than 4,  $[H_3O^+] > [OH^-]$  and the  $[H_3O^+]$  ions react with  $OH^-$  ions from  $Al(OH)_3$ . ie  $H_3O^+ + OH^- \rightarrow 2H_2O$  (OR  $Al(OH)_3(s) + 3H_3O + \rightarrow Al^{3+}(aq) + 6H_2O$ ) The decrease in  $[OH^-]$  from the solubility equilibrium causes the position of equilibrium to shift further to the right so that more  $Al(OH)_3$  is dissolved.

Basic conditions When the pH is greater than 10,  $[H_3O^+] < [OH^-]$  and the OH<sup>-</sup> ions react with  $Al^{3+}$  ions from  $[Al(OH)_4]^-$  ie  $Al^{3+} + 4OH^- \rightarrow [Al(OH)_4]^-$  (OR  $Al(OH)_3(s) + OH^- \rightarrow [Al(OH)_4]^-$ ) The decrease in  $[Al^{3+}]$  from the solubility equilibrium causes the position of equilibrium to shift further to the right so that more  $Al(OH)_3$  is dissolved.

# (2007)

Magnesium hydroxide (known as milk of magnesia) is another substance that the patient consumed to control the acidity of the solution in the stomach.  $K_s$  (Mg(OH)<sub>2</sub>) = 1.25 × 10<sup>-11</sup>

(b) (i) Calculate the solubility of magnesium hydroxide in water in mol L<sup>-1</sup>.  $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH(aq) K_s = 4s^3 = 1.25 \times 10^{-11} s^3 = 3.125 \times 10^{-12} s = 1.46 \times 10^{-4} \text{ solubility is } 1.46 \times 10^{-4} \text{ mol } L^{-1}$ 

### (2006)

Sea-water contains appreciable amounts of ions other than Na $^+$  and Cl $^-$ . One substance that is less soluble than sodium chloride is calcium sulfate. This is precipitated in the first stage of the purification process used to produce table salt (sodium chloride). K<sub>s</sub> (CaSO<sub>4</sub>) =  $2.45 \times 10^{-5}$ 

- (a) (i) Write the equation for the equilibrium reaction in a saturated solution of calcium sulfate.  $CaSO_4(s) = Ca^{2+}(aq) + SO_4^{2-}(aq)$ 
  - (ii) Calculate the solubility of CaSO<sub>4</sub> in water.  $K_s$  (CaSO<sub>4</sub>) = [Ca<sup>2+</sup>][SO<sub>4</sub><sup>2-</sup>] = 2.45 × 10<sup>-5</sup>  $s = 4.95 \times 10^{-3} \text{ mol } L^{-1}$

Evaporating the sea-water to dryness would produce a mixture of salts including NaCl. However, precipitation of NaCl occurs if concentrated hydrochloric acid is added to a saturated NaCl solution.

(b) Explain why this precipitation occurs. The added  $CI^-$  reduces the solubility of the NaCl. For the saturated solution:  $NaCl(s) \rightarrow Na^+$  (aq) +  $CI^-$  (aq). The addition of  $CI^-$  causes the equilibrium to favour the reactants and hence a precipitate will begin to form.

As part of the process for extracting table salt from sea-water, sodium hydroxide is added to the seawater to precipitate the magnesium ions as magnesium hydroxide. The concentration of  $Mg^{2+}$  ions at this stage is 0.555 mol  $L^{-1}$ .

(c) Calculate the minimum hydroxide ion concentration and hence the pH of the solution needed for precipitation to occur.  $K_s$  (Mg(OH)<sub>2</sub>) =  $7.10 \times 10^{-12}$ .  $[Mg^{2+}][OH^-]^2 > 7.10 \times 10^{-12}$   $0.555 \times [OH^-]^2 > 7.10 \times 10^{-12}$   $[OH^-] > 3.58 \times 10^{-6}$  Minimum pH = 8.55

## (2005)

(a) Describe what is meant by the term 'solubility'.

Solubility is the amount of substance that will dissolve in a given volume to form a saturated solution (at that temperature).

(b) The solubility product, Ks, of AgCl has a value of  $1.56 \times 10^{-10}$  at 25°C and this value increases to  $2.15 \times 10^{-8}$  at 100°C. Explain why Ks is higher at 100°C. Include reference to the relevant equilibrium equation in your answer.

Ks is an equilibrium constant for the reaction  $AgCl(s) \Rightarrow Ag^+(aq) + Cl^-(aq)$  and  $K_s = [Ag^+][Cl^-]$  More solid dissolves when the temperature is increased as equilibrium shifts in the endothermic direction, which means it shifts to the right and increases the concentration of ions in solution. This increases  $K_s$ .

The chloride ion concentration in sea water can be determined by titrating a sample with aqueous silver nitrate (AgNO<sub>3</sub>) using potassium chromate ( $K_2CrO_4$ ) as the indicator. As the silver nitrate is added, a precipitate of silver chloride, (AgCl) forms. When most of the AgCl has precipitated, the Ag<sup>+</sup>(aq) concentration becomes high enough for a red precipitate of Ag<sub>2</sub>CrO<sub>4</sub> to form.

- (c) Show that the solubility of  $Ag_2CrO_4$  in pure water at 25°C is higher than that of AgCl.  $K_s$  (AgCl) = 1.56 × 10<sup>-10</sup>,  $K_s$  (Ag<sub>2</sub>CrO<sub>4</sub>) = 1.30 × 10<sup>-12</sup> [Ag<sup>+</sup>] = [Cl<sup>-</sup>] = solubility,  $s_s = 1.25 \times 10^{-5}$  mol  $L^{-1}$   $Ks = [Ag^+]^2[CrO_4^{2-}]$   $s = 6.88 \times 10^{-5}$  mol  $L^{-1}$
- (d) If the concentration of chromate ions is  $6.30 \times 10^{-3}$  mol L<sup>-1</sup> at the point when the Ag<sub>2</sub>CrO<sub>4</sub> starts to precipitate, calculate the concentration of Ag<sup>+</sup> ions in the solution.

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Ks (Ag_2CrO_4) = [Ag^+]^2 [CrO_4]^{2-} = 1.30 \times 10^{-12}

[Ag^+]^2 = 2.06 \times 10^{-10}

[Ag^+] = 1.44 \times 10^{-5} \text{ mol } L^{-1}.
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