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

1 **Investigation of some inorganic and organic reactions**

In this question, you will be investigating some inorganic and organic reactions by carrying out the stipulated tests. Carefully record your observations in Tables 1.1 and 1.2.

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

(a) **Organic analysis**

In this question, you will deduce the structure of an organic compound, **FA 1**.
FA 1 has the molecular formula $C_4H_8O_2$ with **two** functional groups present.

Do not carry out the tests for which observations have been recorded.
Do not use the Bunsen burner for heating in this part of the question. Instead, use the hot water provided.

Table 1.1

	tests	observations
(i)	Place about 2 cm depth of aqueous sulfuric acid in a test-tube. To this test-tube, add about 1 cm depth of **FA 1**, followed by 1 drop of aqueous potassium manganate(VII). Warm the mixture in the hot water bath for two minutes.	• **Purple $KMnO_4$ decolourises / turns colourless.**
(ii)	Add 1 cm depth of aqueous silver nitrate to a test-tube. Then slowly add 1 cm depth of aqueous sodium hydroxide. Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. To this mixture, add about 1 cm depth of **FA 1**. Place the test-tube containing the mixture in the water bath for two minutes.	• **Black / brown / grey ppt formed** • **Black / brown / grey ppt dissolves to give a colourless solution** • **No silver mirror observed.**
(iii)	Place about 1 cm depth of **FA 1** in a test-tube. To this test-tube, add 2,4-dinitrophenylhydrazine dropwise.	Orange ppt. formed
(iv)	Place about 1 cm depth of **FA 1** and add 8 drops of aqueous sodium hydroxide in a test-tube. Then, add aqueous iodine dropwise, until a permanent yellow / orange colour is obtained. Warm the mixture in the hot water bath for two minutes.	• **Brown / Orange solution decolourises.** • **Pale yellow ppt observed.**
(v)	Place 1 cm depth of **FA 1** in a test-tube. To this test-tube, cautiously add a small piece of anhydrous phosphorus pentachloride.	Dense white fumes, which turns moist blue litmus paper red.

Markers' Comments

- Some candidates were unfamiliar with the expected observations for these common reagents used in Organic Qualitative Analysis.
- Many candidates omitted the observations that accompanied the preparation of Tollens' reagent. Candidates also wrongly wrote "no observable change" for the negative Tollens' reagent test, even though it was not permissible to write so.

4 to 6 marking points – [M1] and [M2]
2 to 4 marking points – [M1] only

[2]

M1	M2

(b) **(i)** Observations from **(a)(ii) and (a)(iii)** can be used to identify one of the functional groups present in **FA 1**.

Identify the functional group and explain your answer, showing clearly your reasoning.

functional group: **ketone**

explanation: **Since FA 1 undergoes condensation with 2,4–DNPH** in **(a)(iii), FA 1 contains either a ketone or aldehyde. However, since FA 1 does not undergo oxidation with Tollens' reagent in (a)(ii)** and it does not contain an aldehyde**. [M3]** [1]

(ii) Using observations from **either (a)(iv) or (a)(v)**, identify the other functional group present in **FA 1**.

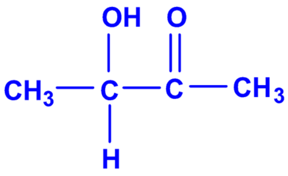
Quote evidence from the relevant test to support your conclusion.

functional group: **alcohol**

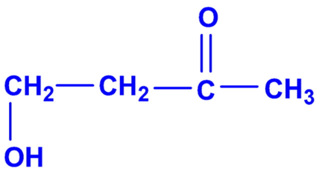
evidence: **Since FA 1 undergoes nucleophilic substitution with PCl_5 in (a)(v) to give HCl, it contains an alcohol functional group. [M4]** [1]

Markers' Comments
- Some candidates were unfamiliar with the requirements of this question. They did not indicate
    - type of reaction with the reagent
    - reference to the test / reagent
    - reference to the observations
- Some candidates also failed to consider the molecular formula while proposing the functional group present and wrongly proposed having carboxylic acid with a ketone.

(iii) Suggest a possible structure of **FA 1** that are consistent with all the observations in Table 1.1.

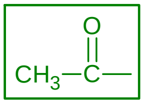
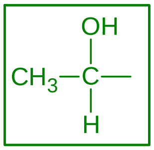

$CH_3-\overset{OH}{\underset{H}{C}}-\overset{O}{C}-CH_3$

OR


$\underset{OH}{CH_2}-CH_2-\overset{O}{C}-CH_3$

[M5]

[1]

- Molecular Formula: $C_4H_8O_2$
- Contains ketone & alcohol functional group
- Contains  $CH_3-\overset{O}{C}-$ AND / OR  $CH_3-\overset{OH}{\underset{H}{C}}-$

M3	M4	M5

Markers' Comments
- This question was generally well attempted by candidates who deduced the correct functional groups in the earlier part.
- Some candidates failed to account for the molecular formula while proposing the structural formula. Common mistakes include omitting hydrogen atoms / not having a structure with correct bonding.

(c) Inorganic analysis

FA 2 is an aqueous solution containing Fe^{3+}.
FA 3 contains one cation and **FA 4** contains one anion listed in the Qualitative Analysis Notes on pages 23 – 24.

You should indicate clearly at what stage in a test a change occurs. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

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

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitate in an excess of the reagent added

No additional tests for ions present should be attempted.

Table 1.2

	tests	observations
(i)	Test the **FA 2** solution using Universal Indicator paper.	• **Universal indicator paper turns** o **red (pH 1)** o **orange-red (pH 2)** o **orange (pH 3)** **Must include colour and pH of UI paper**
(ii)	To 1 cm depth of **FA 2**, add 1 cm depth of hydrochloric acid followed by a small spatula of zinc powder. Shake well. Leave the mixture to stand for five minutes.	• **Effervescence observed.** • **H_2(g) "pops" with a lighted splint / extinguishes a lighted splint with a pop.** **Must include identity of gas and the confirmatory test for gas** • **Yellow solution decolourises / fades / becomes lighter in colour.**
(iii)	To 1 cm depth of **FA 2**, add a few drops of aqueous sodium thiosulfate with shaking. Leave the mixture to stand.	• Yellow solution **turns purple/ dark violet / brown.** • **Solution turns back to yellow**.

4 – 6 marking points – [M6] and [M7]
2 – 3 marking points – [M6] only

[2]

Markers' Comments

- This question was not well attempted by candidates. Many candidates missed out on the required observation points that they should be familiar with by now.
- Some candidates also did not carry out the procedure, e.g. not following the specified quantities of reagent specified, which resulted in erroneous observations; not observing again after leaving the mixture to stand.

M6	M7

	tests	observations
(iv)	To 1 cm depth of **FA 3**, add an equal volume of aqueous potassium iodide, then	- white / off-white / cream **ppt formed** - **brown / yellow-brown / orange-brown / red-brown solution formed**
	add aqueous sodium thiosulfate dropwise with shaking until no further change is observed.	- **Brown solution fades / decolourises / turns lighter / turns pale yellow / pale brown etc.** - **Cream / white / off-white ppt observed.**
(v)	To 1 cm depth of **FA 3**, add aqueous ammonia slowly, with shaking, until no further change is seen.	- **(pale) blue ppt formed** - **ppt soluble in excess NH_3 to give a dark blue solution**

5 – 6 marking points – [M8], [M9] and [M10]
3 – 4 marking points – [M8] and [M9] only
2 marking points – [M8] only

[3]

Markers' Comments

- This question was not well attempted by candidates. Candidates struggled with distinguishing the observations involving a precipitate forming in a coloured solution, e.g. only describing ppt but not solution, or describing the ppt using the colour of the solution or vice versa.
- Many candidates missed out on the required observation points that they should be familiar with by now.

(d) **(i)** Explain your observations in **(c)(i),** given that the cation present in **FA 2** is Fe^{3+}.

Fe^{3+} has high charge density and can distort the electron cloud of the surrounding H_2O molecules, weakening and breaking the O–H bond, **thus releasing H^+. The hydrolysis of Fe^{3+} in water** accounts for the acidic nature of the solution which turns the Universal Indicator paper red / orange. **[M11]** [1]

(Slight) Hydrolysis

$$[\mathbf{Fe}(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [\mathbf{Fe}(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(l)$$

Markers' Comments

- This question was generally well attempted by most candidates. Some candidates however did not relate the hydrolysis to the high charge density of Fe^{3+}.

(ii) State the type of reaction that is likely to have occurred in **(c)(iii).**

Ligand exchange reaction / (Homogenous) Catalysis / Redox [M12] [1]

Ligand Exchange $[Fe(H_2O)_6]^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(H_2O)_2(S_2O_3)_2]^{-}(aq) + 2H_2O(l)$

yellow purple

Catalysis - indicated by the regeneration of the yellow Fe^{3+} catalyst at the end of the reaction.

Redox – Homogenous catalysis usually entail a change in oxidation state of Fe^{3+} catalyst

Markers' Comments

- This question was generally well attempted by most candidates.

(iii) Identify the cation present in **FA 3**. Use evidence from your observations in **1(c)** to support your deduction.

cation: **copper(II), Cu^{2+}**

evidence: **In test (v), blue ppt** of $Cu(OH)_2(s)$ **soluble in excess $NH_3(aq)$ to form dark blue solution** of $[Cu(H_2O)_2(NH_3)_4]^{2+}$ complex

[M13] for both correct identification and evidence [1]

Markers' Comments

- This question was well attempted by most candidates who made clear reference to the observations in **1(c)(v)**.

M8	M9	M10	M11	M12	M13

(iv) Write an ionic equation to account for the observations made for the **first** reaction in **(c)(iv)**. Include state symbols.

$$2\,Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$ **[M14] for correct equation** [1]

blue colourless off–white ppt brown solution

Markers' Comments

- This question was not well attempted by most candidates, as many did not account for the formation of iodine as evidenced by the brown I_2 (aq) solution formed in **1(c)(iv)**.
- There are essentially two reactions ongoing concurrently.
  - **Precipitation reaction** involving Cu^+ (aq) and I^- (aq) to **form the insoluble CuI precipitate (off-white ppt).**
  - **Redox reaction** involving the **oxidation of colourless I^- (aq) to brown I_2 (aq)** and the **reduction of blue Cu^{2+} (aq) to colourless Cu^+ (aq).**

[Turn Over

(e) Devise and perform a series of **three** simple tests to identify the anion in **FA 4**.

Your tests should be based on the Qualitative Analysis Notes on pages 23 – 24 and should use only the bench reagents provided. Record your tests and observations in the space below.

Any test requiring heating MUST be performed in a boiling tube.

The anion is not a nitrite, sulfate or sulfite ion. **Possible anions: CO_3^{2-} ; Cl^- / Br^- / I^-; NO_3^-**

test	observations
Test for CO_3^{2-} ✓ To a 1 cm depth of **FA 4** in a test-tube, add 1 cm depth of aqueous **HNO_3 / HCl / H_2SO_4.** *Note: any mineral acid in Bench reagent* If effervescence is observed, bubble the gas produced through limewater.	✓ **No effervescence** observed. [CO_3^{2-} absent] [Follow-up confirmation using limewater is not required as there is no effervescence.]
Test for halide (Cl^- / Br^- / I^-) ✓ To a 1 cm depth of **FA 4** in a test-tube, add 1 cm depth of **aqueous HNO_3**. Then, add **aqueous $AgNO_3$** dropwise until no further change. Note: HNO_3 (aq) is the only mineral acid that can be used to acidify the reagent before testing with $AgNO_3$ (aq). The other mineral acids will give a ppt with $AgNO_3$(aq). Acidification is necessary to minimise the risk of false positive test with $AgNO_3$ (aq). If a ppt is formed, add aqueous NH_3 with shaking until no further change is observed.	✓ **No precipitate** (of silver halide type) formed. [⇒ Cl^- / Br^- / I^- absent] [Follow-up confirmation using NH_3 (aq) is not required as there is no ppt formed.]
Test for NO_3^- ✓ To a 1 cm depth of **FA 4** in a **BOILING TUBE**, add 1 cm depth of **NaOH (aq), then add a piece of Al foil and warm.** Note: Boiling tube should be used as heating is involved.	✓ **Effervescence observed.** **NH_3 (g) evolved which turns moist red litmus paper blue.** [NO_3^- present, since NO_2^- is already precluded]

5 – 6 marking points ✓ [M15], [M16], [M17]
3 – 4 marking points ✓ [M15] and [M16] only
1 – 2 marking points ✓ [M15] only [3]

Use your observations above to deduce the identity of the anion in **FA 4**.

anion: **NO_3^- / nitrate [M18]** [1]

Markers' Comments

- This question was generally well attempted by most candidates who exercised their attention to details and planned a series of test(s) to identify the anion.
- Some candidates performed the halides test incorrectly. They WRONGLY included the use of NaOH (aq) which is necessary for the nucleophilic substitution of the halogenoalkane. Some candidates also used the wrong choice of acid to acidify $AgNO_3$(aq).

2 Determination of the kinetics of the reaction between iron(III) and iodide ions

You are provided with the following reagents.

FA 5 is an acidified solution of aqueous iron(III) chloride, $FeCl_3$.
FA 6 is aqueous potassium iodide, KI.
FA 7 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch solution

In an acidic medium, iron(III) ions, Fe^{3+} oxidises iodide ions, I^-, to iodine, I_2 as shown in equation 1.

equation 1 $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

It is possible to determine the rate of this reaction by measuring the time to produce a certain amount of iodine. To do this, a fixed and small amount of thiosulfate ions, $S_2O_3^{2-}$, and starch indicator are added to the reaction mixture. The thiosulfate ions react immediately with the iodine produced by the reaction and convert it back to iodide ions as shown in equation 2.

equation 2 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

The reaction in equation 2 stops once all the thiosulfate ions have reacted. The concentration of iodine now increases and is detected by starch indicator in the reaction mixture, which causes the reaction mixture to turn blue-black.

You will perform a series of **four** experiments. Then, you will graphically analyse your results to determine the order with respect to the concentration of Fe^{3+} ions, $[Fe^{3+}]$.

For each experiment, you will note the volume of **FA 5** added, $V_{\textbf{FA 5}}$, and the time taken, t, for the reaction mixture to become blue-black. In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding deionised water as required.

You will then calculate values for

- $\frac{1}{t}$,
- $\lg\left(\frac{1}{t}\right)$,
- $\lg(V_{\textbf{FA 5}})$.

(a) **(i)** **Experiment 1**

1. Fill the burette labelled **FA 5** with **FA 5**.
2. Transfer 20.00 cm^3 of **FA 5** to a 100 cm^3 conical flask.
3. Use the measuring cylinders to place the following in a 100 cm^3 beaker.
   - 10.0 cm^3 of **FA 6**
   - 15.0 cm^3 of **FA 7**
   - 10.0 cm^3 of starch solution
4. Add the contents of the beaker rapidly to the conical flask and start the stopwatch.
5. Swirl the mixture and place the conical flask on the white tile.
6. Stop the stopwatch when the **blue-black colour first appears**. Ignore any colour changes that occur before the intense blue-black colouration.
7. Record the time taken, *t*, to nearest second in your table.
8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

(ii) **Experiment 2**

1. Run 8.00 cm^3 of **FA 5** into a 100 cm^3 conical flask.
2. Using another measuring cylinder, add 12.0 cm^3 of deionised water into the conical flask containing **FA 5**.
3. Use the measuring cylinders to place the following in a 100 cm^3 beaker.
   - 10.0 cm^3 of **FA 6**
   - 15.0 cm^3 of **FA 7**
   - 10.0 cm^3 of starch solution
4. Add the contents of the beaker rapidly to the conical flask and start the stopwatch.
5. Swirl the mixture and place the conical flask on the white tile.
6. Stop the stopwatch when the **blue-black colour first appears**. Ignore any colour changes that occur before the intense blue-black colouration.
7. Record the time taken, *t*, to nearest second in your table.
8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

In Experiment 1 you will have obtained the time taken for a ‘fast’ reaction and in Experiment 2 the time taken for a ‘slow’ reaction.

Carry out **two** further experiments to investigate the effect of changing the concentration of $Fe^{3+}(aq)$ by altering the volume of **FA 5** used. In each case, you will need to ensure that the **same total volume** of reaction mixture is used by adding deionised water as required.

Do not use a volume of **FA 5** that is less than 8.00 cm^3.

You should alternate the use of the two 100 cm^3 conical flasks.

Record all required volumes, time taken and calculated values in your table.

(iii) **Results**

The volumes of **FA 6**, **FA 7** and starch indicator are not changed in these experiments, and do not need to be recorded.

Prepare a table in the space provided below to record, to an appropriate level of precision:

- volumes of **FA 5** and deionised water,
- all values of t,
- all calculated values of $\frac{1}{t}$, $\lg\left(\frac{1}{t}\right)$ and $\lg(V_{\textbf{FA 5}})$.

Experiment	$V_{\text{FA 5}}$ / cm^3	$V_{\text{deionised } H_2O}$ / cm^3	t / s	$\frac{1}{t}$ / s^{-1}	$\lg\left(\frac{1}{t}\right)$	$\lg(V_{\text{FA 5}})$
1	20.00	0.0	16	0.0625	-1.20	1.30
2	8.00	12.0	40	0.0250	-1.60	0.903
3	12.00	8.0	26	0.0385	-1.41	1.08
4	16.00	4.0	20	0.0500	-1.30	1.20

[4]

Descriptor	**Mark**
• Tabulates data in appropriate manner. Tabulation may be vertical or horizontal; lines are not essential but there should be no absence of headers. • Tables have correct headers and units. Where units have not been included in the header, there should be the appropriate unit for each entry in the tables. o Volume of **FA 5 / cm³** Volume of deionised water **/ cm³** o Time taken, ***t* / s** $\frac{1}{t}$ **/ s⁻¹** o lg (1/t) and lg ($V_{FA\ 5}$) (ignore units for lg values)	**M19**
• Volume of **FA 5** recorded to **nearest 0.05 cm³** (measured using burette) • Volume of deionised water recorded to **nearest 0.5 cm³** (measured using 25.0 cm³ measuring cylinder) • Time taken recorded to **nearest s**. **[**Award based on students' presented data**;** Do **not** award this mark if any measurements (volumes and time taken) is missing	**M20**
• **Volume of deionised water + Volume of FA 5 = 20.0 cm³** Do not award this mark if V_{H_2O} is not recorded as total volume could not be assessed to be kept constant • **Volumes of FA 5 chosen are uniformly spaced over the range between 8.00 cm³ and 20.00 cm³ (at least 3 cm³ difference between any two self-chosen $V_{FA\ 5}$)** • If **$V_{FA\ 6}$, $V_{FA\ 7}$, V_{starch}** is also shown, then the **volumes used must be kept constant**; ensure the **total volume of the mixture is constant at 55.0 cm³**.	**M21**
• Calculate $\frac{1}{t}$, $\lg\left(\frac{1}{t}\right)$ and **lg ($V_{FA\ 5}$)** correctly [Do not penalise if values are not presented to 3 s.f.]	**M22**

Markers' Comments

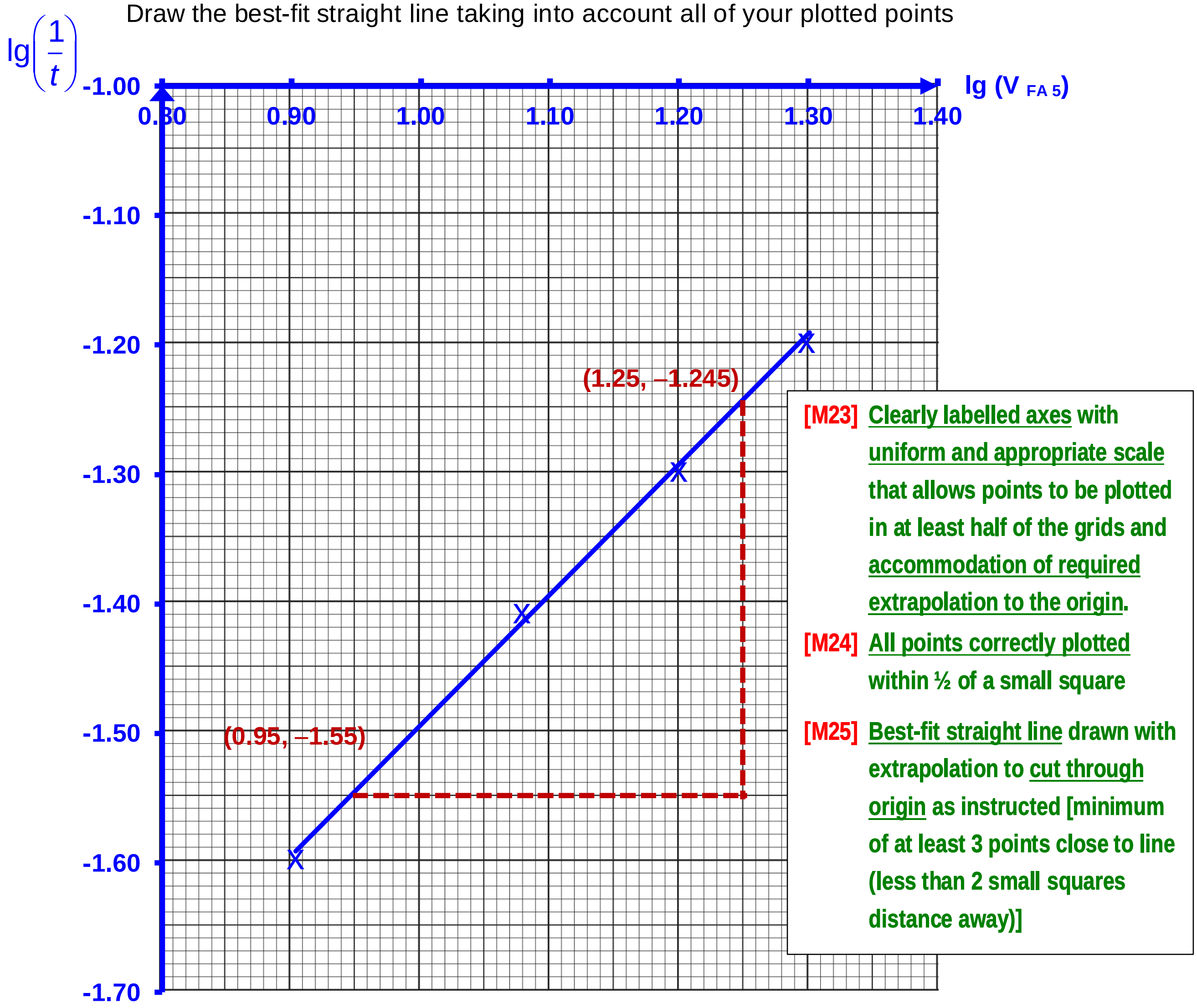
- Many candidates still made the same mistakes in using inappropriate d.p. for the various measurements, which is unacceptable.
- Although it is not a marking point, all calculated values (1/t, lg 1/t and lg V_{FA5}) should be in 3 s.f.
- Candidates should learn to choose **well spaced-out data** for V_{FA5} so that data points on the graph plotted using these points can be more reliable.

M19	M20	M21	M22

[Turn Over

(b) **(i)** Plot a graph of $\lg\left(\frac{1}{t}\right)$ on the y–axis against $\lg(V_{\text{FA 5}})$ on the x–axis.

Draw the best-fit straight line taking into account all of your plotted points



[M23] <u>Clearly labelled axes</u> with <u>uniform and appropriate scale</u> that allows points to be plotted in at least half of the grids and <u>accommodation of required extrapolation to the origin</u>.

[M24] <u>All points correctly plotted</u> within ½ of a small square

[M25] <u>Best-fit straight line</u> drawn with extrapolation to <u>cut through origin</u> as instructed [minimum of at least 3 points close to line (less than 2 small squares distance away)]

[3]

(ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, state the order of reaction with respect to $[Fe^{3+}]$.

$$\text{Gradient} = \frac{-1.245 - (-1.55)}{1.25 - 0.95} = \mathbf{1.01} \text{ (3 s.f.)}$$

[M26] for correct determination of gradient with working; choice of coordinates (coordinates chosen should not be too close – use at least ½ of the best-fit line for gradient construction) and correct reading of coordinates

Hence, the **gradient of the graph of** $\lg\left(\frac{1}{t}\right)$ **vs** $\lg(V_{\text{FA 5}})$ is the order of the reaction w.r.t. $[Fe^{3+}]$. **<u>Order of reaction with respect to $[Fe^{3+}]$ is 1.</u>**

[M27] for correct determination of order of reaction based on gradient calculated

[For understanding – not required in answers]

Rate = $k\,[Fe^{3+}]^{x}\,[I^{-}]^{y}$

Since total volume of reaction mixture and amount of I^{-} (**FA 6**) used is kept constant, $[I^{-}]$ is constant across all experiments.

Hence, rate = $k'\,[Fe^{3+}]^{x}$; where $k' = k\,[I^{-}]^{y}$

$$\text{Rate} \propto \frac{1}{t} \text{ and } [Fe^{3+}] \propto V_{FA\,5}$$

$$\frac{1}{t} = k''\,(V_{FA\,5})^{x}$$

$$\lg\left(\frac{1}{t}\right) = \lg k'' + x\,\lg(V_{FA\,5})$$

y = c + m X ➔ Gradient of the best-fit line gives the order of reaction w.r.t. Fe^{3+}.

gradient = ...

order = ... [2]

M23	M24	M25	M26	M27

Markers' Comments

- For the plotting of graph, candidates should choose a scale which can be easily read, otherwise time will be wasted plotting the points and careless mistakes will be easily made.
- Try to fit all the points onto the graph to achieve the best fit line.
- For determining of the order of reaction, candidates should round off their gradient value instead of rounding down or forcing it to be 1st order. Try to understand the mathematical relationship when the log function is applied in the rate equation.

[Turn Over

(c) **(i)** Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$, used in each experiment in **2(a)**.

$$\text{Amount of } S_2O_3^{2-} \text{ used in each experiment} = \underbrace{\frac{15.0}{1000}}_{V_{FA\,6}} \times \underbrace{0.0060}_{[S_2O_3^{2-}]} = \underline{\mathbf{9.00 \times 10^{-5}\ mol}}\ \mathbf{[M28]}$$

amount of $S_2O_3^{2-}$ = ... **9.00×10^{-5} mol** .... [1]

(ii) Use your answer to **(c)(i)**, and the equations for the reactions involved, to calculate the amount of iron(III) ions, Fe^{3+}, that reacted when the blue-black colour first appear in each experiment in **2(a)**.

$2S_2O_3^{2-} \equiv I_2 \equiv 2Fe^{3+}$ Correct application of mole ratio

Amount of Fe^{3+} reacted in each experiment = Amount of $S_2O_3^{2-}$ reacted in each experiment

= $\underline{\mathbf{9.00 \times 10^{-5}\ mol}}$ **[M29]**

amount of Fe^{3+} = ... **9.00×10^{-5} mol** .... [1]

(iii) Hence, calculate the change in concentration of Fe^{3+} that occurred when the blue-black colour first appear in each experiment in **2(a)**.

$$\text{change in } \left[Fe^{3+}\right] = \frac{-9.00 \times 10^{-5}}{\frac{55.0}{1000}} = -1.636 \times 10^{-3} = \underline{\mathbf{-1.64 \times 10^{-3}\ mol\ dm^{-3}}}\ \mathbf{[M30]}$$

Total volume of reaction mixture = 55.0 cm^3

–ve sign denotes that Fe^{3+} is consumed / used up in the reaction and hence its concentration is decreasing per unit time.

change in $[Fe^{3+}]$ = ... **$\underline{-1.64 \times 10^{-3}\ mol\ dm^{-3}}$** .... [1]

Markers' Comments

- This question is an unusual one as it asks for the change in $[Fe^{3+}]$. Look at the equation and understand what is going on.
- Most candidate did not get this right as they did not know what the question wanted.
- The other problem is the sign. Since this is a change, hence a sign is needed. As $[Fe^{3+}]$ is decreasing, thus there should be a -ve sign.

M28	M29	M30

(iv) The $\frac{1}{t}$ calculated in the results table in **(a)(iii)** is a relative rate. The experimental rate of this reaction can be monitored by the change in concentration of Fe^{3+} per unit time as given in the expression below.

$$\text{experimental rate} = -\frac{\text{change in } [Fe^{3+}]}{\text{time, } t} \times 10^6 \ \mu\text{mol dm}^{-3} \text{ s}^{-1}$$

(1 μmol = 10^{-6} mol)

Calculate the experimental rate of reaction for **Experiment 1**, taking into consideration the required units.

$$\text{experimental rate} = -\frac{-1.636 \times 10^{-3}}{16} \times 10^6 = \underline{\mathbf{102.3\ \mu mol\ dm^{-3}\ s^{-1}}}$$ **[M31]**

Markers' Comments

- It is surprising that many candidates are not able to follow instructions and apply the formula correctly.

experimental rate of reaction for experiment 1 = **102** μmol dm^{-3} s^{-1} [1]

(d) The order of reaction with respect to [I^-] is one.

With reference to **Experiment 1**, state and explain the expected time taken for the appearance of the dark blue-black colour when the experiment is carried out using a mixture comprising the following:

- 20.00 cm^3 of **FA 5**
- 5.0 cm^3 of **FA 6**
- 7.5 cm^3 of **FA 7**
- 12.5 cm^3 of deionised water
- 10.0 cm^3 of starch

When **[I^-] is halved, the time taken for appearance of blue-black colour should be doubled** (volume of **FA 6** is halved) as the reaction is first-order with respect to I^-.

When **volume of FA 7 ($S_2O_3^{2-}$) is halved, the time taken for appearance of blue-black colour should also be halved** as there is **less (halved) $S_2O_3^{2-}$ to react.**

Hence, the expected measured time should be **the same as in experiment 1**, *i.e.* **16 s.**

[M32] with correct analysis and conclusion [1]

- **On effect of rate/ time taken after halving [I^-];**
- **On effect of halving amount of $S_2O_3^{2-}$ on the effect on time taken for blue black to appear**

Markers' Comments

- Very few candidates got this correct.
- They did not understand how $S_2O_3^{2-}$ works as a delay agent. Halving its amount will allow the iodine to appear earlier, hence the time taken will be halved.

M31	M32

[Turn Over

(e) Step **8** of Experiment 1 in **2(a)** instructs you to wash **and** drain the conical flask before it is used again.

State and explain the likely effect on time taken, *t*, if a student had washed the conical flask but had failed to drain it before starting another experiment.

effect on *t* The time taken will be **longer than expected.**

explanation The **residual water present** in the conical flask **decreases the concentration of the reactants** in the reaction mixture, **decreasing the rate of reaction.**

[M33] [1]

Markers' Comments

- This question was well answered, except that most candidates did not relate the effect of dilution to the slowing down of the rate.

ADDITIONAL QUESTION

(f) Thiosulfate ions can also reduce iron(III) ions.

A student carried out the same investigation as in **(a)** but the solutions were mixed in a different order. The student places **FA 6** and an appropriate volume of deionised water in one conical flask and all the other reactants (**FA 5**, **FA 7** and starch) in a second beaker. The student then transfers the mixture from the second beaker to the first and starts timing.

The student proposed that, even though thiosulfate ions are known to reduce iron(III) ions, his method was as good as the method used in **(a)**. Suggest why his assessment is justifiable.

With any of the following reasons:

- **[$S_2O_3^{2-}$] is very small**, so **reaction with Fe^{3+} / FA 5 will be slow and hence negligible effect** on **[$S_2O_3^{2-}$]**

OR

- **[$S_2O_3^{2-}$] decrease by similar extent** throughout **each run of the experiment**, so the **effect is cancelled out** / the **relative rate between experiments is not affected**. [1]

M33

[Total: 15]

3 **To determine the composition of a mixture of sodium carbonate and sodium hydrogen carbonate**

FA 8 contains 3.90 g dm^{-3} of a mixture of sodium carbonate, Na_2CO_3 and sodium hydrogen carbonate, $NaHCO_3$.
FA 9 is 0.0700 mol dm^{-3} hydrochloric acid, HC*l*.
Solution **M** is methyl orange indicator.

Sodium carbonate in aqueous solution acts as a *Brønsted-Lowry* base. It reacts with acid in two stages.

In the first stage, it accepts a proton to form sodium chloride and sodium hydrogen carbonate. In the second stage, sodium hydrogen carbonate combines with another proton to form sodium chloride, carbon dioxide and water.

Stage 1 $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$

Stage 2 $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

The end-point for Stage 1 occurs at pH 8.3 and is determined using thymol blue indicator.

The end-point for Stage 2 occurs around pH 3.7 and is determined using methyl orange indicator.

In this experiment, you are required to determine the end-point for Stage 2 for this reaction and determine the concentrations of sodium carbonate, and that of sodium hydrogen carbonate,
in **FA 8**.

(a) Titration of FA 8 against FA 9, using methyl orange as the indicator

1. Fill the burette with **FA 9**.
2. Use a pipette to transfer 25.0 cm^3 of **FA 8** into a 250 cm^3 conical flask.
3. Add a few drops of solution **M** to the conical flask.
4. Run **FA 9** from the burette into this conical flask. The end-point is reached when the solution changes from yellow to orange. If the solution becomes red, you have passed the end-point.
5. Record your titration results in Table 3.1 on page 15.
6. Repeat steps 1 to 5 until consistent results are obtained.

Results

Table 3.1

Titration	**1**	**2**	3	
Initial burette reading / cm^3	0.15	9.45	0.65	
Final burette reading (second end-point) / cm^3	23.45	60	23.85	
Volume of **FA 9** used to complete both Stages 1 and 2, V_t / cm^3	23.30	23.15	23.20	
		✓	✓	

[2]

• ALL **burette readings and volume of FA 9 used** (including 0.00) are **recorded to nearest 0.05 cm^3** • Do **not** award this mark if: o 50.(00) is used as an initial burette reading **OR** o More than one final burette reading is 50.(00) **OR** o any burette reading is greater than 50.(00)	**M34**
• Has at least **two uncorrected titres within 0.10 cm^3** (even if volumes were not indicated with '✓'s.) • Do **not** consider the titre value if it is labelled "rough" [Ignore calculation errors in titres]	**M35**

(b) Using your titration results, obtain a suitable volume of **FA 9** for the second end-point (total volume of **FA 9** used to complete both stages 1 and 2).

Show clearly how you obtained this volume.

Volume of **FA 9** used to obtain second end-point, $V_t = \dfrac{23.15 + 23.20}{2} = \mathbf{23.18\ cm^3}$

volume of **FA 9** used for second end-point = **23.18** cm^3

• **Titre / Volume of FA 9 used for each titration is correctly calculated.** • **Average / mean titre** is **correctly calculated** from **clearly selected values [uncorrected titre values within ± 0.10 cm^3] (ticks or working); average / mean titre in 2 d.p and units** Do **not** award this mark if • there are any arithmetic errors in the calculation of titre • the rough titre was used to calculate the mean; • candidate carried out only 1 accurate titration	**M36**
Accuracy for second end-point – Supervisor's Result: 23.15 cm^3 **M37 & M38** if difference from Supervisor's results: ≤ 0.30 cm^3 **M37 only** if difference Supervisor's results: > 0.30 cm^3 but ≤ 0.60 cm^3 **[0]** if difference Supervisor's results: > 0.60 cm^3	**M37** **&** **M38**

[3]

Markers' Comments

- Most candidates who exercised their attention to details performed well and scored full credit for their presentation of their data.
- Some candidates did not understand what consistent titres entail (titre values within ± 0.10 cm^3).
- A significant number of candidates struggled with obtaining accurate titration results, indicating poor manipulative and measurement skills.

(c) **(i)** For the titration of **FA 8** against **FA 9** using thymol blue as the indicator, the titre value for the first end-point, V_1 (volume of **FA 9** used to complete stage 1) is determined to be 9.15 cm^3.

Calculate the amount, in moles, of sodium carbonate, Na_2CO_3, and sodium hydrogen carbonate, $NaHCO_3$, present in 25.0 cm^3 of **FA 8**.

Volume of **FA 9** used to obtain first end-point = 9.15 cm^3 (V_1)
Volume of **FA 9** used to obtain second end-point in **(b)** = 23.18 cm^3 (V_t)

Stage 1 $\quad Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$
x mol $\qquad x$ mol
$V_1 = 9.15\ cm^3$

Stage 2 $\quad NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$
($x + y$**)** mol

HC*l* is needed to neturalise both x mol of Na_2CO_3 & ($x + y$) mol of $NaHCO_3$

$2\ V_1 + V_3 = V_{total}$

Amount of **Na_2CO_3** = Amount of HC*l* neutralising Na_2CO_3 in Stage 1

$= 0.0700 \times \frac{9.15}{1000}\ \left(\frac{V_1}{1000}\right)$

$= 6.405 \times 10^{-4}$ mol

= **6.41×10^{-4} mol** **[M39]**

= Amount of $NaHCO_3$ generated at the end of Stage 1

$Na_2CO_3 \equiv 2\ HCl$

Volume of **FA 9** (HC*l*) neutralising **original $NaHCO_3$** = **$V_{total} - 2V_1$**
$= 23.18 - 2\ (9.15)$
= **4.88 cm^3** (V_3)

$NaHCO_{3\ original} \equiv HCl$

Amount of **$NaHCO_3$ original** = Amount of HC*l* neutralising original $NaHCO_3$

$= 0.0700 \times \frac{4.88}{1000}\ \left(\frac{V_3}{1000}\right)$

$= 3.416 \times 10^{-4}$ mol

= **3.42×10^{-4} mol** **[M40]**

amount of Na_2CO_3 in 25.0 cm^3 of **FA 8** = **6.41×10^{-4} mol**

amount of $NaHCO_3$ in 25.0 cm^3 of **FA 8** = **3.42×10^{-4} mol** [2]

Markers' Comments

- Many candidates struggled with the determination of amount of $NaHCO_3$ as they failed to realise that the second end-point of the titration **involves the neturalisation of the original $NaHCO_3$ present** and **$NaHCO_3$ formed from the initial neutralisation of Na_2CO_3 at the first end-point**.

(ii) Calculate the concentrations, in mol dm^{-3}, of Na_2CO_3 and $NaHCO_3$ in **FA 8**.

$$[Na_2CO_3] \text{ in } \mathbf{FA\ 8} = (\mathbf{6.405 \times 10^{-4}}) \div \frac{25.0}{1000} = \mathbf{0.02562} = \underline{\mathbf{0.0256\ mol\ dm^{-3}}}$$

$$[NaHCO_3] \text{ in } \mathbf{FA\ 8} = (\mathbf{3.416 \times 10^{-4}}) \div \frac{25.0}{1000} = \mathbf{0.01576} = \underline{\mathbf{0.0137\ mol\ dm^{-3}}}$$

[M41] for both concentrations correctly calculated.

Allow ECF from [M39] and [M40] based on amount calculated in (c)(i))

If no values were calculated in (c)(i), no marks for (c)(ii).

concentration of Na_2CO_3 in **FA 8** = **0.0256 mol dm^{-3}**

concentration of $NaHCO_3$ in **FA 8** = **0.0137 mol dm^{-3}** [3]

[M42] Shows appropriate significant figures (3 or 4 sf) in all final answers in **2(c)(i), 2(c)(ii), 2(c)(iii), 2(c)(iv), 3(c)(i) and 3(c)(ii)**.
Any calculation not attempted loses this mark.
Any calculations must be relevant although they may not be complete or correct.

[M43] Shows appropriate units for all answers in **2(c)(i), 2(c)(ii), 2(c)(iii), 3(c)(i) and 3(c)(ii)**.
Any calculation not attempted loses this mark.
Any calculations must be relevant although they may not be complete or correct.

Markers' Comments

- Many candidates generally attempted this question well, despite not able to correctly determine the amount of $NaHCO_3$ earlier.
- Some candidates left calculation part(s) blank / unattempted and was further penalised in M42 and M43.

M39	M40	M41	M42	M43

(d) Explain why methyl orange can be used as the indicator for Stage 2 of this titration.

The **pH transition range of methyl orange** **lies within the region of rapid pH change over the second equivalence point** (pH = ~3.7) **of the titration**. **[M44]** [1]

Markers' Comments

- This question was generally well-attempted by candidates who did their bookwork with attention to details.
- Many candidates also failed to comprehend the technical terms in this bookwork question and gave answer in which the meaning is distorted.
  - **pH transition range of indicator** (pH range in which the indicator changes colour)
  - **region of rapid pH change** (region of titration curve where there is a shape change in pH with a small increase in the volume of titrant added, this usually correspond to the equivalence point)

(e) A student used 25.0 cm^3 of **FA 8** and obtained a **FA 9** titre value of 25.15 cm^3 for the second end point. The errors (uncertainties) associated with each apparatus is given below.

pipette	± 0.06 cm^3
burette	± 0.05 cm^3

Calculate the percentage error arising from the use of the following apparatus.

- 25.0 cm^3 pipette

$$\% \text{ error in pipette} = \frac{\pm 0.06}{25.0} \times 100\ \% = \pm 0.240\ \%$$

Note: The absolute uncertainity for the pipette should NOT be multipled by two, as only a single reading of the pipette is needed to determine the volume of aliqout used.

% error (pipette) **± 0.240 %**

- burette

$$\% \text{ error in burette} = \frac{\pm 2\ (0.05)}{25.15} \times 100\ \% = \pm 0.398\ \%$$

Note: The absolute uncertainity of each burette reading will need to be multipled by two, as two readings of the burette is needed (initial and final) to determine the volume of titrant used.

% error (burette) **± 0.398 %** [1]

[M45] for both

Markers' Comments

- o Some candidates still struggled with calculation of percentage uncertainty despite this concept being repeatedly featured throughout the practical tasks over these two years.

(f) A student performed the titration using CH_3CO_2H(aq) instead of HCl(aq). State and explain the effect on the volume of acid required for the first end-point.

The volume of acid required for the first endpoint will be inaccurate / hard to determine as there is no suitable indicator for a weak acid-weak base titration.

OR [1]

The **volume of acid required will be the same**. Both acids are **monoprotic acids** and will **react with Na_2CO_3 and $NaHCO_3$ in similar mole ratio**. **[M46]**

Markers' Comments

- o This question was not well-attempted by candidates. Many candidates have the misconception that using a weak acid as the titrant will result in a larger titre value due to less H^+ present. They failed to recognise that as H^+ are used up initially in the neutralisation, the weak acid will proceed to dissociate further to form more H^+, and eventually this leads to the complete dissociation of the weak acid.

M44	M45	M46

[Total: 13]

4 Planning

The reaction between aqueous sodium chloride, NaC*l* and aqueous lead(II) nitrate, $Pb(NO_3)_2$ produces an insoluble white precipitate of $PbCl_2$.

$$Pb(NO_3)_2(aq) + 2\ NaCl(aq) \rightarrow PbCl_2(s) + 2\ NaNO_3(aq)$$

The concentration of an aqueous solution of lead(II) nitrate can be determined gravimetrically by monitoring the mass of precipitate formed as different volumes of aqueous sodium chloride and aqueous lead(II) nitrate are mixed. A graph of mass of precipitate against volume of aqueous sodium chloride added allows for the graphical determination of the equivalence point through careful extrapolation. At this equivalence point, stoichiometric quantities of reactants are present.

Plan an experiment to determine the concentration of an aqueous solution of lead(II) nitrate gravimetrically.

You may assume that you are provided with:

- solid sodium chloride, NaC*l*
- 250 cm^3 of approximately 0.1 mol dm^{-3} aqueous solution of lead(II) nitrate
- the equipment normally found in a school or college laboratory

(a) Describe how you would make 250 cm^3 of a solution of sodium chloride of concentration 0.200 mol dm^{-3} for your experiment.
[A_r: Na, 23.0; C*l*, 35.5] [2]

M_r of NaC*l* = 23.0 + 35.5 = 58.5

Mass of NaC*l* required = $\frac{250}{1000}\times 0.200\times 58.5$ = **2.925 g**

Prepare 250 cm^3 of the required solution using a 250 cm^3 volumetric flask

1. Using a **mass balance**, weigh 2.925 g of **solid NaC*l*** in a clean and dry beaker.
2. Add about 100 cm^3 **deionised water** and **stir to dissolve the solid NaC*l*.**
3. Using a filter funnel, **carefully transfer the solution and all washings into a 250 cm^3 volumetric flask**. **Make up to the mark with deionised water**.
4. Stopper and **shake the flask well** to **obtain a homogeneous solution**.

☐ **relevant pre-calculations to determine mass of solid NaC*l* required**	**[M47]**
☐ **use of relevant apparatus** ▪ mass balance to determine mass of solid solute used ▪ volumetric flask ☐ **relevant procedure to prepare standard solution.** ▪ dissolving solid solute; ensuring complete transfer of solute; ▪ topping up to mark; shaking to obtain homogenous solution	**[M48]**

Markers' Comments

- Many candidates forgot the procedure in making a standard solution. Some did not even use a volumetric (standard) flask, while some poured solid NaC*l* directly into the volumetric flask. These are incorrect techniques.

M47	M48

(b) In order to determine the concentration of the solution of lead(II) nitrate, sufficient data must be collected to plot a graph of mass of precipitate formed against the volume of sodium chloride used.

In your plan, you should only use the solution of sodium chloride you planned to make in **(a)** and the aqueous solution of lead(II) nitrate provided. No additional chemicals are provided.

The choice for the individual volumes of aqueous sodium chloride and aqueous lead(II) nitrate should be chosen in a way such that mixing the two together gives a reaction mixture of the same total volume for each experiment.

Your plan should include brief details of:

- the apparatus you would use,
- the quantities of reagents you would use in each experiment,
- the procedure you would follow to obtain dry and pure precipitate,
- the measurements you would take to allow for the graph to be drawn,
- how you would ensure that the results obtained are **accurate** and **reliable**.

[5]

1) Place the aqueous Na*Cl* solution and aqueous $Pb(NO_3)_2$ solution in two separate **burettes**.

2) Using the burettes, transfer the Na*Cl* solution and $Pb(NO_3)_2$ solution in **five separate beakers in the proportions by volume shown** in the table below.

Total volume of the two solutions adds up to 50.00 cm^3.

Beaker	volume of 0.200 mol dm^{-3} Na*Cl*(aq) / cm^3	volume of ~ 0.1 mol dm^{-3} $Pb(NO_3)_2$(aq) / cm^3
1	10.00	40.00
2	20.00	30.00
3	25.00	25.00
4	30.00	20.00
5	40.00	10.00

3) Using **filter funnel and a filter paper**, filter the contents of each beaker to **collect the precipitate on the filter paper**.

4) Rinse the beaker with deionised water and pour the washing through the filter paper on the filter funnel to ensure complete transfer of ppt onto the filter paper.

5) **Wash the precipitate with cold deionised water** to remove any unreacted Na*Cl* and $Pb(NO_3)_2$.

6) **Dry the precipitate for a few minutes** in an **oven and allow to cool.**

[Turn Over

7) Using a **mass balance**, weigh and record the mass of precipitate produced in each beaker.

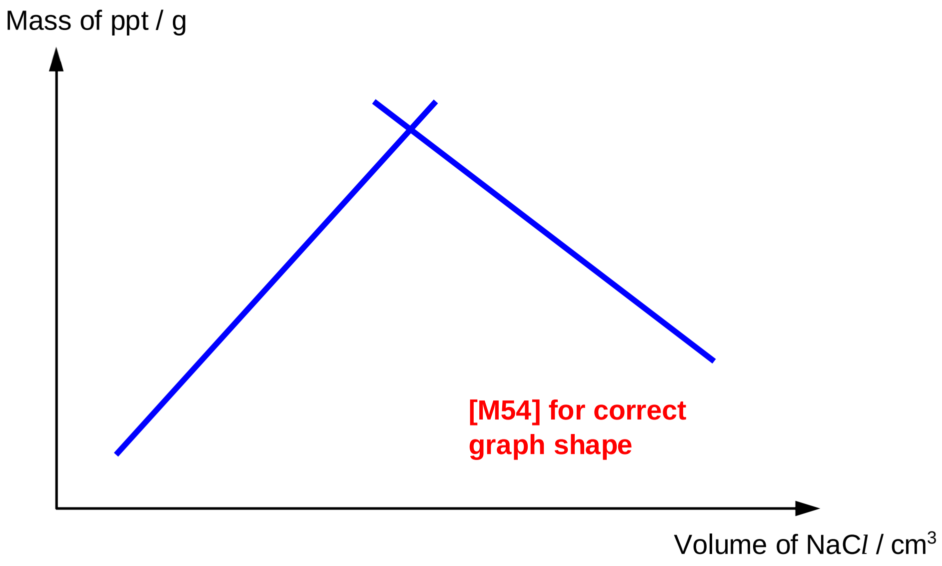
8) Reheat, cool and reweigh until the **mass is constant** to ensure **all the water has been removed.**

9) Repeat **Steps 1–8 to ensure consistent results are obtained (for reliability)**.

• the apparatus you would use	
☐ appropriate apparatus (burettes, beakers, filter funnel, mass balance) o burettes for measuring volume of reagents o filter funnel for filtering of precipitate residue o mass balance for measuring mass of residue.	**M49**
• the quantities of reagents you would use in each experiment	
☐ suitable volumes of each reagent such that they add up to the same total volume for each reaction mixture ☐ total volume used for the volumes suggested for each reagent cannot exceed 250 cm^3 (i.e. no additional chemicals were used)	**M50**
• the procedure you would follow to obtain dry and pure precipitate	
general procedure include ☐ mixing planned quantities of each reagent into different beakers followed by filtering to obtain the ppt residue ☐ washing ppt residue with deionised water to remove impurities, followed by drying the ppt	**M51**
• the measurements you would take to allow for the graph to be drawn	
☐ takes at least 5 data points in order for a graph to be plotted ☐ weighs and record the mass of precipitate for each reaction mixture	**M52**
• how you would ensure that the results obtained are accurate and reliable	
☐ accuracy (any one of the following) o rinse washings into the filter to ensure all solid has been transferred into the filter o reheat-cool-reweigh till constant mass to ensure all water is removed ☐ reliability o repeats the entire experiment for consistent results	**M53**

M49	M50	M51	M52	M53

(c) **(i)** Sketch the graph that you would expect to obtain on the axes provided in Fig. 4.1. [1]



[M54] for correct graph shape

Fig. 4.1

(ii) Describe how you would use your graph to determine the concentration of the lead(II) nitrate solution. [1]

The x–coordinate value of the point of intersection (equivalence point corresponding to maximum amount of ppt formed) gives the value for the volume of NaC*l* solution used to be *P* cm^3

Volume of $Pb(NO_3)_2$ used will be (50 – *P*) cm^3.

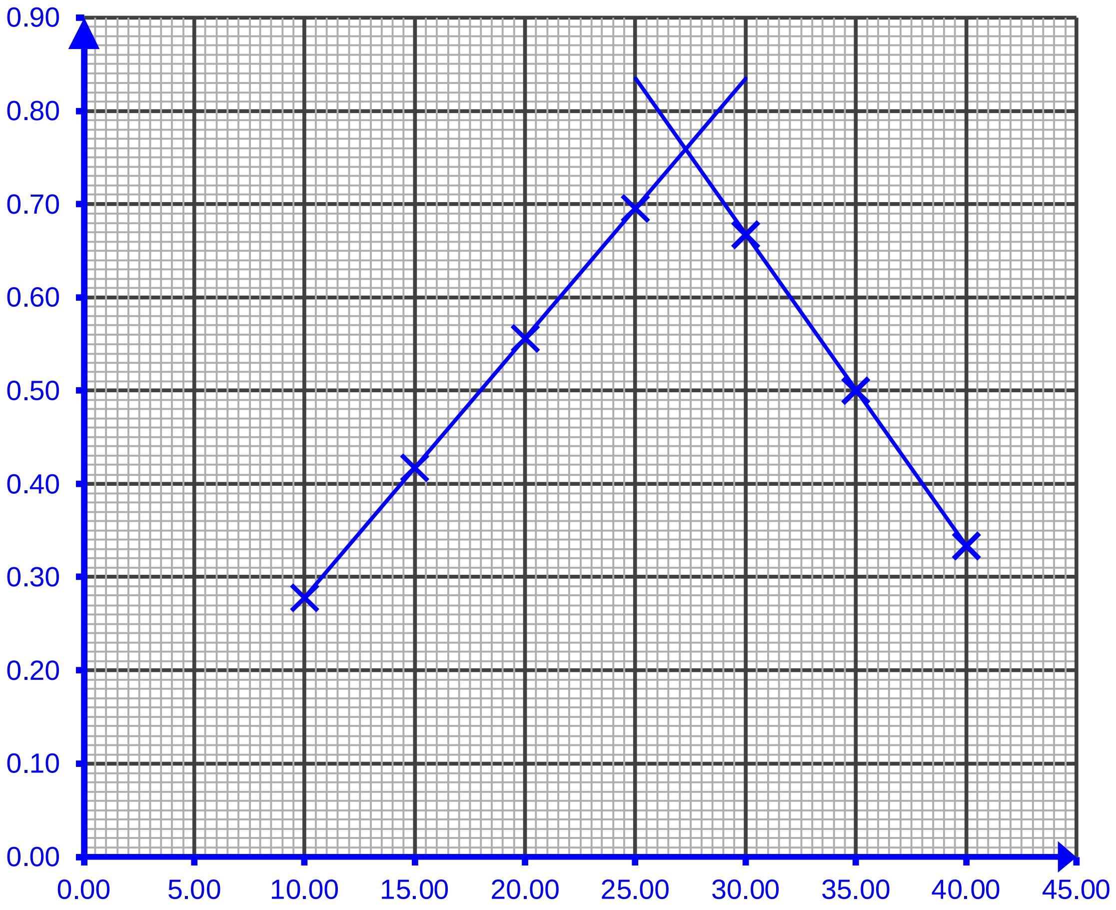
At equivalence point, 2 NaC*l* ≡ $Pb(NO_3)_2$

$$[Pb(NO_3)_2] = \frac{n(Pb(NO_3)_2)}{V(Pb(NO_3)_2 \text{ used})} = \frac{\frac{1}{2} \times n(NaCl)}{\frac{50-P}{1000}}$$

$$= \frac{\frac{1}{2} \times \left(\frac{P}{1000} \times 0.200\right)}{\frac{50-P}{1000}} = = \frac{0.100\,P}{50-P} \quad \textbf{[M55]}$$

M54	M55

[Total: 9]



Markers' Comments

- Not many candidates could appreciate the design of this experiment, hence they were not able to sketch a proper graph and subsequently used the graph to determine the [$Pb(NO_3)_2$].
- Candidates need to appreciate that the total volume need to be kept constant, and vary volumes of $NaCl$ and $Pb(NO_3)_2$. The stoichiometric volumes of $NaCl$ and $Pb(NO_3)_2$ will result in the **max** amount of ppt produced.