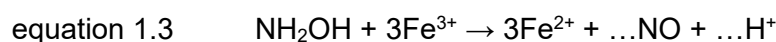
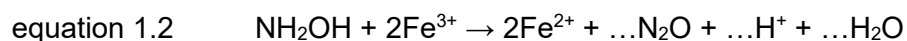
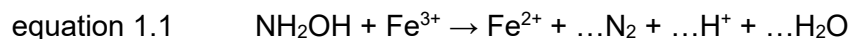


# 1 Determination of the stoichiometry of the reaction between hydroxylamine and iron(III) ion

A redox reaction takes place between hydroxylamine,  $\text{NH}_2\text{OH}$ , and iron(III) ion,  $\text{Fe}^{3+}$ , in an acidic medium. The iron(III) ion is converted to iron(II) ion,  $\text{Fe}^{2+}$ . The reaction is slow at room temperature, but is completed in a few minutes when heated to  $90^\circ\text{C}$ . The iron(II) ions formed can then be oxidised by manganate(VII) ions for quantitative analysis.

You are to determine, by titration, which of the following **unbalanced** equations represents the reaction between hydroxylamine and iron(III) ion.



**FA 1** is  $0.0150 \text{ mol dm}^{-3}$  potassium manganate(VII),  $\text{KMnO}_4$

**FA 2** is a solution prepared by boiling a  $1.00 \text{ dm}^3$  aqueous mixture of  $3.30 \text{ g}$  of hydroxylamine hydrochloride,  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , excess iron(III) chloride,  $\text{FeCl}_3$ , and excess sulfuric acid,  $\text{H}_2\text{SO}_4$

**FA 3** is  $1.00 \text{ mol dm}^{-3}$  sulfuric acid,  $\text{H}_2\text{SO}_4$

## (a) Procedure

1. Fill the burette with **FA 1**.
2. Using the pipette, transfer  $25.0 \text{ cm}^3$  of **FA 2** into the conical flask.
3. Using a measuring cylinder, transfer  $10.0 \text{ cm}^3$  of **FA 3** to the same conical flask.
4. Titrate the mixture in the conical flask with **FA 1**. The end-point is reached when the first permanent pale pink colour is seen.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat steps 2 to 5 to obtain consistent results.

## (i) Titration results

Final burette reading / $\text{cm}^3$	24.70	24.70
Initial burette reading / $\text{cm}^3$	0.00	0.00
Volume of FA 1 used / $\text{cm}^3$	24.70	24.70

[2]

- (ii) From your titration results in (b)(i), obtain a suitable volume of **FA 1**,  $V_{\text{FA 1}}$ , to be used in your calculations. Show clearly how you obtained this volume.

$$V_{\text{FA 1}} = (24.70 + 24.70) / 2 = \underline{24.70 \text{ cm}^3}$$

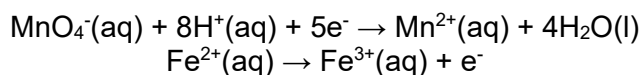
$$V_{\text{FA 1}} = \dots\dots\dots [4]$$

- (b) (i) Calculate the amount of  $\text{MnO}_4^-$  present in  $V_{\text{FA 1}}$  obtained in (a)(ii).

$$24.70/1000 \times 0.0150 = 0.0003705 = \underline{3.71 \times 10^{-4} \text{ mol}} \text{ (3 s.f.)}$$

$$\text{amount of } \text{MnO}_4^- = \dots\dots\dots [1]$$

- (ii) Calculate the amount of  $\text{Fe}^{2+}$  in  $25.0 \text{ cm}^3$  of **FA 2**.



$$5 \times 0.0003705 = 0.0018525 \text{ mol} = \underline{0.00185 \text{ mol}} \text{ (3 s.f.)}$$

$$\text{amount of } \text{Fe}^{2+} = \dots\dots\dots [1]$$

- (iii) Calculate the amount of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  that reacted in the **FA 2** pipetted into the conical flask.

[ $A_r$ : H, 1.0; N, 14.0; O, 16.0; Cl, 35.5]

Other than the fact that the reaction to prepare **FA 2** was complete and there were no impurities in the chemicals used, state an assumption made in your calculation.

$$M_r \text{ of } \text{NH}_2\text{OH} \cdot \text{HCl} = 69.5$$

$$\text{Amount of } \text{NH}_2\text{OH} \cdot \text{HCl} \text{ in } 1.0 \text{ dm}^3 = 3.3 / 69.5 = 0.04748 \text{ mol}$$

$$\text{Amount of } \text{NH}_2\text{OH} \cdot \text{HCl} \text{ in } 25.0 \text{ cm}^3$$

$$= 25/1000 \times 0.04748$$

$$= 0.001187 = \underline{0.00119 \text{ mol}} \text{ (3 s.f.)}$$

$$\text{amount of } \text{NH}_2\text{OH} \cdot \text{HCl} = \dots\dots\dots [2]$$

assumption There was no significant water loss through boiling, such that the total volume of **FA 2** remained at  $1.00 \text{ dm}^3$ .

OR Any water lost through boiling was replaced by topping up with deionised water to  $1.00 \text{ dm}^3$  after cooling.

OR  $\text{NH}_2\text{OH} \cdot \text{HCl}$  is fully soluble in aqueous solution, such that 1 mol of the solid gives 1 mol of  $\text{NH}_2\text{OH}$ . [1]

- (iv) Determine which equation represents the reaction between hydroxylamine and iron(III) ion. Show your working.

Amount of  $\text{NH}_2\text{OH}$  : Amount of  $\text{Fe}^{2+}$   
0.001187 : 0.001845  
1 : 1.55  $\approx$  1 : 2

Hence, it is equation 1.2.

equation ..... [1]

- (v) From your answer to (b)(iv), write the balanced chemical equation, with state symbols, for the reaction between hydroxylamine and iron(III) ion.

..... [2]  
 $\text{NH}_2\text{OH}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \frac{1}{2}\text{N}_2\text{O}(\text{g}) + 2\text{H}^+(\text{aq}) + \frac{1}{2}\text{H}_2\text{O}(\text{l})$

- (vi) Hence, with reference to the oxidation number of nitrogen, explain whether hydroxylamine acts as an oxidising agent or a reducing agent in the reaction with iron(III) ion.

Hydroxylamine acts as a reducing agent. It is oxidised as the oxidation number of nitrogen increases from  $-1$  in hydroxylamine to  $+1$  in  $\text{N}_2\text{O}$ .  
..... [1]

- (d) Another student prepared **FA 2** in a similar way, but found out later that the 3.30 g of hydroxylamine hydrochloride,  $\text{NH}_2\text{OH}.\text{HCl}$ , contained a small amount of inert impurities.

Suggest what effect this would have on the average titre. Explain your answer.

With impurities, the actual mass and therefore the amount of  $\text{NH}_2\text{OH}.\text{HCl}$  and, in turn, the amount of  $\text{Fe}^{2+}$  would be lower than expected.  
As such, a lower amount  $\text{MnO}_4^-$  is required to react completely with  $\text{Fe}^{2+}$ , resulting in a lower average titre than expected.  
..... [2]

[Total: 17]

## 2 Determination of a value for the molar enthalpy change of reaction for citric acid and sodium hydrogen carbonate.

Citric acid is a weak acid that is found naturally in all citrus fruits.

Citric acid reacts with sodium hydrogen carbonate according to equation 2.1 and produces temperature change.



The maximum temperature change,  $\Delta T_{\text{max}}$ , can be determined by direct measurement of the initial temperature and the final temperature reached.

In this question, you are to plan a procedure that would provide sufficient data to allow you to determine an accurate and reliable value for the molar enthalpy change of reaction,  $\Delta H_{\text{reaction}}$ , may be determined.

- (a) Plan an investigation to determine the maximum temperature change,  $\Delta T_{\text{max}}$ , for the reaction between an aqueous citric acid solution and solid sodium hydrogen carbonate.

Measurements should be taken:

- before the reaction starts,
- during the reaction,
- for some time after the reaction is complete.

You are provided with:

- **FA4** (approximately 120 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> of citric acid solution)
- **FA5** (approximately 8 g of solid sodium hydrogen carbonate)
- 250 cm<sup>3</sup> beaker
- 2 polystyrene cups
- 0.2 °C division thermometer
- 50 cm<sup>3</sup> measuring cylinder
- glass rod
- weighing bottle
- weighing balance

In your plan you should include brief details of how you would:

- prepare and set up the apparatus to minimise heat loss,
- measure the initial temperature of the citric acid solution,
- add the sodium bicarbonate (**do not exceed 3 g**) and monitor the temperature change,
- ensure the temperature is recorded accurately,
- repeat the experiment for reliability,
- record and process your data, including how to calculate the average temperature change,  $\Delta T_{\text{average}}$ .

[Ar: C, 12.0; H, 1.0; O, 16.0; Na, 23.0]

[9]

### Pre-calculation

Let the volume of citric acid used be  $50.0 \text{ cm}^3$ .

Amount of citric acid =  $\frac{50.0}{1000} \times 0.100 = 0.00500 \text{ mol}$

Amount of  $\text{NaHCO}_3$  needed for complete reaction =  $0.005 \times 3 = 0.0150 \text{ mol}$

Mass of  $\text{NaHCO}_3$  for complete reaction =  $0.0150 \times 84.0 = 1.26 \text{ g}$

Therefore, for citric acid to be in excess, mass of  $\text{NaHCO}_3$  should be less than  $1.26 \text{ g}$ .

### Procedure

1. Using a  $50.0 \text{ cm}^3$  measuring cylinder, transfer  $50.0 \text{ cm}^3$  of citric acid solution into a polystyrene cup. Note that the volume used should result in excess amount of citric acid.
2. Place this cup inside a second polystyrene cup, which is placed in a  $250 \text{ cm}^3$  beaker.
3. Stir and measure the temperature of the citric acid solution. Record this temperature as  $T_{\text{initial}}$ .
4. Weigh exactly  $1.00 \text{ g}$  of solid sodium bicarbonate into a dry weighing bottle using a weighing balance. Record the mass in the table below.
5. Add the sodium hydrogen carbonate quickly into the citric acid solution in the polystyrene cup.
6. Stir the mixture continuously using the thermometer. Monitor the temperature until it reaches its minimum. Record this temperature as  $T_{\text{final}}$ .
7. Replace the wet polystyrene cup with a clean, dry polystyrene cup. Repeat steps 1 to 6 to obtain a second value for  $T_{\text{final}}$ .
8. Complete a results table, calculating the average of the initial temperatures and the change in temperature ( $\Delta T$ ) for each experiment.

	Expt 1	Expt 2
mass of weighing bottle and $\text{NaHCO}_3$ / g		
mass of weighing bottle and residue / g		
mass of $\text{NaHCO}_3$ / g		

For  $50 \text{ cm}^3$  of citric acid and  $1 \text{ g}$  of  $\text{NaHCO}_3$ ,

	Run A	Run B
$T_{\text{initial}} / ^\circ\text{C}$		
$T_{\text{final}} / ^\circ\text{C}$		
$\Delta T / ^\circ\text{C}$	$T_A$	$T_B$

$$\Delta T_{\text{average}} = (T_A + T_B) / 2 = T ^\circ\text{C}$$

- (b) Calculate the average heat change,  $q$ , for your experiment in **2(a)**, and hence determine a value for the enthalpy change of reaction for the reaction between citric acid and sodium hydrogen carbonate reaction,  $\Delta H_{\text{reaction}}$ , with reference to equation 2.1.

You should assume that:

- specific heat capacity of the mixture is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ;
- density of the mixture is  $1.00 \text{ g cm}^{-3}$

$$\text{Heat absorbed} = mc\Delta T_{\text{average}} = 50 \times 4.18 \times 3.0 = \underline{627 \text{ J}}$$

$$q = \dots\dots\dots$$

For  $\text{NaHCO}_3$ , being limiting reagent, average mass should be used for calculating  $n_{\text{NaHCO}_3}$  since  $\Delta T_{\text{average}}$  was obtained from 2 sets of experiments.

$$\begin{aligned}\Delta H_{\text{limiting reagent}} &= q/n_{\text{NaHCO}_3} \\ &= +627 \div [1.00 / (23.0+1.0+12.0+3(16.0))] \\ &= +627 \div 0.0119 \\ &= +52.7 \text{ kJ mol}^{-1}\end{aligned}$$

To find the  $\Delta H$  for equation 2.1, the calculation should be based on **per mole of citric acid** reacting with **3 moles** of  $\text{NaHCO}_3$ .

$$\begin{aligned}\text{Since 3 moles of } \text{NaHCO}_3 \text{ react per mole of citric acid,} \\ \Delta H_{\text{reaction}} &= +52.7 \times 3 = +158.1 = \underline{+158 \text{ kJ mol}^{-1}} \text{ (3 s.f.)}\end{aligned}$$

$$\Delta H_{\text{reaction}} = \dots\dots\dots$$

- (c) Another student performed a similar experiment that you performed in **2(a)** but measured the temperature at timed intervals. He added 3.00 g of sodium hydrogen carbonate to 50.0 cm<sup>3</sup> of citric acid at  $t = 30$  s and obtained the data shown in Table 2.1 below.

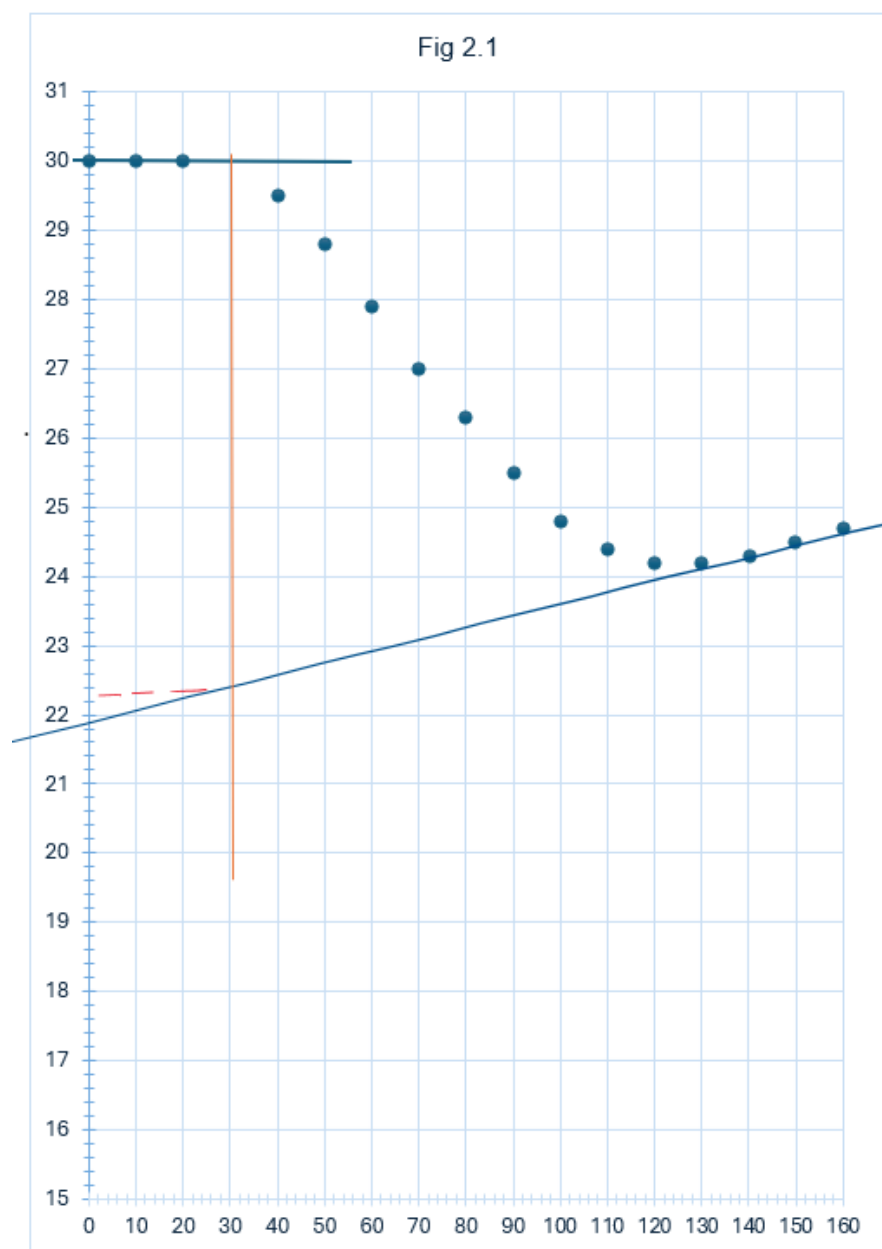
**Table 2.1**

time/ s	temperature/ °C
0	30.0
10	30.0
20	30.0
30	–
40	29.5
50	28.8
60	27.9
70	27.0
80	26.3
90	25.5
100	24.8
110	24.4
120	24.2
130	24.2
140	24.3
150	24.5
160	24.7

- (i) Plot, on Fig 2.1, a graph that the student would obtain using the data in Table 2.1.

Show using construction lines, on Fig 2.1, how the minimum temperature,  $T_{\min}$ , and the maximum temperature,  $T_{\max}$ , and  $\Delta T$  may be obtained at  $t = 30$  s.

[3]



- (ii) From your graph in Fig 2.1, read the minimum temperature,  $T_{\min}$  and the maximum temperature,  $T_{\max}$ , at  $t = 30$  s. Record these values in the spaces provided. Deduce the temperature change at  $\Delta T$  at  $t = 30$  s.

$$T_{\min} = \dots 22.4^{\circ}\text{C} \dots$$

$$T_{\max} = \dots 30.0^{\circ}\text{C} \dots$$

$$\Delta T = \dots 7.6^{\circ}\text{C} \dots$$

[2]

- (iii) Hence, using the graphical method, calculate a value for the enthalpy change of reaction for the reaction between citric acid and sodium hydrogen carbonate reaction,  $\Delta H_{\text{reaction}}$ , with reference to equation 2.1.

Since citric acid the limiting reagent, to find the  $\Delta H$  for the reaction, the calculation should be based on per mole of citric acid.

$$\text{Heat absorbed} = mc\Delta T = 50 \times 4.18 \times 7.6 = 1588.4 = 1590 \text{ J}$$

$$\begin{aligned}\Delta H &= q / n(\text{citric acid}) \\ &= +1588.4 \div (\text{volume} \times \text{conc}) \\ &= 1588.4 / 0.005 = \underline{\underline{+318 \text{ kJ mol}^{-1}}}\end{aligned}$$

$$\Delta H_{\text{reaction}} = \dots\dots\dots [2]$$

- (iv) Explain whether the graphical method in **2(c)(ii)** gives a more accurate value for  $\Delta T$  than  $\Delta T_{\text{average}}$  determined in **2(a)**. [2]

The graphical method is more accurate as it accounts for heat gained from (or exchange with) the environment.

[Total: 21]

### 3 Inorganic qualitative analysis

You will carry out tests on **FA 10** and **FA 11**.

Unless otherwise stated, the volumes given in the procedure are approximate and should be estimated rather than measured.

(a) (i) **FA 10** is an aqueous solution containing two cations and one anion.

Carry out the tests in Table 3.1 and record your observations.  
Test and identify any gases evolved.

**Table 3.1**

tests		observations
1	Test solution <b>FA 10</b> with a blue litmus paper.	<ul style="list-style-type: none"><li>Blue litmus paper turns red</li></ul>
2	To a 0.5 cm depth of <b>FA 10</b> in a test-tube, add aqueous sodium carbonate dropwise.	<ul style="list-style-type: none"><li>Pale blue / bluish-white precipitate forms</li><li>Effervescence due to colourless, odourless gas seen</li><li>Moist blue litmus paper turns red (note: no delivery tube was given!)</li><li>CO<sub>2</sub> evolved</li></ul>
3	To a 0.5 cm depth of <b>FA 10</b> in a test-tube, add aqueous sodium hydroxide dropwise, with shaking, until no further change is seen.  Filter the mixture. Retain the filtrate and the residue for use in Tests 4, 5 and 6.	<ul style="list-style-type: none"><li>Pale blue ppt</li><li>Insoluble in excess</li><li>Blue solid as residue</li><li>Colourless solution as filtrate</li></ul>
4	Divide the filtrate from step 3 into two portions.  To the <b>first portion</b> of the filtrate in a test-tube, add 5 to 6 drops of aqueous NaOH, followed by a spatula full of Zn powder and warm.	<ul style="list-style-type: none"><li>Pungent, colourless gas evolved</li><li>Moist red litmus paper turns blue</li><li>Ammonia evolved</li></ul>
5	To the <b>second portion</b> of the filtrate in a test-tube, add aqueous sulfuric acid dropwise, with shaking, until no further change is seen.	<ul style="list-style-type: none"><li>White ppt reforms</li><li>Dissolves in excess acid to form a colourless solution</li></ul>
	Add aqueous ammonia to the mixture obtained dropwise, with shaking, until no further change is seen.	<ul style="list-style-type: none"><li>White ppt forms</li><li>Insoluble in excess</li></ul>

6	Use a spatula to transfer the washed residue from the filter paper to a test-tube.  Add aqueous sulfuric acid dropwise, with shaking, until the solid dissolves.	<ul style="list-style-type: none"> <li>Blue solid dissolves to form a pale/light-blue solution</li> </ul>
	Add aqueous potassium iodide dropwise, with shaking, to the solution.	<ul style="list-style-type: none"> <li>White / cream ppt forms in an orange / brown / yellow solution</li> </ul>
7	To a 0.5 cm depth of <b>FA 10</b> , add aqueous ammonia dropwise until in excess.  Filter the mixture. Retain the filtrate for use in Test 8.	<ul style="list-style-type: none"> <li>Blue ppt forms</li> <li>Dissolves in excess ammonia to form a deep blue solution</li> <li>Dark blue solution as filtrate</li> </ul>
8	To the filtrate in a test-tube, add aqueous sulfuric acid dropwise, with shaking, until no further change is seen.	<ul style="list-style-type: none"> <li>Blue ppt reforms</li> <li>Dissolves in excess acid to give a pale blue solution</li> </ul>
	Add aqueous potassium iodide dropwise, with shaking, to the mixture.	White / cream ppt forms in an orange / brown / yellow solution

[6]

- (ii) From the observations in (a)(i), deduce the identity of the two cations and one anion in **FA 10**.

$\text{Al}^{3+}$  and  $\text{Cu}^{2+}$

cations .....

$\text{NO}_3^-$

anion .....

[2]

- (iii) Giving essential supporting evidence from (a)(i), state and explain which tests allow you to deduce the identity of the anion present in **FA 10**.

- In test 4, powdered Zn reduced the nitrate or nitrite present to ammonia upon warming, thus indicating the presence of either nitrate or nitrite
- Test 1 and/or 5 rules out nitrite because if nitrite was present, a brown pungent gas should have been evolved and hence the absence of which confirms that it must be nitrate

[2]

- (iv) Explain why it would not be meaningful to add Zn powder to a portion of the filtrate obtained in Test 7 to confirm the anion identified in the earlier tests.

- The filtrate from test 7 already contains an excess of the aqueous ammonia added in that step
- Hence, any ammonia evolved will be from the excess aqueous ammonia present in the filtrate and not necessarily due to the reaction with Zn

[1]

- (b) (i) **FA 11** is an aqueous solution containing one cation.

Carry out the tests in Table 3.2 and record your observations.

**Table 3.2**

tests		observations
1	To a 0.5 cm depth of <b>FA 11</b> in a test-tube, add aqueous ammonia dropwise, with shaking, until no further change is seen.	<ul style="list-style-type: none"> <li>White ppt forms</li> <li>Insoluble in excess</li> </ul>
	Add 1 to 2 spatula full of solid ammonium chloride and shake the mixture.	<ul style="list-style-type: none"> <li>White ppt dissolves to form a colourless solution</li> </ul>
2	To a 0.5 cm depth of <b>FA 11</b> in a test-tube, add 1 to 2 spatula full of solid ammonium chloride, with shaking, until no further change is seen.	<ul style="list-style-type: none"> <li>Solid ammonium chloride dissolves to form a colourless solution</li> </ul>
	Add aqueous ammonia dropwise, with shaking, until no further change is seen.	<ul style="list-style-type: none"> <li>No ppt formed</li> <li>Solution remains colourless</li> </ul>

[3]

- (ii) Explain your observations for Test 1 in (b)(i) using the principles of solubility equilibrium.

- White ppt of  $\text{Mg}(\text{OH})_2$  formed as  $[\text{Mg}^{2+}][\text{OH}^-]^2 > K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2$
- Ppt dissolved when common ion in the form  $\text{NH}_4^+$  was introduced, causing the  $[\text{Mg}^{2+}][\text{OH}^-]^2$  to become lower than  $K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2$
- $\text{NH}_4^+$  as a common ion suppressed the dissociation of aqueous ammonia, resulting in the lowering of the  $[\text{OH}^-]$  and hence the lowering of the ionic product,  $[\text{Mg}^{2+}][\text{OH}^-]^2$

[2]

- (iii) Explain your observations for Test 2 in (b)(i) using the principles of solubility equilibrium.

- No ppt of  $\text{Mg}(\text{OH})_2$  was formed when aqueous ammonia was added as the  $[\text{NH}_4^+]$  was already very high due to the dissolved  $\text{NH}_4\text{Cl}$ , which suppressed the ionisation of the aqueous ammonia
- Hence, the low  $[\text{OH}^-]$  in the mixture resulted in  $[\text{Mg}^{2+}][\text{OH}^-]^2 < K_{\text{sp}}$  of  $\text{Mg}(\text{OH})_2$

[1]

[Total: 17]