Answer **all** the questions in the spaces provided.

1 Determination of concentrations of sodium hydroxide, and of sodium carbonate in a mixture

FA 1 is a solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.
FA 2 is an aqueous solution containing 0.90 mol dm^{-3} of hydrochloric acid, HC*l*.

Sodium hydroxide reacts with hydrochloric acid according to the equation below:

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Sodium carbonate reacts with hydrochloric acid in two separate stages. The reactions that occur are:

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$
Reaction 3 $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

You are required to find the concentrations of sodium hydroxide, and of sodium carbonate, in **FA 1**, by means of a *double-indicator* titration.

In a *double-indicator* titration, **two different** indicators are used, separately, in the **same** titration. In this experiment, thymolphthalein indicator, followed by methyl orange indicator, will be used.

Thymolphthalein indicates the end-point when **Reaction 1** and **2** are complete, while methyl orange indicates the end-point when **Reaction 3** is complete.

(a) (i) Dilution of FA 2

Using a burette, measure between 35.00 cm^3 and 36.00 cm^3 of **FA 2** into the 250 cm^3 volumetric flask.

Record your burette readings and the volume of **FA 2** added to the flask in the space below.

Final (burette) reading /cm^3	46.30
Initial (burette) reading / cm^3	11.00
Volume of FA2 (used for dilution) /cm^3	35.30

Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. This solution is **FA 3**.

(ii) Titration of FA 1 against FA 3

Fill a second burette with **FA 3**.

Pipette 25.0 cm^3 of **FA 1** into a conical flask.
Replace the cap over the FA 1 bottle to prevent absorption of carbon dioxide from the atmosphere.

Add a few drops of thymolphthalein indicator and titrate **FA 1** with **FA 3**. The end-point is reached when the solution turns colourless. Ignore any cloudiness that you may observe in the conical flask. Record your titration results in the space below. **The volume of FA 3 used to reach the first end-point need not be consistent.**

Do not discard this solution.

To **this** solution, add a few drops of methyl orange indicator and **continue** to titrate with **FA 3** until the second end-point is reached. Record your titration results in the space below.

Perform sufficient titrations to obtain accurate results for the **second end-point**, which refers to the **total** volume of **FA 3** required for the whole titration.

Make certain that all your recorded results show the precision of your working.

Initial (burette) reading /cm^3	4.90	4.30
Final (burette) reading 1 /cm^3	24.60	24.10
Final (burette) reading 2 / cm^3	35.50	34.90
Titre 1 /cm^3	19.70	19.80
Titre 2 /cm^3	30.60	30.60

Tables have correct headers and units [1]
All readings recorded to correct precision [1]
Dilutes between 35.00 cm^3 and 36.00 cm^3 of **FA 2**. [1]

[3]

(b) From your titrations, obtain suitable volumes of **FA 3** for the:
- first end-point
- second end-point.

Show clearly how you obtained these volumes.

mean titre 1 = ½ (19.70 + 19.80) = 19.75 cm^3
mean titre 2 = ½ (30.60 + 30.60) = 30.60 cm^3

Correct average titre from values within 0.10 cm^3 [1]
Accuracy (difference between teacher's and student's scaled mean titre) [2]

volume of **FA 3** for first end-point = ...

volume of **FA 3** for second end-point = ...
[3]

(c) **(i)** Calculate the concentration, in mol dm^{-3}, of HC*l* in **FA 3**.

[HC*l*] in FA3 = 35.30 / 250 × 0.90 = 0.127 mol dm^{-3}

concentration of HC*l* in **FA 3** = ... [1]

(ii) Calculate the amount of sodium carbonate, Na_2CO_3, present in 25.0 cm^3 of **FA 1**.

vol. FA3 reacted with $NaHCO_3$ formed = 30.60 – 19.75
= 10.85 cm^3

ηNa_2CO_3 in 25 cm^3 **FA 1**
= η$NaHCO_3$ formed
= ηHC*l* reacted
= 0.1271 × 10.85/1000
= 0.00138 mol

amount of Na_2CO_3 in 25.0 cm^3 of **FA 1** = ... [1]

(iii) Calculate the amount of sodium hydroxide, NaOH, present in 25.0 cm^3 of **FA 1**.

vol. FA3 reacted with NaOH = 19.75 – 10.85
= 8.90 cm^3 [1]

ηNaOH in 25 cm^3 **FA 1** = ηHC*l* reacted
= 0.1271 × 8.90/1000 = 0.00113 mol [1]

amount of NaOH in 25.0 cm^3 of **FA 1** = ... [2]

(iv) Use your answers from **(c)(ii)** and **(c)(iii)**, calculate the concentrations, in mol dm^{-3}, of Na_2CO_3 and NaOH in **FA 1**.

[Na_2CO_3] in **FA 1** = 0.001379 x 1000/25 = 0.0552 mol dm^{-3}

[NaOH] in **FA 1** = 0.001131 x 1000/25 = 0.0452 mol dm^{-3}

concentration of Na_2CO_3 in **FA 1** = ...

concentration of NaOH in **FA 1** = ...
[1]

(d) The maximum error in a single burette reading is ±0.05 cm^3.

When making up the diluted acid, **FA 3,** a student recorded that 35.00 cm^3 of **FA 2** was used. What are the smallest and largest possible volumes of acid that were run into the volumetric flask?

smallest volume used = 34.90 cm^3 largest volume used = 35.10 cm^3

[1]

(e) A student suggested doing the titration in **(a)(ii)** differently – **FA 3** is placed in the conical flask and **FA 1** in the burette, using methyl orange indicator followed by thymolphthalein indicator.

Explain if this method will allow you to determine the concentrations of NaOH and Na_2CO_3 in **FA 1**.

As there is **excess HC*l*** in the conical flask, methyl orange only changes colour when **both** Na_2CO_3 and NaOH have completely reacted i.e. only **one end-point** will be obtained.
Hence this method does **not** allow [Na_2CO_3] and [NaOH] to be determined.

.....

.....

.....[1]

[Total: 13]

2 Heat of reaction between copper(II) ions and iron metal

In this experiment, you will measure the heat given out by the reaction of excess iron with copper(II) sulfate solution and use this to find the concentration of the copper(II) sulfate.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

FA 4 is iron powder.
FA 5 is aqueous copper(II) sulfate, $CuSO_4$.

In an appropriate format in the space below, prepare a table in which you may record each temperature and the time it was taken.

1. Wash thoroughly a burette and fill it with **FA 5**. Place a Styrofoam cup into a 250 cm^3 beaker to prevent it from tipping over. Transfer 40.00 cm^3 of **FA 5** into the Styrofoam cup.

2. Place the lid onto the cup and insert the thermometer through the lid. Measure and record the initial temperature of the **FA 5** solution in the cup.

3. Start the stopwatch. Measure and record the temperature of the solution in the cup **every <u>half minute</u>** up to and including the temperature at 1.5 min. Stir the solution using the thermometer.

4. At time *t* = 2.0 min, add all the powdered iron **FA 4** to the solution. Stir the mixture **thoroughly** with the thermometer to **ensure the solid mixes well with the solution**.

5. Record the temperature of the mixture **every <u>minute</u>** from *t* = 2.5 min. Continue stirring **thoroughly** and mixing the contents of the cup well **throughout** your recordings.

6 Once the temperature starts to drop, continue recording **every <u>half minute</u>** for a **further 3 minutes**. Constantly stir the solution **thoroughly**.

(a) Experimental Results

Time / min	Temperature / °C
0.0	29.6
0.5	29.6
1.0	29.6
1.5	29.6
2.0	–
2.5	29.8
3.5	32.4
4.5	35.8
5.5	38.6
6.5	40.6
7.5	41.8
8.5	42.5
9.5	42.6
10.5	42.3
11.0	42.2
11.5	42.0
12.0	41.8
12.5	41.7
13.0	41.6

Correct headers and units **[1]**
All temperatures recorded to correct precision **[1]**
Full set of results with **at least 6 more readings** once the temperature starts to drop **[1]**
Accuracy (difference between teacher's and student's highest recorded T) **[1]**

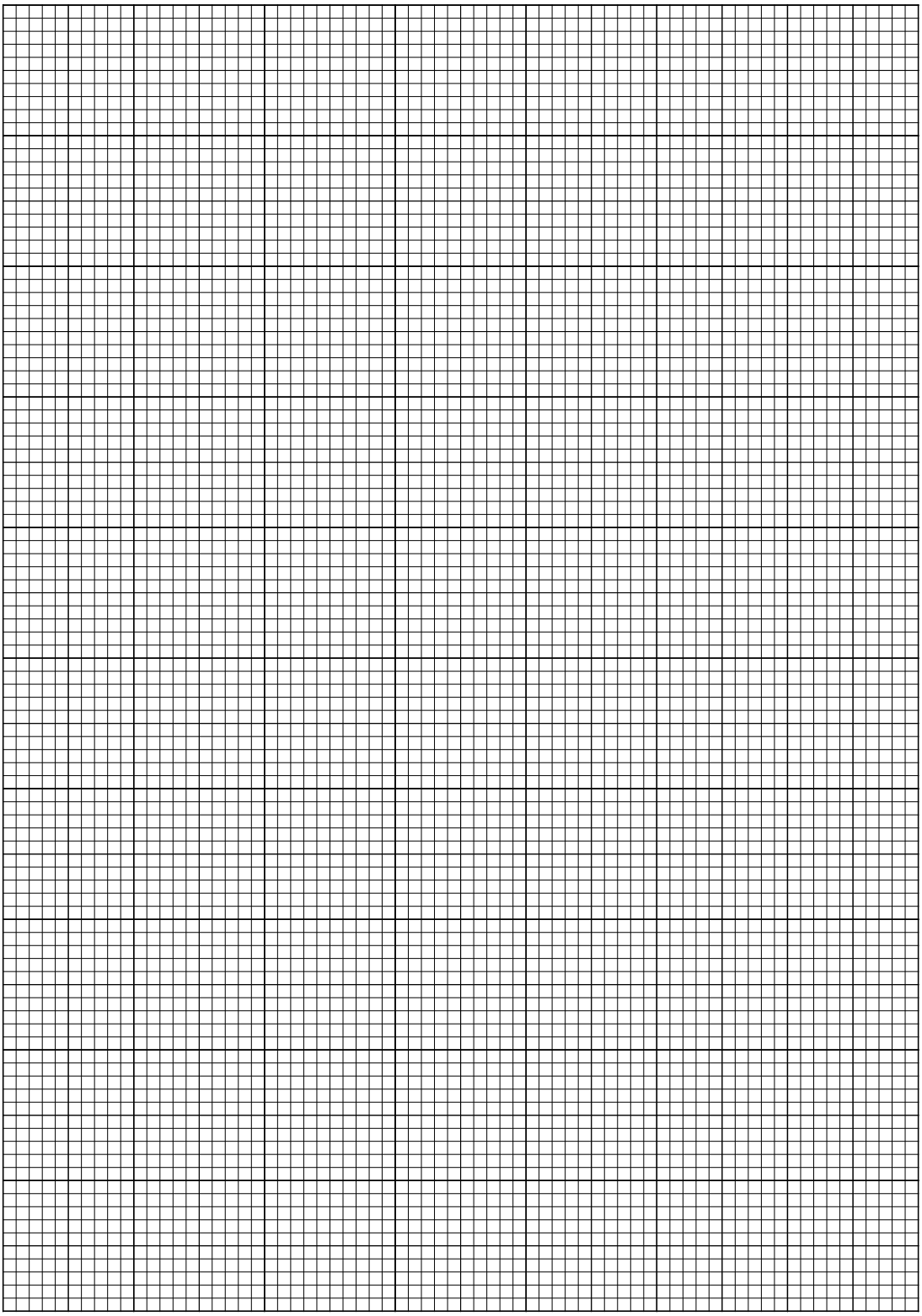
Correct axes + labels + units + sensible scale + plotted points (inclusive of 5 °C) occupy at least half the graph grid in both x and y directions **[1]**
Correct plotting **[1]**
Correctly draws the two best-fit lines **[1]**

[4]

(b) **(i)** Plot on the grid below, a graph of the temperature on the y-axis, against time, *t,* on the x-axis. The scale for the temperature axis must allow you to plot a point with temperature 5 ^{o}C greater than the maximum temperature you recorded.

Draw the following **best-fit** straight lines on the graph.

- a line through the points before addition of **FA 4**.
- a line through the points once temperature starts to drop.



(ii) Use the best-fit straight lines to determine the theoretical temperature change at time t = 2.0 min.

45.0 – 29.6 = 15.4 ^{o}C

Correctly determines theoretical T_{max} using graph [1]

Accuracy (difference between teacher's and student's change in T) [1]

change in temperature = ... [5]

(c) **(i)** Use your answer to **(b)(ii)** to calculate the heat energy produced in the reaction. (Assume that **4.2 J** are required to increase the temperature of 1 cm^3 of solution by 1 ^{o}C.)

q = 40.00 x 4.2 x 15.4 = 2587.2 = 2590 J

heat energy produced = ... [1]

(ii) The molar enthalpy change, ΔH, for the reaction shown below is –152 kJ mol^{-1}.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

Use this value and your answer to **(c)(i)** to calculate the concentration of copper(II) sulfate, in mol dm^{-3}, in **FA 5**.

nCu^{2+} in 40.00 cm^3 of **FA 4** = 2587 / 152000 = 0.01702 mol [1]

[Cu^{2+}] in **FA 4** = 0.01702 / (40.00/1000) = 0.426 mol dm^{-3} [1]

Shows working in **all** calculations in Q1 and Q2 [1]
Shows appropriate significant figures in **all** final answers [1]
Shows appropriate units in **all** answers [1]

concentration of copper(II) sulfate = ... [5]

(d) **(i)** Calculate the maximum percentage error in the highest temperature that you recorded in your results table.

maximum percentage error = 0.1 / 42.6 x 100 % = 0.23 %

maximum percentage error = ... [1]

(ii) What would be the expected change in temperature obtained in **(b)(ii)** if the volume of copper(II) sulfate used was halved? Explain your answer.

Since $CuSO_4$ is the limiting reagent, using half the volume of $CuSO_4$ means only half the original amount of Cu^{2+} is reacted, hence only half the heat will be released. However, the volume of solution to be heated is also halved. Hence the change in temperature will be the same.

.....

.....[1]

[Total: 17]

3 Planning

The concentration of copper(II) sulfate in **FA 5** in Question 2 may be determined instead, by titration of the aqueous solution obtained after step 5, with aqueous potassium manganate(VII).

The reaction mixture obtained after step 5 in Question 2 contains $FeSO_4(aq)$ and solids iron and copper. This mixture needs to be first filtered. The filtrate is then diluted to obtain a solution suitable for titration with aqueous potassium manganate(VII) of known concentration, in the presence of acid.

The manganate(VII) ions react with iron(II) ions as shown in the following equation.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(a) Using information from Question 2, determine a suitable concentration of aqueous potassium manganate(VII) to use in this titration. The concentration of manganate(VII) should not exceed 0.0500 mol dm^{-3}.

You are to assume that the concentration of copper(II) sulfate in **FA 5** is 0.800 mol dm^{-3}. (Note that this is not the correct value.)

Show clearly your calculations and any assumptions.

$n(Cu^{2+})$ in 40.00 cm^3 of **FA 5**
= 0.800 x 40/1000 = 0.032 mol = $n(Fe^{2+})$ produced in mixture [1]

Assume pipette 25 cm^3 (out of 40 cm^3) of Fe^{2+} and dilute to 250 cm^3, then draw out 25 cm^3 for titration,

$n(Fe^{2+})$ used for titration = 0.032 x 25/40 x 1/10 = 0.0020 mol

$n(MnO_4^-)$ needed for titration = 0.0020 / 5 = 0.00040 mol [1]

Assume titre to be 25 cm^3,
$[KMnO_4]$ = 0.00040 / (25/1000) = **0.0160 mol dm^{-3}** [1]

[3]

(b) Plan an experiment to determine the concentration of copper(II) sulfate in **FA 5** using the titration method described above.

In your plan, you should include details of:
- the quantities of chemicals you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take.

1. Filter the mixture into a dry conical flask, using dry filter funnel and dry filter paper.
2. Pipette 25.0 cm^3 of the filtrate into a 250 cm^3 volumetric flask. Top up to the mark with deionised water. Stopper and shake to ensure a homogeneous solution.
3. Fill a burette with 0.0160 mol dm^{-3} aqueous $KMnO_4$ solution. Record the initial burette reading.
4. Pipette 25.0 cm^3 of the diluted solution into a conical flask.
5. Add 10 cm^3 of 1.0 mol dm^{-3} H_2SO_4 solution into the conical flask.
6. Titrate the solution in the conical flask with $KMnO_4$ until the end-point where the solution turns from yellow to orange/pink. Record the final burette reading.
7. Repeat steps 4-6 until consistent results within +/-0.10 cm^3 are obtained.

Filters reaction mixture into volumetric flask and ensure quantitative transfer of all Fe^{2+}
OR: Filters reaction mixture using dry filter funnel, dry filter paper and dry conical flask into beaker/conical flask and draws out suitable volume of filtrate using pipette for dilution [1]
Proposes correct dilution steps and apparatus from Question 1 [1]
Proposes correct titration steps and apparatus from Question 1 [1]
Adds excess dilute H_2SO_4 into conical flask before titration [1]
Gives correct colour change at end-point (yellow to orange/pink) [1]

.....

.....

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.....[5]

[Total: 8]

4 Qualitative analysis

In this question you will perform a series of test-tube reactions and use the observations to help you deduce the identities of two solids present in a given mixture **FA 6**.

You will also **devise a plan**, consisting of test-tube reactions, and **carry out** the plan to distinguish between three solutions **FA 9**, **FA 10** and **FA 11**, so that each is identified.

At each stage of any test you are to record details of the following:

- details of colour changes and precipitates formed
- the names of gases evolved and details of the test used to identify each one

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

(a) **FA 6** is a mixture of two solids: **FA 7**, which is soluble in water and **FA 8**, which is insoluble in water. Each contains one cation and one anion listed in the Qualitative Analysis Notes on pages 15 and 16.

Carry out the following tests and record your observations in the table.

	test	*observations*
(i)	Place all of the solid, **FA 6**, into a boiling tube. Add 10 cm^3 of deionised water and shake to dissolve **FA 7**. Filter the mixture, collecting the filtrate in a test-tube. Keep the filtrate for tests **(ii)** to **(iv)**. Wash the residue, **FA 8**, with deionised water. Collect the washings in the previous boiling tube. Keep the residue for tests **(v)** to **(vii)**.	colourless filtrate green residue
(ii)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add aqueous sodium hydroxide. Carefully warm the mixture.	no ppt no pungent/NH_3 gas evolved
(iii)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add aqueous ammonia.	no ppt
(iv)	To a 1 cm depth of filtrate, **FA 7**, in a test-tube, add 5 drops of aqueous silver nitrate, followed by aqueous ammonia.	white ppt white ppt soluble in NH_3(aq)

	test	*observations*
(v)	Transfer half a spatula of the residue, **FA 8**, into a clean boiling tube. Using a measuring cylinder, measure out 10 cm^3 of dilute nitric acid. Transfer the acid to the boiling tube in portions. Mix the contents of the boiling tube thoroughly. Filter if necessary. This solution is **FA 12**.	green residue dissolves to give blue solution effervescence, gas gives white ppt with limewater
(vi)	To a 1 cm depth of **FA 12** in a test-tube, add 1 cm depth aqueous edta.	blue solution turns dark blue
(vii)	To a 1 cm depth of **FA 12** in a test-tube, add 1 cm depth aqueous sodium hydroxide, followed by aqueous ammonia. **Do not discard the remaining FA 12. Keep the solution for (b).**	blue ppt blue ppt dissolves to give dark blue solution

[4]

10 observations [4]

(viii) From the observations, identify the ions in **FA 7** and **FA 8**.

FA 7 contains the cation Ba^{2+}/Ca^{2+} and the anion Cl^-

FA 8 contains the cation Cu^{2+} and the anion CO_3^{2-}

[2]

(ix) Explain in terms of the chemistry involved, your observations in **(a)(iv)**.

Cl^- reacts with $AgNO_3$ to form white ppt of **AgCl**. With $NH_3(aq)$, complex **$[Ag(NH_3)_2]^+$** is formed. [1]
This reduces $[Ag^+]$ and shifts the equilibrium: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ to the right / ionic product becomes lower than K_{sp}, so AgCl solid dissolves. [1]

.....

..... [2]

(x) State the type of reaction that occurred in **(a)(vi)**.

Ligand exchange
..... [1]

(b) Planning

FA 9, **FA 10** and **FA 11** each contains one of the following but not in that order:

hydrogen peroxide iron(II) sulfate potassium iodide

You are required to plan and **perform** a series of test-tube reactions using only **FA 9**, **FA 10**, **FA 11** and, **FA 12** from **(a)(v)**, to identify the three solutions, **FA 9** to **FA 11**.

You should commence your plan by adding **FA 12** to each of **FA 9**, **FA 10** and **FA 11**.

Each solution should be identified by at least one positive test. It is **not** sufficient to identify a solution simply by eliminating all the others.

You should aim to use the **minimum number** of reactions.

You may find it useful to consider the standard electrode potentials given below.

$O_2 + 2H^+ + 2e$	$\rightleftharpoons$	H_2O_2	+0.68 V
$H_2O_2 + 2H^+ + 2e$	$\rightleftharpoons$	$2H_2O$	+1.77 V
$Fe^{3+} + e$	$\rightleftharpoons$	Fe^{2+}	+0.77 V
$Fe^{2+} + 2e$	$\rightleftharpoons$	Fe	–0.44 V
$I_2 + 2e$	$\rightleftharpoons$	$2I^-$	+0.54 V

You may use the space below to plan your tests.

In the table in the next page, record
- details of the tests, including quantity of solutions used,
- observations of the tests,
- identities of the products that gave rise to the observations,
- identity of each solution.

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	observations, identities of products and identity of each solution		
tests	**FA 9**	**FA 10**	**FA 11**
1. To 1 cm depth FA solution, add 1 cm depth **FA 12**	no yellow/ orange/ brown solution formed	no yellow/ orange/ brown solution formed	cream ppt in brown solution cream ppt is CuI brown solution is I_2 ∴ **FA 11** is KI
2. To 1 cm depth FA solution, add 1 cm depth **FA 11**	no yellow/ orange/ brown solution formed	yellow solution formed, effervescence of gas which relights a glowing splint yellow solution is I_2 gas is O_2 ∴ **FA 10** is H_2O_2	
3. To 1 cm depth FA solution, add 1 cm depth **FA 10**	yellow solution formed, effervescence of gas which relights a glowing splint yellow solution is Fe^{3+} gas is O_2 ∴ **FA 9** is $FeSO_4$		

Correct sequence and quantities [1]
All negative tests observations correct [1]
5 positive observations, 5 products and 3 identities [6]

Conclusion

Solution **FA 9** contains .....

Solution **FA 10** contains .....

Solution **FA 11** contains .....

[8]

[Total: 17]