Planning Experiments

[Planning]: Titration 1 – Acid-Base

1 Citrus fruits such as limes, lemons and oranges are an excellent source of vitamins and they also contain a mixture of weak acids such as citric acid, tartartic acid and ascorbic acid.

You are required to plan an experiment involving titration that will enable you to determine an accurate value for the concentration of H^+ present in lemon juice. (Assume that the acid present in lemon juice is a monobasic acid.)
You are provided with:

- **FA 1** 100 cm^3 of fresh (filtered) lemon juice
- **FA 2** 400 cm^3 of 0.150 mol dm^{-3} aqueous sodium hydroxide
- Phenolphthalein and methyl orange indicator
- Deionized water
- Common laboratory apparatus

(a) It is found that 1 drop of **FA 1** required 5 drops of **FA 2** for complete reaction. Explain why the given **FA 1** should not be titrated with **FA 2** directly.

The given **FA 1** is too concentrated.
25.0 cm^3 of **FA 1** will require 125 cm^3 of **FA 2** ($\frac{5}{1} \times 25.0 = 125$ cm^3) for a complete neutralisation, which exceeds the capacity of the burette.

(b) State the dilution factor for the **FA 1** solution so that 25 cm^3 of this diluted solution would require approximately 25 cm^3 of **FA 2** for complete reaction.

Since H^+ and OH^- reacts in 1:1 mole ratio, **FA 1** needs to be diluted to ~ 0.150 mol dm^{-3}.
Dilution factor = $\frac{5}{1}$ = 5

(c) Outline, step by step, how you would prepare 250 cm^3 of diluted solution of **FA 1** based on your answer in **part (b)**.

Vol. of **FA 1** required to dilute to 250 cm^3 = $\frac{250}{5}$ = 50.00 cm^3
Step 1: Transfer 50.00 cm^3 of **FA 1** using a burette into a 250 cm^3 graduated flask.
Step 2: Add deionized water to the graduated flask and top it up to the graduated mark
Step 3: Stopper the flask, invert and shake well to obtain a homogeneous solution and label the diluted **FA 1** as **FA 3**

(d) Give a detailed sequence of steps to produce a set of consistent titres that could be used to find the concentration of H^+ present in lemon juice.

In your plan, you should include

- details of apparatus and quantities of reagent to be used;
- the essential details of the titration procedure;
- the appropriate data to be recorded .

Procedure:

1. Top up a 50.00 cm^3 burette with **FA 2**. Record the initial burette reading.
2. Transfer 25.0 cm^3 of **FA 3** into a conical flask using a 25.0 cm^3 pipette and add 2 - 3 drops of **phenolphthalein**.
3. Titrate it against **FA 2** until the solution turns from colourless to pale pink. Record the final burette reading and calculate volume of **FA2** used .
4. Repeat the titration until results are consistent within $\pm$ 0.10 cm^3.

Titration	Rough	1	2
Final burette reading / cm^3			
Initial burette reading / cm^3			
Vol. of **FA 2** used / cm^3			

(e) A student carried out your plan and obtained an average titre value of **y** cm^3. Outline how you would use this result to determine the concentration of H^+ present in **FA 1**.

Amt of H^+ in 25.0 cm^3 of diluted lemon juice, **FA 3** = Amt of NaOH reacted

$$= \frac{y}{1000} \times 0.150 = \left(1.50 \times 10^{-4}\right) y \text{ mol}$$

Amt of H^+ in 250 cm^3 of **FA 3** = $\frac{250}{25.0} \times \left(1.50 \times 10^{-4}\right) y = \left(1.50 \times 10^{-3}\right) y \text{ mol}$

Amt of H^+ in 50.00 cm^3 of **FA 1** = $\left(1.50 \times 10^{-3}\right) y \text{ mol}$

Conc. of H^+ in **FA 1** = $\frac{1000}{50.00} \times \left(1.50 \times 10^{-3}\right) y = 3.00 \times 10^{-2} y \text{ mol}$

[Planning]: Titration 2 – Acid-Base

2(a) Outline a stepwise titration method by which you can determine whether a solid organic acid provided is monobasic or dibasic.

You are provided with:

- 1.0 g of an anhydrous solid organic acid of M_r of 90
- 0.010 mol dm^{-3} aqueous sodium hydroxide
- deionized water
- common laboratory apparatus

In your plan, you should

- indicate the mass of acid to be used and the indicator;
- justify the amount and concentration of the chemicals used and,
- show the appropriate recording of data.

(b) Explain how you would interpret the data to determine obtain the basicity of the organic acid.

(a) Preliminary consideration:

Dependent variable in this expt is volume of NaOH(aq) required.

For the same no. of moles of acid to reach end-point:

For monobasic acid:

Same no. of moles of NaOH(aq) required since: $HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$

For dibasic acid:

TWICE no. of moles of NaOH(aq) required since $H_2A(aq) + \mathbf{2}\ NaOH(aq) \rightarrow Na_2A(aq) + 2H_2O(l)$

Suitable volumes of 0.010 mol dm^{-3} NaOH(aq) used are 20.00 cm^3 (to neutralise monobasic acid) and 40.00 cm^3 (to neutralise dibasic acid).

Note:

1. To choose an appropriate **minimum volume** of NaOH(aq) used for titration, the percentage error/uncertainty due to apparatus measurement should not exceed 0.5%.

   Percentage error = $\frac{\text{uncertainty} \times \text{no. of reading taken}}{\text{quantity measured}} \times 100\%$ (**≤ 0.5%**)

2. To choose an appropriate **maximum volume** of NaOH(aq) used for titration, the max. volume should be kept to 80% of the capacity of the measuring apparatus.

To determine the mass of acid used to prepare standard solution of acid using 250 cm^3 graduated flask:

Amt of NaOH(aq) in 20.00 cm^3 = 0.02 × 0.01 = 2.0 × 10^{-4} mol

Amt of acid present in 25.0 cm^3 = 2.0 × 10^{-4} mol (Since $H^+ \equiv OH^-$ for monobasic acid)

Amt of acid present in 250 cm^3 graduated flask = 2.0 × 10^{-3} mol

Mass of acid needed = 2.0 x 10^{-3} × 90 = 0.18 g

Phenolphthalein is used as an indicator. At equivalence point, pH >7 (a weak acid-strong base titration), since organic acids are weak acids.

Procedure:

1. Weigh accurately about 0.18 g of **the organic acid solid** in a dry and clean weighing bottle using an electronic balance.

2. Transfer the **organic acid solid** into a small beaker and re-weigh the residual solid in the weighing bottle. Record the actual mass transferred to the beaker.

Mass of weighing bottle and **organic acid solid** / g	
Mass of weighing bottle and **residual organic acid solid** / g	
Mass of **organic acid solid** used / g	

3. Add deionised water into the small beaker to dissolve the **organic acid solid** and transfer all solution and washings into a 250 cm^3 graduated flask. Make up to mark with deionised water. Stopper the flask, invert and shake thoroughly to obtain a homogenous solution. Label as **FA 2**.

4. Pipette 25.0 cm^3 of **FA 2** into a conical flask and add 2 - 3 drops of **phenolphthalein** to the solution.

5. Top up a **50.00 cm^3 burette** with NaOH. Record the initial burette reading**.** Titrate against the 0.010 mol dm^{-3} of NaOH(aq) until the solution turns from **colourless to pale pink.** Record the final burette reading and calculate volume of NaOH used.

6. Repeat the titration until results are consistent **(two titres within ±0.10 cm^3)**.

(b) Interpretation of data to determine basicity of the organic acid

- If volume of NaOH(aq) used for the titration is 20.00 cm^3, organic acid is monobasic.
- If volume of NaOH(aq) used for the titration is 40.00 cm^3, organic acid is dibasic.

[Planning]: Titration 3 – Redox Reaction

3 You are to devise a method to determine the percentage purity of potassium nitrite in an impure sample **Y**. The percentage purity of KNO_2 in the given sample **Y** is around 95% – 98%.

Nitrite ions, NO_2^-, are oxidised to NO_3^- by acidified potassium manganate(VII), $KMnO_4$. However, nitrite ions decompose in contact with dilute acids.

$$NO_2^-(aq) + H^+(aq) \rightarrow HNO_2(aq)$$
$$3HNO_2(aq) \rightarrow H_2O(l) + HNO_3(aq) + 2NO(g)$$

You are provided with:

- solid sample **Y**
- 0.20 mol dm^{-3} potassium manganate(VII)
- 1.0 mol dm^{-3} sulfuric acid

(a) Bulk solution of **Y** is prepared by dissolving 1 g of **Y** in deionised water to form 250 cm^3 of solution. Using calculations, explain why the 0.20 mol dm^{-3} $KMnO_4$ solution provided is **not** suitable for the titration in this case. [Hint: % purity of KNO_2 in the given sample **Y** is around 95% – 98%]

[O]: $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e$ -------- eqn 1 (×5)

[R]: $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ ------- eqn 2 (×2)

Balanced equation: $5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn^{2+} + 3H_2O$

Assuming % purity of KNO_2 in **Y** is 95%, mass of KNO_2 in 1 g **Y** = 0.95 × 1 = 0.95 g

(Note: Lower percentage of 95% (instead of 98%) is chosen to determine whether the volume of $KMnO_4$ is suitable with lesser KNO_2 present)

Amt of KNO_2 in 1 g **Y** dissolved in 250 cm^3 graduated flask

= 0.95 / (39.1 + 14.0 +32.0) = 0.01116 mol

Amt of KNO_2 in 25.0 cm^3 (conical flask for titration)

= 0.01116 × 25/250 = 0.001116 mol

$$\frac{\eta_{KMnO_4}}{\eta_{KNO_2}} = \frac{2}{5}$$

Amt of $KMnO_4$ needed = 2/5 × 0.001116 = 4.465 × 10^{-4} mol

Volume of $KMnO_4$ needed = [(4.465 × 10^{-4})/0.20] × 1000 = 2.23 cm^3

Volume of $KMnO_4$ (i.e. 2.23 cm^3) is too small, percentage error due to measurement will be significant. Hence, the 0.20 mol dm^{-3} $KMnO_4$ solution provided is **not** suitable for the titration in this case.

Alternatively, if $KMnO_4$ is in the conical flask:

25.0 cm^3 of $KMnO_4$ will need [5/2 × 0.2 × 0.025] ÷ [(0.01116 × 4)/1000] = 280 cm^3 of sample **Y**, this is beyond the capacity of burette.

(b) Give an appropriate sequence of steps which enable you to use titration results to determine the percentage purity of KNO_2. Your plan should include

- suitable starting quantities of $KMnO_4$ and H_2SO_4 to carry out the above titration by considering the answer in part **(a)**.
- steps to prepare solution **Y** mentioned in part **(a)**.
- steps taken to prevent significant decomposition of NO_2^- ion taking place during titration. You may assume that the rate of redox reaction is faster than rate of decomposition of NO_2^- ion caused by acid.
- the endpoint colour change by considering the colour of the ions in reactants and products.

NOTE: It is stated in the question that nitrite ions decompose in acidic solution; hence **nitrite should not come into contact with acid before titration.**

Preliminary calculation:

1. Since nitrite ions decompose in dilute acid, sulfuric acid has to be added to $KMnO_4$ before titration.
2. Dilute $KMnO_4$ by a factor of 10 to increase the volume of $KMnO_4$ required to become 22.3 cm^3.
   $\therefore$ pipette 25.0 cm^3 $KMnO_4$ into a 250 cm^3 graduated flask
3. Amt of H^+ needed for redox reaction in 25.0 cm^3 of aliquot = $6/5 \times 0.001116 = 1.339 \times 10^{-3}$ mol
   Total amt of H^+ in 250 cm^3 graduated flask = 1.339×10^{-2} mol
4. Amt of H_2SO_4 required = $(1.354 \times 10^{-2})/2 = 0.006696$ mol
   Volume of H_2SO_4 required = $(0.06696/1.0) \times 1000 = 6.70$ cm^3
5. Volume of H_2SO_4 to be added into graduated flask = 7 cm^3 to 10 cm^3 (in excess)

Procedure

Preparation of acidified dilute solution of $KMnO_4$:

1. Pipette 25.0 cm^3 of $KMnO_4$ into a 250 cm^3 graduated flask. Use a 10.0 cm^3 measuring cylinder to measure 10.0 cm^3 of H_2SO_4 into the flask and top it up to the mark with deionised water. Stopper, invert and shake the graduated flask to obtain a homogeneous solution. This is **FA 1**.

Preparation of solution Y

1. Weigh accurately about 1.0 g of **Y** in a dry and clean weighing bottle using an electronic balance.
2. Transfer the solid to a small beaker and re-weigh the residual solid in the weighing bottle. Record your data in Table 1. Calculate the actual mass of **Y**, used.

Table 1:

Mass of weighing bottle and solid **Y**/ g	
Mass of weighing bottle and residual **Y**/ g	
Mass of **Y** used/ g	

3. Dissolve the solid using a small amount of deionised water in the small beaker and transfer into another 250 cm^3 volumetric flask. Transfer all washings into the flask and make up to the mark with deionised water.
4. Stopper the flask, invert and shake well to obtain a homogenous solution by inverting the flask several times. Label the flask **Y1**.

Titration:

1. Fill a 50.00 cm^3 burette with the acidified dilute solution of $KMnO_4$, **FA 1**. Record the initial burette reading.

2. Use a 25.0 cm^3 pipette to transfer 25.0 cm^3 of solution **Y1** into a conical flask. Titrate it against **FA 1** till a first permanent pale pink colour is obtained. Record the final burette reading and calculate volume of **FA 1** used.

3. Repeat the titrations until results are within $\pm$ 0.10 cm^3.

Titration	Rough	1	2
Final burette reading / cm^3			
Initial burette reading / cm^3			
*Vol. of **FA 1** used / cm^3*			

(c) Show, step by step, how you will calculate the percentage purity of potassium nitrite in sample **Y**. Assume that the titration result is 22.50 cm^3.

$\eta(MnO_4^-) = \frac{0.020 \times 22.5}{1000}$ = 4.5×10^{-4} mol

η (NO_2^-) in 25.0 cm^3 **Y** = $\frac{5 \times 4.5 \times 10^{-4}}{2}$ = 1.125×10^{-3} mol

η (NO_2^-) in 250 cm^3 of **Y** = $\frac{1.125 \times 10^{-3}}{25.0} \times 250 = 1.125 \times 10^{-2}$ mol

mass of KNO_2 = $85.1 \times 1.125 \times 10^{-2}$ = 0.957g

% by mass of KNO_2 in **Y** = $\frac{0.957}{1} \times 100\%$ = 95.7 %

[Planning]: Titration 4 – Iodine-thiosulfate

4 Iodine is an essential element in the human body. It is normally obtained through the diet but in regions of many countries there is an iodine deficiency.

Sodium chloride, NaC*l*, used in food industry can have a very small amount of potassium iodide, KI, added as a source of iodine. The product is sold as 'iodised salt'.

In the manufacture of 'iodised salt', sodium chloride and potassium iodide are dry mixed to give a mixture containing 2000 parts per million of potassium iodide.

> In a manufacturing of 'iodised salt', too much potassium iodide was accidentally added to the sodium chloride.
>
> You are required to **outline** a plan involving titration to determine the percentage by mass of potassium iodide present in the 'iodised salt' sample.

You are provided with:

- 0.100 mol dm^{-3} copper sulfate
- 0.100 mol dm^{-3} of thiosulfate ions
- starch solution
- 'iodised salt'
- usual apparatus for titration
- an electronic balance

In your plan, you should include

- masses and volumes of reagents to be used from the preliminary consideration **(You may assume 20 g of iodised salt can easily dissolve in deionised water to form 25.0 cm^3 of solution.)**
- reagents that must be in excess
- how the mass of potassium iodide is to be calculated from the titre obtained by working with arbitrary values like **A** cm^3

Reactions involved:

Copper(II) ions are reduced by iodide to form insoluble copper(I) iodide and iodine as shown below.

$$2Cu^{2+} + 4I^- \rightarrow 2CuI\ (s) + I_2 \text{ ------- eqn 1}$$

To ensure that all iodide are completely reacted, copper(II) sulfate must be added in excess.

To determine the amount of iodide present in the 'iodised salt', the titration of iodine with sodium thiosulfate, known as iodometric titration, is carried out as shown below.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^- \text{ ------- eqn 2}$$

Preliminary calculation on the mass and volumes of each reagent used:

Assume mass of iodised salt used = 20 g (as given in the Qn)

mass of KI present = 20 × (2000/1000000) = 0.04 g

Amt of iodide = Amt of KI = 0.04/166.1 = 2.408×10^{-4} mol

From eqn 1: Amt of iodine = $2.408 \times 10^{-4} / 4 = 6.020 \times 10^{-5}$ mol

Amt of copper(II) sulfate reacted with iodide = $2.408 \times 10^{-4} / 2 = 1.204 \times 10^{-4}$ mol

Volume of $CuSO_4$ needed = $(1.204 \times 10^{-4} / 0.1) \times 1000 = 1.204$ cm^3

As $CuSO_4$ is added in excess to ensure all iodide are reacted away, can just use a 10 cm^3 measuring cylinder to measure 2 cm^3 of $CuSO_4$

According to eqn 2: volume of 0.1 mol dm^{-3} of thiosulfate ions $= [(6.020 \times 10^{-5} \times 2) / 0.1] \times 1000$
$= 1.204$ cm^3

Volume required is too small, will incur large percentage error in measurement, therefore there is a need to dilute the given 0.1 mol dm^{-3} of thiosulfate by a factor of 20 so that the volume required now becomes 1.204 x 20 = 24.08 cm^3

Therefore 24.08 cm^3 contain 1.204×10^{-4} mol of $S_2O_3^{2-}$, 250 cm^3 of it will contain 1.25×10^{-3} mol

Volume of $S_2O_3^{2-}$ needed for dilution to form 250 cm^3 solution = $(1.25 \times 10^{-3} / 0.1) \times 1000 = 12.5$ cm^3

[diluted $S_2O_3^{2-}$] = $12.5/250 \times 0.1 = 5.00 \times 10^{-3}$ mol dm^{-3}

Procedure

(1) Transfer 12.50 cm^3 of 0.1 mol dm^{-3} thiosulfate ions from a 50.00 cm^3 burette into a 250 cm^3 graduated flask and make up to 250 cm^3 mark with deionised water. Stopper, invert and shake the flask well to obtain a homogeneous solution.

(2) As 20 g of iodised salt can readily dissolve in deionised water to form 25.0 cm^3 solution and 20 g in 25.0 cm^3 solution requires 24 cm^3 of $S_2O_3^{2-}$. Therefore weigh 200 g of iodised salt directly into a 250 cm^3 beaker using an electronic balance, dissolve solid in minimum volume of deionised water and transfer to a 250 cm^3 graduated flask. Rinse the sides of 250 cm^3 beaker with deionised water and transfer all washings to the graduated flask. Top up to the mark with deionised water, stopper and invert and shake the flask well to obtain a homogeneous solution.

Note: Formation of bulk solution of the analyte (iodised salt) is necessary so that solution of the same concentration can be used for repeated titrations to get rid of anomalous result.

(3) Use a pipette to transfer 25.0 cm^3 of the iodised salt solution into a conical flask.

(4) Use a 10 cm^3 measuring cylinder to transfer 2.0 cm^3 of copper(II) sulfate into the same conical flask.

Titration

(5) Titrate the solution with the diluted sodium thiosulfate in the burette until a pale yellow solution is obtained.
(6) Add 10 drops of starch solution and continue to titrate until the blue-black colouration disappears.
(7) Repeat steps 3-6 to obtain at least 2 consistent results within $\pm$ 0.10 cm^3. Record the volume of sodium thiosulfate used.

To determine the mass of potassium iodide (KI) from the titre

Assume the titre volume= A dm^3

Amt of $S_2O_3^{2-}$ = **A × 0.005 mol**

Amt of iodine in 25.0 cm^3= (**A × 0.005) /2 mol**

Amt of iodine in 250 cm^3= **[(A × 0.005) /2]** × 10 = 0.025 × **A** mol

Amt of iodide = 4 × (0.025 × **A**) mol

Amt of KI = 4 × (0.025 × **A**) mol

Mass of KI = [4 × (0.025 × **A**)] × 166.1

[Planning]

[Planning] : Gas Collection 1

When the nitrates of the Group 1 metals (Li, Na, K, Rb, Cs) are heated they decompose in one of the following ways.

$$2M\text{NO}_3(s) \rightarrow 2M\text{NO}_2(s) + \text{O}_2(g)$$

$$4M\text{NO}_3(s) \rightarrow 2M_2\text{O}(s) + 4\text{NO}_2(g) + \text{O}_2(g)$$

M represents a Group 1 metal.

You are to design an experiment in which the **oxygen** gas evolved from the thermal decomposition of a known quantity of potassium nitrate is collected and its volume measured.

Nitrogen dioxide, NO_2, is **soluble** in water.

Oxygen gas, O_2, can be regarded as **insoluble** in water.

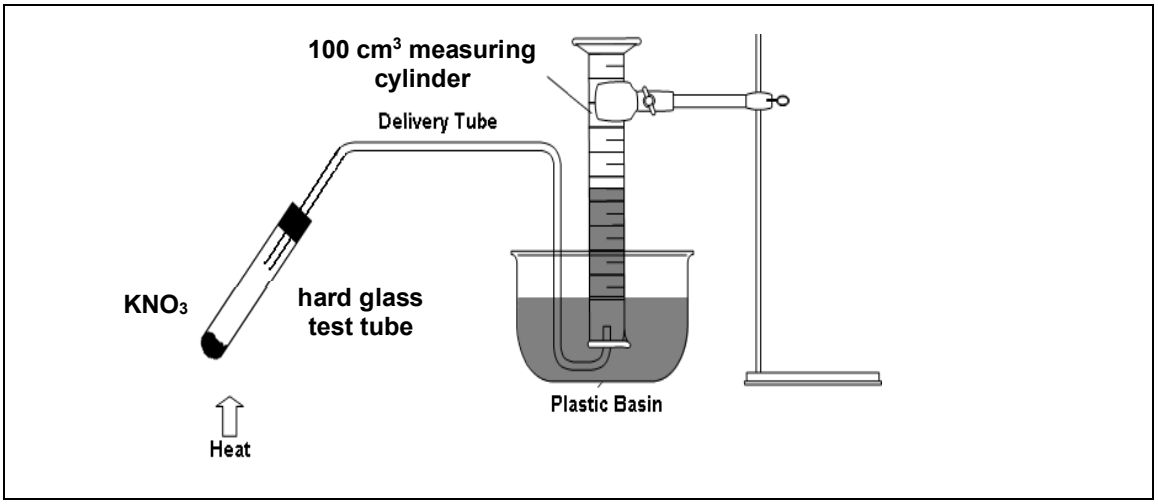
From the data collected in the experiment, you should be able to determine which of the above equations correctly represents the decomposition of potassium nitrate.

(a) Draw a labelled diagram of the apparatus you would use to

- decompose the potassium nitrate by heating,
- remove any nitrogen dioxide formed,
- collect the oxygen gas evolved, and
- measure the volume of the gas collected.

Your diagram should show how standard pieces of laboratory apparatus are to be assembled.

You should show clearly how these pieces of apparatus are connected together.



(b) What is the maximum volume of oxygen gas that can be collected in the apparatus shown in your diagram?

The maximum volume of oxygen gas is 100 (or 50) cm^3 depending on the capacity of the inverted cylinder. (can also use burette – 50.00 cm^3)

(c) **(i)** For each of the following equations, calculate the mass of potassium nitrate, KNO_3, that, when completely decomposed, will produce the volume of oxygen you have stated in **(b).**

(You may assume that all gases are measured at room temperature and pressure.)

$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$

$4KNO_3(s) \rightarrow 2K_2O(s) + 4NO_2(g) + O_2(g)$

If O_2 is the only gaseous product:	If O_2 and NO are evolved on heating:
$2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$	$4KNO_3(s) \rightarrow 2K_2O(s) + 4NO_2(g) + O_2(g)$
At r.t.p:	At r.t.p:
Mass of KNO_3 to produce 100 cm^3 of O_2	Mass of KNO_3 to produce 100 cm^3 of O_2
$= \frac{100}{24000} \times 2 \times 101.1$	$= \frac{100}{24000} \times 4 \times 101.1$
= 0.843 g	**= 1.69 g**

(ii) What is the maximum mass of potassium nitrate that should be used in the experiment? Explain your answer.

The maximum mass that should be used is 0.843 g.

Explanation : If the decomposition follows reaction 1, a mass greater than 0.843g would result in a volume of oxygen greater than 100 cm^3.

Note: Mass of 1.69 g should not be used as the volume of O_2 gas produced will exceed the maximum capacity of the apparatus if the reaction follows equation 1 (volume of O_2 collected is 200 cm^3)

(d) List, in the order in which they will be made, the measurements you would take during the experiment.

- Mass of empty tube, mass of tube + contents before heating
- Initial volume and final volume of water in the inverted measuring cylinder
- Mass of tube + residue after heating

(e) The residue after heating the potassium nitrate will be either potassium oxide, K_2O, or potassium nitrite, KNO_2.

Use your knowledge of the chemistry of metal oxides to suggest an appropriate test and observations to distinguish between potassium oxide and potassium nitrite.

Add H_2SO_4 acid

Observation: K_2O will dissolve in acid to give a colourless solution (neutralization since K_2O is basic)

Observation: KNO_2 will liberate brown pungent fumes, NO_2. (acid decomposition of nitrite)

[Planning] : Gas Collection 2

GRAVIMETRY, GAS COLLECTION, BACK TITRATION

A solid sample contains a mixture of NaC*l* and $Mg(HCO_3)_2$. The mixture contains approximately 30% by mass of magnesium hydrogencarbonate.

The analysis of the solid mixture can be carried out using three methods:

(i) gravimetric analysis
(ii) gas collection
(iii) back titration

You are provided with the following chemicals:

- 0.01 mol dm^{-3} NaOH(aq)
- 1.0 mol dm^{-3} HC*l*
- solid mixture of NaC*l* and $Mg(HCO_3)_2$

Copy the table into your answer sheet and complete it.

	Preliminary calculation to determine suitable starting quantities of the chemical reagents	Outline of step-by-step procedure taking precautions to ensure reliability of results	Table of data to be collected
Gravimetric analysis			
Gas collection			
Back titration			

<table>
<tr><th></th><th>Preliminary calculation to determine suitable starting quantities of the chemical reagents.</th><th>Outline of step-by-step procedure taking precautions to ensure reliability of results.</th><th>Table of data to be collected</th></tr>
<tr><td>Gravimetric analysis</td><td>
Δm= 0.2 g to keep error due to measurement to 5%.
$\frac{\pm 2(0.01)}{\text{mass lost}} \times 100\% \leq \pm 5\%$
mass lost ≤ 0.400 g
Mass lost = Mass of CO_2 and H_2O in 2:1 ratio
If mass lost = 0.4 g,
mass of H_2O = $\frac{18.0}{2(44.0)+18.0} \times 0.4$ = 0.06792 g
Amount of H_2O lost = 0.06792/18.0 = 3.774×10^{-3} mol
$Mg(HCO_3)_2(s) \rightarrow MgO(s) + 2CO_2(g) + H_2O(g)$
Amt of $Mg(HCO_3)_2 = 3.774 \times 10^{-3}$ mol
Mass of $Mg(HCO_3)_2 = (3.774 \times 10^{-3}) \times 146.3 = 0.552$ g
Mass of solid mixture = 0.552 g × 100/30 = 1.84 g
Note: Mass used for heating must not be too large (incomplete decomposition) or too small (large percentage error in measurement).
</td><td>
1. Weigh and record the mass of a dry and clean boiling tube.
2. Weigh accurately about 1.80 g of solid mixture in hard glass boiling tube using an electronic mass balance. Record the total mass of sample and boiling tube.
3. Using a test tube holder, heat the boiling tube and its contents gently at first.
4. Continue heating the solid mixture using non-luminous flame with intermittent tapping on the heat proof mat. (This is to ensure all solid are exposed to heat.)
5. Leave the hot boiling tube on heat proof mat to cool before weighing.
6. Repeat heat-cool-weigh process until difference in the mass of residue after every heating is within ± 0.01g. (This is to verify that all solid are completely decomposed.)
7. Record data in Table 1.
</td><td>
Table 1
<table>
<tr><td>Mass of boiling tube used / g</td><td>A</td></tr>
<tr><td>Mass of solid mixture + boiling tube initially / g</td><td>B</td></tr>
<tr><td>Mass of solid mixture used / g</td><td>B – A = C</td></tr>
<tr><td>Mass of sample + boiling tube after repeated heating / g</td><td>D_1
D_2
...
D</td></tr>
<tr><td>Mass loss / g</td><td>D - B</td></tr>
</table>
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Gas collection

$Mg(HCO_3)_2 + 2HCl \rightarrow MgCl_2 + 2CO_2 + 2H_2O$

Vol of gas collected = 80% of 100 cm^3 gas syringe
= 80 cm^3.

Amount of CO_2 = $\frac{80}{24000}$ = 3.333×10^{-3} mol

Amount of $Mg(HCO_3)_2$ to produce 80 cm^3 of CO_2
= ½ (3.333×10^{-3}) = 1.667×10^{-3} mol

Mass of $Mg(HCO_3)_2$ = $1.667 \times 10^{-3} \times 146.3 = 0.2438$ g

Since the mixture contains approximately 30% by mass of magnesium hydrogencarbonate,

mass of solid mixture required = $0.2438 \div \frac{30}{100} = 0.813$g

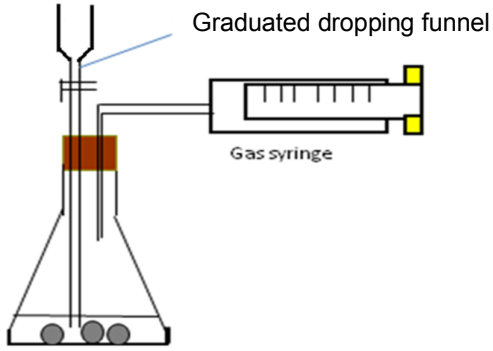
Given that [HCl] = 1.0 mol dm^{-3},
volume of HCl required to react with $Mg(HCO_3)_2$

= $(3.33 \times 10^{-3}) \div \frac{1.0}{1000}$ = 3.33 cm^3

To ensure complete reaction, an excess of HCl of 10 cm^3 is used.

1. Weigh accurately about 0.80 g of solid mixture in a clean and dry weighing bottle using an electronic balance and add the solid to a 250cm^3 conical flask. Measure the mass of weighing bottle and residual solid. Record data in Table 1.

2. Set up the apparatus according to the diagram below using a 100 cm^3 frictionless gas syringe.



3. Add 10.0 cm^3 HCl using a 10 cm^3 measuring cylinder into a graduated dropping funnel/thistle funnel.

4. Open the tap to release 5.0 cm^3 of HCl into the conical flask and leave some HCl behind. Then close the tap. (it's important to use excess HCl so as to achieve air-tight conditions at all times). Swirl the conical flask 10 times (or continuously).

5. Record the volume of the gas collected when no more effervescence is seen or the piston of the syringe stopped moving (constant value), indicating reaction is complete, wait for a few minutes (cool

Table 1

	1	2
Mass of weighing bottle + solid mixture/ g		
Mass of weighing bottle + residual solid / g		
Mass of solid transferred / g		
Volume of CO_2/ cm^3		
V_{CO_2}/ mass used		

		down) before reading the volume of CO_2 in the gas syringe and record the result. 6. (if repeat expt) Repeat steps 1-5 and check that the difference in V_{CO2}/ mass used of two experiments is within 5% difference.	

Back titration	Back Titration involves addition of excess HC*l* to $Mg(HCO_3)_2$. The amount of remaining unreacted HC*l* can be determined by titrating with NaOH(aq). Let the mass of solid mixture used be 1.00 g. Since 1.00 g of solid mixture contains 0.300 g of $Mg(HCO_3)_2$, amt of $Mg(HCO_3)_2$ = 0.300 / 146.3 = 2.051×10^{-3} mol $Mg(HCO_3)_2 + 2HCl \rightarrow MgCl_2 + 2CO_2 + 2H_2O$ Amt of acid required = $(2.051 \times 10^{-3}) \times 2$ mol = 4.101×10^{-3} mol V_{HCl} needed = $(4.101 \times 10^{-3}/1) \times 1000 = 4.10$ cm^3 $HCl + NaOH \rightarrow NaCl + H_2O$ Assume titre (NaOH) obtained for titrating with 25.0 cm^3 of reaction mixture (containing unreacted HC*l*) = 25.0 cm^3, Amt of 0.01 mol dm^{-3} NaOH(aq) required = 0.00025 mol	1. Weigh accurately about 1.00 g of solid mixture in a weighing bottle using an electronic balance. Transfer solid into a clean and dry 100 cm^3 beaker. Reweigh mass of weighing bottle and content. Record data in Table 1. 2. Add 6.60 cm^3 of 1 mol dm^{-3} HC*l* from a burette to beaker. Swirl mixture until no more effervescence. 3. Transfer solution to 250 cm^3 graduated flask. 4. Rinse the sides of beaker with some deionised water and transfer all washings to the graduated flask. 5. Top up to the mark with deionised water. 6. Stopper, invert and shake to ensure solution is homogeneous. Label as **FA 1**. 7. Pipette 25.0 cm^3 of **FA 1** into a clean conical flask and add 2 – 3 drops of phenolphthalein. 8. Fill the burette with **NaOH**. Record initial burette reading. 9. Titrate against **NaOH** until solution turns from colourless to pale pink. Record the final burette reading and calculate volume of **NaOH** used. **10. Repeat titration until results are within ± 0.10 cm^3.** 11. Record data in Table 2.	Table 1 | | 1 | 2 | | Mass of weighing bottle + solid mixture/ g | | | | Mass of weighing bottle + residual solid / g | | | | Mass of solid transferred / g | | | Table 2 | | 1 | 2 | | Initial burette reading / cm^3 | | | | Final burette reading / cm^3 | | | | Volume of NaOH(aq) used / cm^3 | | |

	= amt of unreacted HC*l* in 25.0 cm^3 Amt of unreacted HC*l* in 250 cm^3 = 0.0025 mol Hence, additional volume of 1.0 mol dm^{-3} HC*l* needed = 2.5 cm^3 Total vol of HC*l* required = 4.10 + 2.5 = 6.60 cm^3		

(a) A student carried out gravimetric analysis and back titration to verify the percentage by mass of $Mg(HCO_3)_2$ in the solid mixture.

The following data were obtained

Gravimetric analysis	Back titration
Mass of solid mixture = 1.850 g Mass of residue after repeated heating = 1.453 g	Volume of 0.01 mol dm^{-3} of NaOH(aq) needed to neutralise the unreacted acid in 25.0 cm^3 = 25.60 cm^3 Mass of solid mixture = 0.950 g Total volume of 1 mol dm^{-3} HC*l* used to prepare 250 cm^3 solution = 6.60 cm^3

Use the above data to determine the percentage by mass of $Mg(HCO_3)_2$ in solid mixture for each method used. [29.6%, 31.1%]

Gravimetric analysis	Back titration
$Mg(HCO_3)_2(s) \rightarrow MgO(s) + H_2O(g) + 2CO_2(g)$ (**Note:** $MgCO_3$ is initially formed, it decomposes to yield MgO and CO_2) Mass loss = Mass of CO_2 and H_2O in 2:1 ratio = 1.850 – 1.453 = 0.397 g Mass of $H_2O = \frac{18}{2(44)+18} \times 0.397 = 0.006742$g Amount of H_2O = 0.006742/18.0 = 3.745×10^{-3} mol Amount of $Mg(HCO_3)_2 = 3.745 \times 10^{-3}$ mol Mass of $Mg(HCO_3)_2 = 3.745 \times 10^{-3} \times 146.3$ = 0.5479 g percentage by mass of $Mg(HCO_3)_2$ = (0.5479 / 1.85) × 100 = 29.6% **(3.s.f.)**	Total amount of HC*l* in 250 cm^3 $= \frac{6.60}{1000} \times 1 = 6.6 \times 10^{-3}$ mol Amount of unreacted HC*l* in 25.0 cm^3 = Amount of NaOH(aq) reacted $= \frac{25.60}{1000} \times 0.01 = 2.56 \times 10^{-4}$ mol Amount of unreacted HC*l* in 250 cm^3 $= 2.56 \times 10^{-3}$ mol Amount of HC*l* reacted with $Mg(HCO_3)_2$ $= 6.6 \times 10^{-3} - 2.56 \times 10^{-3}$ $= 4.04 \times 10^{-3}$ mol ($Mg(HCO_3)_2 + 2HCl \rightarrow MgCl_2 + 2CO_2 + 2H_2O$ Amount of $Mg(HCO_3)_2 = (4.04 \times 10^{-3})/2$ $= 2.02 \times 10^{-3}$ mol Mass of $Mg(HCO_3)_2$ $= (2.02 \times 10^{-3}) \times 146.3$ = 0.2956 g percentage by mass of $Mg(HCO_3)_2$ = (0.2956/0.950) × 100 = 31.1% **(3.s.f.)**

Planning Exercises

[Planning]: Gravimetric Analysis Practical 1

1 Sodium carbonate, Na_2CO_3, does not decompose on heating with a Bunsen burner. In contrast, sodium hydrogencarbonate, $NaHCO_3$, decomposes on heating.

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

You are to design an experiment in which the percentage by mass of $NaHCO_3$ in a mixture of Na_2CO_3 and $NaHCO_3$ can be determined by heating and weighing alone.

You are provided with:

- solid sample containing a mixture of Na_2CO_3 and $NaHCO_3$
- boiling tube and test-tube holder
- electronic balance
- Bunsen burner and heat proof mat

(a) Your plan should give a step-by-step description of the method, including

- appropriate weighings you would take,
- the sequence of steps to ensure that decomposition was complete,
- the recordings using the letters A, B, C etc to represent the measurement taken and present it with an appropriate table format.

Procedure:

1. Weigh a dry, empty boiling tube using an electronic balance and record its mass.
2. Weigh about 5.0 g of the mixture into the boiling tube. Record the total mass of the boiling tube and its contents.
3. Heat the boiling tube and its contents gently first, then strongly for about 5 to 10 minutes.
4. After heating, place the hot boiling tube on a heat proof mat to cool.
5. Once the boiling tube has cooled down, weigh the boiling tube containing the residue and record its mass.
6. Repeat the heat-cool-weigh process until mass of boiling tube and residue is constant (± 0.01 g). Record all the masses.

Mass of empty boiling tube / g	/	A
Mass of boiling tube and solid sample used / g	/	B
Mass of boiling tube and residue after first heating / g	/	C
Mass of boiling tube and residue after second heating / g	/	D

	Mass of boiling tube and residue after third heating / g	/	D
	Mass of solid used	/g	B – A
	Maximum mass loss	/g	B – D

(b) Use the letters from your plan in **(a)** to show how you would process the results to find the percentage by mass of $NaHCO_3$ in the mixture.

$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$

Mass loss due to loss of CO_2 and H_2O during heating = B – D g

Amount of (H_2O + CO_2) loss = $\frac{B-D}{(44.0+18.0)}$ mol

Since mole ratio of $NaHCO_3$: (H_2O + CO_2) is 2 : 1,

Hence amount of $NaHCO_3$ in the weighed sample = $2\left(\frac{B-D}{(44.0+18.0)}\right)$ = E mol

Mass of $NaHCO_3$ = E × 84.0 = F g

% by mass of $NaHCO_3$ in the mixture = $\left(\frac{F}{B-A}\right)\times 100\%$

(c) The solid sample should be heated gently at first before applying strong heating for thermal decomposition to occur. Suggest a reason why this is necessary.

To prevent the spurting of solid due to sudden expansion of the air trapped in the solid sample if the mixture is heated too strongly at first.

(d) By considering the products of the decomposition, suggest a reason why a crucible, without a lid, might be more appropriate than a boiling tube.

Crucible without lid allows for gases or volatile products to escape more easily.

If product of decomposition involves water vapour: water vapour will condense on the upper cooler surface of boiling tube and may drop onto red hot part of the tube, causing the tube to crack.

Other advantages:
A crucible provides greater surface area to heat so that decomposition of the solid can be faster and more efficient.

[Planning]: Gravimetric Analysis Practical 2

2 When aqueous sodium chloride, NaC*l*, is added to aqueous lead nitrate, $Pb(NO_3)_2$, a white precipitate of lead chloride, $PbCl_2$, is produced. A suggested stoichiometric equation is as shown.

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

In separate experiments, different volumes of 0.20 mol dm^{-3} aqueous sodium chloride are added to a fixed volume of 0.10 mol dm^{-3} aqueous lead nitrate. In each case, the precipitate is filtered, washed with deionised water and thoroughly dried. The mass of the precipitate is recorded.

You are to plan an experiment to investigate this reaction in order to confirm or reject the stoichiometry of the equation.

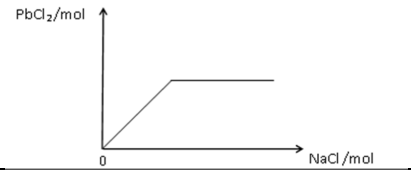
(a) By considering the suggested stoichiometric equation, predict and explain how the number of moles of the precipitate, $PbCl_2$, will change as the number of moles of NaC*l* added increases.

As the number of moles of NaC*l* added increases (as long as it is the limiting reagent), the number of moles of precipitate of $PbCl_2$ will increase proportionately.

(b) State a limiting factor that must be taken into account when increasing the volume of the aqueous sodium chloride added.

Sketch the graph which would result if, after some of the experiments, the NaC*l* is in excess. Start your graph with no NaC*l* added.

Lead(II) nitrate must always be in excess when increasing the volume of sodium chloride.



(c) In the experiment you are to plan, identify the following:

(i) independent variable

(ii) dependent variable

(iii) another variable to be controlled

(i) Independent variable: volume of NaC*l*

(ii) Dependent variable: mass of $PbCl_2$

(iii) Another variable to be controlled: Temperature

(d) Design a laboratory experiment to test your prediction in **(a)**.

You are provided with 250 cm^3 of 0.20 mol dm^{-3} aqueous sodium chloride.

(i) Outline how you would prepare 250 cm^3 of 0.10 mol dm^{-3} aqueous lead nitrate.

[*Ar*: N, 14.0; O, 16.0; Pb, 207]

Amt of $Pb(NO_3)_2$ in 250 cm^3 graduated flask = (250/1000) × 0.1 = 0.0250mol

Mass of $Pb(NO_3)_2$ required = 0.0250 × 331.0 = 8.275 g

- Weigh accurately 8.275 g of $Pb(NO_3)_2$ directly into a 100 cm^3 beaker using an electronic balance, dissolve solid in minimum volume of deionised water and transfer to a 250 cm^3 graduated flask.
- Rinse the sides of 100 cm^3 beaker with deionised water and transfer all washings to the graduated flask. Top up to the mark with deionised water, stopper and invert and shake the flask well to obtain a homogeneous solution.

(ii) Give a step by step description of how you would carry out **one** experiment.

In your plan, you should state:

- the volumes of each solution to be used,
- how the volumes will be measured,
- how you would dry the precipitate.

1. Using a pipette, transfer 25.0 cm^3 of 0.10 mol dm^{-3} $Pb(NO_3)_2$ into a DRY and CLEAN 250 cm^3 beaker. (2.5 x 10^{-3} mol $Pb(NO_3)_2$; in excess)
2. Using a burette, transfer 10.00 cm^3 of 0.20 mol dm^{-3} NaC*l* into the same beaker. (2.0 × 10^{-3} mol NaC*l*; limiting agent)
3. Stir the mixture in the beaker thoroughly using a glass rod.
4. Filter the mixture into a new 250 cm^3 conical flask and collect the residue ($PbCl_2$) precipitate on the **pre-weighed** filter paper.
5. Rinse the beaker and glass rod with small/limited volume of cold deionised water and transfer the washings and continue to filter.
6. Wash the precipitate with limited cold deionised water to get rid of aqueous ions adsorbed on the surface of $PbCl_2$ precipitate.
7. Drain off excess water by pressing the solid between filter papers.
8. Dry the $PbCl_2$ precipitate in the oven OR under infra-red lamp.
9. Cool and weigh the dried $PbCl_2$ precipitate.
10. Repeat the heat-cool-weigh process until mass of $PbCl_2$ precipitate is constant to $\pm$ 0.01g.

11. Keeping the volume of $Pb(NO_3)_2$ fixed, vary volumes of NaC*l* (10, 15, 20, 25, 30 cm^3), and repeat step 1-10 of the above procedures.

Sample table for recording of data:

Mass of filter paper + content after 1st heating / g Mass of filter paper + content after 2nd heating / g Mass of filter paper + content after 3rd heating / g Mass of filter paper + content after 4th heating / g	**K1** **K2** **K3** **K4**
Mass of filter paper / g	**L**
Mass of $PbCl_2$ precipitate / g	**K4 - L**

(e) Prepare a table to:

Show data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in (**a**).

	Data to be recorded				**Values to be calculated**
Expt No	Vol of $Pb(NO_3)_2$ / cm^3	Vol of NaC*l* / cm^3	Mass of $PbCl_2$ / g (total mass of filter paper and residue – mass of filter paper)	Amt of NaC*l* / mol	Amt of $PbCl_2$ / mol
1					
2					
3					
4					
5					

Planning Experiment

[Planning] : Thermochemistry 1

1 Given:

The enthalpy change of neutralisation of strong acid and strong base is –57.3 kJ mol^{-1}.

The enthalpy change of neutralisation of weak acid and strong base is approximately –54 kJ mol^{-1}.

You are required to plan an experiment using the solutions provided below to determine the enthalpy change of ionisation of ethanoic acid.

$$CH_3CO_2H(aq) \rightarrow CH_3CO_2^-(aq) + H^+(aq)$$

The enthalpy change of ionisation of ethanoic acid cannot be measured directly. Hence, the construction of an energy cycle and applying of Hess' Law are required.

You are provided with:

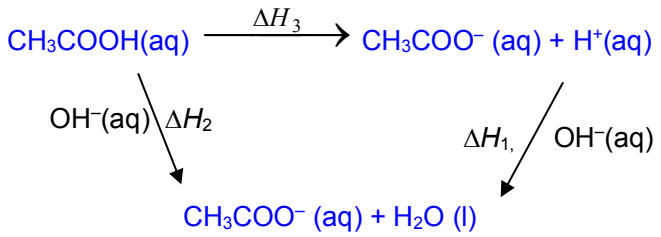
- dilute ethanoic acid, 2.00 mol dm^{-3}
- dilute sodium hydroxide, 2.00 mol dm^{-3}
- 0.2 °C division thermometer
- Styroform cups and lid

In your plan, you should include

- details of apparatus and quantities of reagents to be used;
- procedures involved in the experiment;
- table to show appropriate data to be capture and use the letters A, B, C etc to represent the measurement taken;
- how you would construct energy cycle, use the experiment results (with the letters) for calculation of enthalpy change and apply Hess' Law to determine the enthalpy change of ionization of ethanoic acid.

Enthalpy change of ionisation of ethanoic acid **cannot be measured directly**.

Hence**, Hess' Law** must be applied:



Since $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H_1 = -57.3$ kJ mol^{-1}

Need to conduct experiment to find ΔH_2 :

$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

By Hess' Law, $\Delta H_3 = \Delta H_2 - \Delta H_1$

Preliminary consideration in determining the quantity of the reagent used in energetics:

1. ΔT
   - ΔT must be with 5 – 10 °C.
   - When ΔT > 10 °C, there will be **significant heat exchange** with the environment.
   - When ΔT is too small, there will be high percentage error due to measurement.
2. Volume of the mixture
   - For reaction involves mixing of two solutions, total volume should not exceed 80% of the max capacity of styrofoam cup so that spillage will not occur upon swirling.
   - The volume of mixture must cover the bulb of thermometer to ensure reliable temp measurement (**approximate volume between 30 - 80 cm^3**).

100 cm^3 styrofoam cup is used, **assume 40 cm^3 of NaOH(aq) and 20 cm^3 of acid are mixed, total volume is 60 cm^3**.

Magnitude for enthalpy change of neutralisation between CH_3COOH (weaker acid) and NaOH(aq) ≈ 54 kJ mol^{-1} (< 57. 3 kJ mol^{-1})

If acid is limiting reagent:

Amt of CH_3COOH in 20 cm^3 = $\frac{20}{1000} \times 2.00$ = 0.0400 mol

Heat released from reaction = heat absorbed by solution

$0.0400 \times 54000 = m_{aq} c \Delta T$

$= (60)(4.18)(\Delta T)$

ΔT = 8.61 °C (within 5 - 10 °C)

Procedure (To determine ΔH_2):

1. Using a 50 cm^3 measuring cylinder, add 20.0 cm^3 of 2.00 mol dm^{-3} CH_3COOH(aq) into a 100 cm^3 dry clean styrofoam cup placed in another Styrofoam cup supported by a beaker. Once the temperature stablises, measure its temperature with a 0.2 °C division thermometer and record in **Table 1**.
2. Measure 40.0 cm^3 of 2.00 mol dm^{-3} NaOH(aq) with a 50 cm^3 measuring cylinder and measure its temperature once it stablises and record in **Table 1**.
3. Add NaOH(aq) to the cup and cover the cup with a lid to minimize heat loss to surroundings.
4. Gently stir the mixture with a thermometer continuously and measure record the highest temperature reached and record in **Table 1**.

Table 1

Temperature of CH_3COOH / °C	E
Temperature of NaOH(aq) / °C	F
Average Initial Temperature / °C	$T_{average} = \frac{(V_{CH3COOH} \times E) + (V_{NaOH} \times F)}{V_{CH3COOH} + V_{NaOH}}$ = G
Highest Temperature reached / °C	H
Temperature rise, ΔT_2/ °C	H – G

Sample Calculations

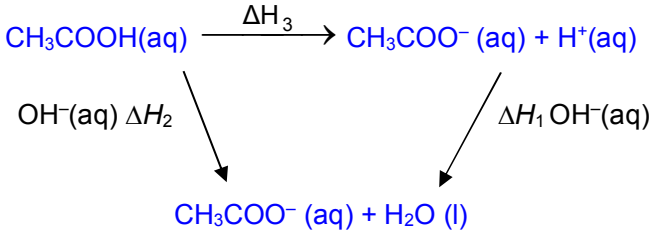
$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$ ΔH_2

Limiting reagent is the acid:

Amt of CH_3COOH in 20 cm^3 = 0.0400 mol

Heat released from reaction = (60)(4.18)(ΔT_2) J

$$\Delta H_2 = -\left(\frac{(4.18)(60)(\Delta T_2)}{0.0400} \div 1000\right) \text{ kJ mol}^{-1}$$



By Hess' Law,

enthalpy change of ionisation of ethanoic acid, $\Delta H_3 = \Delta H_2 - \Delta H_1$

[Planning] : Thermochemistry 2

2 Zinc reacts with aqueous copper(II) sulfate as shown by the following equation

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq) \quad \Delta H \approx -200 \text{ kJ mol}^{-1}$$

Using an excess of Zn powder, the reaction takes a **few minutes** to go to completion.

Note: zinc, copper and all of their compounds are toxic.

A 1.50 mol dm^{-3} solution of copper(II) sulfate is provided.

Apparatus provided are:

- two 100 cm^3 styrofoam cups and lids
- 0.2 °C division thermometer
- 100 cm^3 measuring cylinder
- electronic balance
- weighing bottle
- 250 cm^3 beaker
- stop watch
- burette

Using the information above, describe how you would determine the enthalpy change of the reaction between zinc and copper(II) sulfate.

In your plan, you must include

- the volume of copper(II) sulfate solution to be used;
- a suitable mass of zinc to be used and its justification;
- description of the experiment you would perform with details of the apparatus and the precautions you would take to determine a more accurate enthalpy change of reaction. (**A diagram is not essential but may help your answer**.)
- how you would use the experimental results to calculate the enthalpy change of the reaction between zinc and copper(II) sulfate.
- the potential safety hazards and the relevant safety precautions you would take.

You may find the following questions useful for preliminary calculations.

(i) Suggest and explain a suitable volume of $CuSO_4$ solution to be used for the above reaction.

Preliminary Considerations

- 100 cm^3 Polystyrene cup is used.
- $CuSO_4(aq)$ is the limiting reagent.
- The volume of $CuSO_4$ solution must cover the bulb of thermometer to ensure reliable temp measurement. (**approximate volume between 30 - 80 cm^3**.)

  (If reaction involves mixing of two solutions, total volume should not exceed 80% of the max capacity of styrofoam cup so that spillage will not occur upon swirling.)

(ii) Calculate the amount of $CuSO_4$ present in the suggested volume and the expected rise in temperature on reaction with zinc. Hence discuss whether there is a need to make adjustments to the chemical reagents provided.

In 80 cm^3 of 1.50 mol dm^{-3} $CuSO_4(aq)$, amt of $CuSO_4$ present = $\frac{80}{1000} \times 1.50$ = 0.12 mol **(limiting reagent)**

Heat released from reaction = heat absorbed by solution

0.12 x 200 000 = $mc\Delta T$

= 80 × 4.18 × ΔT

ΔT = **71.8 °C**

When ΔT > 10 °C, there will be **significant heat exchange** with the environment. Thus **[$CuSO_4(aq)$] is too high** and should be **diluted about 10 times** so that ΔT < 10 °C.

$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$

$[CuSO_4(aq)]_{diluted}$ = 0.15 mol dm^{-3}

Amt of $CuSO_4$ present in 80 cm^3 of 0.15 mol dm^{-3} $CuSO_4(aq)$ = 0.012 mol

Amt of Zn required = 0.012 mol

Mass of Zn required = 0.012 x 65.4 = 0.785 g

percentage error due to measurement = ±0.001/0.785 × 100 =±0.127% < 5% (acceptable)

(iii) With reference to the answer in part **(ii)**, provide details of how the adjustment should be made.

To dilute $CuSO_4(aq)$ 10 times:

Use burette to measure 25.00 cm^3 of 1.50 mol dm^{-3} $CuSO_4$ into a 250 cm^3 volumetric flask and top up to the mark with deionised water. Stopper, invert and shake well to get a homogeneous solution.

Note: Dilution should be carried out appropriately to allow ΔT to be within 5 – 10 °C.

Too small a ΔT will incur high percentage error; while too high a ΔT will result in significant heat exchange with the surrounding.

(i) By considering the precision of the apparatus used to measure the mass and temperature, calculate the total percentage uncertainty incurred in these measurements. Suggest how the percentage error can be reduced.

Total percentage uncertainty = $\pm \left[\frac{0.001}{0.785} + \frac{0.5}{80} + \frac{2(0.1)}{7} \right] \times 100\% = \pm 3.61\%$

Largest source of error is from temperature measurement; use digital thermometer (temperature sensor) that can read up to 2 dp.

Procedure:

1 Weigh accurately about **1.0 g of Zn** in a clean and dry weighing bottle. Record the mass in **Table 1**. (Zn is in excess, so can use more than the required 0.785 g)

2 Use a burette to measure 25.00 cm^3 of 1.50 mol dm^{-3} $CuSO_4$ into a 250 cm^3 volumetric flask and fill up to mark with deionised water. Stopper, invert and shake well to get a homogeneous solution. Record burette readings in **Table 2**.

3 Use a 100 cm^3 measuring cylinder to transfer **80.0 cm^3 of diluted $CuSO_4$** solution into a Styroform cup placed in another Styrofoam cup supported by a beaker.

4 Gently stir the solution in the cup with a 0.2 °C division thermometer and measure and **record the temperature of diluted $CuSO_4$ solution every 0.5 min for 2.5 min** in **Table 2**.

5 At **exactly 3.0 min**, add Zn solid to the Styrofoam cup. Cover the cup with a lid to minimize heat exchange with environment. Continue to stir the mixture, **measure** and **record the temperature at 3.5 min**, then **every 0.5 min after mixing** until the temperature reaches a maximum. **Continue to measure temperature every 0.5 min for a further 2 - 3 min**. Record data in **Table 3**.

6 Plot a temperature vs time graph using the data in **Table 3**.

7 By **extrapolation, estimate the maximum and minimum temperatures** of the solution at the time of mixing, i.e. 3rd minute. Record the temperatures as T_{max} and T_{min} respectively and calculate the temperature change, $\Delta T = T_{max} - T_{min}$.

Table 1

Mass of weighing bottle / g	
Mass of Zn and weighing bottle / g	a
Mass of residual Zn and weighing bottle / g	b
Mass of Zn added / g	a–b

Table 2

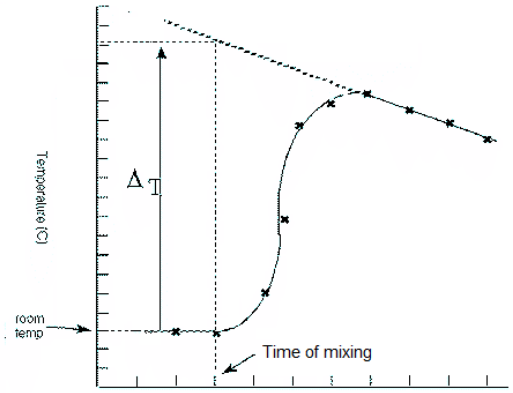
Final burette reading / cm^3	c
Initial burette reading / cm^3	d
Volume of $CuSO_4$ added / cm^3	c–d

Table 3

Temp/°C	Time/ min	Temp/°C	Time/ min
	0.00	N.A.	3.00
	0.50		3.50
	1.00		4.00
	1.50		4.50
	2.00		5.00
	2.50		

[No need to draw temperature vs time graph]

FYI only



Sample Calculations:

Excess Zn is used and $CuSO_4(aq)$ is limiting.
Assume that the 4.18 J of heat is required to raise the temperature of 1 cm^3 of the solution by 1 K,
Heat released from reaction
= heat absorbed by solution
= (80)(4.18) (ΔT) J

$$\Delta H_r = \frac{(80)(4.18)(\Delta T)}{0.012} \times 10^{-3} \text{ kJ mol}^{-1}$$

Note:

As the **reaction between Zn and $CuSO_4$ is slow**, there will be significant heat loss to the environment as the reaction proceeds. Hence the highest temperature is determined by extrapolation, which is more accurate.

Lagging is NOT necessary as the cooling curve takes into account heat exchange with environment.

[Planning] : Thermochemistry 3

3 You are to plan an experiment to determine the enthalpy change per mole of magnesium for the reaction shown below:

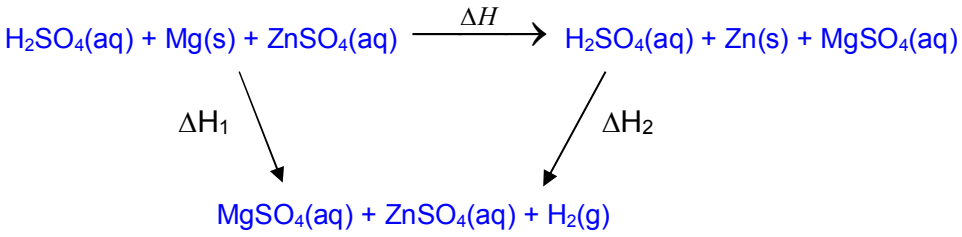
$$Mg(s) + ZnSO_4(aq) \rightarrow Zn(s) + MgSO_4(aq)$$

You are supplied with

- 100 cm^3 of 0.50 mol dm^{-3} sulfuric acid
- magnesium ribbon
- pieces of zinc metal (granulated zinc)
- the usual laboratory equipment

(a) Explain how you would use the chemical reagents provided to devise an alternative pathway which enables you to calculate a value for the enthalpy change per mole of magnesium for the reaction by applying Hess' law.

$$Mg(s) + ZnSO_4(aq) \rightarrow Zn(s) + MgSO_4(aq)$$



$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$ **ΔH_1**

$Zn(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$ **ΔH_2**

By Hess' Law: $\Delta H = \Delta H_1 - \Delta H_2$

Add solid Mg and Zn separately to $H_2SO_4(aq)$ to determine ΔH_1 and ΔH_2.

(b) Given the following information, suggest the quantities of reagents you would use to carry out reactions. justify your answer through appropriate calculations or explanation:

- When 0.2 g of Mg reacts with 50 cm^3 of H_2SO_4, it causes a temperature rise of 3.6 °C.
- Enthalpy change of reaction between Zn and H_2SO_4 is approximately +80 kJ mol^{-1}.

Amt of H_2SO_4(aq) in 50 cm^3= $\frac{50}{1000} \times 0.500$ = 0.0250 mol

Amt of Mg in 0.20 g = 0.2 ÷ 24.3 = 0.00823 mol

∴ Mg is limiting.

Given ΔT < 5 °C and is too small (not within 5-10 °C),

It is appropriate to double ΔT to become 7.2 °C (within acceptable range) by doubling the amt of Mg (limiting) to **0.4 g**.

$$Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g) \quad \mathbf{\Delta H_2 \approx} +80 \text{ kJ mol}^{-1}$$

Use 50.0 cm^3 of 0.500 mol dm^{-3} sulfuric acid. Let ΔT be 8 °C.

Heat absorbed by solution = heat released in the reaction

$$n_{zinc} \times 80000 = (\text{vol of } H_2SO_4)(4.18)(8)$$

n_{zinc} × 80000 = 50 × 4.18 × 8

n_{zinc} = 0.0209 mol

min amt of Zn required = 0.0209 mol

mass of Zn required = 0.0209 × 65.4 = 1.37 g

Note: The basis of calculation is to ensure the dependent variable (ΔT in this case) to be within 5 – 10 °C.

(c) Give step-by-step description of how the experiments are going to be carried out. Stating clearly

- apparatus used for **measurements**
- suitable data for collection of data
- how the data collected can be used to determine the unknown enthalpy change

Procedure: the following procedure is carried out assuming that the reaction between metal and dilute acid is a relatively fast reaction. Hence the use of cooling curve method is NOT crucial. [See qn 10 as a contrast]

1. **Sandpaper** the Mg ribbons.
2. Weigh accurately about 0.4 g of Mg in a clean and dry weighing bottle using an electronic balance. Record the mass in **Table 1**.
3. Using a 50 cm^3 measuring cylinder, add 50.0 cm^3 of 0.50 mol dm^{-3} sulfuric acid into a dry, clean 100 cm^3 styrofoam cup placed in a second styrofoam cup seated in a beaker.
4. Stir the sulfuric acid with a **0.2 °C division thermometer and record** the temperature as T_i in **Table 1** when it stablises.

5. Add Mg into the cup. Stir the mixture continuously and measure the highest temperature reached. Record the temperature in **Table 1** as T_f.

(NOTE: Given that this is an exothermic reaction, it is appropriate to state the highest / maximum temperature reached. If reaction is endothermic, then state the lowest / minimum temperature reached instead.)

6. **Reweigh the weighing bottle** and its content, and record the mass in **Table 1**.

Table 1

Mass of weighing bottle / g	**a**
Mass of weighing bottle plus Mg solid / g	**b**
Mass of weighing bottle plus Mg residue / g	**c**
Mass of Mg used / g	**b – c**
Initial temp of Soln / °C	T_i
Highest Temp of Soln / °C	T_f
ΔT / °C	$T_f - T_i$

7. **Weigh** accurately about 1.4 g of Zn in a clean and dry weighing bottle. Record the mass in **Table 2**.
8. Repeat steps 2 to 6 using Zn to determine the **lowest temp reached** (endothermic) and the average ΔT_{Zn}. Record all values in **Table 2**.

Table 2

Mass of weighing bottle / g	**d**
Mass of weighing bottle plus Zn solid / g	**e**
Mass of weighing bottle plus Zn residue / g	**f**
Mass of Zn used / g	**f – e**
Initial temp of Soln / °C	T_i
Lowest Temp of Soln / °C	T_f
ΔT / °C	$T_f - T_i$

NOTE: A measuring cylinder is used to measure volume of H_2SO_4 since it is in excess.

Sample Calculations

$H_2SO_4(aq) + Mg(s) + ZnSO_4(aq) \xrightarrow{\Delta H} H_2SO_4(aq) + Zn(s) + MgSO_4(aq)$

ΔH_1 ↘ ↙ ΔH_2

$MgSO_4(aq) + ZnSO_4(aq) + H_2(g)$

Amt of $H_2SO_4(aq)$ in 50 cm^3= $\frac{50}{1000} \times 0.500$ = 0.0250 mol; amt of Mg used = $\frac{m_{Mg}}{24.3}$ mol

∴ Mg is limiting.

Since there is residual Mg from weighing, the mass of Mg used is < 0.400 g; thus, we CANNOT assume that mass of Mg is 0.400 g as stated in the procedure.

Assume that specific heat capacity of solution and container, c = 4.18 J g^{-1} K^{-1},

Heat absorbed by solution = (4.18)(50) (ΔT_{Mg}) J

$$\Delta H_1 = -\frac{(4.18)(50)(\Delta T_{Mg})}{\frac{m_{Mg}}{24.3}} \times 10^{-3} \text{ kJ mol}^{-1}$$

Amt of Zn used = $\frac{m_{Zn}}{64.5}$ mol

Heat lost by reaction = (4.18)(50) (ΔT_{Zn}) J

$$\Delta H_2 = \frac{(4.18)(50)(\Delta T_{Zn})}{\frac{m_{Zn}}{65.4}} \times 10^{-3} \text{ kJ mol}^{-1}$$

By Hess' Law, $\Delta H = \Delta H_1 - \Delta H_2$

(d) Suggest three modifications that you might make to the experiment to obtain a more accurate result. Justify your answers.

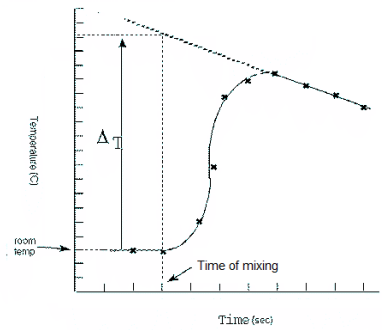
Modification 1:

In contrast to reactions involving aqueous solution, reactions involving solid reactants are slower and would complete in longer times and will incur more heat exchange (gain or loss) with environment. Error due to heat exchange is more significant for slower reactions.

A possible way to increase reaction is to use zinc **powder** / **cut Mg ribbon into smaller pieces**.

Modification 2:

Use **cooling curve method** where **temperature changes after mixing are measured at 0.5 min intervals** for about 3 min, then **max/ min temperature is extrapolated to time of mixing**.



Modification 3:

Calibration of the calorimeter by **making use of reaction with a known enthalpy change**.

The calibrated heat capacity, C, of the calorimeter takes the percentage of actual heat transfer between the reaction and solution into but the **rate of this reaction must be similar to the reaction of unknown enthalpy**.

(e) The experiments that you have planned in **(a)** and **(b)** are to be repeated using the same volumes of 0.50 mol dm^{-3} hydrochloric acid in place of the sulfuric acid.

Explain what differences, if any, it would make to the results.

$2HCl + Mg \rightarrow MgCl_2 + H_2$ ---------- eq (1)

$2HCl + Zn \rightarrow ZnCl_2 + H_2$ ---------- eq (2)

Must check if the solid metal or the acid is limiting (stoichiometry ratio is 2 mole of HC*l* to 1 mole of Zn or Mg.

If **solid is limiting**: amount of heat change in **reaction is not affected** as both H_2SO_4 and HC*l* are both strong acids and the volume of solutions used are the same; i.e. **no change to ΔT and ΔH_r obtained**.

If **HC*l* is limiting**: amount of heat liberated will be half if the same volume of HC*l* is used, **ΔT would be halved**, but **ΔH_1 and ΔH_2 and ΔH_r obtained would be unchanged.**

Heat absorbed by solution = (50)(4.18) (ΔT_{Mg}) J

$\Delta H_1 = -\frac{(50)(4.18)(\Delta TMg)}{amt\ of\ HCl}$ x 2 x 10^{-3} kJ mol^{-1}

Heat lost by reaction = (50)(4.18) (ΔT_{Zn}) J

$\Delta H_2 = -\frac{(50)(4.18)(\Delta TZn)}{amt\ of\ HCl}$ x 2 x 10^{-3} kJ mol^{-1}

By Hess' Law, $\Delta H = \Delta H_1 - \Delta H_2$

[Planning] : Thermochemistry 4

4 You are provided with solutions **FA 3, FA 4** and **FA 5.** The solutions are:

- 1.0 mol dm^{-3} sodium hydroxide
- 1.0 mol dm^{-3} sulfuric acid
- 0.5 mol dm^{-3} sulfuric acid

You are to plan experiments that will enable you to identify the solution that matches each of **FA 3**, **FA 4** and **FA 5**.

You have the following apparatus available:

- –10 °C to 110 °C thermometer
- 100 cm^3 beaker

a measuring cylinder (Note: No indicator is provided)

(a) You are to identify, by the **minimum number** of practical steps, the solution which contains sodium hydroxide.
Outline your method – with an explanation of the expected results.

Your experiment(s) must use only the solutions and apparatus provided above.

General Method:

Mix equal volumes any two unknown solutions in a Styrofoam cup and measure the temperature of mixture.

- **No change in temperature** when **1 mol dm^{-3} H_2SO_4 is mixed with 0.5 mol dm^{-3} H_2SO_4** since no chemical reaction occurs.
- There will be a **rise in temperature when NaOH(aq) is added to any one of the acids due to exothermic neutralisation**. Thus, **NaOH(aq)** can be identified.

	30 cm^3 of 0.5 mol dm^{-3} H_2SO_4	30 cm^3 of 1 mol dm^{-3} H_2SO_4
30 cm^3 of 1 mol dm^{-3} NaOH(aq)	Rise in temp	Rise in temp
30 cm^3 of 0.5 mol dm^{-3} H_2SO_4	-	No change in temp

Table 1

- The next step is confirmed which acid is in which container. This can be done by adding the same volume of NaOH(aq) (excess) separately to the same volume of 0.5 mol dm^{-3} and 1 mol dm^{-3} H_2SO_4, a higher temperature will be observed for the reaction with 1 mol dm^{-3} H_2SO_4, because more moles of water is formed, releasing more heat.

Procedure

[There is no need for precise measurement for temperature changes.]

1 Use a 50 cm^3 measuring cylinder to add 30.0 cm^3 of **FA 3** into a styrofoam cup. Measure the initial temperature, T_1 °C once the temperature stabilises. Record the results in Table 2.

2 Use another clean 50 cm^3 measuring cylinder to add 30.0 cm^3 of **FA 4** into the styrofoam cup. Stir continuously and note if there is a temp rise.

3 Repeat Steps 1 to 2, between **FA 3** and **FA 5** as well as between **FA 4 and FA 5**.

	30 cm^3 of **FA 4**	30 cm^3 of **FA 5**
30 cm^3 of **FA 3**	ΔT_1	ΔT_2
30 cm^3 of **FA 4**	-	ΔT_3

Table 2

4 Compare **Table 2** with **Table 1** to determine whether **FA 3**, **FA 4** and **FA 5** is NaOH(aq).

If there is no change in temperature when 2 solutions are mixed, they both are acids, while the remaining is NaOH(aq).

(b) Plan further experiments to find which of the remaining solutions is 1 mol dm^{-3} sulfuric acid and 0.5 mol dm^{-3} sulfuric acid respectively.

Outline your method – with an explanation of the expected results.

Once NaOH(aq) is identified (assumed to be **FA 3**), use it to identify the H_2SO_4 solutions of different concentrations by adding at least twice the volume of NaOH(aq) as the volume of each acid (**total volume of the reaction mixture is kept constant**).

[Why that is necessary? To ensure the rise in temperatures of the solution is proportional to the amount of heat released from neutralisation.]

1. Use a measuring cylinder to add 50.0 cm^3 of **NaOH(aq)** into a styrofoam cup. Measure and record the initial temperature, T_i °C , once it stabilises. Record data in **Table 3**.
2. Use another clean measuring cylinder to add 20.0 cm^3 of **one acid**. Measure and record its initial temp**.** Transfer it to the cup. Stir, measure and record the maximum temperature reached.
3. Repeat Steps 1 to 3, adding 20.0 cm^3 of **the other acid**..

T_i of **NaOH(aq) /°C**	T_i of 1st acid **/°C**	Avg T_i **/°C**	T_f **/°C**	ΔT_5 **/°C**
T_i of **NaOH(aq) /°C**	T_i of 2nd acid **/°C**	Avg T_i **/°C**	T_f **/°C**	ΔT_6 **/°C**

Table 3

Analyses of results

- If $\Delta T_5 < \Delta T_6$ OR $2\Delta T_5 = \Delta T_6$,

$\Rightarrow$ **FA 5** is 0.5 mol dm^{-3} H_2SO_4(aq) and **FA 6** is 1 mol dm^{-3} H_2SO_4 (aq).

- If $\Delta T_5 > \Delta T_6$ OR $\Delta T_5 = 2\Delta T_6$,

$\Rightarrow$ **FA 5** is 1 mol dm^{-3} H_2SO_4 (aq) and **FA 6** is 0.5 mol dm^{-3} H_2SO_4 (aq).

Planning

[Planning] : Kinetics Practical 1

Iodide ions, I^-, reacts with peroxodisulfate ions, $S_2O_8^{2-}$ as shown:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq) \quad \text{.....(1)}$$

Colourless blue black with starch

The rate of this reaction maybe followed by measuring the time taken to reach an identifiable point early in the reaction.

An identifiable point of reaction (1) is the appearance of blue black iodine-starch complex.

A small and fixed amount of thiosulfate is used to fix the amount of iodine produced by reaction (1) in every repeated experiment. This is because blue-black colouration of an iodine-starch complex appears only when thiosulfate ion, $S_2O_3^{2-}$, present in the mixture have completely reacted with the iodine as shown in equation (2).

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

colourless

You are to plan an experiment to investigate how the rate of reaction between $K_2S_2O_8$ and KI depends on the concentration of $S_2O_8^{2-}$.

(a) A preliminary experiment, using approximate volumes of solution, indicates that time taken for the blue-black colouration to appear doubles when $K_2S_2O_8$ (aq) is diluted with an equal volume of water.

Using the results of the preliminary experiment, deduce the order of reaction with respect to $S_2O_8^{2-}$.

*Since time doubles (rate halved) when $K_2S_2O_8$ (aq) is diluted with an equal amt of water (conc halved), the order of reaction w.r.t $S_2O_8^{2-}$ is **1st order.***

(b) Identify **(i)** the independent variable and **(ii)** dependent variable in the experiment described in part **(a).**

(i) independent variable: volume of I_2 (aq) added (total volume of reaction mixture kept constant by adding variable volume of deionised water)

(ii) dependent variable: time taken for blue-black colouration to appear.

(c) **(i)** Explain why it is important for the iodine formed via oxidation in reaction (1) is reduced back to iodide ions by thiosulfate.

Appearance of blue-black starch-iodine complex will be instantaneous (too fast for time measurement) if thiosulfate is not present.

(ii) Hence explain why the volume of sodium thiosulfate should be measured precisely, using a burette, in each of the experiments.

A fixed amt of $Na_2S_2O_3$ that is accurately measured ensures that the same amount of iodine is produced in every experiment for the appearance of blue-black coloration. Thus rate of each experiment is proportional to $\frac{1}{time\ taken\ for\ blue-black\ couration\ to\ appear}$.

(d) You are provided with

- 0.60 mol dm^{-3} potassium iodide, KI
- 0.20 mol dm^{-3} potassium peroxodisulfate, $K_2S_2O_8$
- 0.01 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
- deionised water
- starch indicator
- the equipment normally found in laboratory

A first experiment is carried out using the following quantities

Chemical reagent	KI	$K_2S_2O_8$	$Na_2S_2O_3$	starch solution
Volume used / cm^3	20	60	5	5

By considering the points raised in part **(a)** - **(c)**, give a step-by-step description of how you would carry out **5** further experiments to verify that the order of reaction with respect to $S_2O_3^{2-}$ is 1.

In your plan, you are to include:

- the apparatus you would use
- the procedure you would follow
- the measurements you would make
- a table that records the dependent and independent variables.

Principles behind Clock Method

- *Constant, but small amt of $Na_2S_2O_3$ must be added to each mixture to enable the initial rate to be determined. Small amt refers to 5% of total amt of I_2 that can form.*
- *Starch indicator must be added to form a distinct dark colour.*
- *Vary only the volume of of $S_2O_8^{2-}$, keeping all others constant. Top up with deionised water to keep total volume constant if necessary (see Table 1 below).*

No.	*Volume/cm^3*					*Time/s*
	KI	*starch*	*$Na_2S_2O_3$*	*$K_2S_2O_8$*	*water*	
1	*20*	*5*	*5*	*60*	*0*	
2	*20*	*5*	*5*	*50*	*10*	
3	*20*	*5*	*5*	*40*	*20*	
4	*20*	*5*	*5*	*30*	*30*	
5	*20*	*5*	*5*	*20*	*40*	
6	*20*	*5*	*5*	*10*	*50*	

Table 1

Procedure

Expt 1

1) *Using a **100 cm³ measuring cylinder**, add **60.0 cm³** 0.20 mol dm⁻³ $K_2S_2O_8$ into the **conical flask A.***
2) *Using a **10 cm³ measuring cylinder**, add **5.0 cm³** of starch into flask A.*
3) *Using a **burette**, add **5.00 cm³** of 0.01 mol dm⁻³ $Na_2S_2O_3$ into flask A.*
4) *Using a **50 cm³ measuring cylinder**, add **20.0 cm³** of 0.60 mol dm⁻³ KI to flask A and **start the stopwatch when half the volume is added**. Swirl the flask once.*
5) ***Stop the stopwatch** when mixture **turns dark blue**. Record the time taken.*
6) *Wash flask A.*

Expt 2 - 6

7) *Using a 100 cm³ measuring cylinder, add **50.0 cm³** 0.20 mol dm⁻³ $K_2S_2O_8$ and **add deionised water till the 60 cm³ mark**. Pour the solution into flask A.*
8) *Using a 10 cm³ measuring cylinder, add 5.0 cm³ of starch into the flask A.*
9) *Using a burette, add 5.00 cm³ of 0.01 mol dm⁻³ $Na_2S_2O_3$ into the flask A.*
10) *Using a 50 cm³ measuring cylinder, add 20.0 cm³ of 0.60 mol dm⁻³ KI flask A. start the stopwatch when half is added. Swirl the flask once.*
11) *Stop the stopwatch when mixture turns dark blue. Record the time taken.*
12) ***Repeat steps 7 -11 using volumes of solution as shown in table 1**.*

(e) Suggest how the results of the experiment can be manipulated in three different ways to verify the answer to part **(d)**.

Method 1: *Plot a graph of lg $\frac{1}{\text{time}}$ vs lg (volume of $K_2S_2O_8$: (at least 4 sets of data as linear graph is expected)*

- *Calculate $\frac{1}{\text{time}}$ (rate of reaction $\propto \frac{1}{\text{time}}$)*
- *Calculate lg $\frac{1}{\text{time}}$ and lg (volume of $K_2S_2O_8$).*
- *Plot a graph for lg $\frac{1}{\text{time}}$ and lg (volume of $K_2S_2O_8$)*
- *Determine the gradient of the graph. gradient of graph = order of reaction wrt $K_2S_2O_8$*

Method 2: *Plot a graph of* $\frac{1}{\text{time}}$ *vs volume of* $K_2S_2O_8$ *(at least 6 sets of data)*

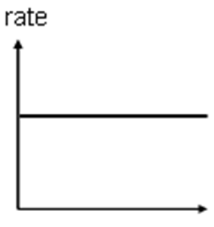
- *Calculate* $\frac{1}{\text{time}}$ *(rate of reaction* $\propto \frac{1}{\text{time}}$*)*

A horizontal line: zeroth order reaction wrt $K_2S_2O_8$

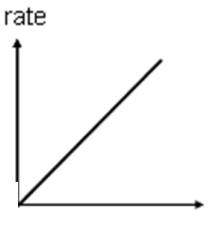
Y = mX, A linear line through origin: 1st order reaction wrt $K_2S_2O_8$

Y = X^2 *Curve: likely* 2^{nd} *order reaction wrt* $K_2S_2O_8$

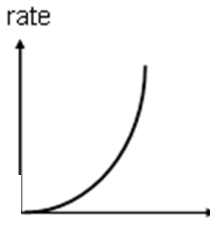
Zero order



First order



Second order



[To confirm if it is a 2^{nd} ***order reaction, plot*** $\frac{1}{\text{time}}$ ***vs (volume of*** $K_2S_2O_8$***)*** ^{2} ***and it should be a straight line graph through origin.]***

Method 3: *vt method (3 sets of data)*

V: volume of $S_2O_8^{2-}$

Mixture	*Volume / cm*^{3}					*Time / s*	*vt / cm*^{3} *s*	v^2t */ cm*^{6} *s*
	KI	$Na_2S_2O_3$	*starch*	$S_2O_8^{2-}$	*water*			
1								
2								
3								

If t is constant $\Rightarrow$ 0^{th} *order reaction*

If vt is constant, vol α *1/t , rate increases linearly with [ ],* $\therefore$ 1^{st} *order reaction*

If v^2t *is constant, vol*^{2} α *1/t t , rate increases linearly with [ ]*^{2} $\therefore$ 2^{nd} *order reaction*

[Planning] : Kinetics Practical 2

The reaction between ethanedioate ions and acidified manganate(VII) ions as shown below takes place very slowly in the cold but can be accelerated with heat or with addition of Mn^{2+} catalyst.

$$2MnO_4^- + 5C_2O_4^{2-} + 10H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The reaction rate for the reaction can be measured by noting the time elapsed for the purple colour of the manganate(VII) ions to disappear.

(a) A teacher demonstrates this experiment as follows:

She prepares two separate solutions **A** and **B**.

- Solution **A** contains 200 cm^3 of 0.08 mol dm^{-3} ethanedioic acid and 200 cm^3 of 0.50 mol dm^{-3} sulfuric acid
- Solution **B** contains a mixture of 400 cm^3 of 0.0080 mol dm^{-3} potassium manganate(VII) solution and 400 cm^3 of 0.0080 mol dm^{-3} manganese(II) sulfate solution.

(b) She mixes 20 cm^3 of solution **A** with 60 cm^3 of solution **B**. The time taken for the purple manganate(VII) solution to decolourise is about 40 s.

By considering the information given above, you are to plan experiments to study the effects of different concentration of catalyst, $MnSO_4$, on rate of reaction between the ethanedioate ions and acidified manganate(VII) ions.

The order of the reaction with respect to $MnSO_4$ may be determined by performing a number of experiments and then analysis by plotting a suitable graph.

Write a plan to show how the series of experiments can be carried out. In your plan, you should use the same proportions of **A** and aqueous $KMnO_4$ as described above.

You should ensure that at least one of your experiments would be expected to take significantly less than 40 sec.

You may assume that you are provided with the following:

- Solution **A**, having the concentrations of reagent given above
- 0.008 mol dm^{-3} potassium manganate(VII) solution
- 0.08 mol dm^{-3} manganese(II) sulfate solution
- Deionised water
- White tile
- The apparatus normally found in a school or college laboratory

Your plan should contain the following:

- the intended concentration of the stock solution of manganese(II) sulfate solution to be used
- details for the preparation of this stock solution from the manganese(II) sulfate solution provided
- appropriate quantities and concentrations of solutions

- all essential experimental details
- an outline of how the results would be used to determine the order with respect to manganese(II) sulfate.

Preliminary consideration:

- *Using teacher's expt as a reference, total volume of each reaction mixture = 80 cm^3, max volume of aq $MnSO_4$ = 30 cm^3 (proportions of **A** and aq $KMnO_4$ = 2 : 3).*
- *At least time for **one** expt must be < 40 sec, $[MnSO_4] > 0.008$ mol dm^{-3}; the $MnSO_4$ solution provided must be diluted.*
- *$[MnSO_4] = 0.016$ mol dm^{-3} is doubled and is appropriate as it can easily be predicted that time taken to decolorise a solution of 30 cm^3 of 0.016 mol dm^{-3} $MnSO_4$ + 20 cm^3 of solution **A** + 30 cm^3 of $KMnO_4$ to be less than 40 s.*

Preparation of dilute manganese(II) sulfate:

$MnSO_4$ solution has to be diluted by 0.08 / 0.016 = 5 times.

If a total volume of diluted solution is 100 cm^3, volume of 0.08 mol dm^{-3} manganese(II) sulfate solution to be added to 100 cm^3 graduated flask is 20.00 cm^3 measured by burette then top up to the mark with deionised water.

Procedure:

For experiment 1

1) *Using a **50 cm^3 measuring cylinder**, add **20 cm^3 of Solution A** to a **250 cm^3 conical flask.***
2) *Using another **50 cm^3 measuring cylinder**, add **30 cm^3** of 0.008 mol dm^{-3} **$KMnO_4$ to a 100 cm^3 measuring cylinder**.*
3) ***Add 5 cm^3 of 0.016 mol dm^{-3} $MnSO_4$** to **the measuring cylinder**. **Top up to 30 cm^3 mark with deionised water**. Pour the solution into the conical flask and **start the stopwatch when half the solution has been added.** Swirl the conical flask once.*
4) ***Stop the stopwatch** when mixture **is decoloirised**. Record the time taken in Table 1.*

For subsequent experiments

5) ***Repeat steps 1 to 6 using volumes of solutions according to Table 1.***
6) *Calculate $\frac{1}{\text{time}}$ as rate of reaction $\propto \frac{1}{\text{time}}$.*
7) *Calculate lg $\frac{1}{\text{time}}$ and lg (volume of 0.016 mol dm^{-3} of $MnSO_4$).*
8) *Plot a graph for lg $\frac{1}{\text{time}}$ and lg (volume of $MnSO_4$)*
9) *Determine the gradient of the graph where gradient = order of reaction wrt $MnSO_4$.*

Table 1

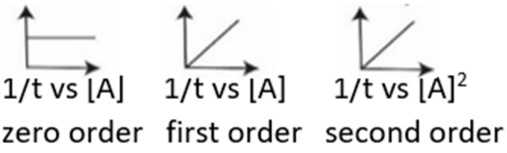
No.	Volume/cm^3				Time / s	Rate $\propto \frac{1}{\text{time}}$
	Solution **A**	0.008 mol dm^{-3} $KMnO_4(aq)$	0.016 mol dm^{-3} $MnSO_4(aq)$	water		
1	20	30	5	25		
2	20	30	10	20		
3	20	30	15	15		
4	20	30	20	10		
5	20	30	25	5		
6	20	30	30	0		

OR

Plot a graph of $\frac{1}{\text{time}}$ *against volume of* $MnSO_4$ *which is similar to rate against* $[MnSO_4]$*. A straight line through the origin implies a first order reaction.*

Use rate equation or shape of the graph to determine order of reaction wrt A.

rate = $k[A]^x$ where x = 0, 1 or 2



zero order first order second order

[Planning] : Kinetics Practical 3

Catalysed decomposition of aqueous hydrogen peroxide gives O_2 is as shown:

$$2H_2O_2\ (aq) \rightarrow 2H_2O(l) + O_2(g)$$

You are provided with:

- 0.10 mol dm^{-3} aq H_2O_2
- 100 cm^3 gas syringe
- Catalyst $Fe(OH)_3$
- The equipment normally found in a school laboratory

(a) Give a step-by-step description of how the volume of oxygen produced is measured over time to monitor the rate of decomposition of H_2O_2.

Your plan should include:

- Given that the measurements are carried out under room conditions and pressure, calculate a suitable volume of H_2O_2 (aq) which gives a total volume of O_2 gas hat occupies 80% of the gas syringe.
- a labelled diagram of the experimental set-up, showing the apparatus you would use
- the procedure you would follow
- the measurements you would take
- how the data measured enable you to determine the order with respect to H_2O_2.

$2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$

*Maximum volume of O_2 to be collected at r.t.p.= **80%** of 100 cm^3 gas syringe = 80 cm^3.*

No. of moles of O_2 = $\frac{80 \times 10^{-3}}{24}$ = 3.33×10^{-3}

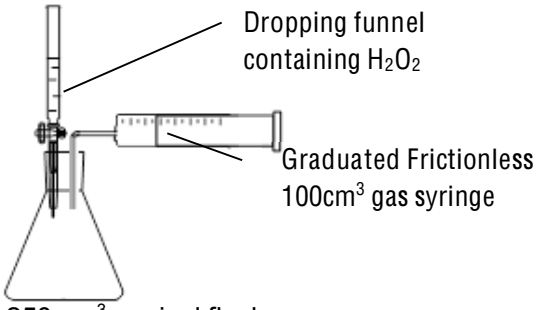
No. of moles of H_2O_2 = $2 \times 3.33 \times 10^{-3} = 6.66 \times 10^{-3}$

Volume of H_2O_2 to be used = $6.66 \times 10^{-3}/0.10 = 66.67\ cm^3$

Procedure

1 *Set up the experiment as shown below.*

2 *Using a **100 cm^3 measuring cylinder**, add **65 - 67 cm^3 of H_2O_2** into a **dropping funnel.***



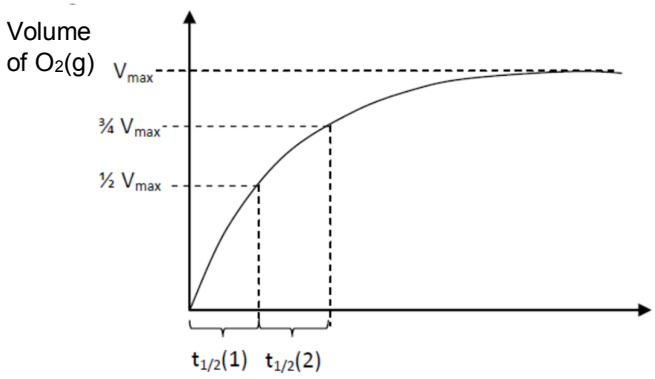
3 ***Open the tap*** *to allow H_2O_2 to drip into the conical flask and* ***close the tap*** *when all H_2O_2 is discharged. (The set up should be air-tight).*

4 ***Read off*** *the volume of O_2 in the* ***syringe*** *at* ***30s intervals*** ***until it reaches a constant value/ the piston of the syringe stops moving****, indicating reaction is complete.*

5 *Plot a graph of volume of O_2 against time.*

6 *Determine two half-lives to see if they are constant. (Refer to diagram below.)*

(If has a constant half-life, it is a 1st order reaction wrt H_2O_2. If not constant but increasing half-life, it could be a 2nd order reaction.)



(b) Identify another variable in the experiment that can also affect the volume of O_2 collected. Hence suggest an improvement that can make the experimental results collected more reliable.

Temperature will affect the volume of gas collected.

Use a water jacket around the gas syringe to maintain a constant temp.

[Planning] : Kinetics Practical 4

The decomposition of hydrogen peroxide can be catalysed by Fe(III) chloride solution

$$2H_2O_2 \rightarrow 2\ H_2O + O_2$$

The rate equation for this reaction is: rate = $k[H_2O_2][Fe^{3+}]$ where k is the rate constant.

The order with respect to H_2O_2 maybe confirmed to be first order by preparing a reaction mixture containing H_2O_2 (aq) and $FeCl_3$(aq).

Portions of the reaction mixture are

- Removed at timed intervals,
- Quenched by adding to ice water
- Titrated against standard solution of $KMnO_4$(aq).

The volume of $KMnO_4$ added in each titration (titre) is proportional to the $[H_2O_2]$.

$$2MnO_4^- + 6\ H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

(a) Describe how you would make a 100 cm^3 of acidified $KMnO_4$ of concentration 0.05 mol dm^{-3} from $KMnO_4$ of original concentration 0.1 mol dm^{-3} and H_2SO_4 (aq). Label this solution as **FA 1**. You are going to use **FA 1** in part **(b)**.

Use a burette to measure 50.00 cm^3 of original $KMnO_4$ (aq).

Top up to the mark with H_2SO_4 (aq) provided.

Stopper and shake to ensure uniform mixture.

(b) Plan a procedure to collect sufficient data to allow a graph of *volume of $KMnO_4$ against time to be drawn* to verify that the order of reaction with respect to H_2O_2 is 1.

You should plan to make a reaction mixture containing,

- 100 cm^3 H_2O_2(aq)
- 10 cm^3 of $FeCl_3$(aq)

You are provided with:

FA 1 prepared by you	$FeCl_3$(aq)
aq H_2O_2	ice water
normal apparatus found in the laboratory	

In your plan, you are to include:

- the apparatus you would use
- the procedure you would follow
- the measurements you would make

Procedure

1 *Using a 100 cm^3 measuring cylinder, transfer 100 cm^3 of hydrogen peroxide into a clean, dry 250 cm^3 beaker.*

2 *Use 10.0 cm^3 measuring cylinder, transfer 10 cm^3 of aqueous iron(III) chloride, swirl the flask and start the stopwatch simultaneously.*

3 *Before 5 minutes have elapsed, pipette 10.0 cm^3 of the reaction mixture into a conical flask.*

4 *At **exactly 5 minutes**, rapidly add about 20 cm^3 of ice water, measured using a measuring cylinder, into the conical flask.*

5 *Swirl the flask and titrate the mixture against **FA1** in a burette until solution just turns pale pink (due to 1 excess drop of $KMnO_4$).*

6 *Repeat Steps 1 – 5 at **10**, **15, 20 and 25 min**. Record all results in **Table 1** below.*

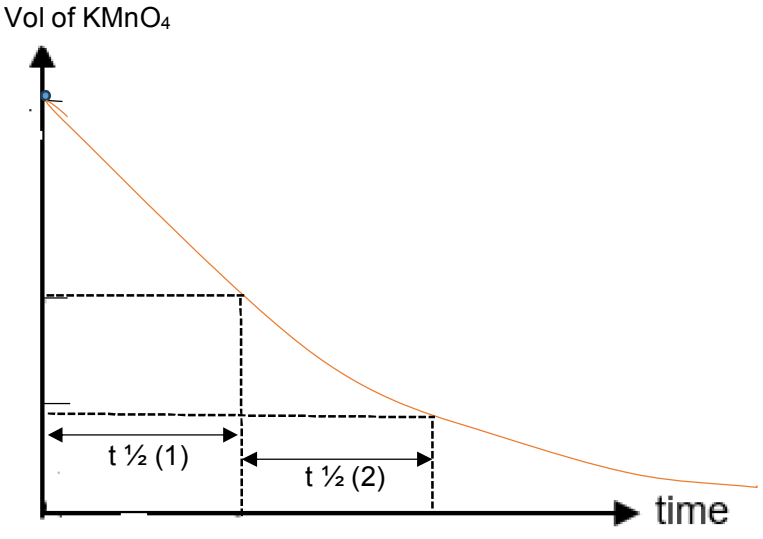
Results

Time when ice water was added to withdrawn sample /min	*0*	*5*	*10*	*15*	*20*	*25*
Final burette reading /cm^3						
Initial burette reading /cm^3						
Volume of $KMnO_4$ used /cm^3						

Table 1

(c) In the space below, sketch the graph you would expect to obtain**.**

Explain your answer.



t ½ (1) = t ½ (2)

Since its 1st order wrt H_2O_2, it should shows a curve with constant half-life. Fe^{3+} is a catalyst, it is used and regenerated, no change in Fe^{3+}(aq) concentration thus exert no effect on rate.

(c) From your observations, provide evidence to identify the ions present in each of the solutions.

Solution	Ions present	Evidence
FA 1	Cation: **Cr^{3+}**	**Cr^{3+} is present as a grey–green ppt** of **$Cr(OH)_3$** was formed in **test (ii)** and was **soluble in excess NaOH (aq) to form a dark green solution.**
	Anion: **NO_3^-**	**NH_3 gas was evolved with NaOH and Al / test (ii) and no NO_2 gas was evolved with HCl / test (iii)**
FA 2	Cation: **Cu^{2+}**	**Cu^{2+} is present as a pale blue ppt** of **$Cu(OH)_2$** was formed in **test (i)** and was **soluble in excess NH_3 (aq) to form a deep blue solution**
	Anion: **NO_2^-**	**NO_2 gas was evolved with HCl / test (iii) / NH_3 gas was evolved with NaOH and Al / test (ii)**

[Planning] : Inorganic Qualitative Analysis Practical 1

1. **FA2** is a green solution containing the following cations: $Al^{3+}(aq)$, $Fe^{3+}(aq)$ and $Cu^{2+}(aq)$.

(a) How does the colour of **FA2** indicate that both the transition metal cations quoted are present?

Green color is a combination of yellow Fe^{3+} and blue Cu^{2+} ions.

(b) State, with reasons, whether each of the following anions could also be present.

i. $NO_3^-(aq)$
ii. $SO_4^{2-}(aq)$
iii. $CO_3^{2-}(aq)$

i) Yes, NO_3^- can be present as all nitrates soluble.

ii) Yes, SO_4^{2-} can be present as sulfates of all given cations are soluble.

iii) No, CO_3^{2-} cannot be present.

– $CuCO_3$ is insoluble.

– $Al^{3+}(aq)$ and $Fe^{3+}(aq)$ have high charge/volume ratio and give acidic solution upon hydrolysis. They can react with $CO_3^{2-}(aq)$ to give CO_2 gas and insoluble $Al(OH)_3$ and $Fe(OH)_3$.

(c) State the reagent, or reagents, needed to test for the presence of $SO_4^{2-}(aq)$.

Add $BaCl_2(aq)$ followed by dilute HNO_3.

Explanation:

- Ba^{2+} can form white ppt with CO_3^{2-}, $SO_3^{2-}$and SO_4^{2-}. ($BaCO_3$, $BaSO_3$ and $BaSO_4$ respectively).
- $BaCO_3$ and $BaSO_3$ will react with acid and the white ppt will dissolve.
- If the white ppt remains insoluble in HNO_3, it must be $BaSO_4$.

(d) Plan a procedure to separate the three cations $Al^{3+}(aq)$, $Fe^{3+}(aq)$ and $Cu^{2+}(aq)$ in **FA 2** so that each cation is present in separate precipitates.

You may assume that you are provided with:

- aqueous sodium hydroxide, NaOH,
- aqueous nitric acid, HNO_3,
- aqueous ammonia, NH_3,
- aqueous sodium carbonate, Na_2CO_3,
- dilute hydrochloric acid, HCl,
- deionised water,
- the equipment normally found in a school or college laboratory.

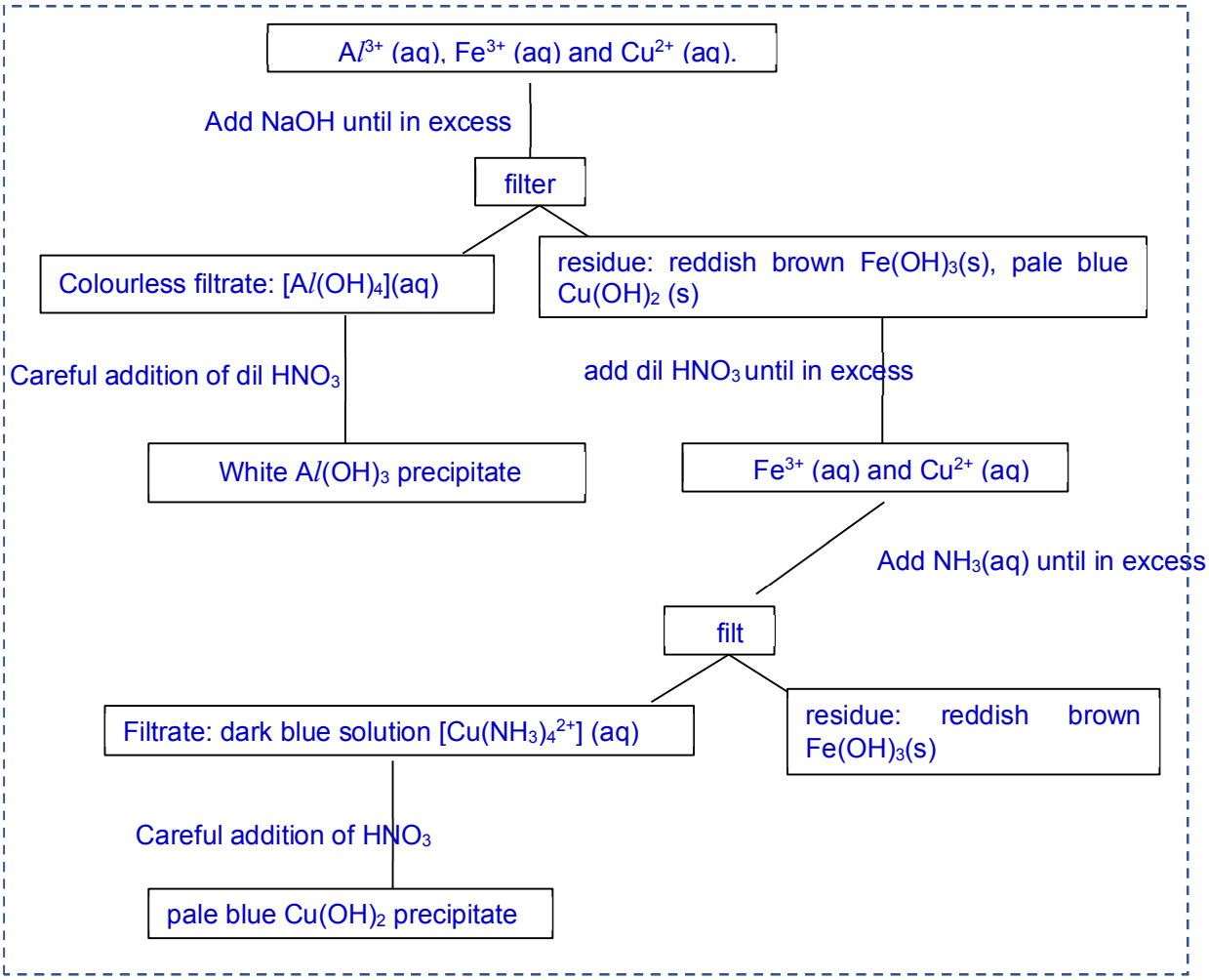
In your plan you should:

- **only** be using the chemicals provided, but **not** necessarily all of them,
- outline the sequence of steps you would follow (You may present using a flow chart),
- give brief details of the quantities of chemicals that you would use i.e. in excess,
- state the observation you would observe,
- identify the cations by the formulae of the precipitates obtained after each separation step.

Preliminary Considerations with reference to QA Table (not required in answer)

	NaOH(aq)	*NH_3(aq)*
Al^{3+}(aq)	*White ppt, soluble in excess NaOH(aq).*	*White ppt, insoluble in excess NH_3 (aq).*
Fe^{3+}(aq)	*Reddish-brown ppt formed, insoluble in excess NaOH(aq).*	*Reddish-brown ppt formed, insoluble in excess NH_3 (aq).*
Cu^{2+}(aq)	*Pale blue ppt formed, insoluble in excess NaOH(aq).*	*Pale blue ppt formed, soluble in excess NH_3 (aq) forming a dark blue solution.*

Suggested answer:



[Planning] : Inorganic Qualitative Analysis Practical 2

2. There are three aqueous solutions. Each of the solutions contains one of the following:

- magnesium sulfate
- sodium hydroxide
- zinc nitrate

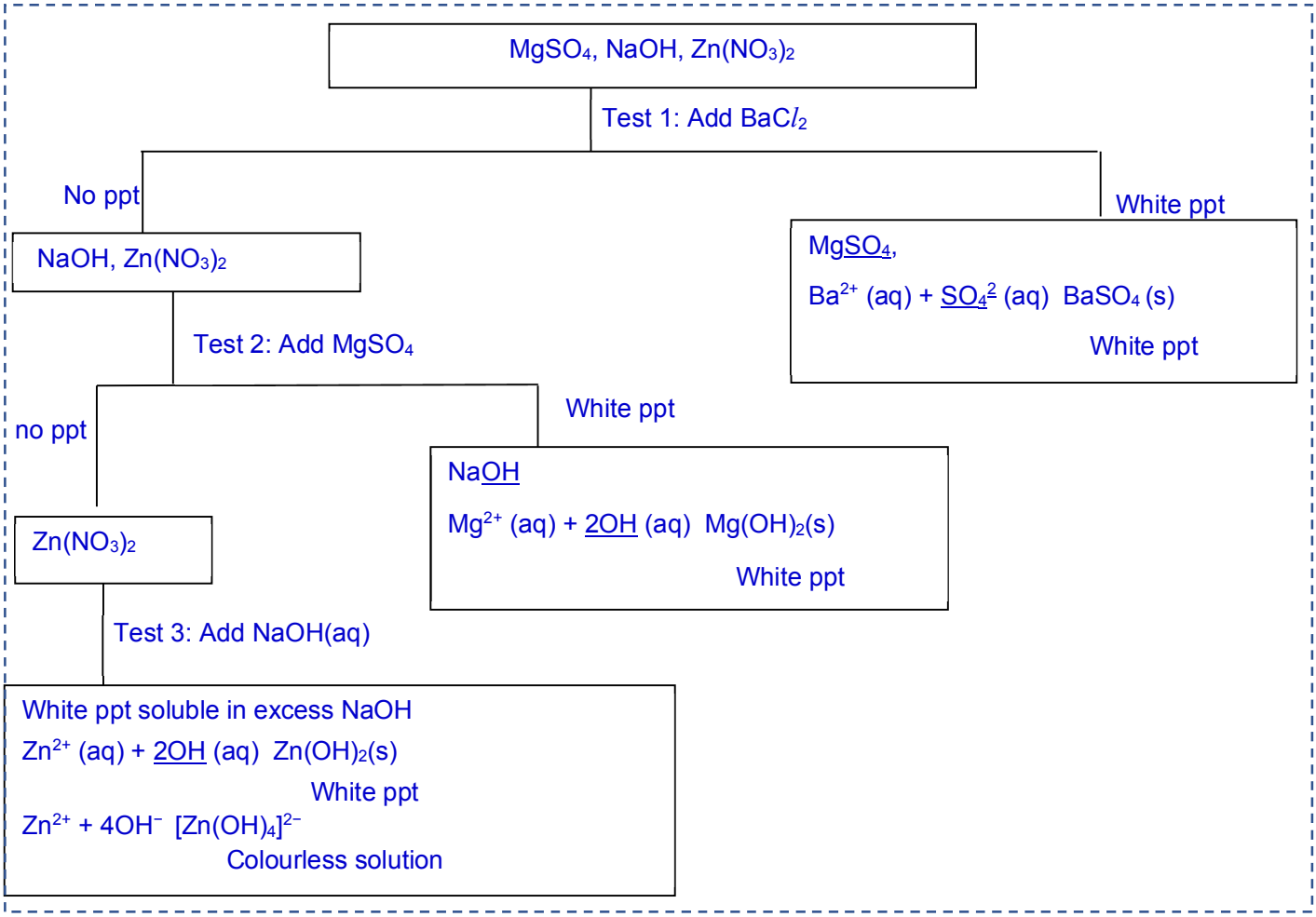
Plan a series of test-tube experiments which will enable you to identify the compounds present in each aqueous solution using only the three solutions and aqueous barium chloride. Use of any form of indicator or additional reagent will be is not allowed.

You may assume that you are provided with:

- three unknown aqueous solutions,
- aqueous barium chloride,
- the equipment normally found in a school or college laboratory.

In your plan you should:

- **only** be using the chemicals provided,
- outline the sequence of steps you would follow (You may present using a flow chart),
- highlight the chemicals that you would use in excess,
- state the observation you would observe,
- identify the solution by the formulae of the precipitates obtained after each separation step.



[Planning] : Inorganic Qualitative Analysis Practical 3

3. In this question, you are to plan an experiment to identify the five colourless solutions listed below.

    - ammonium sulfate,
    - barium chloride,
    - dilute hydrochloric acid,
    - sodium sulfate,
    - sodium sulfite.

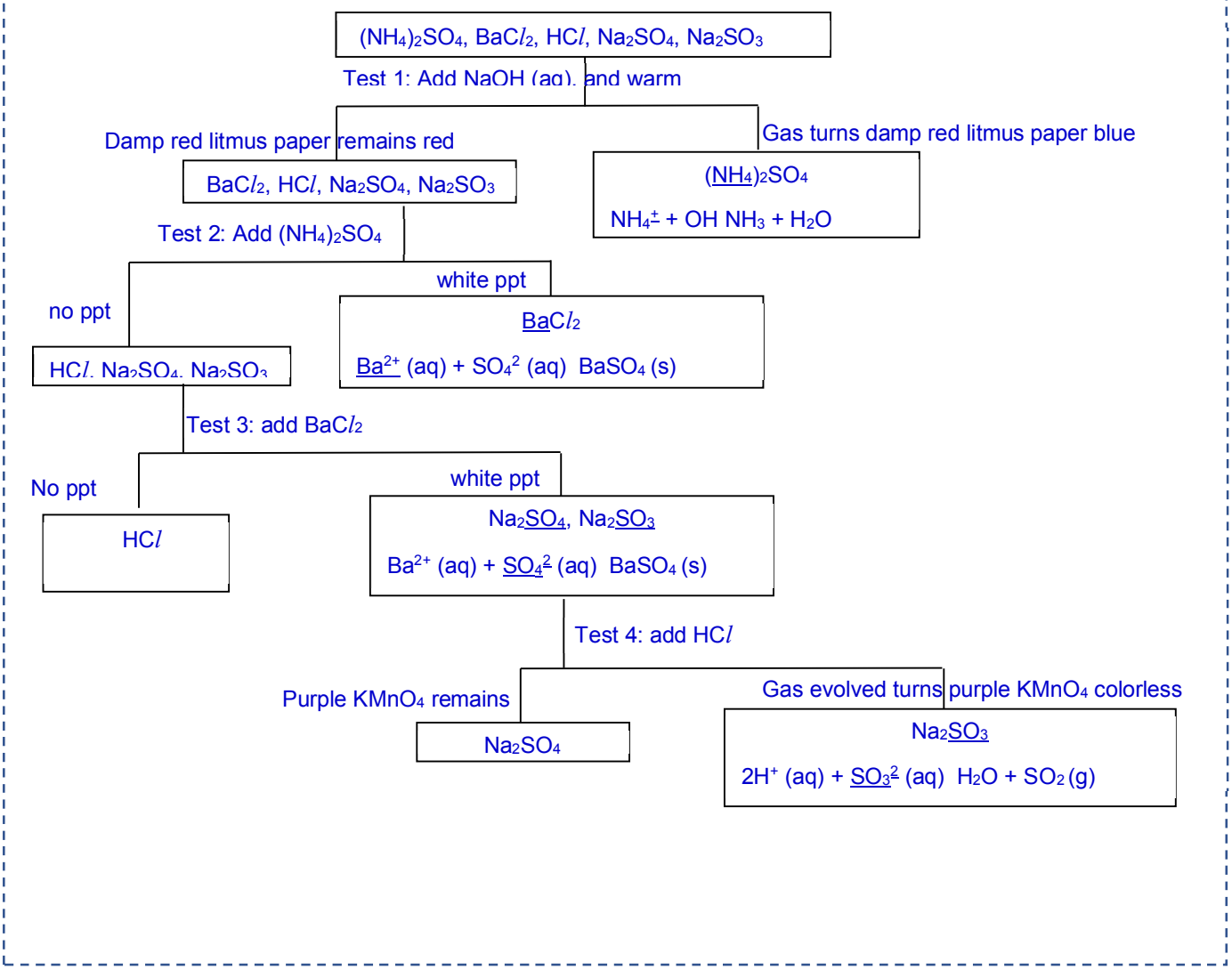
    The five solutions are in unlabelled bottles.

    Plan a series of test-tube tests which will enable you to identify the compound present in each bottle.

    You may assume that you are provided with:
    - five unknown aqueous solutions,
    - aqueous sodium hydroxide,
    - red and blue litmus paper,
    - the equipment normally found in a school or college laboratory.

    In your plan you should:

    - **only** be using the chemicals provided,
    - outline the sequence of steps you would follow (You may present using a flow chart),
    - highlight the chemicals that you would use in excess,
    - state the observation you would observe,
    - state the positive test you would conduct to identify the gas evolved (if any),
    - provide brief explanations of how you identify the solution in each bottle.


(NH4)2SO4, BaCl2, HCl, Na2SO4, Na2SO3
Test 1: Add NaOH (aq), and warm
Damp red litmus paper remains red
Gas turns damp red litmus paper blue
BaCl2, HCl, Na2SO4, Na2SO3
(NH4)2SO4
NH4+ + OH NH3 + H2O
Test 2: Add (NH4)2SO4
white ppt
no ppt
BaCl2
Ba2+ (aq) + SO42 (aq) BaSO4 (s)
HCl, Na2SO4, Na2SO3
Test 3: add BaCl2
No ppt
white ppt
HCl
Na2SO4, Na2SO3
Ba2+ (aq) + SO42 (aq) BaSO4 (s)
Test 4: add HCl
Purple KMnO4 remains
Gas evolved turns purple KMnO4 colorless
Na2SO4
Na2SO3
2H+ (aq) + SO32 (aq) H2O + SO2 (g)

[Planning] : Inorganic Qualitative Analysis Practical 4

**The $E^{\ominus}$ concept will be taught in the elctrochemistry topic

4. **FA3** is a dilute aqueous solution which is believed to contain one of the cations, barium or magnesium, and a halide anion (chloride, bromide or iodide).

   You are required to devise an experiment which will enable you to identify the ions present in **FA 3**. You may use **ONLY** the reagents provided below.

aqueous barium chloride	dilute nitric acid
aqueous sodium hydroxide	dilute sulfuric acid
aqueous hydrogen peroxide (an oxidant)	dilute hydrochloric acid
aluminium foil	dilute aqueous ammonia

Half equations

$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	$E^{\ominus} = + 1.77$ V
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	$E^{\ominus} = + 1.36$ V
$Br_2 + 2e^- \longrightarrow 2Br^-$	$E^{\ominus} = + 1.07$ V
$I_2 + 2e^- \longrightarrow 2I^-$	$E^{\ominus} = + 0.54$ V

(a) Plan two test tube experiments to distinguish between barium and magnesium ions in **FA 3**.

In your plan you should:
- **only** be using the chemicals provided,
- an outline of the sequence of steps you would follow,
- highlight the chemicals that you would use in excess,
- state the observation you would observe,
- identify the cations by the formulae of the precipitates obtained in each test.

Test	Reagent(s) and description of the test to be performed	Expected observations	
		for Ba^{2+}	for Mg^{2+}
1	Add dilute NH_3 in drop wise until in excess to 1 cm depth of **FA 3** in a test tube	No ppt	White ppt; insoluble in excess NH_3.
2	Add dilute H_2SO_4 in drop wise until in excess to 1 cm depth of **FA 3** in a test tube	White ppt	No ppt

(b) Plan one test tube experiment to identify the anion present in **FA 3**.

In your plan you should:
- **only** be using the chemicals provided,
- outline the step you would follow,
- state the observation you would observe,
- how you identify the anion based on the observation.

From the $E^{\ominus}$ values, H_2O_2 can oxidise the halides into the halogens.

Test	reagent(s) and description of the test to be performed	Expected observations		
		for Cl^-	for Br^-	for I^-
3	Add H_2O_2 (aq) and H_2SO_4(aq) to 1 cm depth of **FA 3** in a test tube	yellowish-green gas produced or solution turns yellowish	Solution turns orange	solution turns brown, black solid formed

[Planning] : Organic synthesis Practical 1

1. The preparation of *N-phenylethanamide* from phenylamine is termed ***acylation.*** Both ethanoyl chloride, CH_3COCl, and ethanoic anhydride, $(CH_3CO)_2O$, may be used as acylating agents. The reactivity of ethanoic anhydride is lower than that of ethanol chloride, and allows the reaction rate to be more easily controlled. Phenylamine is most conveniently used in the form of the salt phenyl ammonium chloride.

The ***acylation*** reaction is performed in two stages.

Stage 1: A solution of sodium ethanoate is treated with phenylammonium chloride, forming phenylamine, ethanoic acid and sodium chloride.

Stage 2: Phenylamine then reacts with ethanoic anhydride to form *N-phenylethanamide* as a white solid, together with ethanoic acid.

An aqueous solution of phenylammonium chloride (5.0 g in 150 cm^3) is mixed with ethanoic anhydride (10 cm^3). To this mixture is added a second aqueous solution of sodium ethanoate (30 g in 125 cm^3). The sodium ethanoate causes the reaction in step 1 to occur. Once phenylamine is released, it reacts readily with ethanoic anhydride to form *N*- phenylethanamide as a white solid. The crude solid product is isolated and recrystallised from water.

Note: An excess of ethanoic anhydride is used to ensure a good yield.

(a) Write an equation for each of the two stages in the preparation of *N-phenylethanamide*.

Stage 1: $C_6H_5NH_3Cl + CH_3CO_2Na \rightarrow C_6H_5NH_2 + CH_3CO_2H + NaCl$
Stage 2: $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3CO_2H$

(b) Assuming that this reaction typically yields around 70% of the theoretical maximum, calculate the mass of phenylammonium chloride needed to make 2.0 g of *N-phenylethanamide*.

2.0 g of product (N-phenylethanamide) at 70% yield,
Thus mass obtained at 100 % yield should be
= 2.0 ÷ (70/100) = 2.857 g

Amount of N-phenylethanamide in 2.857 g = 2.857 / 135 = 0.0212 mol
Amount of phenyl ammonium chloride needed = 0.0212 mol

Mass for phenyl ammonium chloride needed = 0.0212 × M_r = 2.74 g

(c) Write a plan to obtain a **pure** and **dry** crystalline *N-phenylethanamide* from the crude solid N-phenylethanamide obtained from stage 2.

You may assume that you are provided with:

- the equipment normally found in a school or college laboratory.

In your plan, you should include details of:

- the apparatus you would use,
- the procedure you would follow to obtain pure and dry crystalline N-phenylethanamide.

1. Dissolves the crude solid N-phenylethanamide obtained from stage 2 in minimum quantity of hot water.
2. Filter it while hot to get rid of insoluble impurities
3. Allow the hot solution to cool and crystallise.
4. Filter the crystals and dry it on a watch glass/IR lamp/press between filter papers
5. weighs dry sample

(d) Describe how you will assess the purity of the product obtained and how to interpret the results.

Melting point determination
A pure solid will have a fixed melting point, whereas an impure solid will melt over a range of temperatures.

(e) Suggest a reason why a student may obtain a higher yield than expected.

Product may be damp or contain impurities.

(a) Identify a potential safety hazard and suggest a safety precaution to minimise this risk.

Hazards :
- phenyl ammonium chloride and *N-phenylethanamide* are both **toxic**
- ethanoic anhydride is **corrosive**

Precautions:
- wear gloves to avoid direct skin contact

[Planning] : Organic Qualitative Analysis Practical 2

2. 1–iodopropane can be synthesized from 1–bromopropane and sodium iodide, using dry propanone as a solvent.

$$CH_3CH_2CH_2Br + NaI \rightleftharpoons CH_3CH_2CH_2I + NaBr$$

(a) **Table 1** shows the solubilities of sodium bromide and sodium iodide in propanone.

Table 1

compound	solubility at 55 °C in g / 100 g of propanone
sodium bromide	0.00841
sodium iodide	39.9

Use this information in **Table 1**, explain why the reaction produces a very high yield of $CH_3CH_2CH_2I$.

$CH_3CH_2CH_2Br + NaI \rightleftharpoons CH_3CH_2CH_2I + NaBr$

The NaBr that is formed has a very low solubility in propanone. By Le Chatelier's Principle, the equilibrium position of the reaction will favour the formation of NaBr to partially offset the low concentration of NaBr in propanone. This results in a very high yield of $CH_3CH_2CH_2I$.

(b) The preparation of 1–iodopropane is described as follows:

1–bromopropane, excess sodium iodide and propanone solvent are mixed and then heated under reflux conditions for around thirty minutes.

The crude product is then shaken with water, before the layer containing 1–iodopropane is separated out and distilled to isolate pure 1–iodopropane.

Table 2 gives the boiling points and densities of 1–bromopropane, 1–iodopropane and propanone.

Table 2

compound	boiling point / °C	density / g cm^{-3}
1–bromopropane	71.0	1.35
1–iodopropane	102.6	1.75
propanone	56.0	0.784

[A_r: C, 12.0; H, 1.0; O, 16.0; Br, 79.9; I, 126.9; Na, 23.0]

(i) Assuming that the reaction goes to completion, calculate the volume of 1–bromopropane and mass of sodium iodide you would need to prepare **at least 10.0 g** of pure 1–iodopropane. Show your working clearly.

Amount of $CH_3CH_2CH_2I$ = 10.0 ÷ 169.9
= 0.0589 mol

Amount of $CH_3CH_2CH_2Br$ = 0.0589 mol

Mass of $CH_3CH_2CH_2Br$ = 0.0589 × 122.9
= 7.23 g

Volume of liq $CH_3CH_2CH_2Br$ = 7.23 ÷ 1.35
= 5.36 cm^3

Amount of NaI = 0.0589 mol

Mass of NaI = 0.0589 × 149.9
= 8.82 g

(ii) Write a plan for the preparation of **at least 10.0 g** of pure and dry 1–iodopropane.

You may assume that you are provided with:

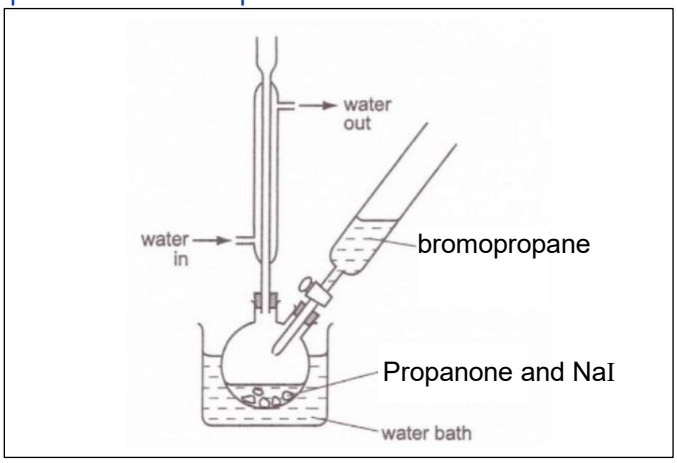
- liquid 1-bromopropane,
- solid sodium iodide,
- 25.0 cm^3 liquid propanone,
- the equipment normally found in a school or college laboratory.

In your plan, you should include details of:

- the quantities of the reactants calculated in **(b)(i)**,
- the apparatus you would use, including well-labelled diagrams of the assembled apparatus,
- the procedure you would follow to obtain pure and dry 1–iodopropane.

Procedure to Prepare Impure $CH_3CH_2CH_2I$:

2. Using an electronic balance, weigh a dry and empty weighing bottle
3. Using an electronic balance, weigh the weighing bottle and 10.0 g of NaI. [Note that NaI just needs to be in excess]
4. Transfer the NaI into a dry and empty two-neck round bottom flask.
5. Using an electronic balance, weigh the weighing bottle and residual NaI.
6. Set up the apparatus for a reflux process as shown below.

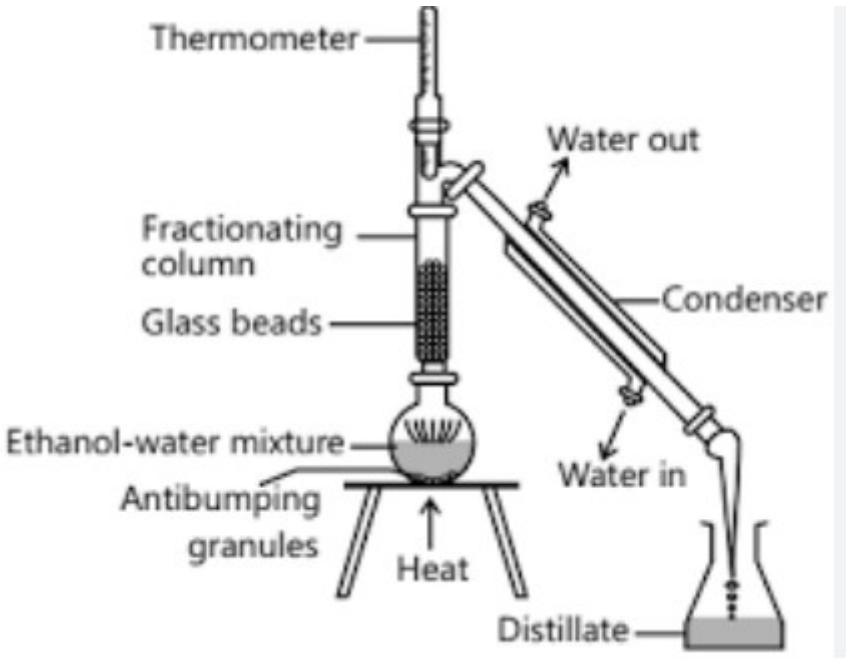


7. A 50 cm^3 measuring cylinder was used to measure 25.0 cm^3 of propanone and 6.0 cm^3 of $CH_3CH_2CH_2Br$, transferred into the two-neck round bottom flask via a dropping funnel.
8. Allow the reaction mixture to heat under reflux for 30 minutes.
9. After heating, allow the reaction mixture to cool to room temperature.

Procedure to Purify and Dry $CH_3CH_2CH_2I$ (Including Apparatus):

10. Using a measuring cylinder, measure out 50.0 cm^3 of distilled water into a clean and dry separating funnel. [Note: The 50.0 cm^3 of distilled water is just an estimate.]
11. Using a filter funnel, transfer the reaction mixture in the round bottom flask into the separating funnel. Stopper separating funnel and shake, releasing pressure intermittently.
12. Collect the bottom organic layer in a clean and dry beaker. Discard the top aqueous layer which contains the NaBr and propanone. [Note: $CH_3CH_2CH_2I$ has a density that is higher than H_2O. Thus $CH_3CH_2CH_2I$ will be in the bottom layer.]
13. Add anhydrous $CaCl_2$ to the organic layer. Remove hydrated $CaCl_2$ via filtration when the organic layer is no longer cloudy. Collect the filtrate into a round bottom flask.

14. Set up the apparatus for a distillation process shown below.



15. Heat the reaction mixture with distillation.
16. Collect the fraction at the range of 102.6 ± 2 °C.
17. Allow the reaction mixture to cool to room temperature.

[Planning] : Organic Qualitative Analysis Practical 3 (2024 A level P4)

Consider the following six organic compounds, which are all liquids at room temperature.

C	butanal	**D**	butan-1-ol	**E**	butan-2-ol
F	2-methylpropan-2-ol	**G**	pentan-2-one	**H**	pentan-3-one

Plan an investigation, using test-tube reactions, which would allow you to identify each of the these six organic compounds.

Your plan should include:

- Details of the reagents to be used
- An outline of the sequence of steps you would follow
- How the results of your tests would identify each compound.

Compounds may be identified by positive or negative results in the tests.

You should use as few different tests as possible.

You may present your answer in a flow-chart or table. [8]