Raffles Institution
H2 Chemistry Practical 2022

Planning Experiments – Introduction

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1 Practical Assessment

1.1 Scheme of Assessment

Paper	Type of paper	Duration	Weighting (%)	Marks
1	Multiple Choice	1 h	15	30
2	Structured Questions	2 h	30	75
3	Free Response Questions	2 h	35	80
4	Practical Paper	2 h 30 min	20	55

1.2 Assessment Objectives

A Knowledge with understanding
B Handling, applying and evaluating information
C Experimental skills and investigations

Candidates should be able to:

1. follow a detailed set or sequence of instructions and use techniques, apparatus and materials safety and effectively
2. make, record and present observations and measurements with due regard for precision and accuracy
3. interpret and evaluate observations and experimental data
4. **identify a problem, devise and plan investigations, select techniques, apparatus and materials**
5. evaluate methods and techniques, and suggest possible improvements

1.3 Paper 4 (2 h 30 min)

- This paper will assess appropriate aspects of objectives C1 to C5 in the following skill areas: P, MMO, PDO and ACE.

<table>
<tr><td colspan="2">1. Planning (P)
Candidates should be able to:
• define the question/problem using appropriate knowledge and understanding
• give a clear logical account of the experimental procedure to be followed
• describe how the data should be used in order to reach a conclusion
• assess the risks of the experiment and describe precautions that should be taken to keep risks to a minimum</td><td>5%</td><td rowspan="2">20%</td></tr>
<tr><td>2. Manipulation, measurement and observation (MMO)
3. Presentation of data and observations (PDO)
4. Analysis, conclusions and evaluation (ACE)</td><td>Note: The assessment of PDO and ACE may also include questions on data-analysis which do not require practical equipment and apparatus.</td><td>15%</td></tr>
</table>

- One, or more, of the (experimental) questions may incorporate some assessment of Skill P, set in the context of the syllabus content, requiring candidates to apply and integrate knowledge and understanding from different sections of the syllabus. It may also require the treatment of given experimental data to draw a relevant conclusion and analyse a proposed plan.

2 Overview

2.1 Main components of a written report for the plan of an experiment

	Headings	Remarks
1	Aim	• Always read the given question carefully and understand the aim of the experiment.
2	Theory • identify the topic (e.g. kinetics) • define the problem and give the theoretical basis of why a certain method is used • give outline of method	• May be asked to write briefly about the chemistry principles underlying the experiment. • May be asked to state the **dependent** variable and the **independent** variable in the experiment.
3	**Pre-experimental calculations** ✓ • show calculations of quantities of reagents to be used	• **Make suitable assumptions to work out appropriate quantities** (masses or volumes of chemicals) to be used.
4	**Procedure** ✓ • state chemicals and apparatus used • propose detailed sequence of steps	• Give a detailed **sequence of steps** to be carried out to collect experimental data. • Within the procedure, ➢ all **apparatus** used and their capacities (if relevant) should be stated. ➢ the **mass or volume** of each chemical used should be stated (pre-experiment calculations have to be done beforehand)
5	**Results** ✓ • construct appropriate tables to record experimental data	• Construct appropriate tables to record experimental data.
6	**Treatment of results** ✓ • preferably use a hypothetical experimental result (e.g. y cm^3) and show how it can be used to achieve the aim of the experiment	• Use relevant formulae to perform calculations • Plot relevant graphs
7	**Safety considerations** ✓ • identify one or more safety risks • suggest ways to overcome safety risks	• Suggestion should **always** tackle the accompanying risk e.g. "*gloves and lab coat should be worn as concentrated sulfuric acid is corrosive and can cause burns if it comes in contact with the skin*". **NOT** just "gloves should be worn" or "gloves should be worn as the chemical is flammable."
8	Reliability of results • state and explain measures taken to ensure reliability of results	

2.2 Types of experimental variables

- In an experiment, there are generally three types of variables.

1 independent variable	• The independent variable is the **variable** that is **changed** in an experiment to investigate its effect. • This is the variable that is being investigated in the experiment and its value is chosen to be varied.
2 dependent variable	• The dependent variable is the **variable** that is **measured** in an experiment. • This is the variable with value that depends on the independent variable and is being measured in the experiment.
3 constant variable(s)	• These are other key factor(s) that can affect the dependent variable. • These variables must be controlled (usually kept constant) in the experiment to help ensure valid conclusion can be made. • These are also termed controlled variables.

- **Example 1**

Hydrochloric acid and magnesium ribbon react to produce hydrogen gas.

$$2HCl(aq) + Mg(s) \rightarrow MgCl_2(aq) + H_2(g)$$

You are to plan the details of an experiment, based on the volume of gas produced in the reaction, to investigate how the rate of reaction depends on the concentration of the hydrochloric acid.

independent variable	• concentration of HCl
dependent variable	• volume of H_2 gas collected in a specified time • time taken to produce a specified volume of H_2 gas
constant variable	• temperature • amount/length/mass/surface area of magnesium ribbon

- **Example 2**

When aqueous sodium chloride, $NaCl$, 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

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

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 distilled 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.

independent variable	• volume/amount/mass of $NaCl$
dependent variable	• mass/amount of $PbCl_2$
constant variable	• temperature

2.3 Writing the procedure

- Each procedural step must be properly described and typically comprises three parts:

1. A **verb** (an action word – "weigh", "transfer", etc)
2. **Quantity and identity of chemical** to be measured and recorded e.g. (20.00 cm^3 of NaOH)
3. **Instrument / apparatus (specifying their capacity**, if relevant) to be used (e.g. 100 cm^3 beaker, electronic balance, 25.0 cm^3 pipette, etc)

- Examples:

- Using a 25 cm^3 measuring cylinder, measure 20.0 cm^3 of NaOH(aq).
- Using an electronic balance, weigh accurately about 2.5 g of Na_2CO_3 into a clean and dry weighing bottle.

3 Types of Planning Experiments

- There are many types of planning experiments. They can be classified based on topics as listed below.

3.1 Planning volumetric analysis experiments

3.2 Planning gravimetric analysis experiments

3.3 Planning gas collection experiments

3.4 Planning energetics experiments

3.5 Planning equilibrium experiments

3.6 Planning kinetics experiments

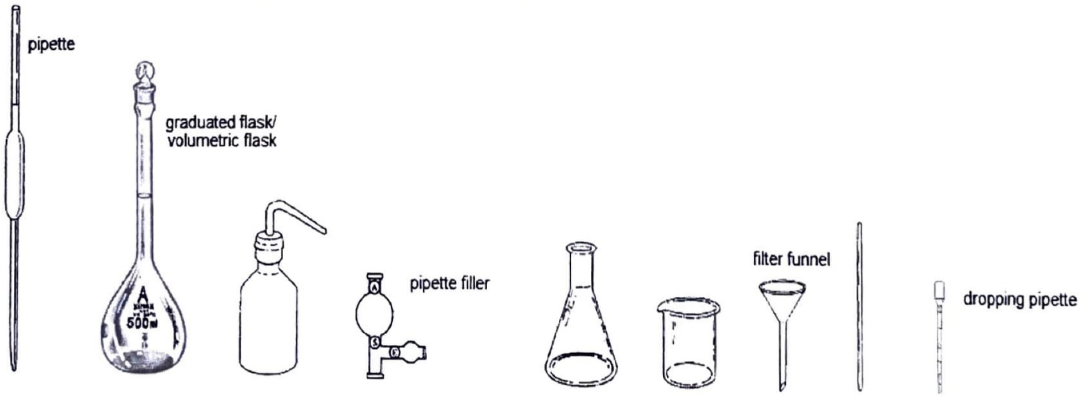
3.7 Planning electrochemistry experiments

3.8 Planning organic qualitative analysis experiments

3.9 Planning inorganic qualitative analysis experiments

3.10 Planning organic synthesis experiments

- Some common apparatus used in the laboratory:



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Planning Experiments 1 – Volumetric Analysis

Lecture Outline
1 Important Points to Consider
2 Acid-Base Titrations
3 Redox Titrations
4 Other Considerations (including micro-titration)
5 Worked Examples

Reference
1 Understanding Experimental Planning for Advanced Level Chemistry: The Learner's Approach (by Jeanne Tan and Kim Seng Chan)

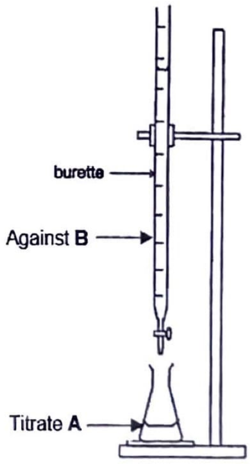
1 Important Points to Consider

(a) Identify the aim of the experiment and the **type of titration** to be carried out.

	Type of titration	Remarks and Examples
1	acid-base titration	The type of acid and base used in the titration will determine the **choice of indicator** to be used. • Determination of concentration of sodium hydroxide in a given sample. • Determination of concentration of an acid in a sample of apple juice.
2	redox titration	Titrating an oxidising agent ($KMnO_4$, $K_2Cr_2O_7$, H_2O_2, etc.) against a reducing agent (Fe^{2+}, H_2O_2, $C_2O_4^{2-}$, etc.) or vice versa. • Determination of x in $FeSO_4.xH_2O$. • Determination of concentration of H_2O_2 in a given sample.
3	back titration	Back titrations are employed when the determination of the amount of a substance poses some difficulty in the direct titration method, e.g. solid substances and volatile substances. Excess of one reagent reacted with compound of interest and titration is used to determine amount of **unreacted** reagent. • Determination of percentage by mass of $CaCO_3$ in a sample of limestone. • Determination of percentage by mass of NH_4^+ in a given ammonium salt.
4	double indicator titration	Titrating a base or acid with two end-points will require two types of indicators. • Determination of percentage by mass of Na_2CO_3 in a mixture containing NaOH and Na_2CO_3. • Determination of percentage by mass of $NaHCO_3$ in a mixture of $NaHCO_3$ and Na_2CO_3.
5	precipitation titration	• Determination of concentration of Ag^+ in a given solution. • Determination of concentration of Cl^- in a given solution.

(b) Decide on whether a graduated flask (or volumetric flask) is needed.
- Can the given solutions be titrated directly?
- Is there a need to prepare a solution from a given solid sample?
- Is there a need to dilute a given solution to an appropriate concentration?
- What is the capacity of the graduated flask to be used? 250 cm³ or 100 cm³?

(c) Decide on which solution is to be placed in the 50.00 cm³ **burette** and which solution is to be **pipetted** into the 250 cm³ **conical flask** for titration.
For example, the diagram on the right shows the titration of **A** (in conical flask) against **B** (in burette).



(d) State clearly the **volume of solution to be pipetted**. Common pipette sizes are 10.0 cm³, 20.0 cm³ and 25.0 cm³.

(e) If 25.0 cm³ of solution is to be pipetted into a conical flask for titration, assume **titration result of between 20.00 cm³ and 25.00 cm³** when working out the quantity of reagent needed during pre-experimental calculations. The ratio of the volume of solution pipetted for titration to the volume of solution added from the burette should be approximately 1:1.

- If the titration result obtained is too low (e.g. 8.00 cm³), the percentage uncertainty (error) associated with this titre volume would be rather high and this would lead to problems of accuracy of measurement.
- If the titration result obtained is too high (e.g. 55.00 cm³), the titration process would be time-consuming and may incur a higher percentage uncertainty (error), as there would be a need to refill the burette during each titration.

2 Acid-Base Titrations

2.1 Common indicators

- Know the colour change at the end-point for different indicators.

Indicator	**Approximate pH range**	**Colour**		
		in 'acidic' solution	**at end–point**	**in 'alkaline' solution**
Methyl orange	3.2 – 4.4	red	orange	yellow
Screened methyl orange	3.2 – 4.4	violet	grey	green
Thymol blue	8.0 – 9.6	yellow	green	blue
Thymolphthalein	9.4 – 10.6	colourless	light blue (if titrant is alkali) colourless (if titrant is acid)	blue
Bromothymol blue	6.0 – 7.6	yellow	green	blue
Phenolphthalein **Note:** Not used in school labs due to potential risk of carcinogenicity.	8.3 – 10.0	colourless	light pink (if titrant is alkali) colourless (if titrant is acid)	pink

2.2 Choosing an indicator

- Identify the **type of acid-base titration** to be carried out and select a **suitable indicator** to be used.

	Type	**Marked pH change**	**Suitable indicator**	
1	strong acid – strong base	4 – 10	thymolphthalein, thymol blue, methyl orange, screened methyl orange	**Note:** More details will be given in the lecture notes on Ionic Equilibria.
2	strong acid – weak base	3.5 – 6.5	methyl orange, screened methyl orange	
3	weak acid – strong base	7.5 – 10.5	thymolphthalein, thymol blue	
4	weak acid – weak base	no marked change	No suitable indicator	

- Note that candidates can be asked to explain their choice of indicator for a planned titration.

  Example: Explain your choice of indicator for this titration.

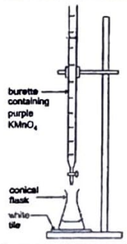
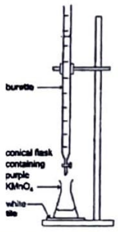
  - This titration involves the reaction between a strong acid and weak base.
  - Methyl orange (or screened methyl orange) is a suitable indicator since its pH range (pH 3.1 to 4.4) coincides with the region of rapid pH change (about pH 3.5 to 6.5) in this titration.

3 Redox Titrations

3.1 Types of redox titrations

	Type	Examples	Remarks
1	Manganate(VII) titration	- $KMnO_4$(aq) and Fe^{2+}(aq) - $KMnO_4$(aq) and H_2O_2(aq)	- No indicator is needed.
		- $KMnO_4$(aq) and $C_2O_4^{2-}$(aq)	- No indicator is needed. - The $C_2O_4^{2-}$ solution is acidified and usually heated to about 65 °C before being titrated against $KMnO_4$(aq).
		- $KMnO_4$(aq) and NO_2^-(aq)	- No indicator is needed. - The $KMnO_4$ solution is acidified and pipetted into conical flask and titrated against NO_2^-(aq) in the burette.
2	Dichromate(VI) titration	- $K_2Cr_2O_7$(aq) and Fe^{2+}(aq)	- A redox indicator is needed.
3	Iodine-thiosulfate titration (or iodometric titration)	- I_2(aq) and $S_2O_3^{2-}$(aq) - Iodine is usually generated *in situ* by mixing KI(aq) and a suitable oxidising agent (with either one in excess)	- Starch solution is commonly used as the indicator.

3.2 Colour change at the end-point for manganate(VII) titration

Manganate(VII) titration	**End-point colour change**	
	with acidified $KMnO_4$ placed in the burette	**with acidified $KMnO_4$ placed in the conical flask**
	 	
$KMnO_4$(aq) and H_2O_2(aq)	from colourless to pale pink Note: Just before the end-point, the conical flask contains Mn^{2+} (colourless in dilute solution) and very little unreacted H_2O_2 only. At the end-point, the addition of one drop of excess $KMnO_4$ which remains unreacted and this gives a pale pink colour (pale pink due to very dilute purple).	from pale pink to colourless Note: Just before the end-point, the conical flask contains very little unreacted $KMnO_4$ (pale pink due to low concentration) and Mn^{2+} (colourless in dilute solution) only. At the end-point, the addition of one drop of excess H_2O_2 which remains unreacted and the solution will be colourless (since all $KMnO_4$ has been reacted).
$KMnO_4$(aq) and Fe^{2+}(aq)	from yellow to pale orange/pink Note: Just before the end-point, the conical flask contains very little unreacted Fe^{2+} (almost colourless due to low concentration), Fe^{3+} (yellow) and Mn^{2+} (colourless in dilute solution) only. At the end-point, the addition of one drop of excess $KMnO_4$ which remains unreacted and this gives a pale pink colour (pale pink due to very dilute purple). Mixture of yellow and pink gives an orange colour.	from pale orange to yellow Note: Just before the end-point, the conical flask contains Fe^{3+} (yellow), very little unreacted $KMnO_4$ (pale pink due to low concentration) and Mn^{2+} (colourless in dilute solution) only. Mixture of yellow and pink gives an orange colour. At the end-point, the addition of one drop of excess Fe^{2+} which remains unreacted and colour will be yellow due to the Fe^{3+} present (note: all $KMnO_4$ has been reacted).

- To decide on the colour change at the end-point of any unfamiliar redox titration, consider both the colours of the reactants used and the products formed in the conical flask during the course of titration.

3.3 Acidifying solutions – choice of acids

- Some redox titrations require acidification with an appropriate acid. This is usually apparent from the question or the balanced chemical equation. For example:

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + \mathbf{8H^+(aq)} \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

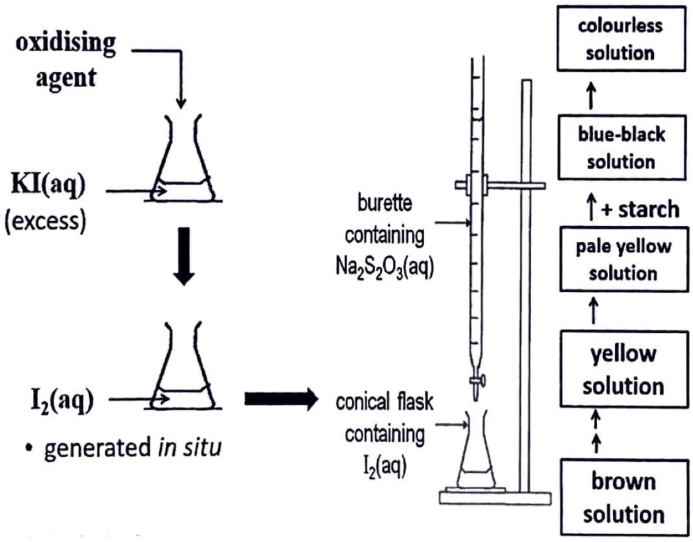
- The choice of acid used must be considered carefully. For example, hydrochloric acid <u>cannot</u> be used to provide the acidic medium for the titration between $KMnO_4$ and H_2O_2. The Cl^- ion from $HCl(aq)$ would be oxidised by either $H_2O_2(aq)$ or MnO_4^- to $Cl_2(g)$.

- Dilute $H_2SO_4(aq)$ is commonly used to provide the acidic medium for redox titrations and is usually added in excess using a measuring cylinder.

3.4 Colour change at the end-point for iodometric titration

Iodometric titration	**End-point colour change**	
	with iodine and starch indicator placed in the conical flask	**with iodine (and no starch indicator) in the conical flask**
$I_2(aq)$ and $Na_2S_2O_3(aq)$	from blue-black to colourless	from pale yellow to colourless

- For iodometric titrations, iodine is usually generated *in situ* in the conical flask. The brown iodine solution is then titrated against a standard solution of sodium thiosulfate placed in the burette. When the solution in the conical flask becomes pale yellow, starch indicator is added and a blue-black (or deep blue) starch-iodine complex is formed. The titration is continued until the blue-black solution turns colourless.



- The addition of the starch indicator makes the colour change at the end-point more obvious. However, the starch indicator should not be added right at the start of the titration.

- At the start of the titration, the concentration of iodine is relatively high. If the starch indicator is added at the start of the titration, many iodine molecules will be trapped in the starch molecules. Since the liberation of the iodine molecules from the starch molecules takes time, the titration results will be inaccurate.

4 Other Considerations

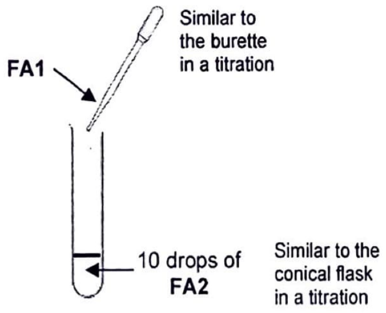
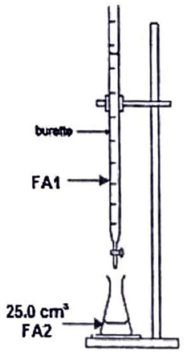
4.1 Suitability of the concentrations of solutions used for titration

(a) Titrant Volume

- When a titration is performed, the titrant volume is preferably between 10.00 cm³ and 30.00 cm³.
- Since % uncertainty (or error) for $V_{titrant} = \frac{\pm 0.10}{V_{titrant}} \times 100\%$, % uncertainty is high if $V_{titrant}$ is too low.
- Since the capacity of burette used is 50.00 cm³, it is important that $V_{titrant}$ is smaller than 50.00 cm³ (or the capacity of the burette). Otherwise, the burette needs to be refilled to complete the titration, making it time-consuming and may incur a higher % uncertainty.

(b) Using micro-titration to check suitability of concentrations of solutions used

- Let the two solutions used in a titration be **FA1** and **FA2**. **FA1** is the titrant (placed in burette) while **FA2** is pipetted into conical flask.
- If $V_{FA1} < 10.00$ cm³, **FA1** is too concentrated and needs to be diluted.
- If $V_{FA1} > 30.00$ cm³, **FA2** is too concentrated and needs to be diluted.
- A micro-titration is a simple and fast method to check if the solutions used are of suitable concentrations.
- Procedure for micro-titration:
  - ❖ Using a dropping pipette (or dropper), add 10 drops of **FA2** to a boiling tube (If necessary, add a suitable indicator or acid).
  - ❖ Next, wash the dropping pipette with deionised water and then with **FA1**.
  - ❖ Using the <u>same</u> dropping pipette, add **FA1** drop by drop to the boiling tube. Count the number of drops and shake the boiling tube to ensure good mixing until a colour change is observed (end-point of reaction). Record the number of drops of **FA1** used.
- Determining the suitability of [**FA1**] and [**FA2**] from micro-titration results:
  - ❖ Let D_{FA1} and D_{FA2} be the number of drops of **FA1** and **FA2** used in a micro-titration.
  - ❖ Let V_{FA1} and V_{FA2} be the volumes of **FA1** and **FA2** used in a normal titration;

	Micro-titration	**Normal titration**
		
FA2	D_{FA2} = 10 drops	V_{FA2} = 25.0 cm³
FA1	D_{FA1}	V_{FA1}

- ❖ The number of drops of **FA1** used in a micro-titration can be used to <u>estimate</u> the volume of **FA1** needed when a normal titration is carried out.

$$V_{FA1} = \frac{25}{10} D_{FA1}$$

❖ Fill in the table below which shows the corresponding volume of **FA1** expected with D_{FA1} obtained.

D_{FA2} in test tube / drops	D_{FA1} required in micro-titration/ drops	Corresponding V_{FA1} in normal titration/ cm³	Remarks
10	10	25.00	ideal
10	12	30.00	Dilute FA2
10	4	10.00	Dilute FA1

(c) Using micro-titration results to determine the volume required to be used for dilution

- Let V_D be the volume of solution required to be used for dilution.
- Dilution is done by the following procedure:
  - ❖ Using a burette, introduce V_D cm³ of **FA2** into a clean 250 cm³ volumetric flask.
  - ❖ Add deionised water to the 250 cm³ mark. Stopper and shake the volumetric flask to ensure that the solution is well mixed.

Example:
A student performed a micro-titration using 10 drops of **FA2**. She found that 67 drops of **FA1** were required to reach the end point of the titration.

(i) Which solution should be diluted? FA2

(ii) Calculate the volume of the solution needed for dilution in **(i)** if the total volume of the diluted solution is 250 cm³

Points to consider	Decisions
How much of each solution used in each titration?	Let **FA2** be diluted to the concentration such that V_{FA1} used is about 25 cm³ when 25.0 cm³ of diluted **FA2** is titrated against **FA1.**
Dilution factor The number of times **FA2** is to be diluted is called the dilution factor. $$\text{Dilution factor, DF} = \frac{\text{number of drops of } \mathbf{FA1}}{\text{number of drops of } \mathbf{FA2}}$$	Dilution factor = $\frac{67}{10} = 6.7$
Volume required for dilution If the final volume that **FA2** was to be diluted to is 250 cm³, the volume of **FA2** needed for the dilution, $$V_D = \frac{250}{DF}$$	$V_D = \frac{250}{6.7} = 37.31 = 37.30 \text{cm}^3$ (2dp)

4.2 Safety

- Students can be asked to **suggest safety precautions** that should be undertaken during the experiment and to **state the reasons** for them.

- Examples of some basic safety precautions related to titration.

	Safety precaution	**Reason**
1	Fill the burette with hydrochloric acid with the aid of the funnel and preferably do so at below eye-level.	To prevent any accidental spillage of the corrosive acid solution into the eyes which will cause irritation and harm.
2	Pipette the aqueous sodium hydroxide solution with the aid of the pipette filler. The solution should not be drawn into the pipette by mouth.	To avoid any accidental contact or swallowing of corrosive and toxic chemicals which can cause serious harm.
3	Wear safety goggles and safety gloves when diluting the 1 mol dm^{-3} H_2SO_4.	To avoid any direct skin and eye contact with the dilute sulfuric acid, which is corrosive and can cause irritation to the skin.

- Students can also be asked to **identify one or more safety risks** unique to the experiment and to **suggest ways to overcome or minimise** these safety risks.

- Examples

	Safety risk/hazard	**Way to minimise or overcome the risk/hazard**
1	To prepare **FA3** solution for titration, magnesium ribbon has to be added to hydrochloric acid. This produces hydrogen gas which is highly inflammable.	During the preparation of **FA3**, ensure that there is no naked flame lying around to avoid any hydrogen gas produced catching fire and causing an explosion.
2	**FA1** contains $Na_2C_2O_4$ which is highly toxic and also an irritant.	Wear safety goggles, safety gloves and laboratory coat when handling **FA1** to avoid any direct contact with the skin and also any accidental contact with the eyes.

4.3 Reliability of results

- Candidates can be asked to state measures to take to ensure reliability of results in a titration. Some measures are:
    - Stopper and shake the volumetric flask well to ensure a homogeneous solution is obtained.
    - Swirl the solution in the conical flask continuously during titration to ensure that the reactants are well mixed.
    - Repeat the titration to get at least two consistent titration readings (i.e. at least two titre values that are within 0.10 cm^3 of each other).

- The experiment can be repeated to check for the reliability of the titration results.

4.4 Checklist of skills

Students should be able to

(a) draw a simple diagram of a titration setup, with labelling of the solutions in the burette and conical flask

(b) write procedures for each of the following:

- the preparation of a standard solution using the 250 cm^3 graduated flask,
- the dilution of a given solution using the 250 cm^3 graduated flask,
- the steps to carry out an acid-base titration
- the steps to carry out a redox titration

5 Worked Examples

◆◆ Worked Example 1 ◆◆

A solid sample contains about 80% by mass of Na_2CO_3.

You are to design an experiment in which the percentage purity by mass of Na_2CO_3 in the impure sample can be determined accurately using a titrimetric method.

You may assume that the following are available:

- 3 g of impure Na_2CO_3 sample
- 0.100 mol dm^{-3} dilute HCl
- acid-base indicators
- usual titration apparatus

(a) Write a plan involving volumetric analysis for the determination of the percentage purity by mass of Na_2CO_3 in the given solid sample.

Your plan should include the following:

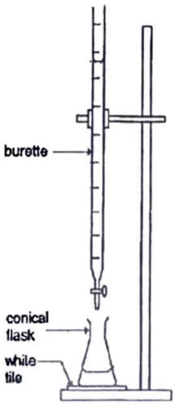
- calculation of a suitable mass of sample to be used
- procedure for the preparation of Na_2CO_3 solution
- details of the titration procedure

(b) Show how the experimental results may be used to find the percentage purity of Na_2CO_3 in the sample.

(c) State any assumptions made regarding the impurity in the sample.

Guiding questions

- What is the type of titration to be conducted? Is there a need for back titration?
- Is there is a need to prepare a solution using a graduated flask? If so, what is the capacity of the graduated flask to be used?
- Which solution, Na_2CO_3 or HCl, is to be placed in the conical flask or burette?
- What is a suitable indicator? What is the expected colour change at the end-point of titration?



Solution - (a)

- Do pre-experimental calculation.
- Include appropriate headings

- State clearly if there is a need to prepare a solution using a 250 cm^3 graduated flask.

- State clearly the volume of the solution to be pipetted into a 250 cm^3 conical flask and the solution to be placed in the burette.

- **Assume** a suitable value for the desired titration result and use it to 'back-calculate' the mass of impure Na_2CO_3 to be used.

Pre-experimental calculation

- Include relevant equations, if necessary.
- Show all essential steps in the calculation.
- Write proper statements.
- Use appropriate number of significant figures.
- Include relevant units.

- Include appropriate headings for clarity.
- **Number each step** in the procedure.

Each procedural step typically comprises three parts:

- A **verb**
- (an action word – weigh, transfer, dissolve, etc).
- **Quantity and identity of chemical** to be measured and recorded.
  (e.g. 20.0 cm^3 of NaOH)
- **Instrument / apparatus (specifying their capacity)** to be used.
  (e.g. electronic balance, 100 cm^3 beaker, etc.)

Calculation of mass of impure Na_2CO_3 to be used

- The mass of impure Na_2CO_3 to be used needs to be calculated first. This mass of impure Na_2CO_3 has to be dissolved in water and the solution made up to 250 cm^3 in a 250 cm^3 graduated flask.

- 25.0 cm^3 of the prepared Na_2CO_3 solution is pipetted into a conical flask and the solution titrated against standard $HCl(aq)$ placed in the burette.

Let the **average** volume of HCl used in the titration be **25.00 cm^3**.

Amount of HCl reacted = 25.00/1000 x 0.100 = 2.50 x 10^{-3} mol

$$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Amount of Na_2CO_3 in 25.0 cm^3 of solution = (½) (2.50 x 10^{-3})
= 1.25 x 10^{-3} mol

Amount of Na_2CO_3 in 250 cm^3 of solution = (10) (1.25 x 10^{-3})
= 1.25 x 10^{-2} mol

Molar mass of Na_2CO_3 = 106.0 g mol^{-1}
Mass of Na_2CO_3 = (1.25 x 10^{-2}) (106.0) = **1.325 g**

The impure solid contains about 80% Na_2CO_3 by mass.
Mass of impure Na_2CO_3 to be used = 1.325/0.80 = **1.66 g**

Preparation of 250 cm^3 of Na_2CO_3 solution

Procedure:

1. Using an **electronic balance**, weigh out accurately about **1.66 g** of the impure Na_2CO_3 sample in a clean and dry weighing bottle.
2. **Dissolve** the sample in some deionised water in a 100 cm^3 beaker. Transfer the sample quantitatively from the weighing bottle to the beaker by rinsing the weighing bottle a few times with deionised water and transfer all the washings into the beaker.
3. **Transfer** the solution in the beaker quantitatively into a **250 cm^3 graduated flask** with the aid of a funnel and a glass rod. Rinse the beaker a few times with deionised water and transfer all the washings into the graduated flask.
4. **Fill** the graduated flask to the 250 cm^3 mark with more **deionised water**. Use a dropping pipette (or dropper) to add the deionised water drop by drop when nearing the mark.
5. **Stopper** the graduated flask and **shake** the solution thoroughly to ensure that it is homogeneous. Label the solution **FA 3**.

- Include appropriate headings for clarity.
- State the capacity of the pipette.
- Name the indicator used.
- State the number of drops of indicator to be added.
- State the colour change at the end-point of the titration.
- Include the criterion for 'consistent' results.

Titration of Na_2CO_3 solution against standard $HCl(aq)$

Procedure:

6. Fill the burette with the 0.100 mol dm^{-3} HCl provided.
7. Pipette **25.0 cm^3** of **FA 3** into a 250 cm^3 conical flask. Add 2 drops of **methyl orange** indicator. **Titrate** this solution in the conical flask against the standard $HCl(aq)$ placed in the burette.
8. **Stop** the titration when the end-point is reached i.e. when one drop of the $HCl(aq)$ added from the burette changes the colour of the solution in the conical flask from **yellow to orange**.
9. Record the titration results using an appropriate table.
10. **Repeat** the titration until at least **two consistent results** are obtained (i.e. the two titre volumes are **within 0.10 cm^3** of each other).

Solution - (b)

Treatment of results

- For this part, show how the primary data collected can be used to achieve the aim of the experiment.
- Use hypothetical result (e.g. **m** g and **V** cm^3) to represent the primary data collected.
- Express the final answer in terms of **m** and **V** with the appropriate units.
- Always check whether the final expression is correct by substituting **m** and **V** using suitable numerical values.

Let the mass of impure Na_2CO_3 sample used be **m g**
Volume of Na_2CO_3 solution pipetted for titration = 25.0 cm^3
Let the **average** volume of dilute HCl for used for titration be **V** cm^3.

Amount of HCl reacted = (**V**/1000) (0.100) = 1.00 x 10^{-4} **V** mol

$$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Amount of Na_2CO_3 in 25.0 cm^3 of solution = (½) (1.00 x10^{-4} **V**)
= 5.00 x 10^{-5} **V** mol

Amount of Na_2CO_3 in 250 cm^3 of solution = (10) (5.00 x 10^{-5} **V**)
= 5.00 x 10^{-4} **V** mol

Molar mass of Na_2CO_3 = 106.0 g mol^{-1}
Mass of Na_2CO_3 = (5.00 x 10^{-4} **V**) (106.0) = 0.0530 **V** g
Mass of impure Na_2CO_3 sample used to prepare 250 cm^3 of solution = **m** g

Percentage purity by mass of Na_2CO_3 = (0.0530 **V/m**) (100%) = 5.30 **V/m** %

Solution - (c)

The impurity present is assumed to be **water soluble** and **does not react with dilute HCl.**

◆◆ **Worked Example 2** ◆◆

An old bottle of methanoic acid solution was found in a laboratory.

It is known that methanoic acid is a weak acid that decomposes slowly according to the following equation.

$$HCO_2H \longrightarrow CO + H_2O$$

You are to design an experiment to determine the concentration of methanoic acid remaining in the bottle using a titration method.

You may assume that the following are available:

- 150 cm^3 of the partially decomposed solution from the bottle (**FA1**)
- 0.200 mol dm^{-3} NaOH (**FA2**)
- 250 cm^3 graduated flask
- deionised water
- thymolphthalein and methyl orange indicators
- the apparatus and materials normally found in a school or college laboratory

The solutions were tested and it was found that 20 drops of **FA1** required 4 drops of **FA2** for complete reaction.

(a) Write a plan for the volumetric analysis of **FA1**.

In your plan you should give:

- details, including quantities, for the preparation of a suitable NaOH solution (i.e. **FA3**) from **FA2** to be used during titration
- the essential details of the titration procedure.

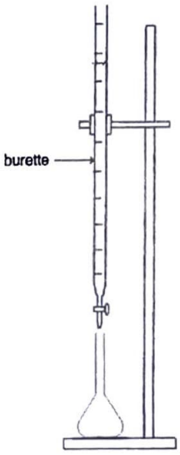
Present your plan as a sequence of numbered steps. [5]

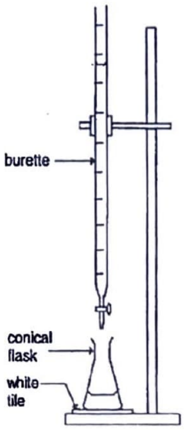
(b) The label on the bottle reads "0.1 mol dm^{-3} methanoic acid".

Show how the experimental results may be used to determine the percentage decomposition of methanoic acid in the sample. Assume that the average titre value is x cm^3. [2]

Guiding questions

- Based on the micro-titration results, is there a need to dilute any solution? If so, what volume of solution is to be used for dilution? What is the capacity of graduated flask to be used?
- What type of titration is to be conducted and which indicator, thymolphthalein or methyl orange, is suitable?
- Which solution is to be placed in the conical flask and burette?
- What is the expected colour change at the end-point of titration?





Solution – (a)

- For this pre-experimental calculation, make use of the preliminary titration (micro-titration) results to determine which solution needs to be diluted.
- See **section 4.1** on page 9.
- The HCOOH and NaOH solutions to be used for this acid-base titration should preferably have similar concentrations so that 25.0 cm^3 of the acid will react with about 25.0 cm^3 of the base.
- Key points to consider here:
  - dilution of **FA2** is necessary
  - volume of **FA2** to be used for dilution needs to be determined
  - this is a weak acid-strong base titration, so the suitable indicator is thymolphthalein.

Pre-experimental calculation

Since 20 drops of **FA1** required only 4 drops of **FA2** for complete reaction, **FA2** is too concentrated to be used for titration and needs to be diluted.

Dilution factor = 20/4 = 5

In this case, **FA2** needs to be diluted 5 times so that 20 drops of **FA1** will require 20 drops of diluted **FA2** (i.e. **FA3**) for complete reaction.

The diluted **FA2** solution will be labelled as **FA3**.
250 cm^3 of **FA3** is to be prepared using a 250 cm^3 graduated flask.

Volume of **FA2** to be used for dilution = 250/5 = 50 cm^3

Preparation of FA3 (i.e. diluted FA2 solution)

Procedure:

1. Using a burette, add 50.00 cm^3 of **FA2** into a 250 cm^3 graduated flask.
2. **Fill** the graduated flask to the 250 cm^3 mark with **deionised water**. Use a dropping pipette (or teat pipette) to add deionised water drop by drop when nearing the mark.
3. **Stopper** the graduated flask and **shake** the solution to ensure that it is homogeneous. Label the solution **FA3**.

Titration of FA1 against FA3 placed in the burette

Procedure:

4. Fill another burette with **FA3**.
5. Pipette **25.0 cm^3** of **FA1** into a 250 cm^3 conical flask and add 2 drops of **thymolphthalein** indicator. Titrate this **FA1** against **FA3**.
6. **Stop** the titration when the end-point is reached i.e. when one drop of **FA3** added changes the colour of the solution in the conical flask from **colourless to pale blue**.
7. Record the titration results using an appropriate table.
8. **Repeat** the titration until at least **two consistent results** are obtained (i.e. the titre volumes are within 0.10 cm^3 of each other).

Solution – (b)

Treatment of results

- For this part, express the final answer in terms of *x*.

Concentration of NaOH in **FA3** = 0.200/5 = 0.0400 mol dm^{-3}

Amount of NaOH used = $\frac{x}{1000} \times 0.0400 = 4 \times 10^{-5}x$ mol

$HCOOH(aq) + NaOH(aq) \rightarrow HCOO^-Na^+(aq) + H_2O(l)$

Amount of HCOOH in 25.0 cm^3 **FA1** = $4 \times 10^{-5}x$ mol

Concentration of HCOOH in **FA1** = $4 \times 10^{-5}x \div \frac{25.0}{1000} = 0.0016x$ mol dm^{-3}

% of HCOOH that remains = (0.0016x / 0.1) (100%) = 1.6x %

% decomposition of HCOOH = **(100 – 1.6*x*) %**

Raffles Institution
Year 6 H2 Chemistry 2023
Planning Experiments Lecture 2
Gravimetry, Gas Collection, Energetics and Kinetics

TAMP Framework

When approaching planning questions, it is important to

1. know the typical steps (processes) involved in different types of experiments
2. interpret and incorporate information provided in the question in your plan.

We are going to use the TAMP framework to help you organise information from the question to write a clear and coherent plan.

What does it stand for:	What do you have to do:
Topic & Aim	Identifying the **T**opic tested and the **A**im of the experiment narrows the scope of your thinking quickly. The **P**rocess involved for the experiment should come to mind.
Analyse clues	Identify and **A**nalyse the clues / information given in the question which can be found in 1. description of experiment 2. apparatus provided 3. chemicals provided 4. bulleted points in question **A**nalyse the clues / information allows you to appropriately adapt the typical **P**rocess for that particular experiment.
Measurements	Decide and write down the quantities of the chemicals to be used and measured. Some of these quantities may be • assumed to take particular values, or • calculated based on **C**lues or your assumptions.
Process	**TAM** involves you responding the unique question presented. Each type of experiment has a typical series of steps and considerations i.e. **P**rocess, which you can / should remember. How much of the typical series of steps and considerations is used in your answer depends on what you have **A**nalysed previously.

In these lecture, we will be

1. going into the considerations in planning the different topics.
2. highlight the typical steps and considerations i.e. **P**rocess in the different topics.
3. solve worked examples using the **TAMP** framework to adapt the **P**rocess to situation presented in the question.

GRAVIMETRIC ANALYSIS

Gravimetry involves the accurate measurement of mass as a means of quantifying a sample. The substance to be weighed may be formed from thermal decomposition or by precipitation.

THERMAL DECOMPOSITION

This method involves heating a compound until it decomposes to give a solid residue and a gaseous product.

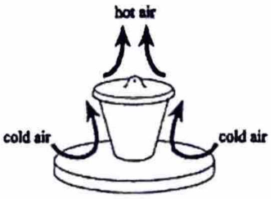
General procedure:

- Record the mass of an empty boiling tube/crucible.
- Weigh accurately *m* g of the compound in the boiling tube. Record total mass.
- Heat the sample gently in the boiling tube using a Bunsen burner.
- Then heat strongly for at least 10 min.
- Cool and weigh the boiling tube and its contents.
- The process of heating, cooling and weighing is repeated until constant mass is achieved.

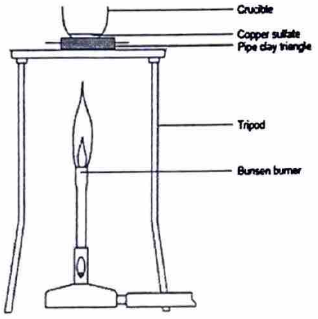
Common apparatus for gravimetric analysis using thermal decomposition
- electronic mass balance
- crucible / boiling tube
- desiccator

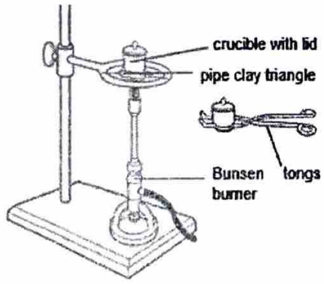
Points to take note:

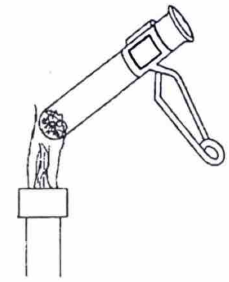
- Apparatus used for heating: dry and clean boiling tube or crucible
- Heating should be gentle at first to prevent spattering of the sample. Strong heating is then carried out for about 10 min.
- The crucible and its contents should be cooled to room temperature. If the crucible and its contents are weighed when they are hot, the measured mass will be less than their true mass. Why? As hot air rises above the crucible, cold air is drawn in and as it heats up and rises, it lifts the crucible very slightly from the balance pan.
- Ideally, the crucible and its contents should be cooled in a desiccator (see below). The desiccator provides a dry atmosphere and allows the crucible and its contents to cool without absorbing moisture.



- The procedure of reheating, cooling and weighing of the solid until constant mass is important in gravimetric analysis because this ensures that the sample is completely decomposed.
- Possible source of error: Due to uneven heating, part of the sample may not have decomposed.







Basic safety considerations:

- Allow the crucible to cool sufficiently before handling and handle a hot crucible with crucible tongs. This is to ensure that your hands do not get burnt.
- While heating a sample using a boiling tube, move the boiling tube up and down, and do not heat it at one spot. This is to prevent the contents of the boiling tube from spurting due to intensive heating at one spot.
- Handle the boiling tube with a test tube holder at all times. This ensures that your hands do not get burnt.
- Point the boiling tube away from yourself and others. This ensures that no one gets hurt in case of spurting.

The table below shows some substances that decompose on heating.

Substance	Effect on heating	Examples
Carbonate	• Many carbonates decompose to produce oxide and carbon dioxide on heating. • Example: $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ • Na_2CO_3 and K_2CO_3 are stable to heat and do not decompose on heating.	• Determine the identity of **M** in MCO_3 • Determine the % composition of $MgCO_3$ contaminated with K_2CO_3 (Na_2CO_3 and K_2CO_3 are stable to heat and do not decompose on heating.) • Determine the % by mass of $NaHCO_3$ in a mixture of $NaHCO_3$ and Na_2CO_3. *[see worked example 2]*
Hydroxide	• Group 2 hydroxides decompose on heating to give their respective oxides and water • Example: $Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$	• Determine the identity of **M** in $M(OH)_2$ • Determine the % composition of $Mg(OH)_2$ in a mixture of $Mg(OH)_2$ and MgO.
Salts with water of crystallisation	• The water of crystallisation can be driven off, leaving the anhydrous salt. • Example: $CuSO_4{\bullet}5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(g)$ • Difference in the mass before and after heating allows us to find the number of water of crystallisation present.	• Determine the value of *n* in $CuSO_4{\bullet}nH_2O$ *[see worked example 1]* • Determine the relative molecular mass of **X** in $X{\bullet}5H_2O$

Gravimetry (Thermal decomposition)

<table>
<tr><td>Topic & Aim</td><td colspan="3"></td></tr>
<tr><td>Analyse clues</td><td colspan="3"></td></tr>
<tr><td>Measurements</td><td colspan="3">Mass (see below)</td></tr>
<tr><td rowspan="4">Process</td><td rowspan="3">• Weighing</td><td>Mass of empty container / g</td><td></td></tr>
<tr><td>Mass of container + solid / g</td><td></td></tr>
<tr><td>Mass of container + contents after heating / g</td><td></td></tr>
<tr><td colspan="3">• Heat gently, then strongly
• Heat-cool-weigh until constant mass</td></tr>
</table>

♦♦ Worked Example 1 ♦♦

A sample of hydrated copper(II) sulfate has a formula of $CuSO_4{\bullet}nH_2O$.

You are to design an experiment in which the value of n can be determined accurately using a method involving weighing (i.e. gravimetric analysis) but not titration.

You may assume that the following are available:

- 5 g of $CuSO_4{\bullet}nH_2O(s)$
- crucible
- weighing balance
- Bunsen burner

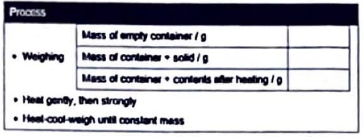
(a) Outline a step-by-step procedure, giving full experimental details.

(b) Show how the experimental data may be tabulated.

(c) Show how the results may be used to find the value of n in the sample of $CuSO_4.nH_2O$.

Aim

Topic (Gravimetry – thermal decomposition)



Process

• Weighing	Mass of empty container / g	
	Mass of container + solid / g	
	Mass of container + contents after heating / g	

- Heat gently, then strongly
- Heat-cool-weigh until constant mass

Analyse clues

Heat 5 g of solid in crucible to drive off water of crystallisation.

(a) Procedure

1. Using an analytical balance, weigh and record the mass of a clean, empty and dry crucible.
2. Weigh out accurately about 5.00 g of solid $CuSO_4{\bullet}nH_2O$ into the crucible. Record the total mass of the crucible and the solid $CuSO_4{\bullet}nH_2O$.
3. Using a Bunsen burner, heat the crucible and its contents gently at first, and then heat strongly for 10 minutes.
4. Cool and weigh the crucible and its contents.
5. Repeat the heating-cooling-weighing process until constant mass is achieved.

(b) Tabulation of results

Mass of empty crucible / g	A
Mass of crucible and $CuSO_4{\bullet}nH_2O$ / g	B
Mass of crucible and its contents	
after first heating / g	C
after second heating / g	D
after third heating / g	D

(c) Analysis of results – to determine the value of n

Mass of $CuSO_4$ left after heating = (D – A) g

Molar mass of $CuSO_4$ = 159.6 g mol^{-1}

Amount of $CuSO_4$ = $\dfrac{D-A}{159.6}$ mol

Mass of H_2O driven off = (B – D) g

Amount of H_2O driven off = $\dfrac{B-D}{18.0}$ mol

$$CuSO_4{\bullet}nH_2O(s) \longrightarrow CuSO_4(s) + nH_2O\,(g)$$

$$n = \frac{amt\ of\ H_2O}{amt\ of\ CuSO_4} = \frac{\dfrac{B-D}{18.0}}{\dfrac{D-A}{159.6}} = \left(\frac{159.6}{18.0}\right)\left(\frac{B-D}{D-A}\right)$$

◆◆ Worked Example 2 ◆◆

Sodium carbonate, Na_2CO_3, does not decompose on heating with a Bunsen burner. Sodium hydrogen carbonate, $NaHCO_3$, decomposes on heating.

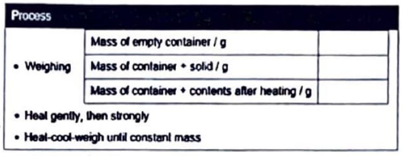
$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

You are provided with a mixture of $NaHCO_3$ and Na_2CO_3.

(a) Plan an investigation to determine the percentage by mass of $NaHCO_3$ in this mixture of $NaHCO_3$ and Na_2CO_3 by heating and weighing alone.

You may assume that you are provided with

- 2 g of a mixture of $NaHCO_3$ and Na_2CO_3,
- a boiling tube and a holder,
- weighing balance,
- Bunsen burner,
- the equipment normally found in a school or college laboratory.



Process		
• Weighing	Mass of empty container / g	
	Mass of container + solid / g	
	Mass of container + contents after heating / g	

- Heat gently, then strongly
- Heat-cool-weigh until constant mass

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements that you would take and how you would tabulate the experimental data,
- how you would use the results to determine the percentage by mass of $NaHCO_3$ in this mixture of $NaHCO_3$ and Na_2CO_3,

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

Solutions

(a)

Procedure

1. Weigh an empty, dry and clean boiling tube and record its mass.
2. Transfer about 2.00 g of the mixture of Na_2CO_3 and $NaHCO_3$ provided into the boiling tube. Weigh the boiling tube and its contents and record the total mass.
3. Using a Bunsen burner, heat the boiling tube with its contents gently at first, and then strongly for 10 minutes. Ensure that the water droplets that condensed on the cooler parts of the boiling tube is driven off during heating.
4. Allow the boiling tube and its contents to cool. Then weigh the cooled boiling tube and its contents and record the total mass.
5. Repeat this heating-cooling-weighing process until constant mass is achieved.

Tabulation of results

Mass of empty boiling tube / g	A
Mass of boiling tube and sample / g	B
Mass of boiling tube and contents after first heating / g after second heating / g after third heating / g	 C D D

Mass of mixture of Na_2CO_3 and $NaHCO_3$ used = (B – A) g
Mass of H_2O and CO_2 lost = (B – D) g

Analysis of results

Total mass of H_2O and CO_2 lost = (B – D) g
Total mass of 1 mole of H_2O and 1 mole of CO_2 = (18.0 + 44.0) = 62.0 g

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

$$n(H_2O)\text{ lost} = n(CO_2)\text{ lost} = \frac{B-D}{62.0}\text{ mol}$$

$$n(NaHCO_3) = \frac{2(B-D)}{62.0} = \frac{B-D}{31.0}\text{ mol}$$

Molar mass of $NaHCO_3$ = 84.0 g mol^{-1}

Hence mass of $NaHCO_3$ in the mixture = $\frac{84.0(B-D)}{31.0}$ g

Mass of sample (mixture of Na_2CO_3 and $NaHCO_3$) used = (B – A) g

Percentage by mass of $NaHCO_3$ in the mixture = $\frac{84.0(B-D)}{31.0(B-A)} \times 100\% = \frac{8400(B-D)}{31.0(B-A)}\%$

(b)

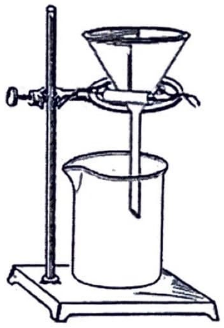
Heating the sample using an open crucible will allow water vapour to be lost more easily. With a boiling tube, the water vapour evolved will condense on the upper inner walls of the boiling tube to form tiny water droplets. Further heating will be needed to remove these water droplets.

PRECIPITATION

This may be used to determine the amount of an insoluble compound formed when two solutions are mixed.

General Procedure:

- Mix two solutions.
- Filter the mixture through a filter funnel lined with a sheet of pre-weighed filter paper.
- Wash the precipitate with several portions of cold deionised water.
- Dry the precipitate with the pre-weighed filter paper in the oven.
- Cool the precipitate with the pre-weighed filter paper in a desiccator for about 10 min.
- Weigh accurately the precipitate and the pre-weighed filter paper.
- Repeat the last 3 steps until constant mass is achieved.



	Type of salt	Solubility in water	Examples
1	Na^+, K^+, NH_4^+	All sodium, potassium and ammonium salts are soluble.	—
2	NO_3^-	All nitrates are soluble.	—
3	NO_2^-	All nitrites are soluble except $AgNO_2$.	—
4	Cl^-, Br^-, I^-	All halides are soluble except $AgCl$, $AgBr$, AgI, $PbCl_2$, $PbBr_2$ and PbI_2. $PbCl_2$, $PbBr_2$ and PbI_2 are soluble in hot water.	Determine the identity of the metal cation in MCl.
5	SO_4^{2-}	All sulfates are soluble except $BaSO_4$, $CaSO_4$ and $PbSO_4$.	Determine the identity of a sulfate MSO_4. Determine the value of n in $CuSO_4{\cdot}nH_2O$. Determine the solubility of cerium(IV) sulfate in water. *(Refer to worked example in Planning Notes 3 on Equilibria)*
6	SO_3^{2-}	Only sulfites of sodium, potassium and ammonium are soluble.	
7	CO_3^{2-}	Only carbonates of sodium, potassium and ammonium are soluble.	Determine the amount of Zn^{2+} in a sample by precipitating out $ZnCO_3$.
8	OH^-	Only hydroxides of sodium, potassium and barium are soluble. $Ca(OH)_2$ has limited solubility in water.	Determine the solubility and K_{sp} of $Ca(OH)_2$ in water.

Some common ions and their precipitating reagents are shown below:

Ion	Precipitating Reagent	Remarks
sulfate, SO_4^{2-}	$BaCl_2$(aq) or $Pb(NO_3)_2$(aq)	**Question:** If contaminants such as halide ions are present, $Pb(NO_3)_2$(aq) should not be used. Why? **Answer:** Lead(II) halides are insoluble and they will precipitate out together with $PbSO_4$.
halide ions: Cl^-, Br^-, I^-	$AgNO_3$(aq) or $Pb(NO_3)_2$(aq)	**Question:** If sulfate is also present, $Pb(NO_3)_2$(aq) should not be used. Why? **Answer:** $PbSO_4$ is insoluble and it will precipitate out together with the lead(II) halides.
lead(II) ion, Pb^{2+}	H_2SO_4(aq) or Na_2SO_4(aq)/ HCl(aq) or NaCl(aq)/ KBr(aq)/ KI(aq)	**Question:** $PbCO_3$, $BaCO_3$ and Ag_2CO_3 are insoluble in water. Theoretically, Na_2CO_3(aq) may also be used to precipitate out Pb^{2+}, Ba^{2+} and Ag^+, but it is usually the least preferred compared to the reagents shown. Why? **Answer:** Many carbonates are insoluble. If the impurities contain metal ions that form insoluble salts with carbonate ions, the impurities will be precipitated out as well. **Question:** Why is NaOH(aq) not used to precipitate out any of these three ions? **Answer:** • $Pb(OH)_2$ is amphoteric and dissolves in excess NaOH(aq). • $Ba(OH)_2$ has appreciable solubility. • AgOH is unstable and decomposes to form Ag_2O.
barium ion, Ba^{2+}	H_2SO_4(aq) or Na_2SO_4(aq)	
silver ion, Ag^+	HCl(aq) or NaCl(aq)/ KBr(aq)/ KI(aq)	

Gravimetry (Precipitation)

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Mass during dry-cool-weigh cycle.
Process	• Mix reactants • Filter • Wash • Dry (in oven) – cool – weigh until constant mass

♦♦ Worked Example 3 ♦♦

A $PbCO_3$ solid sample has been contaminated with solid $BaCO_3$.The percentage purity of the sample can be found using the gravimetric method.

The following sequence of steps has been proposed.

Step 1: Weigh accurately 0.5 g of the sample into a small beaker.
Step 2: Add 20 cm^3 of dilute nitric acid to the sample. Stir and mix well.
Step 3: Add 20 cm^3 of hot dilute hydrochloric acid to the resulting solution and stir vigorously.
Step 4: Allow the mixture to cool and the precipitate to settle.
Step 5: Filter the mixture and wash the precipitate using a suitable solvent.
Step 6: Transfer the precipitate into a pre-weighed crucible.
Step 7: Dry the precipitate and crucible in the oven for about 10 min.
Step 8: Cool the precipitate and crucible in a desiccator.
Step 9: Weigh the precipitate and crucible.

(a) Suggest a reason for adding dilute nitric acid to the sample in step 2.

Dilute nitric acid has been added to dissolve the sample.

(Note: The sample and the precipitating agent must be combined in solution form. If either the sample or the precipitating agent is in solid form, the precipitate formed may coat the solid, preventing further reaction.)

(b) Suggest a suitable concentration for the hydrochloric acid used in step 3.

Assume that the sample contains 100% $PbCO_3$.

$n(PbCO_3)$ present = $\frac{0.5}{267.2} = 1.873 \times 10^{-3}$ mol

$n(Cl^-)$ needed to fully precipitate out all the Pb^{2+} ions = $1.873 \times 10^{-3} \times 2 = 3.746 \times 10^{-3}$ mol

$[HCl]$ needed = $\frac{3.746 \times 10^{-3}}{20 \times 10^{-3}} = 0.187$ mol dm^{-3}

Suitable concentration to use: 0.200 mol dm^{-3} (Any concentration above 0.187 mol dm^{-3} is fine. However, due to corrosive nature of the acid, the concentration should not be above 2 mol dm^{-3}.)

(c) A student proposed the use of dilute sulfuric acid in place of the dilute hydrochloric acid. Comment on whether this is feasible.

This is not feasible since sulfate ions will precipitate out both the Pb^{2+} and Ba^{2+} ions.

(d) After all the precipitate has settled in step 4, suggest what can be done to check that all the Pb^{2+} ions have been precipitated out.

A small amount of the solution above the precipitate can be decanted and tested with a few drops of concentrated hydrochloric acid (or any solution containing chloride ions). If no precipitate is formed, it confirms that all the Pb^{2+} are in the precipitate and none are in the solution.

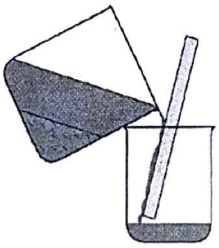


Figure shows the decanting process

(e) In an analysis, the mass of the precipitate obtained was found to be **m** g. Outline how you would use the result to determine the percentage purity of the sample.

Molar mass of $PbCl_2$ = 278.2 g mol^{-1}; Molar mass of $PbCO_3$ = 267.2 g mol^{-1}

$n(PbCl_2)$ formed = $\frac{m}{278.2}$ mol

Mass of $PbCO_3$ present in the sample = $\frac{m}{278.2} \times 267.2$ g = 0.9604 **m** g

Percentage purity = $\frac{0.9604m}{0.5} \times 100\%$ = 192 **m** %

(f) Suggest a significant modification to the given procedure to improve the reliability of the results.

Repeat steps 7 to 9 until a constant mass is obtained to ensure that the precipitate is completely dry.

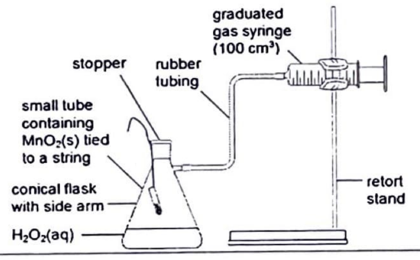
GAS COLLECTION

- Some reactions give out gas when a reagent is added in excess to another.
- For a reaction that evolves a gas, the gas can be collected using suitable apparatus and the experimental data (e.g. total volume of gas evolved, volumes of gas at regular time intervals, etc.) can be used to study selected aspects of the reaction.

	Reaction which produces a gas	**Experiments based on gas collection**
1	$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$	• Determination of percentage purity of a sample of impure Na_2CO_3 *[see worked example 5]* • Determination of relative formula mass of Na_2CO_3 • Study on kinetics of the reaction based on the rate of evolution of CO_2
2	$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$	• Determination of percentage of zinc by mass in a sample of zinc sheet • Determination of relative atomic mass of Zn • Determination of molar gas constant, R
3	$H_2O_2(aq) \xrightarrow{MnO_2(s)} H_2O(l) + \frac{1}{2}O_2(g)$	• Determination of concentration of H_2O_2 in a given H_2O_2 sample *[see worked example 4]* • Determination of volume strength of a given sample of H_2O_2 • Study on kinetics of the reaction based on the rate of evolution of O_2

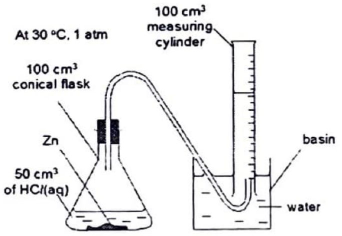
- A labelled diagram for the apparatus set-up should preferably be drawn.
  - Consider how the reactants will be mixed and how the gas should be collected.
- Common apparatus used to collect a gas:
  - graduated gas syringe
  - inverted burette filled with water
  - inverted measuring cylinder filled with water

Some common set-ups used in experiments involving gas collection are shown below.



Results:

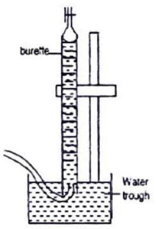
Final gas syringe reading / cm^3	V_2
Initial gas syringe reading / cm^3	V_1
Volume of gas evolved / cm^3	$V_2 - V_1$

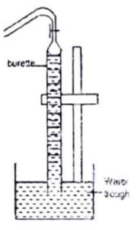


Results:

Final measuring cylinder reading / cm^3	V_2
Initial measuring cylinder reading / cm^3	V_1
Volume of gas evolved / cm^3	$V_2 - V_1$

Note:
For collection of gas over water, the gas should be insoluble in water or has poor solubility in water. Examples of gases which are soluble are CO_2, NH_3, SO_2, NO_2 and HX(X=Cl, Br, I)





Results:

Final burette reading / cm^3	V_1
Initial burette reading / cm^3	V_2
Volume of gas evolved / cm^3	$V_2 - V_1$

Note:
When a burette is used to collect the gas, the maximum volume of gas that can be collected is 50.00 cm^3.

- Gas collection method is fast, but it is not so accurate because
    - some gases, e.g. CO_2, may dissolve in the water if the water displacement method is used.
    - some gas may escape from the experimental set-up instead of being collected in the burette/measuring cylinder/gas syringe.
    - swirling of the conical flask is variable, which will vary the volume of gas collected in the measuring cylinder;
    - air and the gas evolved are both compressible, and heat of reaction may cause fluctuation in gas volumes due to thermal expansion;
    - volume of gas collected in the gas syringe or by water displacement method is dependent on temperature and pressure.
    - the ideal gas equation must be used to determine the amount of substance present from the volume of gas collected. However, this is not a good estimate, especially for gases which deviate greatly from the ideal gas behaviour.

General Guideline

For planning gas collection experiments, we assume the volume of gas collected to be between **50% and 90%** of the capacity of the collection apparatus and use it to determine the amounts of reagents required in the pre-calculations.

Gas collection

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and final readings of gas collection apparatus
Process	• May assume $V_{gas} \approx 50 - 90\%$ of gas collection apparatus capacity. • Setup diagram as shown in diagram o Vessel for reaction o Gas collection apparatus

◆◆ Worked Example 4 ◆◆

Hydrogen peroxide decomposes slowly in accordance to the following equation:

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

This reaction can be catalysed by MnO_2.

(a) Plan an investigation to determine the actual concentration of a sample of aqueous H_2O_2.

You may assume that you are provided with:

- 100 cm³ sample of aqueous H_2O_2 with an approximate concentration of 0.140 to 0.160 mol dm^{-3},
- 2.0 g of powdered MnO_2,
- 100 cm³ graduated gas syringe,
- the equipment normally found in a school or college laboratory.

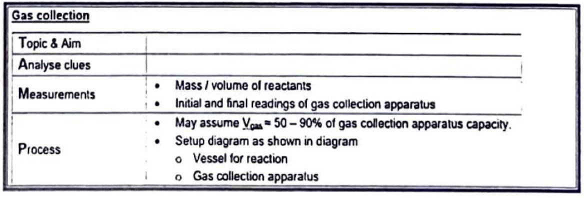
In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- a fully-labelled diagram of the set-up you would use,
- the procedure you would follow and the measurements that you would take,
- how you would use the results to determine the actual concentration of H_2O_2,
- how you would ensure that an accurate and reliable value of the actual concentration of aqueous H_2O_2 is obtained.

You may assume that 1 mole of gas occupies a volume of 24 dm³ under laboratory conditions.

(b) The actual concentration of H_2O_2 in the sample can also be determined via titration.

Suggest whether a more accurate value would be obtained compared to the gas collection method in **(a)**.



Gas collection

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and final readings of gas collection apparatus
Process	• May assume $V_{gas} \approx$ 50 – 90% of gas collection apparatus capacity. • Setup diagram as shown in diagram o Vessel for reaction o Gas collection apparatus

Solutions

(a) Pre-calculations

Since a 100 cm^3 gas syringe is used, let the volume of $O_2(g)$ collected be 72.0 cm^3

As 1 mole of gas occupies a volume of 24 dm^3 under laboratory conditions,

Amount of O_2 evolved = $72.0 \times 10^{-3} \div 24$

= 3.00×10^{-3} mol

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

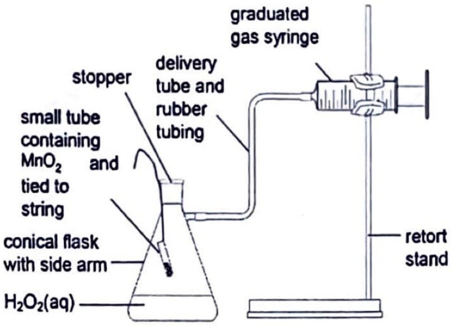
Amount of H_2O_2 used = $2 \times 3.00 \times 10^{-3}$

= 6.00×10^{-3} mol

Assume that the concentration of $H_2O_2(aq)$ used is 0.150 mol dm^{-3}.

Thus, volume of H_2O_2 to be used = $6.00 \times 10^{-3} \div 0.150 \times 1000 = 40.0$ cm^3

Experiment set-up



Procedure

1. Using a burette, add 40.00 cm^3 of $H_2O_2(aq)$ into a clean and dry 250 cm^3 conical flask with a side arm.
2. Weigh accurately about 1.00 g of $MnO_2(s)$ and place it in a small tube tied to a string.
3. Set up the apparatus as shown above.
4. Lower the filled tube into the conical flask taking care that the reagents do not mix. Stopper the conical flask.
5. Check that the initial reading of the 100.0 cm^3 graduated gas syringe is set at the zero mark.
6. At a suitable time, loosen the stopper slightly to release the string to allow mixing of MnO_2 and $H_2O_2(aq)$. Stopper the conical flask immediately.
7. Swirl the conical flask to ensure that the reagents are well mixed.
8. Allow the reaction to progress until it has ceased as indicated by a constant reading of the syringe.
9. Record the final reading, **V** cm^3, on the graduated gas syringe.
10. Repeat the experiment again to get consistent results of volume of $O_2(g)$ collected.

Note: Both steps 8 and 10 help to ensure accuracy and reliability.

Step 8 ensures that after the reaction has ceased, time is allowed for the pressure and/or temperature to stabilise before measurement of volume. Step 10 ensures that the experiment is repeated to obtain consistent values of $O_2(g)$ collected.

Calculations

Assume **average** volume of $O_2(g)$ evolved = **V** cm^3

As 1 mole of gas occupies a volume of 24 dm^3 under laboratory conditions,

Amount of O_2 evolved = $\frac{V}{24000}$ mol

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

Amount of H_2O_2 = $\frac{2V}{24000} = \frac{V}{12000}$ mol

Since volume of H_2O_2 used = 40.00 cm^3, concentration of H_2O_2 = $\frac{V}{12000} \times \frac{1000}{40.00} = \frac{V}{480}$ mol dm^{-3}

(b) The actual concentration of H_2O_2 obtained via titration is more accurate than gas collection. In gas collection, the volume of the gas collected fluctuates with temperature and pressure, which affects the accuracy of the amount and concentration of H_2O_2 obtained. Also, some $O_2(g)$ may have escaped when the flask is being stoppered.

◆◆ Worked Example 5 ◆◆

Sodium carbonate reacts with hydrochloric acid to produce carbon dioxide gas:

Clue

$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + \underline{CO_2(g)} + H_2O(l)$

FA 1 is a solid mixture containing about <u>80% by mass of sodium carbonate and 20% by mass of sodium chloride.</u> Clue

Plan an investigation to determine the <u>percentage by mass</u> of sodium carbonate in **FA 1**.

You may assume that you are provided with:

- 1.00 g of **FA 1** (a mixture of sodium carbonate and sodium chloride),
- 100 cm³ of 0.200 mol dm⁻³ aqueous hydrochloric acid,
- 100 cm³ graduated gas syringe,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use, so that there is an excess of HC*l*
- a fully-labelled diagram of the set-up you would use,
- the procedure you would follow and the measurements that you would take,
- how you would use the results to determine the percentage by mass of sodium carbonate in **FA 1**.
- how you would ensure that an accurate and reliable value of the percentage by mass of sodium carbonate is obtained.

You may assume that 1 mole of gas occupies a volume of 24 dm³ under laboratory conditions.

Aim

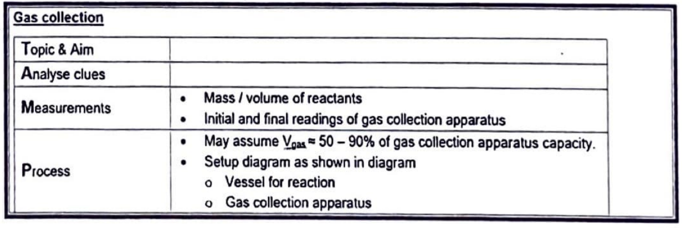
Topic: Gas collection

<u>Reaction flask</u> : mix $Na_2CO_3(s)$ + HCl
<u>Collect CO_2 gas</u> : 100 cm³ gas syringe

Excess HCl
  - *Use calculated mass of solid to check volume of HCl*

Limiting solid mixture
  - *Assume 50 cm³ of CO_2 to determine mass of solid mixture to use.*

- *Mass of solid mixture*
- *Volume of HCl(aq)*
- *Initial reading of syringe*
- *Final reading of syringe*



<u>Gas collection</u>

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and final readings of gas collection apparatus

Process	• May assume $\underline{V_{gas}} \approx 50 - 90\%$ of gas collection apparatus capacity.
	• Setup diagram as shown in diagram
	  o Vessel for reaction
	  o Gas collection apparatus

Solutions

Pre-calculations

Mass of FA1 to be used

Assume that 50.0 cm³ of CO_2 gas is collected.

As 1 mole of gas occupies a volume of 24 dm³ under laboratory conditions,

Amount of $CO_2 = \frac{50.0}{24000} = 2.08 \times 10^{-3}$ mol

$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

Amount of $Na_2CO_3 = 2.08 \times 10^{-3}$ mol

Molar mass of $Na_2CO_3 = 106.0$ g mol^{-1}

Mass of $Na_2CO_3 = (2.08 \times 10^{-3})(106.0) = 0.220$ g

Assume that **FA 1** contains 80% Na_2CO_3. Hence mass of FA 1 to be used = 0.220 / 0.8 = 0.275 g

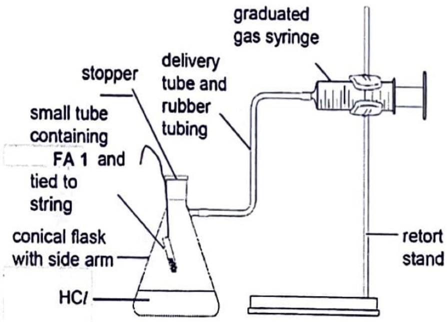
Volume of HCl(aq) to be used

Amount of HCl(aq) = $(2)(2.08 \times 10^{-3}) = 4.16 \times 10^{-3}$ mol

Volume of HCl to be used = $(4.16 \times 10^{-3})/0.200 = 2.08 \times 10^{-2}$ dm³ = 20.8 cm³

Since HCl(aq) has to be in excess such that the Na_2CO_3 used is completely reacted and for the experiment to be repeated, a suitable volume of HCl(aq) to be used is 30 cm³.

Experimental set-up



Procedure

1. Using a burette, add 30.00 cm³ of HCl(aq) into a clean and dry 250 cm³ conical flask with a side arm.
2. Weigh accurately about 0.275 g of **FA 1** and place it in a small tube tied to a string.
3. Set up the apparatus as shown above.
4. Lower the filled tube into the conical flask taking care that the reagents do not mix. Stopper the conical flask.
5. Check that the initial reading of the 100.0 cm³ graduated gas syringe is set at the zero mark.
6. At a suitable time, loosen the stopper slightly to release the string to allow mixing of **FA 1** and HCl(aq). Stopper the conical flask immediately.
7. Swirl the conical flask to ensure that the reagents are well mixed.
8. Allow the reaction to progress until it has ceased as indicated by a constant reading of the syringe.
9. Record the final reading, **V** cm³, on the graduated gas syringe.
10. Repeat the experiment again to get consistent results of volume of $CO_2(g)$ collected.

Calculations

Let the **average** volume of $CO_2(g)$ collected be **V** cm³ and the mass of **FA1** used = **$m_1 - m_2$** g

Amount of CO_2 formed $= \frac{V}{24000}$ mol

Amount of Na_2CO_3 = Amount of $CO_2 = \frac{V}{24000}$ mol

Mass of $Na_2CO_3 = \frac{V}{24000} \times 106.0$ g

Percentage composition by mass of Na_2CO_3 in **FA 1** $= \left(\frac{V}{24000} \times 106.0 \Big/ (m_1 - m_2) \right) \times 100\% = \frac{53V}{120(m_1 - m_2)}\%$

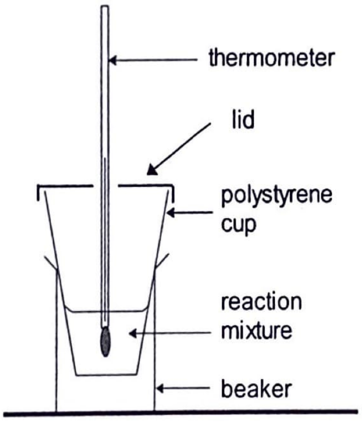
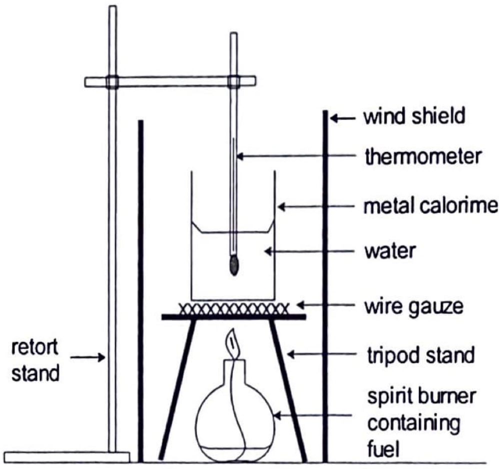
CHEMICAL ENERGETICS

Thermochemistry is the study of heat effects accompanying chemical reactions, the formation of solutions and changes in physical states of substances. The measurement of the heat of a reaction requires the careful determination of a measurable change in temperature, often with the use of a calorimeter.

Refer to your lecture notes on Chemical Energetics for the definitions of important terms. You must be able to construct energy cycles and calculate enthalpy changes of reactions using the experimental data obtained.

Symbol	**Definition**
Standard enthalpy change of reaction, $\Delta H_r^\ominus$	The energy absorbed or released in a chemical reaction when the molar quantities of reactants stated in the chemical equation react at 298 K and 1 bar.
Standard enthalpy change of neutralisation, $\Delta H_{neut}^\ominus$	The energy change when an acid and a base react to form one mole of water at 298 K and 1 bar.
Standard enthalpy change of solution, $\Delta H_{soln}^\ominus$	The energy change when one mole of the substance is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 bar.
Standard enthalpy change of combustion, $\Delta H_c^\ominus$	The energy released when one mole of the substance is completely burnt in excess oxygen at 298 K and 1 bar.

Common Experimental Setups used for

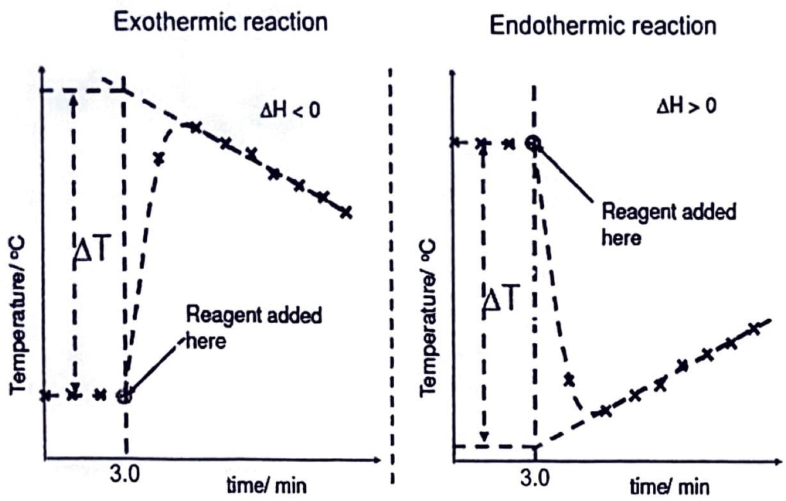
(a) determination of enthalpy change of a reaction	(b) determination of enthalpy change of combustion of a substance
	
• Enthalpy change of neutralisation $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ • Enthalpy change of reaction $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$ • Enthalpy change of solution $NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$	• Enthalpy change of combustion of ethanol $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ • Enthalpy change of combustion of hexane $C_6H_{14}(l) + \frac{19}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$
Methods 1. Measure the highest or lowest temperature attained using a thermometer, then calculate $\Delta T = (T_{highest/lowest} - T_{initial})$. *[see worked example 6 and 2021 Y5 Expt 6 Part 2]* 2. Measure temperature over time and determine ΔT graphically. *[2021 Y5 Expt 6 Part 1]* *Note: The volume of solution should be no more than half the capacity of the cup so as to prevent spillage when the solid is added.*	**Method** Measure the mass of substance that is completely combusted to cause a 5–10°C rise in temperature. *Note: 5–10°C rise in temperature is considered a measurable change in temperature.* *[see worked example 9]*

General Guideline

For planning energetics experiments where the approximate value of the unknown enthalpy change of reaction is given, we will assume that the reaction causes a **5–10 °C** change in temperature and perform pre-calculation to determine the appropriate qualities of reagents to use.

Common Graphs plotted in Chemical Energetics Experiments

Graphs to plot to account for heat lost to or heat absorbed from surroundings:
(refer to 2021 Y5 Expt 6 Part 1)



Time / min	Temperature / °C
0.0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0 (addition of reagent)	---
3.5	
4.0	
. .	

General Procedure:

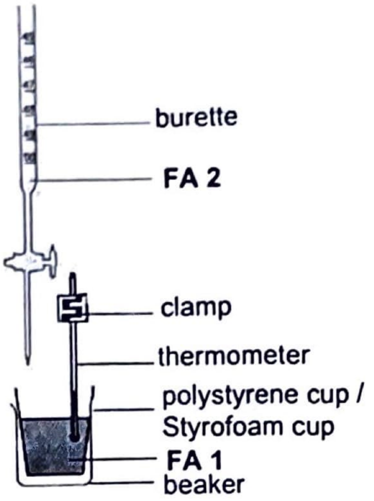
1. Monitor the temperature of a solution at regular time intervals, e.g. 0.5 min intervals. There should be a minimum of 3 (including initial temperature) temperature readings before the addition of the other reagent.
2. At a suitable time (e.g. t = 3min), add the other reagent to the solution and take temperature readings at 0.5 min intervals.
3. Sufficient temperature readings (minimum of 5 readings) must be taken after highest or lowest temperature is reached for reliable plotting of data points to be done.
4. Plot a graph of temperature against time. Draw two straight lines of best fit, one for the temperature of solution before addition of reagent at t = 3 min and the other for the cooling/warming of the solution once the reaction is completed. Extrapolate the two lines to t = 3 min and determine the change in temperature.

[Note: A stopwatch is required for this experimental method.]

Graphs to plot to find unknown concentration of one of the reagents used:

1) Thermometric titration

(refer to Worked Example 7 and 2021 Y5 Expt 7 Part I)

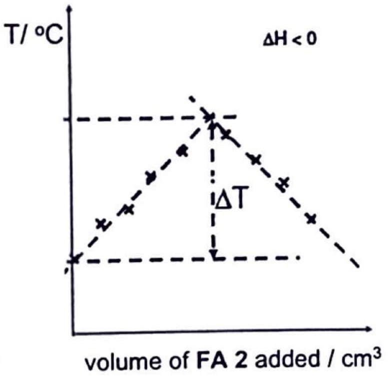


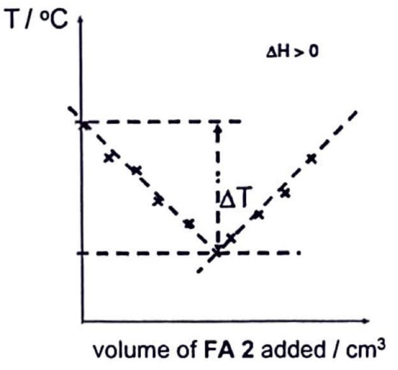
General procedure:

1. Transfer x cm^3 of **FA 1** into a polystyrene cup, supported in a 250 cm^3 beaker.
2. Measure the initial steady temperature of the **FA 1** solution in the cup.
3. Add y cm^3 of **FA 2** from a burette into the polystyrene cup. Measure and record the highest/lowest temperature, T, attained.
4. Repeat step 3 until a total of z cm^3 of **FA 2** has been added.
5. Plot a graph of T/ °C against volume of **FA 2** / cm^3. Draw best-fit lines for the points before and after the maximum/minimum temperature, T, has been reached and extend them until they intersect. The point at which the two best-fit lines meet corresponds to the volume of **FA 2** required for reaction and ΔT.

(values of x, y and z need to be determined based on context of question.)

[Note: The volume of **FA 2** added in step 3 should allow for a <u>minimum of 5 temperature readings</u> before AND after the maximum/minimum T.]





As **FA 2** is added to **FA 1**, the temperature of the reaction mixture will rise (for exothermic reaction) / drop (for endothermic reaction) until the equivalence-point is reached. Upon further addition of **FA 2**, temperature of the reaction mixture will decrease / increase as no further reaction takes place and the **FA 2** added is at a lower / higher temperature than the reaction mixture.

2) Mixing varying volumes of reagents and keeping total volume constant

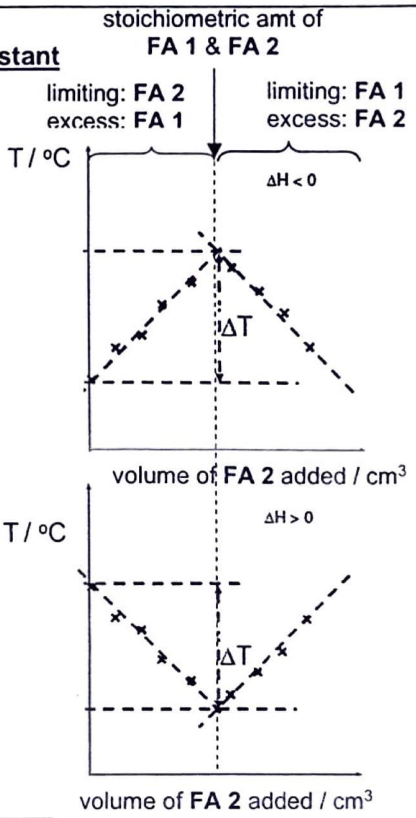
(refer to Worked Example 8 and 2021 Y5 Expt 7 Part II)

General Procedure:

1. Transfer x cm^3 of **FA 1** into a Styrofoam cup, supported in a 250 cm^3 beaker.
2. Measure the initial steady temperature of the **FA 1** solution in the cup.
3. Measure y cm^3 of **FA 2**. Ensure that **FA 1** and **FA 2** are at the same initial temperature.
4. Add y cm^3 of **FA 2** to **FA 1**. Measure and record the highest/lowest temperature, T, attained.
5. Repeat steps 1 to 3 using different volumes of **FA 1**, each time using the appropriate volume of **FA 2** so that the <u>**total volume of the mixture is kept constant**</u>.
6. Plot the graph of T/ °C against volume of **FA 2**/ cm^3. Draw best-fit lines for the points before and after the maximum/minimum temperature, T, has been reached and extend them until they intersect. The point at which the two best-fit lines meet corresponds to the volume of **FA 2** required for reaction and ΔT.

(values of x, y and z need to be determined based on context of question.)

[Note: The volumes of reagents used should allow for a <u>minimum of 5 temperature readings</u> before AND after the maximum/minimum T.]



Energetics

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and highest/lowest temperature
Process	1. Reaction setup a. Reaction involving solution(s) – Styrofoam cup in beaker b. Reaction involving combustion – Spirit lamp 2. Experiment type / data collected a. Continuous (i.e. with time) b. Mix different mass/volume of 2 reagents 3. Initial T, mix, highest/lowest T 4. $\Delta H = -\dfrac{mc\Delta T}{n}$ 5. May assume 5 – 10 °C temperature change

♦♦ Worked Example 6 ♦♦

NH_4Cl is commonly used in ice packs. With a solubility of 383 g dm^{-3}, it is one of the more soluble salts readily available.

$$NH_4Cl(s) + aq \rightarrow NH_4Cl(aq) \quad \Delta H_{soln} \approx +15\ kJ\ mol^{-1}$$

You are to plan an experiment to determine the enthalpy change of solution, ΔH_{soln}, of ammonium chloride.

You may assume you are provided with the following:

- 20g of solid NH_4Cl
- a polystyrene cup
- a thermometer
- other apparatus normally found in a school laboratory

Your plan should include:

- the apparatus you would use,
- calculation of suitable quantities of ammonium chloride and water you would use,
- practical details of how you would
  - ensure a known mass of NH_4Cl is transferred to the water;
  - determine the temperature change of the reaction mixture.
- tabulation of recorded data;
- brief but specific details of how the results would then be used to obtain ΔH_{soln} of ammonium chloride.

Precalculation

Let the volume of water used = 50.0cm^3

Since solubility of NH_4Cl in water is 383 g dm^{-3},

Max mass of NH_4Cl that would dissolve in 50.0cm^3 of water = $\frac{383}{1000} \times 50 = 19.15$ g

Let the temperature change be –7 °C.

Heat change = 50 x 4.18 x –7 = –1463 J

Since ΔH_{soln} (NH_4Cl) ≈ +15 kJ mol^{-1},

n(NH_4Cl) = $-\frac{-1463}{15\times10^3}$ = 0.09753 mol

mass of NH_4Cl = 0.09753 x (14.0+4.0+35.5) = 5.218 g

Procedure

1. Using a 50.0 cm^3 burette (or measuring cylinder), transfer 50.0 cm^3 of deionised water into a clean and dry polystyrene cup supported in a 250 cm^3 beaker. Take the initial temperature of the water using the thermometer provided.
2. Using an analytical balance, weigh accurately about 5.22 g of NH_4Cl in a clean and dry weighing bottle. Record the total mass of the weighing bottle and solid NH_4Cl.
3. Empty the solid NH_4Cl into the polystyrene cup, cover the cup with a lid and stir gently using the thermometer to dissolve all the NH_4Cl. Record the lowest temperature reached.
4. Weigh the emptied weighing bottle and record its mass.
5. Repeat steps 1 to 4. Use the data obtained from each experiment to calculate a value for ΔH. Take the average of these two values.

Table of results

Mass of weighing bottle and solid NH_4Cl / g	
Mass of emptied weighing bottle / g	
Mass of solid NH_4Cl used / g	

Lowest temperature reached / °C	
Initial temperature / °C	
Change in temperature / °C	

The change in temperature (ΔT) will be negative as temperature decreases when NH_4Cl dissolves in water. $\Delta T = T_{min} - T_i$

Calculations to determine ΔH_{soln}

Assume specific heat capacity of solution to be 4.18 J cm^{-1} K^{-1}.
Assume no heat absorbed from surroundings.

Energy change for the reaction, q = (50.0)(4.18)(–T) = –209T J

Let mass of NH_4Cl used be m_A g.
Molar mass of NH_4Cl = 53.5 g mol^{-1}

Amount of NH_4Cl used = $\frac{m_A}{53.5}$ mol

Enthalpy change of reaction

$$= -\frac{q}{\text{amount of } NH_4Cl}$$

$$= -\frac{(-209T)(53.5)}{m_A} = +\frac{11181.5T}{m_A} \text{ J mol}^{-1}$$

Since the reaction is endothermic and temperature decreases, enthalpy change of reaction must be positive.

◆◆ Worked Example 7 ◆◆

The neutralisation of an acid by a base is exothermic.

A student suggests that the concentration of sulfuric acid can be determined by measuring the temperature of the solution as the acid is added in small amounts to a known volume of sodium hydroxide in a styrofoam cup.

The student proposes the following hypothesis.

As the acid is added to the alkali, the temperature will rise until the end-point is reached. Upon further addition of acid, there will be a reduction in the temperature of the solution in the cup as the acid added is not reacting and is at a lower temperature than the solution in the cup.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

(a) Use the equation for the reaction to estimate the volume of approximately 0.75 mol dm^{-3} H_2SO_4 needed to neutralise 25.0 cm^3 of 2.00 mol dm^{-3} NaOH.

(b) Using the information given, you are required to write a plan to determine the precise concentration of sulfuric acid.

You may assume that you are provided with:

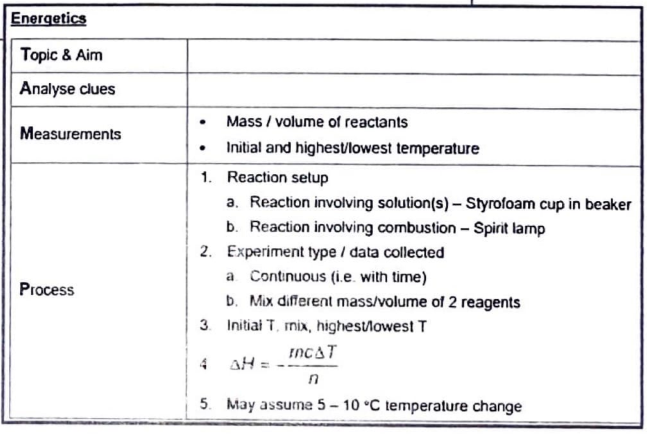
- **FA 1** 2.00 mol dm^{-3} NaOH
- **FA 2** approximately 0.75 mol dm^{-3} H_2SO_4
- burette
- a Styrofoam cup
- a thermometer
- graph paper
- other apparatus normally found in a school or college laboratory

Your plan should include:

- details of the apparatus you would use;
- the procedure you would follow and the measurements that you would take;
- how you would recognise that the end-point had been passed
- an outline of how the results would be obtained and recorded;

(c) Sketch the graph you would expect to obtain as the acid is added. Label the end-point.

(d) Show how the data obtained from the graph would be used to determine the precise concentration of sulfuric acid.



Energetics

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and highest/lowest temperature
Process	1. Reaction setup a. Reaction involving solution(s) – Styrofoam cup in beaker b. Reaction involving combustion – Spirit lamp 2. Experiment type / data collected a. Continuous (i.e. with time) b. Mix different mass/volume of 2 reagents 3. Initial T, mix, highest/lowest T 4. $\Delta H = -\frac{mc\Delta T}{n}$ 5. May assume 5 – 10 °C temperature change

(a) Use the equation for the reaction to estimate the volume of approximately 0.75 mol dm^{-3} H_2SO_4 needed to neutralise 25.0 cm^3 of 2.00 mol dm^{-3} NaOH.

n(NaOH) reacted = 2 x n(H_2SO_4) reacted
Amount of NaOH in 25.0 cm^3 = (25.0 x 10^{-3}) x 2.00 = 5.00 x 10^{-2} mol
Amount of H_2SO_4 needed = ½ x 5.00 x 10^{-2} = 2.50 x 10^{-2} mol

Volume of H_2SO_4 needed = $\dfrac{2.50\times10^{-2}}{0.75} \times 1000$ = 33.3 cm^3

(b) Using the information given, you are required to write a plan to determine the precise concentration of sulfuric acid.

Procedure

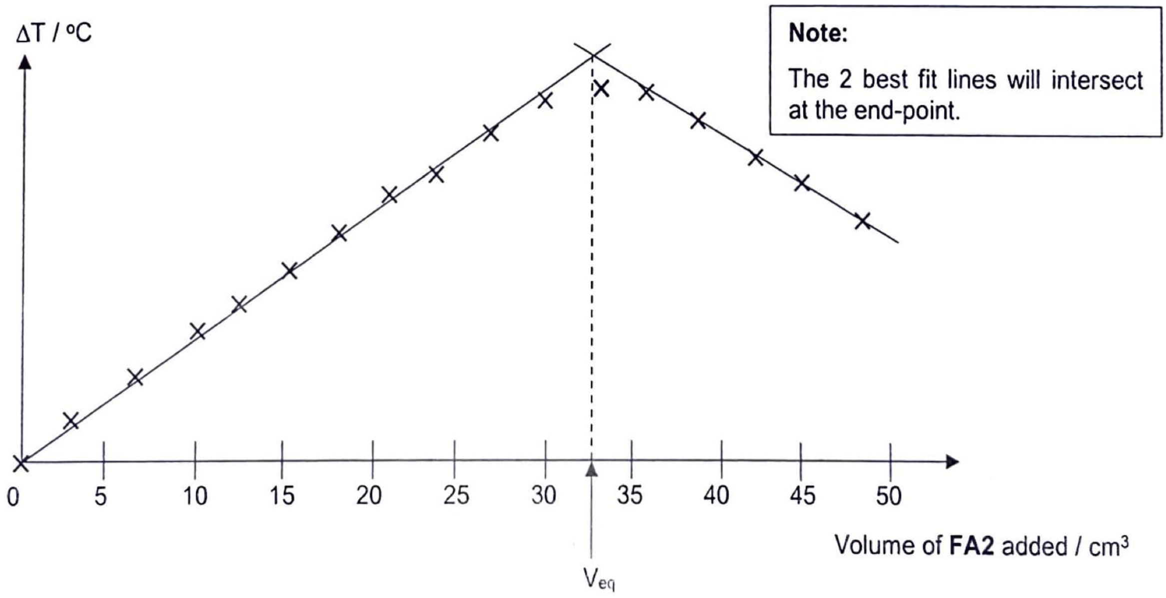
1. Fill a 50.00 cm^3 burette with FA 2.
2. Pipette 25.0 cm^3 of FA 1 into the clean and dry styrofoam cup supported in a 250 cm^3 beaker.
3. Use a thermometer to measure the steady initial temperature of FA 1. Record this temperature, T_i.
4. Run 3.00 cm^3 of FA 2 into the cup. Stir and record the highest temperature observed.
5. Immediately add another 3.00 cm^3 of FA 2 from the burette and repeat the temperature measurement.
6. Repeat step 5 until a total of 48.00 cm^3 of FA 2 has been added.

Results

Volume of **FA2** added / cm^3	Highest temperature / °C	ΔT / °C
0.00		0.0
3.00		
6.00		
9.00		
12.00		
15.00		
18.00		
21.00		

Volume of **FA2** added / cm^3	Highest temperature / °C	ΔT / °C
24.00		
27.00		
30.00		
33.00		
36.00	The end-point is calculated to be 33.3 cm^3. Hence, 5 more readings are taken after the end-point is reached for a reliable plotting of data points. A total of 48.00 cm^3 FA2 is added.	
39.00		
42.00		
45.00		
48.00		

(c) Sketch the graph you would expect to obtain as the acid is added. Label the end-point.



Note:

The 2 best fit lines will intersect at the end-point.

(d) Show how the data obtained from the graph would be used to determine the precise concentration of sulfuric acid.

From **(a)**, amount of H_2SO_4 needed = ½ x 5.00 x 10^{-2} = 2.50 x 10^{-2} mol

Concentration of H_2SO_4 = $\frac{2.50 \times 10^{-2}}{V_{eq} \times 10^{-3}} = \frac{25}{V_{eq}}$ mol dm^{-3}

heat of neutralisation = heat gained by solution

$n(H_2O) \times \Delta H_{neut}^{\ominus} = (m_{soln} \times c_{soln} \times \Delta T)$

$$\Delta H_{neut}^{\ominus} = -\frac{m_{soln} \times c_{soln} \times \Delta T}{n_{H2O}} = -\frac{V_{soln} \times \rho_{soln} \times c_{soln} \times \Delta T}{n_{H2O}} = -\frac{(V_{soln} + V_{soln}) \times \rho_{soln} \times c_{soln} \times \Delta T}{n_{H2O}}$$

♦♦ Worked Example 8 ♦♦

The neutralisation of sulfuric acid by sodium hydroxide is an exothermic reaction.

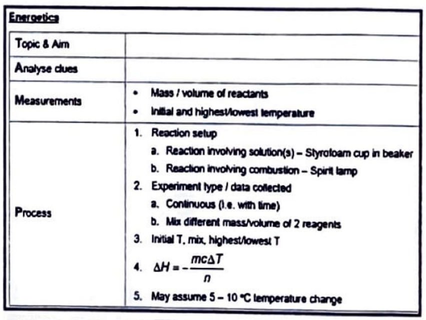
$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l) \quad \Delta H_{neut} < 0$$

The concentration of sulfuric acid and the enthalpy change of neutralisation, ΔH_{neut}, can be determined graphically by measuring the temperature of the solution when different volumes of sulfuric acid and sodium hydroxide are reacted and keeping the total volume of solution constant.

Topic: Energetics
- *mix 2 reagents, measure T after each portion*
- *total volume of solution constant*

(a) Plan an investigation to determine the concentration of sulfuric acid and the enthalpy change of neutralisation, ΔH_{neut}. → *Aim*

You may assume that you are provided with:
- **FA 1** approximately 1.0 mol dm^{-3} H_2SO_4
- **FA 2** 2.0 mol dm^{-3} NaOH
- a Styrofoam cup
- a thermometer
- the equipment normally found in a school or college laboratory



Energetics

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and highest/lowest temperature
Process	1. Reaction setup a. Reaction involving solution(s) – Styrofoam cup in beaker b. Reaction involving combustion – Spirit lamp 2. Experiment type / data collected a. Continuous (i.e. with time) b. Mix different mass/volume of 2 reagents 3. Initial T, mix, highest/lowest T 4. $\Delta H = -\frac{mc\Delta T}{n}$ 5. May assume 5 – 10 °C temperature change

In your plan you should include brief details of:
- the apparatus you would use, → *measuring cylinder, Styrofoam cup*
- the quantities you would use, so that the total volume of solution is 110 cm^3, **Clue**
- the procedure you would follow, → *mix 2 reagents portion by portion, measure T after each portion*
- the measurements that you would take and the tabulation of data.

(b) Sketch the graph you would expect to obtain. On your graph, label
- V_{eq} for the volume of sulfuric acid added
- ΔT_{eq} for the temperature change

when stoichiometric amounts of sulfuric acid and sodium hydroxide has reacted.

(c) Hence, show how the data obtained from the graph would be used to determine the concentration of sulfuric acid and the enthalpy change of neutralisation, ΔH_{neut}.

(d) Explain if the concentration of $Ba(OH)_2(aq)$ be determined using this method.

(a) Plan an investigation to determine the concentration of sulfuric acid and the enthalpy change of neutralisation, ΔH_{neut}.

Pre-calculations

Let V_{eq} cm³ be the volume of sulfuric acid and (110 - V_{eq}) cm³ be the volume of sodium hydroxide used at which stoichiometric amount of sulfuric acid and sodium hydroxide has reacted.

mole ratio of NaOH: H_2SO_4 = 2 : 1
n(NaOH) = 2 x n(H_2SO_4)
$(110 - V_{eq}) / 1000 \times 2.00 = 2 \times V_{eq} / 1000 \times 1.0$
V_{eq} = 55.0 cm³ ; 110 - V_{eq} = 55.0 cm³ *(Note: these are approx. values given approx. conc. of sulfuric acid)*

Hence, there should be at least 5 temperature measurements before AND after V_{eq} = 55.0 cm³

Procedure

1. Using a 100 cm³ measuring cylinder, transfer 10.0 cm³ of **FA 1** into a clean and dry Styrofoam cup supported in a 250 cm³ beaker.
2. Use a thermometer to measure and record the steady initial temperature of **FA 1**.

Experiment	Volume of solutions added / cm³		Initial Temperature of FA 1 / °C	Highest temperature / °C	Temperature change, ΔT / °C
	FA 1	**FA 2**			
1	10.0	100.0			
2	20.0	90.0			
3	30.0	80.0			
4	40.0	70.0			
5	50.0	60.0			
6	60.0	50.0			
7	70.0	40.0			
8	80.0	30.0			
9	90.0	20.0			
10	100.0	10.0			

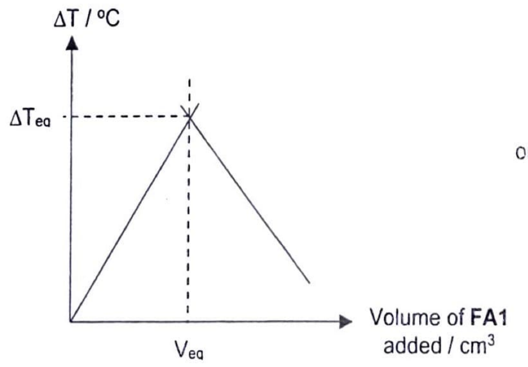
Min. 5 readings before V_{eq} = 55.0 cm³

Min. 5 readings after V_{eq} = 55.0 cm³

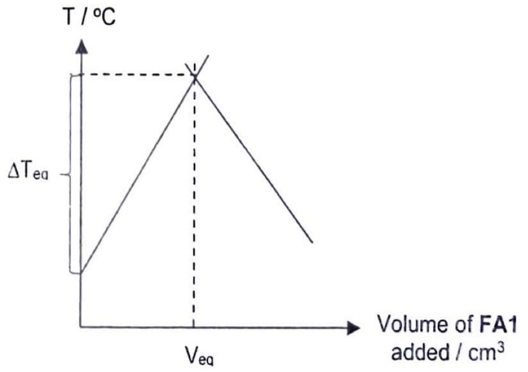
3. Using another 100 cm³ measuring cylinder, measure 100.0 cm³ of **FA 2**. Ensure that both **FA 1** and **FA 2** have the same initial temperature.
4. Add **FA 2** from the measuring cylinder to **FA 1**. Use the thermometer to stir the mixture gently. Measure and record the highest temperature of the mixture.
5. Empty, wash and carefully dry the Styrofoam cup.
6. Repeat steps 1 to 5 using volumes of **FA 1** and **FA 2** in the table below so that the total volume of the mixture is 110 cm³.
7. Record all measurements of volume, temperature and temperature change, ΔT, in the table below.

(b) Sketch the graph you would expect to obtain. On your graph, label
- V_{eq} for the volume of sulfuric acid added
- ΔT_{eq} for the temperature change

when stoichiometric amounts of sulfuric acid and sodium hydroxide has reacted.



or



(c) Hence, show how the data obtained from the graph would be used to determine the concentration of sulfuric acid and the enthalpy change of neutralisation, ΔH_{neut}.

At V_{eq}, n(NaOH) used = $(110 - V_{eq}) / 1000 \times 2.0$ mol = n(H_2O)

n(H_2SO_4) reacted = ½ x n(NaOH) mol

$$\text{Concentration of } H_2SO_4 = \frac{\tfrac{1}{2} \times n(NaOH)}{V_{eq} \times 10^{-3}} \text{ mol dm}^{-3}$$

Assume no heat lost to the surroundings, $q = mc\Delta T_{eq} = +(110 \times c \times \Delta T_{eq})$ J

$$\Delta H_{neut} = -\frac{q}{n_{H2O}} = -\frac{110 \times c \times \Delta T_{eq}}{n_{H2O}} \text{ J mol}^{-1} = -\frac{110 \times c \times \Delta T_{eq}}{n_{H2O} \times 10^{3}} \text{ kJ mol}^{-1}$$

(d) Explain if the concentration of $Ba(OH)_2(aq)$ be determined using this method.

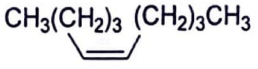
The concentration of $Ba(OH)_2$ cannot be determined using this method as $Ba^{2+}(aq)$ will react with $SO_4^{2-}(aq)$ to form $BaSO_4$ ppt. The enthalpy change of precipitation of $BaSO_4$ will interfere with the temperature measurements leading to inaccurate results.

◆◆ Worked Example 9 ◆◆

Alkynes, which contain C≡C bonds, can undergo partial hydrogenation when added to hydrogen gas in the presence of a poisoned catalyst known as Lindlar catalyst. The partial hydrogenation of 5-decyne to form cis-dec-5-ene is exemplified by the following:

$$CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3 + H_2 \longrightarrow$$

5-decyne



cis-dec-5-ene

However, it is difficult to conduct the experiment in the laboratory to measure the enthalpy change of reaction directly. You are required to plan an experiment to find the enthalpy change of hydrogenation of 5-decyne, ΔH_1, via Hess' Law.

(a) Given that the enthalpy change of combustion of hydrogen is −286 kJ mol⁻¹, state the enthalpy changes that are needed to calculate ΔH_1.

Clue

Topic & Aim

- *Energetics ($\Delta H_{combustion}$)*

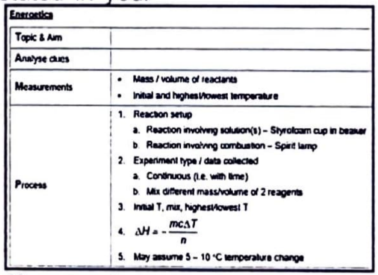
(b) 5-decyne and cis-dec-5-ene are both liquids at room temperature and pressure. Plan an investigation to determine one of the enthalpy changes stated in your answer to **(a)**.

You may assume that you are provided with:

- 5-decyne
- cis-dec-5-ene
- metal calorimeter
- spirit lamp
- a thermometer
- the equipment normally found in a school or college laboratory

In your plan you should include brief details of:

- the experimental set-up and apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements that you would take and the tabulation of data.



Energetics

Topic & Aim	
Analyse clues	
Measurements	• Mass / volume of reactants • Initial and highest/lowest temperature
Process	1. Reaction setup a. Reaction involving solution(s) – Styrofoam cup in beaker b. Reaction involving combustion – Spirit lamp 2. Experiment type / data collected a. Continuous (i.e. with time) b. Mix different mass/volume of 2 reagents 3. Initial T, mix, highest/lowest T 4. $\Delta H = -\frac{mc\Delta T}{n}$ 5. May assume 5 – 10 °C temperature change

Measurements

- *Mass of spirit lamp + 5 decyne*
  - *Before combustion*
  - *After combustion*
- *Blow out flame (stop combustion) when temperature rises by 7 °C.*
- *Temperature of water in calorimeter*
  - *Before combustion*
  - *After combustion*

(c) Describe how you would use the measurements to determine the enthalpy change chosen in **(b)**. You may assume that the density and specific heat capacity of water is 1.0 g cm⁻³ and 4.18 J g⁻¹ K⁻¹ respectively.

(d) List two sources of errors that could affect the accuracy of your results. Discuss how the experimental set-up in your answer to (b) could be improved so as to address these sources of errors.

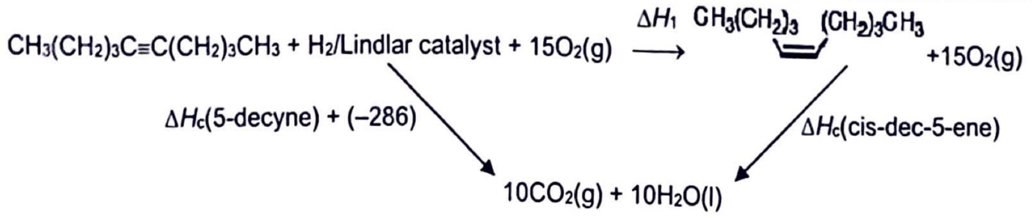
(a) Given that the standard enthalpy change of combustion of hydrogen is –286 kJ mol^{-1}, state the enthalpy changes that are needed to calculate ΔH_1.

Answer

Enthalpy change of combustion of 5-decyne, ΔH_c(5-decyne), and enthalpy change of combustion of cis-dec-5-ene, ΔH_c(cis-dec-5-ene).

Reason

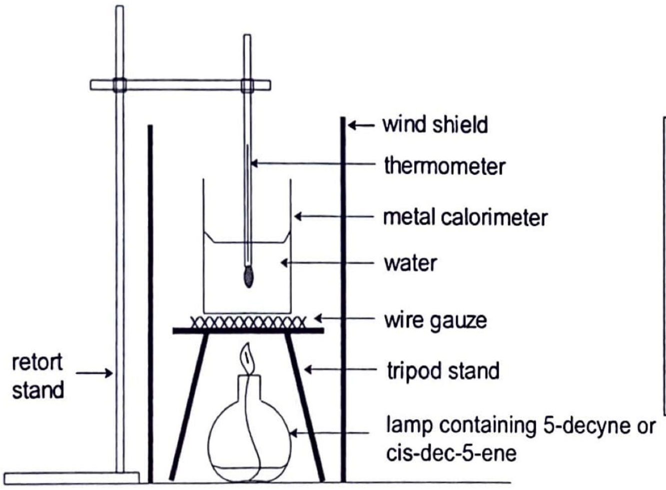
Since the question states that the enthalpy change of hydrogenation of 5-decyne, ΔH_1, is to be determined via Hess' Law and the standard enthalpy change of combustion of hydrogen is given, the following energy cycle can be constructed to determine ΔH_1.



By Hess' Law, enthalpy change of reaction, ΔH_1 = [ΔH_c(5-decyne) – 286] – ΔH_c(cis-dec-5-ene)

Alternatively, you can make use of the equation: $\Delta H_r = \Sigma\, \Delta H_c(\text{reactants}) - \Sigma\, \Delta H_c(\text{products})$

(b) Plan an investigation to determine one of the enthalpy changes stated in your answer to **(a)**.



Set-up should include:

- Spirit lamp with wick partially immersed in fuel (lamp to be placed beneath the calorimeter)
- Calorimeter supported by a tripod stand and wire gauze
- Thermometer (clamped to retort stand) immersed in water inside the calorimeter

Procedure

1. Using a 100 cm^3 measuring cylinder, place 100 cm^3 of water in the calorimeter provided.
2. Using a thermometer, measure and record the steady initial temperature of the water in the calorimeter.
3. Add 5-decyne (or cis-dec-5-ene) to the spirit lamp.
4. Weigh and record the total mass of the spirit lamp and the 5-decyne (or cis-dec-5-ene).
5. Place the spirit lamp under the calorimeter as shown in the set-up.
6. Light the wick of the lamp. When the temperature of the water rises by about 5 – 10 °C, extinguish the flame and record the final temperature of the water.
7. Allow the spirit lamp to cool sufficiently. Then, reweigh the spirit lamp and remaining 5-decyne (or cis-dec-5-ene). Record the new total mass.

Mass of spirit lamp and 5-decyne (or cis-dec-5-ene) before combustion / g	A
Mass of spirit lamp and 5-decyne (or cis-dec-5-ene) after combustion / g	B

Temperature of water in calorimeter before combustion / °C	C
Temperature of water in calorimeter after combustion / °C	D

(c) Describe how you would use the measurements to determine the enthalpy change chosen in **(b)**. You may assume that the density and specific heat capacity of water is 1.0 g cm^{-3} and 4.18 J g^{-1} K^{-1} respectively.

Mass of 5-decyne (or cis-dec-5-ene) combusted = (A – B) g

Amount of 5-decyne (or cis-dec-5-ene) combusted = $\dfrac{(A - B)}{M_r \text{ of 5-decyne (or cis-dec-5-ene)}}$ = E mol

Change in temperature, ΔT = (D – C) °C = (D – C) K
Volume of water used = m cm^3 (or volume of water used in procedure, i.e. 100 cm^3)
Mass of water used = m g
Assume no heat lost to the surroundings,
$q = mc\Delta T = (m)(4.18)(D - C)$ J

Enthalpy change of combustion of 5-decyne (or cis-dec-5-ene)

$$= -\frac{4.18m(D-C)}{E} \text{ J mol}^{-1} = -\frac{4.18m(D-C)}{E \times 10^3} \text{ kJ mol}^{-1}$$

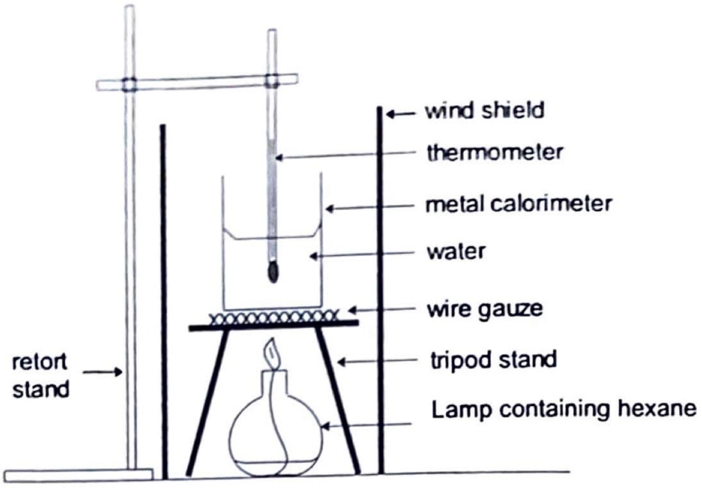
(d) List two sources of errors that could affect the accuracy of your results. Discuss how the experimental set-up in your answer to **(b)** could be improved so as to address the sources of errors.

Possible Errors	**Suggested Improvements**
Incomplete combustion of fuel.	Increase oxygen content of surroundings (e.g. place a beaker of H_2O_2 solution mixed with a small amount of MnO_2 beside the set-up).
Rapid loss of fuel due to evaporation, especially immediately after the flame is extinguished.	Cover the wick with a small cap when the spirit lamp is not in use.
Heat loss from flame due to draughts.	Use a windshield to exclude draughts around the apparatus.
The use of a thermometer with divisions of 1 °C to measure a small temperature change of 5 – 10 °C results in less accurately measured temperatures.	Use a thermometer of higher precision (e.g. measures temperature to 0.1 °C) to improve the accuracy of temperature readings. Or use a thermocouple/data logger with a temperature probe.
The thermometer may have a long response time, e.g. due to a large bulb, leading to lower readings taken (since real/actual readings take longer to be registered). As such, the maximum temperature reached will be lower, making the calculated values of enthalpy changes lower as well.	Use a thermometer with a shorter response time, e.g. smaller bulb, or a thermocouple/data logger with a temperature probe, which would allow fast and easy access to the actual temperature.
*The heat capacity of the calorimeter was not taken into consideration.	*Calibrate the calorimeter used by first conducting a combustion experiment with another fuel for which its ΔH_c is known. (see below - Calibrating a calorimeter)

Calibrating a calorimeter

In most energetics experiment, the heat capacity of the calorimeter is ignored. However, in actual fact, the calorimeter does absorb some of the heat given off by the chemical reaction. If the heat capacity of the calorimeter is to be taken into consideration, the heat capacity of the set-up is first found by using a fuel with a known ΔH_c. E.g. Standard enthalpy change of combustion of hexane, $\Delta H_c^\ominus[C_6H_{14}(l)] = -4163$ kJ mol^{-1} can be used to calibrate the calorimeter. The same set-up (i.e. calorimeter with a specific amount of water) is then used to determine ΔH_c of the sample.

To find the heat capacity of the calorimeter, set up the experiment as shown below, placing hexane inside the spirit lamp. The experiment is conducted as described in the procedure on page 25.



Measurements to be recorded:

Mass of spirit lamp and hexane before combustion / g	P
Mass of spirit lamp and hexane after combustion / g	Q

Temperature of water in calorimeter before combustion / °C	T_i
Temperature of water in calorimeter after combustion / °C	T_f

Treatment of results:
Mass of hexane combusted = (P – Q) g

Amount of hexane combusted = $\dfrac{P-Q}{M_r \text{ of hexane}}$ = R mol

Standard enthalpy change of combustion of hexane, $\Delta H_c^\ominus[C_6H_{14}(l)] = -4163$ kJ mol^{-1}
Heat from combustion of R moles of hexane = – (4163 x R) kJ

Change in temperature, $\Delta T = (T_f - T_i)$ K

Assume no heat lost to the surroundings.
Heat of combustion = Heat absorbed by calorimeter set-up (i.e. metal calorimeter and water)
$-(4163 \times 10^3 \times R) + C\Delta T = 0$ (where C is the overall heat capacity of the metal carlorimeter and water)
$(4163 \times 10^3 \times R) = C(T_f - T_i)$

Heat capacity of calorimeter, $C = \dfrac{4163 \times 10^3 \times R}{T_f - T_i}$ J K^{-1}

Note: With this value, C, we can now conduct the experiment using the same set-up (same metal calorimeter and same mass of water) but replacing hexane with 5-decyne, and subsequently, with cis-dec-5-ene, to determine their respective ΔH_c:

For each compound, $q = C\Delta T$. $\Delta H_c = -\dfrac{q}{n} = -\dfrac{C\Delta T}{n}$, where n is the amount of fuel combusted.

KINETICS

Planning questions in Reaction Kinetics typically fall under two categories.

	"Clock" reaction	Continuous method
Features	Involve measuring the time taken for a stated change to occur. The species responsible for the stated change is the "clock".	Monitor the concentration of a reactant or product species over time. Concentration can be monitored by different methods, including: 1. Sampling and titration 2. Colorimetry 3. Gas collection
Examples	Iodine clock reaction *(2021 Y5 Expt 8)* • Time taken for first appearance of blue-black starch-iodine complex Sulfur clock reaction • Time taken for "X" to be obscured by solid sulfur produced.	• Monitor how concentration of iodine produced changes with time using colorimetry • Monitor how [H_2O_2] changes with time using sampling and titration *(example 11)* • Monitor rate of decomposition of H_2O_2 using gas collection.
Things to note	1. Identify the "clock" 2. If the clock is a reactant, then rate is proportional to V_{clock}/t; if the clock is a product, then rate is proportional to 1/t. 3. Total volume of every experiment is the same. This allows $V_{reactant}$ to be proportional to [reactant]. This can be done by varying the $V_{reactant}$ while keeping the other volumes constant. Water is added to the reaction mixture to keep the total volume constant.	The procedure for a typical sampling and titration consists of the following: 1. Set up reaction. 2. Draw sample from reaction mixture. 3. Quench sample at appropriate time. 4. Use titration to determine concentration of species in quenched sample.

Occasionally, there are planning questions which are even more contextualised and will require the inclusion of more variables (2017 A Levels Planning Question). As such, it is critical to understand the chemistry of the above points and incorporate or modify the experiment according to the context of the question.

First identify whether the experiment involves a clock reaction or uses a continuous method.

Kinetics (Clock reaction)

Topic & Aim	
Analyse clues	
Measurements	• Volume of reactants and water • Time taken for stated change to occur
Process	1. Total volume of every experiment is the same. • Vary volume of one reactant and keep other constant, add water to maintain total volume. 2. $V_{reactant} \propto$ [reactant] 3. Rate $\propto$ 1/t or V_{clock} / t 4. Mix water and reactants. Last reactant added will start reaction. Start stopwatch. 5. Stop stopwatch when stated change occurs.

Kinetics (Continuous method)

Topic & Aim	
Analyse clues	
Measurements	• Time • Concentration (or measure of conc. E.g. colour intensity) at different times.
Process	• Measure concentration (or measure of conc) at different times. • If sampling, quenching, and titration o Mix reactants, last reactant starts the reaction. o Start stopwatch. o Draw **sample** from reaction mixture o **Quench** at pre-determined time. o Use **titration** to determine concentration of species in quenched sample.

◆◆ Worked Example 10◆◆

Topic: Kinetics (Clock reaction)

The initial rate of the reaction between $S_2O_8^{2-}$ and I^- ions can be investigated by the "clock" method, using $S_2O_3^{2-}$ ions. The equations for the reactions are as follow: **Clue**

$$S_2O_8^{2-} + 2I^- \longrightarrow I_2 + 2SO_4^{2-} \qquad \text{reaction I}$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-} \qquad \text{reaction II}$$

When a small but constant amount of $S_2O_3^{2-}$ is added to a reaction mixture, the iodine being slowly produced by reaction I will immediately react in reaction II until all the $S_2O_3^{2-}$ has been used up. At that point, any iodine which is further produced in reaction I will cause a sudden appearance of a deep blue colour in the presence of starch. **Clue**

You are to plan a series of experiments to determine the order of reaction with respect to $S_2O_8^{2-}$ by the "clock" method.

Aim
- *Vary $V_{peroxodisulfate}$ to vary [peroxodisulfate].*

You provided with the following:

- aqueous KI
- aqueous $Na_2S_2O_8$
- aqueous $Na_2S_2O_3$
- stopwatch
- white file
- 100 cm³ beaker
- distilled water
- starch solution
- common apparatus available in a school laboratory

- *Reactants in main reaction : I^- and $S_2O_8^{2-}$*
- *$S_2O_3^{2-}$ is used to delay the observation of I_2.*

The volumes of reagents for the experiment 1 have been predetermined.

Expt No.	Volume of KI / cm³	Volume of $Na_2S_2O_3$ / cm³	Volume of H_2O/ cm³	Volume of $Na_2S_2O_8$, V / cm³
1	5	5	40	10
2				
3				
4				
5				

(a) Complete the table above with appropriate volumes of each reagent.

(b) Describe an experimental procedure that would allow you to determine the order of reaction with respect to $S_2O_8^{2-}$ by the "clock" method.

- *Beaker : mix I^-, $S_2O_3^{2-}$, water and starch.*
- *Add $S_2O_8^{2-}$ from measuring cylinder and start stopwatch.*
- *Stop stopwatch when solution turns blue-black.*

(c) Explain briefly how the results of the experimental procedure can be used to determine the order of reaction with respect to $S_2O_8^{2-}$.

- *$V_{peroxodisulfate} \propto$ [peroxodisulfate]*
- *Rate $\propto$ 1/time*

Note:
- $S_2O_8^{2-}$ will react with the added I^- (from KI) to form I_2
- But, the formed I_2 will react with $S_2O_3^{2-}$ in the solution.
- A constant amt of $S_2O_3^{2-}$ is used, resulting in a constant amt of I_2 being generated to use up the $S_2O_3^{2-}$ before reacting with starch to give the blue black colour.
- The solution will turn blue black (indicating presence of I_2 reacting

(a) Complete the table above with appropriate volumes of each reagent.

Expt No.	Volume of KI / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of H_2O/ cm^3	Volume of $Na_2S_2O_8$, V / cm^3
1	5	5	40	10
2	5	5	30	20
3	5	5	20	30
4	5	5	10	40
5	5	5	0	50

(b) Describe an experimental procedure that would allow you to determine the order of reaction with respect to $S_2O_8^{2-}$ by the "clock" method.

1. Using a 10 cm^3 measuring cylinder, add 5 cm^3 of KI and 5 cm^3 of $Na_2S_2O_3$ to a 100 cm^3 beaker.
2. Using a 50 cm^3 measuring cylinder, add 40 cm^3 of distilled water and 5 drops of starch solution to the same beaker.
3. Place the beaker on a white tile.
4. At an appropriate time, transfer 10 cm^3 of $Na_2S_2O_8$ from a 10 cm^3 measuring cylinder and start the stopwatch at the same time.
5. Record the time taken, t, for the solution to turn blue black.
6. Repeat steps 1 to 5 for Experiments 2 to 5 with varying volumes of distilled water and $Na_2S_2O_8$ according to the table.

Note:

- volume of KI, $Na_2S_2O_3$ and total volume of solution must be kept constant
- rate of reaction ∝ 1/ t and the initial [$S_2O_8^{2-}$] ∝ volume of $S_2O_8^{2-}$ used
- for graph plotting, there should be at least <u>5</u> data points

(c) Explain briefly how the results of the experimental procedure can be used to determine the order of reaction with respect to $S_2O_8^{2-}$.

- Since the same fixed concentration of iodine is formed for each experiment when the stopwatch is stopped, rate of reaction $\propto \frac{1}{t}$.
- Since the total volume of the reaction mixture is kept constant for all the experiments by adding appropriate volumes of water, initial [$S_2O_8^{2-}$] in reaction mixture ∝ V

<u>Method 1 – using $\frac{1}{t}$</u>

Expt No.	Volume of KI / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of H_2O/ cm^3	Volume of $Na_2S_2O_8$, V / cm^3	Time, t / s	$\frac{1}{t}$ / s^{-1}
1	5	5	40	10		
2	5	5	30	20		

Comparing experiments 1 and 2,

When V is doubled and $\frac{1}{t}$ is constant $\Rightarrow \frac{1}{t}$ does not change with change in V ⇒ rate does not change with change in [$S_2O_8^{2-}$] ⇒ order of reaction with respect to $S_2O_8^{2-}$ = 0	When V is doubled, 1/t is doubled $\Rightarrow \frac{1}{t} \propto V$ ⇒ rate ∝ [$S_2O_8^{2-}$] ⇒ order of reaction with respect to $S_2O_8^{2-}$ = 1	When V is doubled, 1/t is increased 4 times $\Rightarrow \frac{1}{t} \propto V^2$ ⇒ rate ∝ [$S_2O_8^{2-}$]^2 ⇒ order of reaction with respect to $S_2O_8^{2-}$ = 2

Method 2 – using $V^n t$

Expt No.	Volume of KI / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of H_2O/ cm^3	Volume of $Na_2S_2O_8$, V / cm^3	Time, t / s	Vt / cm^3 s	V^2t / cm^6 s
1	5	5	40	10			
2	5	5	30	20			

For all the experiments,

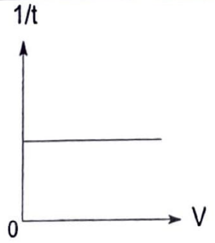
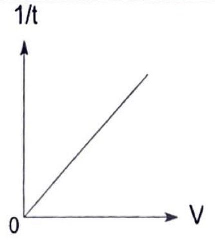
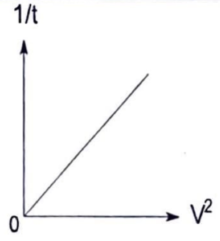
if t = constant,	if Vt = constant,	if V^2t = constant,
$\Rightarrow \frac{1}{t}$ = constant $\Rightarrow \frac{1}{t}$ does not change when V changes $\Rightarrow$ rate does not change with change in $[S_2O_8^{2-}]$ Hence order of reaction with respect to $S_2O_8^{2-}$ = 0	$\Rightarrow V = \frac{constant}{t}$ $\Rightarrow \frac{1}{t} \propto V$ $\Rightarrow$ rate $\propto [S_2O_8^{2-}]$ Hence order of reaction with respect to $S_2O_8^{2-}$ = 1	$\Rightarrow V^2 = \frac{constant}{t}$ $\Rightarrow \frac{1}{t} \propto V^2$ $\Rightarrow$ rate $\propto [S_2O_8^{2-}]^2$ Hence order of reaction with respect to $S_2O_8^{2-}$ = 2

Method 3 – Graphical method using $\frac{1}{t}$

Expt No.	Volume of KI / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of H_2O/ cm^3	Volume of $Na_2S_2O_8$, V / cm^3	Time, t / s	$\frac{1}{t}$ / s^{-1}
1	5	5	40	10		
2	5	5	30	20		
3	5	5	20	30		
4	5	5	10	40		
5	5	5	0	50		

For graphical method, need to have 5 data points for straight line graphs.

Plot a graph of $\frac{1}{t}$ against V

 The graph obtained is a straight horizontal line. $\Rightarrow \frac{1}{t}$ = constant $\Rightarrow$ rate = constant $\Rightarrow$ rate does not change when $[S_2O_8^{2-}]$ changes Hence order of reaction with respect to $S_2O_8^{2-}$ = 0	 The graph obtained is a straight line with a positive gradient and passes through the origin. $\Rightarrow \frac{1}{t} \propto V$ $\Rightarrow$ rate $\propto [S_2O_8^{2-}]$ Hence order of reaction with respect to $S_2O_8^{2-}$ = 1	 The graph obtained is a straight line with a positive gradient and passes through the origin. $\Rightarrow \frac{1}{t} \propto V^2$ $\Rightarrow$ rate $\propto [S_2O_8^{2-}]^2$ Hence order of reaction with respect to $S_2O_8^{2-}$ = 2

NOTE: Alternatively, the graph of $\lg \frac{1000}{time}$ against lgV can also be plotted.

◆◆ Worked Example 11◆◆

You are to investigate the order of reaction with respect to H_2O_2 using a sampling method.

Aim

Topic:
Kinetics (continuous method)
- *Sampling, quench, titration*

Hydrogen peroxide decomposes catalytically according to the following equation:

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

You are provided with the following:

- Aqueous hydrogen peroxide
- Aqueous iron(III) chloride
- Dilute cold sulfuric acid
- 0.02 mol dm^{-3} aqueous potassium manganate(VII)
- 50 cm^3 measuring cylinders
- 50 cm^3 burette
- 25 cm^3 pipettes
- 250 cm^3 beakers
- 250 cm^3 conical flasks
- Stopwatch
- Glass rod

Clue

Iron(III) chloride catalyses the decomposition of hydrogen peroxide

The amount of hydrogen peroxide remaining in the mixture at any time during the reaction may be determined by titration with aqueous acidified potassium manganate(VII). Clue

- ***titration*** *with $KMnO_4$ (need to acidify)*

(a) Write a balanced equation for the reaction between hydrogen peroxide and potassium manganate(VII).

(b) Suggest why cold dilute sulfuric acid needs to be used in this experiment. Clue

- ***Quench*** *using cold reagent (significantly slow down rate of decomposition of H_2O_2)*
- *Acid medium for titration*

(c) Plan an investigation to determine the order of reaction with respect to H_2O_2 using a sampling, quenching and titration method.

You may assume that you are provided with:
- aqueous hydrogen peroxide
- aqueous iron(III) chloride
- cold dilute sulfuric acid
- 0.02 mol dm^{-3} aqueous potassium manganate(VII)
- the equipment normally found in a school or college laboratory

In your plan you should include brief details of:
- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements that you would take and the tabulation of data,
- an outline of how the results would be used to determine the order with respect to hydrogen peroxide.

- *Time (of quenching)*
- *Final burette reading*
- *Initial burette reading*

- *$V(KMnO_4) \propto [H_2O_2]$*
- *Plot $V(KMnO_4)$ against time is equivalent to plotting $[H_2O_2]$ against time.*

(a) Write a balanced equation for the reaction between hydrogen peroxide and potassium manganate(VII).

[O]: $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

[R]: $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

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

(b) Suggest one use of dilute cold sulfuric acid in your experiment.

The addition of the acid dilutes and cools the mixture, significantly reducing the rate of decomposition. H_2SO_4 also serves to provide the acidic medium for the titration with MnO_4^-.

(c) Plan an investigation to determine the order of reaction with respect to H_2O_2 using a sampling, quenching and titration method.

Procedure:

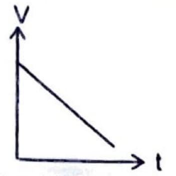
1. Fill a burette with the $KMnO_4$ solution provided.
2. Using a 100 cm³ measuring cylinder, add 100.0 cm³ of the H_2O_2 solution provided to a 250 cm³ conical flask labelled reaction mixture.
3. Using a 10 cm³ measuring cylinder, add 2.0 cm³ of the $FeCl_3$ solution into the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its contents.

   (Note: Since $FeCl_3$ is a catalyst, only a small amount/volume is required.)
4. Using a 50 cm³ measuring cylinder, measure 50.0 cm³ of the cold, dilute H_2SO_4 solution.
5. Using a 10.0 cm³ pipette, transfer 10.0 cm³ aliquot of the reaction mixture to a second 250 cm³ conical flask.
6. At time t = 2 min, transfer the 50.0 cm³ cold, dilute H_2SO_4 solution into the second conical flask and swirl the mixture.
7. Immediately titrate the H_2O_2 in the second conical flask against the $KMnO_4$ solution. The end-point is reached when the solution turns from yellow to orange/pale pink. Record the titration results in the table below.

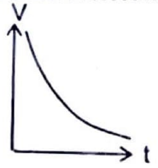
   (Note: End point colour change is yellow (due to Fe^{3+}) to orange (mixture of yellow Fe^{3+} and pink of very dilute MnO_4^-. Also, only one titration is possible for each aliquot)
8. Wash out the second conical flask with water.
9. Repeat steps 4 to 8 at 5-minute interval.

Time from initial mixing, t / min	2	7	12	17	22	27	32	37	42
Final burette reading / cm³									
Initial burette reading / cm³									
Volume of $KMnO_4$ used, V / cm³									

10. Plot a graph of the volume of KMnO4 used against time.



If the graph obtained is a straight downward sloping line, reaction is zero order w.r.t. H_2O_2.



If the graph obtained is a downward sloping curve with a constant half-life, reaction is first order w.r.t. H_2O_2

(Note: Mole ratio of MnO_4^- : H_2O_2 = 2 : 5

At time t, amount of $KMnO_4$ used = $\frac{2}{5}$ x amount of H_2O_2 remaining

volume of $KMnO_4$ x $[KMnO_4]$ = $\frac{2}{5}$ x volume of aliquot x $[H_2O_2]$ remaining

As volume of the aliquots taken were kept constant at 10.0 cm^3,
volume of $KMnO_4 \propto [H_2O_2]$ remaining)

Raffles Institution
Year 6 H2 Chemistry 2023
Planning Experiments 3
Equilibria, Electrochemistry, Organic Synthesis

Lecture Outline

1 Equilibria (Pg 1 – 6)
2 Electrochemistry (Pg 6 – 11)
3 Organic Synthesis (Pg 12 – 22)

Reference

1 Understanding Experimental Planning for Advanced Level Chemistry: The Learner's Approach (by Jeanne Tan and Kim Seng Chan)

EQUILIBRIA

It is important to refer your lecture notes on Chemical Equilibria, Acid-Base Equilibria and Solubility Equilibria for details about the various types of equilibrium systems.

Experiments involving the various equilibria typically involve the following stages.

1. Setup reaction
2. Allow time to reach equilibrium
3. Determine concentrations / amounts of species in equilibrium system using various experimental methods.
4. Use concentrations / amounts to calculate equilibrium constant.

The table below shows the different experimental methods which could be used to determine the concentrations / amounts of species in an equilibrium system.

Experimental Method	Type of Equilibrium	Examples
• Titrimetry (for acid-base, redox or precipitation reactions)	• Equilibrium constant, K_c, of a reversible reaction	• Determine the equilibrium constant, K_c, for the reaction between carboxylic acid and alcohol to form ester and water *[N2015 Planning]*
	• Acid / base dissociation constants of a weak acid / base	• Determine the K_{sp} of potassium hydrogen tartrate (KHT) *[see worked example 3]*
	• Solubility product, K_{sp}, (or solubility) of a sparingly soluble salt	
	• Distribution coefficient, K_D, of a compound which is distributed between two immiscible solvents	• Determine the distribution coefficient, K_D, of iodine between dichloromethane and water *[see worked example 1]*
• Gravimetric analysis (for precipitation reactions)	• Solubility product, K_{sp} (or solubility) of a sparingly soluble salt	• Determine the solubility of cerium(IV) sulfate *[see worked example 2]*
• Colorimetry (relating colour intensity to the concentration of a coloured species)	• Stability constant, K_{stab}, of a complex ion containing an atom or ion of a transition element	• Determine the stability constant, K_{stab}, of a complex ion containing an atom or ion of a transition element

General Guideline

- Identify the type of equilibrium and use a suitable experimental method.
- Bear in mind that any actions you take must not alter the value of the equilibrium constant which you are trying to determine, and that the reaction must have attained equilibrium when measurements are taken.

◆◆ Worked Example 1 ◆◆ [Modified/2015 Y6 CT2/B1]

Dichloromethane (DCM) is a volatile organic solvent. When solid iodine is added to an immiscible mixture of DCM and water, the iodine dissolves completely and is distributed between the aqueous and DCM layers. Subsequently, the following equilibrium is established.

$$I_2(aq) \rightleftharpoons I_2(DCM)$$

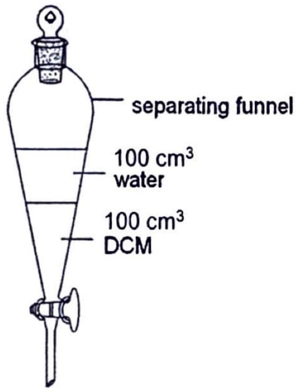
An experiment was conducted to determine the distribution coefficient, K_D, of iodine between DCM and water.

$$K_D = \frac{[I_2]_{DCM}}{[I_2]_{water}}$$

where $[I_2]_{DCM}$ = equilibrium concentration of I_2 in DCM
$[I_2]_{water}$ = equilibrium concentration of I_2 in water

This experiment involves the following stages:
Stage 1 – solid iodine is added to a separating funnel containing DCM and water
Stage 2 – the distribution equilibrium is established and the DCM solution is removed from the separating funnel
Stage 3 – the concentration of iodine in DCM is determined by titration

The experimental set-up is shown below.



To establish the distribution equilibrium in Stage 2, the tap of the separating funnel was held firmly with one hand and the stopper with the other. This is followed by the shaking of the separating funnel vigorously with the tap pointing upwards for 15 mins and opening the tap for a moment and closing it again before shaking the separating funnel again. Lastly, the separating funnel is set aside until the two layers separate.

Clue – how to use separating funnel

Prior to Stage 3, an appropriate concentration of sodium thiosulfate, $Na_2S_2O_3(aq)$, was determined via micro-titration. This involved transferring 10 drops of the DCM solution into a test-tube, followed by 10 drops of deionised water. Sodium thiosulfate was then added drop-wise, *each time stoppering the test tube and shaking vigorously*, until the end point was reached. No starch indicator was required for this titration.

Clue – use titration with $S_2O_3^{2-}$ to determine $[I_2]$
Clue – unusual detail in titration
Clue –no need for indicator

The titration reaction is shown below.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

From the micro-titration results, the sodium thiosulfate solution was diluted to 0.200 mol dm^{-3}.

(a) Suggest why the tap of the separating funnel has to be opened momentarily in Stage 2.

The vigorous shaking causes rapid vaporisation of the volatile dichloromethane. The tap is opened momentarily to release the pressure inside the separating funnel.

(b) Suggest why it was necessary to shake the mixture vigorously during the micro-titration in Stage 3.

The vigorous shaking is necessary to enable the iodine in DCM to migrate to the aqueous layer for reaction with thiosulfate. (Some DI water was added to DCM layer before titration as thiosulfate ions are only soluble in water.)

(c) In Stage 1, 2.00 g of solid I_2 was added to the set-up shown above.

Plan an investigation, from Stage 2 to Stage 3, to determine the partition coefficient, K_D.

Aim - determine K_D of I_2 between DCM and water

You may assume that you are provided with:

- 2.00 g of solid I_2
- 0.200 mol dm^{-3} of aqueous $Na_2S_2O_3$
- 100 cm^3 glass bottle with a screw cap (This must be used instead of a conical flask for titrations involving organic solvents.)
- the apparatus and chemicals normally found in a school or college laboratory

Clue –instead of conical flask

In your plan you should include brief details of:	
• the apparatus you would use, • the quantities you would use,	• *Separation – separating funnel* • *Titration – burette, 25.0 cm^3 pipette, glass bottle with screw cap, no indicator required.*
• the procedure you would follow, ensuring proper use of the separating funnel and careful removal of DCM from the separating funnel,	*Stopper separating funnel, shake vigorously, release pressure, let layers separate.* *Open tap to drain DCM, close tap when DCM is almost drained out.*
• the measurements that you would take to determine the [I_2] in the DCM layer,	*Burette readings of titration of $S_2O_3^{2-}$ against I_2 in DCM layer* *End point colour change - Purple to colourless*
• how you would determine the value of K_D.	*From titration results,* *calculate amt of $S_2O_3^{2-}$* *$\Rightarrow$ amt of I_2 in DCM layer* *$\Rightarrow$ amt of I_2 in aq = amt of I_2 added – amt of I_2 in DCM layer* *Calculate [I_2] in aq and DCM layers $\Rightarrow K_D$*

Procedure

1. Stopper and shake the separating funnel vigorously with the tap pointing upwards. Open the tap for a moment and closing it again before shaking the separating funnel again.
2. Allow the layers to separate in the separating funnel.
3. Remove the stopper. Open the tap of separating funnel and drain the DCM layer into a clean and dry 250 cm^3 beaker. Close the tap when the DCM layer is almost completely drained out. (Note: Beaker needs to be dry to ensure the concentration of I_2 is not affected.)
4. Pipette 25.0 cm^3 of DCM into the 100 cm^3 glass bottle.
5. Fill the 50.00 cm^3 burette with the sodium thiosulfate solution. Record the initial reading.
6. Add 10 cm^3 of water to the glass bottle using a 10.0 cm^3 measuring cylinder.
7. Add small quantities of the sodium thiosulfate from the burette into the glass bottle, stopper the bottle with the screw cap and shake the bottle well.
8. Continue titrating until the DCM layer turns from purple to colourless. Record the final reading of the burette.
9. Repeat the titration until at least 2 consistent titres are obtained (± 0.10 cm^3).

Calculations

Let the **average** volume of $Na_2S_2O_3$ used in titration = **V** cm^3

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

Amount of I_2 in the 25.0 cm^3 DCM layer = (V x 0.200) / 2 = 0.10V mol

Concentration of I_2 in the DCM layer = (0.10V / 25) x 1000 = **4V mol dm^{-3}**

Amount of I_2 in the 100 cm^3 DCM layer = 0.10V x 4 = 0.4V mol

Amount of I_2 in 100 cm^3 aqueous layer = [2.0/2(127) – 0.4V] = (0.00787 – 0.4V) mol

Concentration of I_2 in aqueous layer = (0.00787 – 0.4V) / 0.100 = **(0.0787 – 4V) mol dm^{-3}**

K_D = 4V / (0.0787 – 4V)

(d) Identify one potential safety hazard in this experiment and state how you would minimise the risk.

- Experiment should be carried out in the fume cupboard to avoid inhalation of the toxic DCM fumes/vapour.
- There should be no naked flames near the set-up as DCM is flammable.

◆◆ Worked Example 2 ◆◆ [modified from 2012 Y6 CT2/B1]

The **solubility** of cerium(IV) sulfate, at a particular temperature, is defined as:
*the mass of cerium(IV) sulfate that will dissolve in and just **saturate** 100 g of solvent at that temperature.*

Clue – definition of solubility

A **saturated** solution is one in which no more solid can dissolve at a particular temperature. In a saturated solution with undissolved solid, the following equilibrium is established.

$$Ce(SO_4)_2(s) \rightleftharpoons Ce^{4+}(aq) + 2SO_4^{2-}(aq)$$

Cerium(IV) sulfate is unusual as its solubility decreases when the temperature of the solution increases.

Clue – temperature of mixture must be maintained

(a) Plan a procedure to determine the solubility of cerium(IV) sulfate in water.

Aim – determine the solubility of cerium (IV) sulfate in water

You may assume that you are provided with:

- 60 cm³ deionised water in a 150 cm³ conical flask
- solid cerium(IV) sulfate, $Ce(SO_4)_2$,
- filter funnel and filter paper
- water bath
- thermometer
- the apparatus and equipment normally found in a school or college laboratory.

Your plan should include • practical details of how you would - prepare a saturated solution in 60 cm³ of deionised water,	• add small portions of solid to the water, stir to dissolve, until some solid remain undissolved, let it reach equilibrium.
- maintain the temperature of the mixture,	• use thermostatically controlled water bath
- separate the saturated solution from the undissolved solid,	• filter mixture using **dry** filter funnel and **dry** filter paper
- ensure that an **accurate** and **reliable** value of solubility of cerium(IV) sulfate in water is obtained.	To determine solubility, I need • mass of $Ce(SO_4)_2$ dissolved in filtrate • mass of water in filtrate Heat-cool-weigh filtrate. *Reliable results – repeat expt*
• brief, but specific details of how the results would then be used to obtain - the mass of cerium(IV) sulfate in the saturated solution, - the solubility of cerium(IV) sulfate in water.	

1. Place the conical flask with the deionised water in a thermostatic water bath which is maintained at the temperature at which the solubility of $Ce(SO_4)_2$ is to be found. Place a thermometer into the flask to monitor the temperature of the water.
2. Add a little $Ce(SO_4)_2$ to the deionised water and stir the mixture with a glass rod. Continue adding $Ce(SO_4)_2$, with stirring, until some remained undissolved. Allow time (e.g. 10 min) for the mixture to reach equilibrium.
3. Using an electronic balance, weigh a clean and dry evaporating dish. Let its mass be m_1.
4. Using a dry filter funnel and filter paper, filter the mixture into the evaporating dish. Weigh the mass of the evaporating dish with the filtrate. Let the mass be m_2.
5. Using a Bunsen burner, heat the evaporating dish with its contents gently at first, then strongly for 10 minutes.
6. Cool and weigh the evaporating and its contents.
7. Repeat the heat-cool-weigh process until there is no further change in mass. Let the final mass be m_3.

8. Mass of $Ce(SO_4)_2$ in filtrate = mass of residue after heating = $m_3 - m_1$
Mass of deionised water in filtrate = $m_2 - m_3$
9. Solubility of $Ce(SO_4)_2$ in water

$$= \frac{\text{mass of } Ce(SO_4)_2 \text{ in filtrate}}{\text{mass of DI water in filtrate}} \times 100$$

$$= \frac{m_3 - m_1}{m_2 - m_3} \times 100$$

10. Repeat steps 1-9 for to obtain another value of the solubility of $Ce(SO_4)_2$ in water to ensure reliability.

◆◆ Worked Example 3 ◆◆ [modified 2016 Y6 CT2/B1]

The extent to which sparingly soluble salts dissolve in water is indicated either by the solubility or solubility product of the salt. A saturated solution is one in which no more solid can dissolve at a particular temperature.

Potassium hydrogen tartrate, $KHC_4H_4O_6$ (KHT), is a sparingly soluble salt. In a saturated solution with the undissolved solid KHT, the following equilibrium is established.

$$KHC_4H_4O_6(s) \rightleftharpoons K^+(aq) + HC_4H_4O_6^-(aq)$$

(a) Write an expression for the solubility product, K_{sp}, of KHT.

$K_{sp} = [K^+][HC_4H_4O_6^-]$

The hydrogen tartrate ion, $HC_4H_4O_6^-$ (HT^-), is a weak monobasic acid and its concentration in the saturated solution of KHT can be determined by titration with a strong base like sodium hydroxide of known concentration.

Use acid-base titration
- *WA-SB titration*
- *Thymolphthalein indicator (not methyl orange)*

(b) The solubility of KHT in deionised water at 25 °C is approximately 0.032 mol dm^{-3}.

In a titration experiment, 20.00 cm^3 of 0.0400 mol dm^{-3} aqueous sodium hydroxide was needed to neutralise a saturated solution of KHT at 25 °C.

Calculate the volume of saturated solution of KHT used in the titration.

$n(HC_4H_4O_6^-) = n(NaOH) = 20.00 / 1000 \times 0.0400 = 0.000800$ mol
Volume of saturated solution of KHT used = $0.000800 / 0.032 \times 1000$ = <u>25.0 cm^3</u>

(c) Plan an investigation to determine the solubility of KHT in deionised water at 25 °C. You should plan to prepare 100 cm^3 of saturated KHT solution, separated from any undissolved solid.

Aim - determine solubility of KHT in DI water at 25 °C

You may assume that you are also provided with:

- solid potassium hydrogen tartrate (KHT)
- deionised water
- 0.0400 mol dm^{-3} aqueous sodium hydroxide
- methyl orange
- thymolphthalein — Indicator for titration
- filter funnel and filter paper
- water bath — Maintain mixture at 25 °C
- thermometer
- the equipment normally found in a school or college laboratory

In your plan, you should include brief details of:

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

Prepare 100 cm^3 saturated KHT solution, w/o any undissolved solid
- *Add KHT(s) into 100 cm^3 of water until no more solid can dissolve, filter through dry filter funnel and filter paper.*
- *Maintain temperature using thermostatically controlled water bath set at 25 °C*
- *Measurements - Volume of water*

Titrate filtrate again NaOH provided
- *Volume of filtrate used = 25 cm^3 from part (b)*
- *Thymolphthalein indicator*
- *Measurements – Initial and final burette readings*

1. Using a 50 cm^3 measuring cylinder, transfer 100 cm^3 of deionised water into a 250 cm^3 conical flask.
2. Immerse the flask in a water bath maintained at 25°C and place a thermometer into the flask to monitor the temperature of the solution.
3. Add solid potassium hydrogen tartrate (KHT) into conical flask, stirring using a glass rod, until no more solid can dissolve.
4. Allow the solution to stand for 30 minutes with occasional stirring or swirling to ensure that the system has reached equilibrium i.e. solution is saturated.
5. Filter the solution through a dry filter paper and dry filter paper into a dry 250 cm^3 conical flask.
   (Note: Dry filter paper and conical flask is used to prevent any water diluting the saturated solution)
6. Pipette 25.0 cm^3 of KHT solution into a 250 cm^3 conical flask. Add 2-3 drops of thymolphthalein indicator into the conical flask.
7. Titrate the solution against 0.0400 mol dm^{-3} aqueous sodium hydroxide in the burette. The end-point is reached when the solution in the conical flask changes from colourless to pale blue colour.
8. Repeat the titration to get at least two consistent results (i.e. at least two titres which do not differ by more than 0.10 cm^3).

ELECTROCHEMISTRY

- Identify the type of cell you are required to plan for

Type of Cell	Examples
Electrochemical (Voltaic) cell • Essentially a battery • Converts chemical energy to electrical energy	• Determine the standard reduction potential of a BrO_3^-/Br^- cell • Construct a battery which produces a cell potential of +2.1 V • Determine the effect of concentration on the cell potential • Determine the concentration of copper(II) sulfate by measuring the cell potential of the zinc/copper electrochemical cell at various concentrations of copper(II) sulfate solution *[see worked example 5]*
Electrolytic cell • Electric current is passed through a chemical system to bring about a redox reaction which is, otherwise, non-spontaneous. • External source of electricity required • Converts electrical energy to chemical energy	• Determine a value for Avogadro's constant via the electrolysis of lead(II) bromide *[see worked example 4]* • Determine the charge of an ion through electrolysis

◆◆ Worked Example 4 ◆◆

Lead(II) bromide is an ionic compound which melts at 373 °C. Lead metal has a melting point of 327 °C.

Plan an investigation to determine a value for Avogadro's constant by using an electrolysis experiment involving molten lead(II) bromide. The electrolysis should be conducted for 30 minutes at a current of 3.0 A.

You may assume that you are provided with:

- powdered $PbBr_2$,
- DC power supply adjustable to 12 V,
- wires and crocodile clips,
- ammeter,
- crucibles,
- pipe-clay triangle
- Bunsen burner,
- graphite rods,
- two-hole rubber bung,
- thermometer (0 to 500 °C)
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- a fully-labelled diagram of the set-up you would use,
- the procedure you would follow,
- the measurements that you would take,
- how you would ensure that an **accurate** and **reliable** value of the Avogadro's constant is obtained.
- how your results can be used to obtain a value of Avogadro's constant.

Aim - *determine value for Avogadro's constant, using electrolysis of molten $PbBr_2$.*

How to determine Avogadro's number, N_A?

- It is the number of particles in one mole.
- amt of Pb = $\dfrac{\text{no. of Pb atoms}}{\text{Avogadro's no}}$

Let mass of Pb
obtained from electrolysis = m
amt of Pb = (m / 207.2) mol

$$\boxed{\begin{aligned} &Q = It = (\text{no. of } e^-)(1.6\times10^{-19}) \\ &\text{no. of } e^- = \frac{(3.0)(30\times60)}{1.6\times10^{-19}} = 3.375\times10^{22} \\ &\text{Since } Pb^{2+} + 2e^- \rightarrow Pb \\ &\text{no. of Pb} = (0.5)(3.375\times10^{22}) = 1.688\times10^{22} \end{aligned}}$$

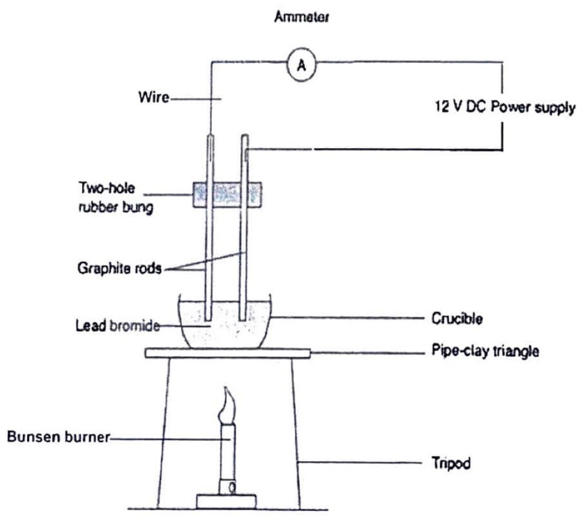
- Tripod stand with pipe clay triangle and crucible
- Bunsen burner to melt $PbBr_2$
- Wires + crocodile clips + ammeter + DC power
- Calculate mass of $PbBr_2$ to use based on 3.0 A and 30 min.

- Melt solid, connect setup, adjust current, run expt for 30 min, lower T to 350°C, decant the liquid Pb to another preweighed crucible and let it cool.

- Current at 3.0A
- 30 min experiment time
- Mass of Pb obtained

- Repeat experiment to ensure reliability.

Solutions



Precalculations

$It = n_eF \Rightarrow (3.0)(30)(60) = n_e(96500)$

$\Rightarrow n_e = 0.05596$ mol

$\Rightarrow n_{Pb^{2+}} = 0.05596(0.5) = 0.02798$ mol $= n_{PbBr2}$

$\Rightarrow$ mass of $PbBr_2 = 0.02898(207.2 + 79.9 + 79.9) = 10.6$g

Mass of $PbBr_2$ used should be more than 10.6g so that the electrons provided by the DC supply are used for reaction. Use 15g of $PbBr_2$ in this experiment.

Procedure:

1. Assemble the set-up, as shown in the diagram above, in a fume cupboard. The two graphite electrodes are inserted into a two-hole rubber bung and clamped to a retort stand.
2. Weigh accurately about 15 g of powdered lead(II) bromide in a crucible.
3. Insert the graphite rods into the solid lead(II) bromide such that the rods almost touch the bottom of the crucible.
4. Light the Bunsen burner and use a non-luminous flame to heat the crucible strongly.
5. When all the solid has melted, switch on the power supply and adjust the current to 3.0 A. Start a stopwatch at the same time.
6. Continue heating the crucible and maintaining the current for 30 minutes.
7. At the end of 30 minutes, switch off the power supply and remove the graphite rods.
8. Turn off (or lower) the Bunsen burner and allow the temperature to decrease to 350 °C. Decant the molten lead metal into a second crucible while keeping any solid $PbBr_2$ in the first crucible. Allow the contents in both crucibles to cool.
9. Rinse the lead metal with hot deionised water to remove any residual $PbBr_2$.
10. Dry the solid lead in a desiccator, weigh the clean and dried lead metal on an electronic balance.
11. Repeat the experiment. Use the mass readings obtained to calculate two different values for Avogadro's constant. Take the average of these two calculated values.

Note: Possible safety considerations

- Bromine gas, which is toxic, is produced during the electrolysis. The experiment must be carried out in a fume cupboard.
- The crucible will be very hot after strong heating. Metal tongs should be used when handling the hot crucible.

Calculations

$Pb^{2+} + 2e^- \rightarrow Pb$

Let the mass of Pb(s) obtained be **m** grams.

Amount of Pb(s) obtained = (**m** / 207) mol

Amount of charge passed = 30 x 60 x 3.0 = 5.40×10^2 C

Charge of 1 e^- = 1.60×10^{-19} C

Number of electrons transferred = (5.40×10^2 C) ÷ (1.60×10^{-19} C) = 3.375×10^{22}

Number of Pb atoms in **m** grams = $3.375 \times 10^{22} \div 2 = 1.688 \times 10^{22}$

Number of Pb atoms in 1 mol of Pb = (1.688×10^{22}) ÷ (m / 207) = (3.49×10^{24}) / **m**

Hence, Avogadro's constant = (3.49×10^{24}) / **m**

◆◆ Worked Example 5 ◆◆

The Nernst equation allows cell potentials to be predicted when the conditions are non-standard.

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{nF}\ln Q$$

where E_{cell} = cell potential at non-standard conditions,
$E^{\ominus}_{cell}$ = standard cell potential,
R = molar gas constant,
T = temperature in Kelvins,
n = amount (in moles) of electrons transferred,
F = Faraday's constant,
Q = reaction quotient.

(a) Write a balanced equation for the reaction in a zinc/copper electrochemical cell when a current is allowed to flow through the cell.
(b) Calculate the standard cell potential, $E^{\ominus}_{cell}$, for the zinc/copper cell in **(a)**.
(c) Write an expression for the reaction quotient, Q.
(d) Using your answers to **(b)** and **(c)**, and appropriate values of n and T, write the Nernst equation for the zinc/copper cell in **(a)**.

(a) $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

(b) $E^{\ominus}_{cell} = (+0.34) - (-0.76) = +1.10$ V

(c) $Q = [Zn^{2+}] / [Cu^{2+}]$

(d) n = 2, T = 298 K

$$\therefore E_{cell} = 1.10 - \frac{8.31(298)}{(2)(96500)}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10 - 0.0128\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

(e) Plan an investigation to determine accurately the concentration of copper(II) sulfate solution, **X**, whose concentration is between 1.00×10^{-4} mol dm^{-3} and 1.00 mol dm^{-3} graphically by measuring the cell potential of the zinc/copper electrochemical cell at various concentrations of copper(II) sulfate solution.

Aim
- obtain graph of cell potential (E_{cell}) of zinc/copper cell at varying $[Cu^{2+}]$
- determine $[Cu^{2+}]$ in solution X from graph obtained.

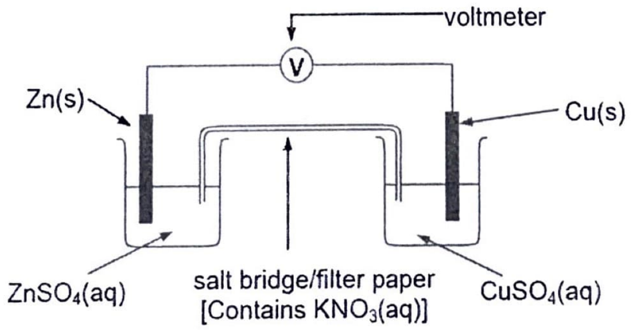
You may assume that you are provided with:

• 1.0 mol dm^{-3} copper(II) sulfate solution	*Dilute Cu^{2+} solutions from this stock solution*
• saturated potassium nitrate solution • filter paper strip	*Salt bridge*
• 25 cm^3 volumetric flasks • 10 cm^3 burette	*For dilution of Cu^{2+}*
• water bath • thermometer	*Maintain temperature*
• copper electrode	*For Cu^{2+}/Cu half cell*
• high resistance voltmeter	
• wires and crocodile clips	
• a standard Zn/$ZnSO_4$ half-cell	
• the apparatus and chemicals normally found in a school or college laboratory	

In your plan you should include brief details of:	*To prepare Cu^{2+} of different concentrations – 10 cm^3 burette, 25 cm^3 volumetric flasks. Do consecutive 10-time dilution. 1 mol dm^{-3} to 0.1 mol dm^{-3} to 0.01 mol dm^{-3}... 0.0001 mol dm^{-3} (5 data points).*
• the apparatus you would use, • the quantities you would use to prepare copper(II) sulfate solution of suitable concentrations	*To measure cell potential* - *Copper half-cell (copper electrode, Cu^{2+} solutions)* - *Zn half-cell (provided)* - *Wires, crocodile clip, voltmeter* - *Salt bridge – filter paper soaked with $KNO_3(aq)$*
• a fully-labelled diagram of the set-up you would use,	*Volume of Cu^{2+} to be diluted – 2.50 cm^3 dilute to 25 cm^3 (10-time dilution) E_{cell} from voltmeter.*
• the measurements that you would take,	*From (d), $E_{cell} = 1.10 – 0.0128 \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$*
• the graph that you would plot, with reference to your answer in **(d)**,	*Plot a graph of E_{cell} against $\ln \frac{1}{[Cu^{2+}]}$ since $[Zn^{2+}] = 1.0$ mol dm^{-3} in standard Zn^{2+}/Zn half cell.*
• how you would ensure that an **accurate** and **reliable** value of **X** is obtained.	*Measure E_{cell} of the unknown copper(II) sulfate solution using same setup. Use the graph plotted and find the corresponding $\ln \frac{1}{[Cu^{2+}]}$ and $[Cu^{2+}] = 1/(e^y)$, where y is the value of $\ln \frac{1}{[Cu^{2+}]}$.*

1. To prepare 1.00×10^{-1} mol dm^{-3} $CuSO_4(aq)$, use a 10.00 cm^3 burette to transfer 2.50 cm^3 of 1.00 mol dm^{-3} $CuSO_4(aq)$ into a 25 cm^3 volumetric flask labelled **A**.
2. Top up the flask to the 25 cm^3 mark with deionised water. Stopper the flask and shake the solution to ensure homogenous mixing.
3. To prepare the solutions in flasks **B**, **C** and **D**, repeat steps 1 and 2 using the solutions from flasks **A**, **B** and **C** respectively.

Volumetric flask	$[Cu^{2+}(aq)]$ / mol dm^{-3}	Volume of solution from appropriate flask / cm^3	E_{cell} / V
--	1.00	--	
A	1.00×10^{-1}	2.50 cm^3 of 1.00 mol dm^{-3} $CuSO_4(aq)$	
B	1.00×10^{-2}	2.50 cm^3 from flask **A**	
C	1.00×10^{-3}	2.50 cm^3 from flask **B**	
D	1.00×10^{-4}	2.50 cm^3 from flask **C**	



<u>Experiment set-up and obtaining readings for cell potential</u>

4. Set up the electrochemical cell shown in the diagram above.
5. Place two clean and dry beakers in a thermostatically controlled water bath. Fill one beaker with 1.00 mol dm^{-3} zinc sulfate solution and fill the other beaker with 1.00 mol dm^{-3} copper(II) sulfate solution.
6. Place a thermometer into each solution and make sure that the temperature in both solutions is the same at 298 K.
7. Connect one end of a wire to the voltmeter and the other end of the wire to the zinc electrode using a crocodile clip. Immerse the zinc electrode into the 1.00 mol dm^{-3} zinc nitrate solution.
8. Repeat step 7 for the copper electrode and the 1.00 mol dm^{-3} copper(II) sulfate solution.
9. Soak a strip of filter paper in saturated potassium nitrate solution. Place one end of the filter paper into the beaker containing the zinc sulfate solution and the other end into the beaker containing the copper(II) sulfate solution. (This is to serve as the salt bridge)
10. Record the reading on the voltmeter.
11. Repeat steps 4 to 10 using copper(II) sulfate solution of four other concentrations, using a new salt bridge each time.

How to use experimental results to determine concentration of X

$[Zn^{2+}] = 1.00$ mol dm^{-3}

$$E_{cell} = 1.10 - 0.0128 \ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Use the data obtained to plot E_{cell} against $\ln\frac{1}{[Cu^{2+}]}$. A straight line should be obtained.

Measure E_{cell} of the unknown copper(II) sulfate solution. Use the graph to find the corresponding value of $\ln\frac{1}{[Cu^{2+}]}$, say Y. $[Cu^{2+}]$ in **X** = $1/(e^{Y})$

The organic chemist works with covalent compounds, in which strong covalent bonds are often broken and made. Such reactions may be very slow and heating may be required. These reactions usually involve side reactions which produce unwanted side products from which the intended products must be separated and purified.

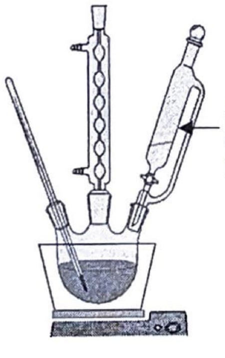
Hence, there are four main steps in organic synthesis experiments:

1	**Reaction**	• the appropriate reaction is carried out and a crude sample of the desired product is obtained at the end of reaction
2	**Isolation / Separation**	• the crude sample of the product is separated from the reaction mixture. • majority of impurities are removed here.
3	**Purification**	• the crude product is purified • remaining trace impurities are removed here.
4	**Identification**	• the identity and purity of the obtained compound is confirmed

1. Reaction

When planning for an organic synthesis reaction, it is important to consider the **type of setup** to be used, **how the reagents should be mixed** and consequently the **temperature control** required.

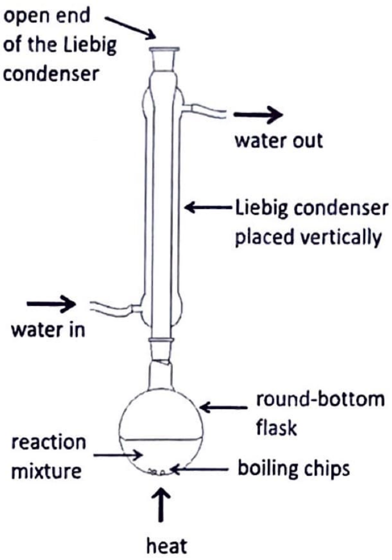
- **Mixing of reagents**
  It is important to consider how the reagents should be mixed. Some reactions require careful mixing of reagents or cooling the reaction flask to reduce side reactions. For example,

Source	Instruction in question	Rationale
N2010/II/Q2	Reaction flask was **1.** cooled in an ice-water bath, before **2.** addition of conc. H_2SO_4 dropwise via a *dropping funnel* into the reaction flask.  ***Dropping funnel*** containing conc. H_2SO_4.	The dilution of a concentrated acid when added to a reaction mixture is highly exothermic and the heat generated causes side reactions (candidates were required to identify possible side products). **1.** cooling the reaction mixture in an ice-water bath prevents temperature from increasing excessively during the addition of the concentrated acid. **2.** dropwise addition using dropping funnel controls the amount of acid being diluted and hence the amount of heat evolved
N2011 Planning	"Equimolar amounts of 2-hydroxybenzenecarboxylic acid and ethanoic anhydride are used, together with about 8-10 drops of 85% phosphoric acid which catalyses the reaction. *When mixing the reactants, the initial reaction may be violent.*"	Candidates were required to mention that the 1. reaction mixture was cooled, and 2. conc. phosphoric acid was added dropwisely with swirling. This controls the heat evolved and prevents the initial reaction from being violent.

- **Reaction setups**
  Some common reaction setups – cooled or room temperature reactions – can be used in some organic

reactions. However due to the volatility of most organic solvents, reactants and products, a reflux setup is often used.

- **Heating under reflux**
  "Heating under reflux" is often used to increase the efficiency and safety of the reaction. In this technique, the reagents are heated together in a flask which has a Liebig condenser fitted **vertically** above it. Vapour from the boiling mixture enters the condenser, cools and condenses, and flows back into the flask. (Note: The cooling water enters the condenser at the bottom to ensure that the temperature is the coolest at the bottom and all vapour will be condensed without any loss.)



  Advantages of boiling under reflux:

  1) The reaction can take place at or near the boiling point of the reactants/products/solvents without any loss of the reagents/products/solvents by evaporation.
  2) Immiscible reactants are constantly agitated and brought into more intimate contact – the contents of the flask not only splash about gently during boiling, but constantly have liquid dripping from above.

  (Note: The boiling chips are to ensure smooth boiling by letting small vapour bubbles form within the porous chips.)

  Safety Considerations:

  As organic reactions often involve flammable organic compounds or solvents, the use of any naked flames should be avoided.

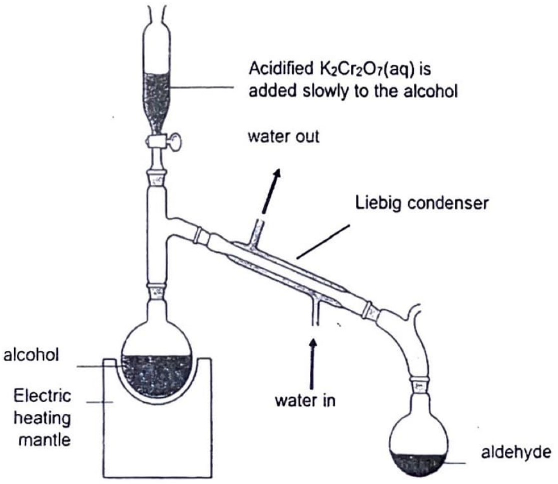
  Refer to section on *Temperature control* for some heat sources which can be used.

- **Distillation**
  Methods such as distillation can be considered a reaction setup even though it is usually used for isolation or purification.

  For example, $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat with immediate distillation}]{K_2Cr_2O_7,\ H_2SO_4(aq)} CH_3CH_2CH_2CHO$

  In the oxidation of butan-1-ol to butanal, the reaction occurs in the round bottom flask and the product, butanal, is immediately distilled out of the reaction mixture to prevent further oxidation. This is possible because the boiling point of butanal is lower than that of butan-1-ol.

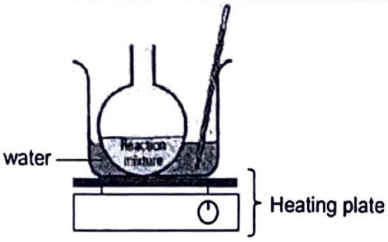
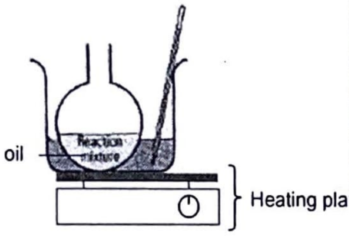
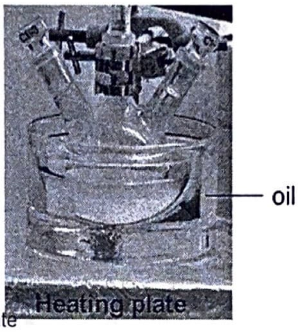
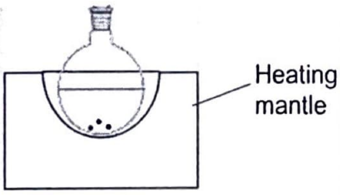
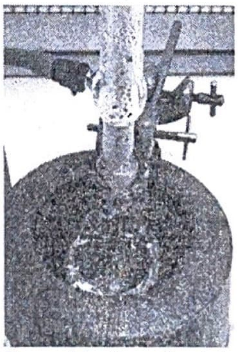
  Note: In the distillation setup, the Liebig condenser is fitted almost horizontally.



- **Temperature control**
  - Bunsen flames should be avoided when planning organic synthesis experiments because most organic

compounds and solvents are highly flammable.

- The table below shows a *general guide* to the temperatures attainable by the different heat sources. Images of these heat sources can be easily found on the Internet.

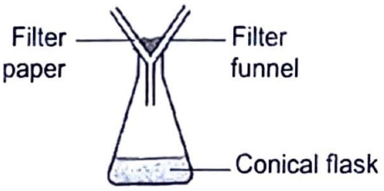
Type	Diagram	Remarks
Ice baths	 Ice bath/thermometer	• By varying the amount of ice added. • For reactions which are highly exothermic • Reagent should be added **with stirring** to prevent localised heating
Water bath (with heating plate)		• By varying temperature setting of heating plate • Highest temperature attainable is limited by boiling point of water • Can be used for reflux setups which boil at temperatures < 100°C
Oil bath (with heating plate) 		• By varying temperature setting of heating plate. • Safety concerns – when droplets of water come into contact with a hot oil bath, the hot oil will splatter out of the bath.
Heating mantle 	 Round bottom flask in heating mantle	• Runs on electricity, no heating plate required. • Vary heat setting of heating mantle • **Convenient heat source** for use with round bottom flasks.  **Heating mantle**

2. Isolation / Separation

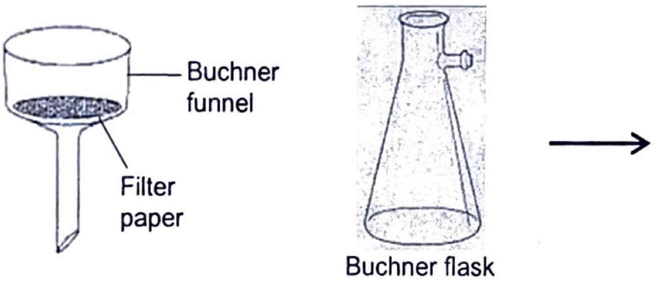
- In this step, majority of the impurities will be removed.
- The technique of separation to be used depends on the type of mixture to be separated. This depends on the nature of the product and impurities.

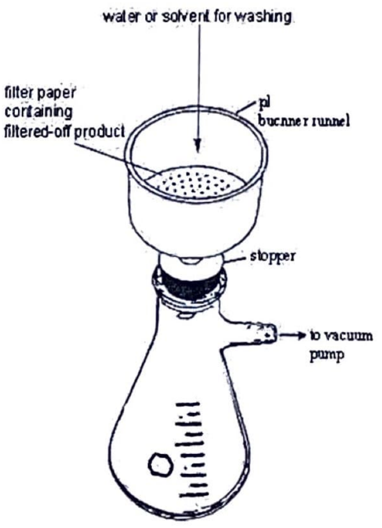
Separation of insoluble solid in a liquid	:	Filtration
Separation of two miscible liquids	:	Distillation
Separation of two immiscible liquids	:	Extraction using separatory funnel

- **Filtration – separation of insoluble solid in a liquid**



1. Gravity filtration
   This technique uses gravity to draw the filtrate through the filter paper, leaving the residue on the filter paper.
2. Vacuum filtration
   This technique uses vacuum (instead of gravity) to separate the filtrate from the residue





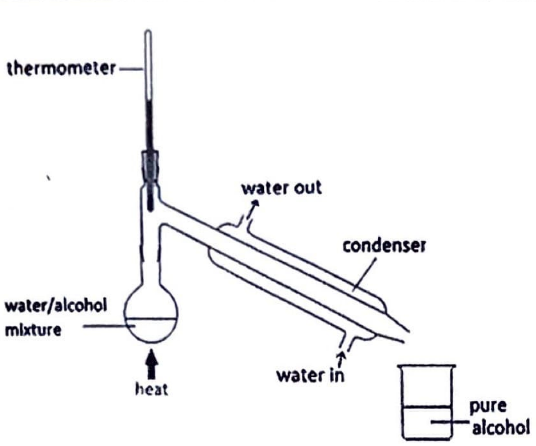
General procedure (vacuum filtration)
1. Place filter paper into the Buchner funnel and attach to Buchner flask.
2. Wet filter paper with solvent and apply vacuum.
3. Swiftly pour the solid–liquid mixture onto the Buchner funnel.
4. Wash the solid residue with some cold solvent to remove impurities on the residue.

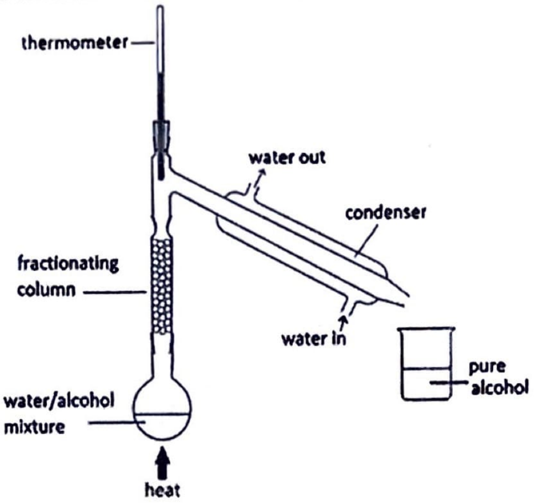
- **Distillation – separation of miscible liquids**

Simple distillation:
If two liquids have boiling points that differ significantly (e.g. by at least 10 °C), it is usually possible to separate them by distillation. The mixture of the two liquids is heated such that the mixture boils. The lower boiling liquid will start to boil first and its vapour will rise from the liquid mixture. The vapour is led to the condenser where it condenses to the liquid state. The lower boiling liquid will be collected first since it boils at a lower boiling point. By repeating this process of distillation, two miscible liquids can be separated.

Fractional distillation:
Introducing a fractionating column into the setup improves the separation between the liquids being distilled, especially when the liquids have similar boiling points. The fractionating column allows the process of distillation to be repeated a large number of times all at once. The vapour rises in the column and as it does so, the higher boiling liquid begins to condense and run down. With suitable adjustment of the heating rate, only the vapour of the lower boiling liquid reaches the side arm and enters the condenser. As the vapour travels up the column, the vapour becomes richer in the lower-boiling component since the higher boiling component condenses. On the other hand, as the liquid runs down the column, it becomes richer in the higher boiling component as the lower boiling component vaporises. This process of fractional distillation can repeat many times the process of boiling and condensing within the single piece of apparatus.

Simple distillation	Fractional distillation

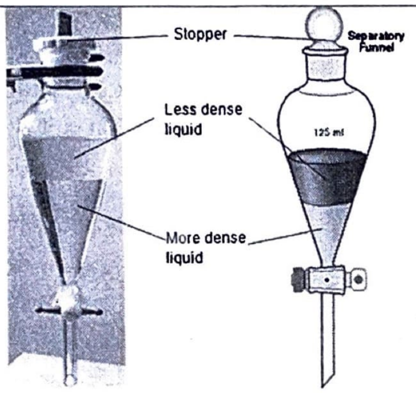




(Note: The column of the fractional distillation is packed with glass beads to provide a greater surface area for the vapour to condense.)

- **Extraction – separation of immiscible liquids**

Mixture of liquids which are immiscible (and with different densities) can be separated using a **separatory funnel** (refer to diagram below). The liquids will separate into layers in the separatory funnel, with the denser liquid at the bottom and the less dense liquid on top. With the stopper removed, the bottom layer is slowly released through the tap until the interface between the layers is just going through the tap. After discarding the interface, the top layer is then run out, from the top of the funnel, into another clean flask.



Solvent	Density (g cm^{-1})
H_2O	1.00
Diethyl ether ($CH_3CH_2OCH_2CH_3$)	0.71
Dichloromethane (CH_2Cl_2)	1.33

For mixture of H_2O and diethyl ether:

- Top layer (diethyl ether)
- Bottom layer (water)

For mixture of H_2O and dichloromethane:

- Top layer (water)
- Bottom layer (dichloromethane)

This technique is particularly **useful in separating organic products from an aqueous reaction mixture.** The cold reaction mixture is shaken with successive amounts of a water-immiscible organic solvent. Each time, the organic layer is run off and collected before fresh organic solvent is added. The organic product will distribute itself between water and organic solvent until equilibrium is reached, but more will dissolve in the organic layer. Two or three extractions with a suitable solvent will remove most of the organic product.

IMPORTANT! When the mixture is shaken in the separatory funnel, the pressure in the funnel should be periodically released. This is to avoid pressure build-up in the separatory funnel, especially if a gas is produced in the process. The pressure build-up will cause the stopper to be pushed out and the organic product might be lost.

In order to remove traces of residual water in the organic solvent, anhydrous reagents such as anhydrous $MgSO_4$ and anhydrous Na_2SO_4 are used. These anhydrous salts absorb water found in the organic solvent and become hydrated, thereby removing the residual water.

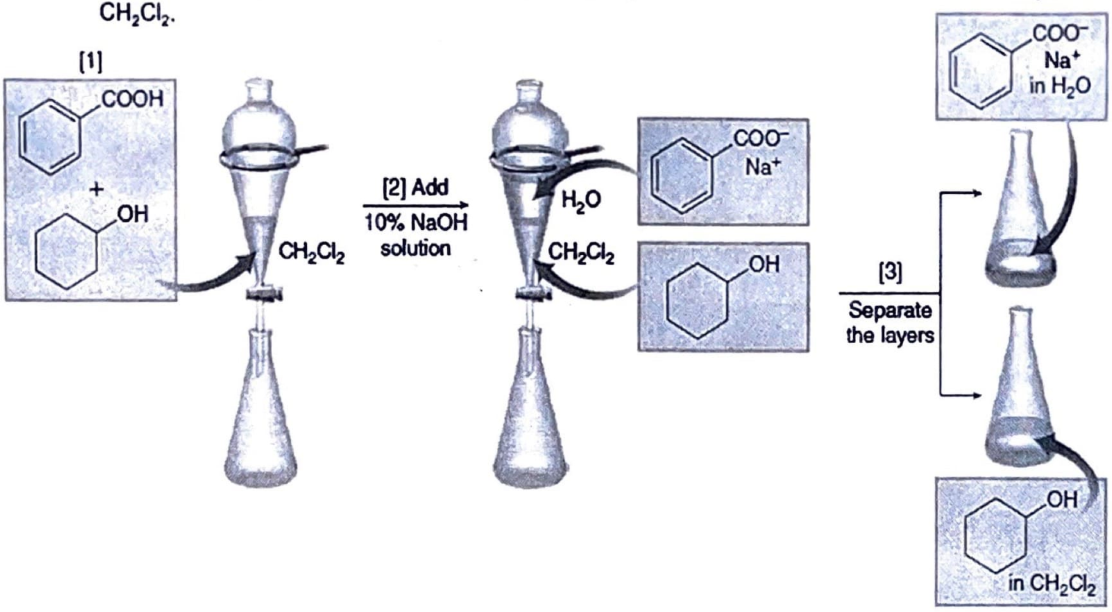
The dehydrating agents can then be removed from the organic solvent via filtration.

Example: Separation of benzoic acid and cyclohexanol by extraction

Step [1] Dissolve benzoic acid and cyclohexanol in CH_2Cl_2.

Step [2] Add 10% NaOH solution to form two layers.

Step [3] Separate the layers.



- Both compounds dissolve in the organic solvent CH_2Cl_2.

- Adding 10% aqueous NaOH solution forms two layers. When the two layers are mixed, the NaOH deprotonates C_6H_5COOH to form $C_6H_5COO^-Na^+$, which dissolves in the aqueous layer.
- The cyclohexanol remains in the CH_2Cl_2 layer.

- Draining the lower layer out the bottom stopcock separates the two layers, and the separation process is complete.
- Cyclohexanol (dissolved in CH_2Cl_2) is in one flask. The sodium salt of benzoic acid, $C_6H_5COO^-Na^+$ (dissolved in water) is in another flask.

3. Purification

The majority of impurities have been removed in the previous separation step. In this step, final traces of impurities will be removed.

- **Distillation – purification of liquids**
  If the intended organic product is a liquid, distillation can be used as a means of purification.

- **Recrystallisation – purification of solids**
  The key feature of this technique is that
  - the solubility of the desired product increases with increasing temperature in a particular solvent, **AND**
  - the impurities are soluble in the solvent at all temperatures

	Solubility in	
	hot solvent	cold solvent
Solid product	Yes	No
Impurities	Yes	Yes

General procedure (in this case, the solvent used is water)

1. Transfer the crude mixture into a 50 cm³ conical flask *(not beaker)* with a few boiling chips.
2. Add about 5 cm³ (small amount) of water into the flask and place it on a heating plate.
3. When the mixture is boiling and the crude mixture does not dissolve, add water slowly to the mixture until the crude mixture just dissolves.
4. Remove the flask from the heating plate and allow it to cool to room temperature slowly before cooling in an ice-water bath. Crystals will grow as the mixture is cooled.
5. Filter the cooled mixture (e.g. using vacuum filtration) and wash the residue (product) with cold deionised water to remove the impurities.
6. Dry the residue under the Infrared lamp.

4. Identification

In this step, the identity and purity of the purified product with be determined.

Identity	Determined through Infra–red spectroscopy and NMR spectroscopy (data is available in the A level *Data Booklet*)
Purity	The melting point of a solid or the boiling point of a liquid can be used to ascertain its purity. For a pure compound, it should melt or boil over a narrow temperature range (~1°C)

Measurement of melting point:

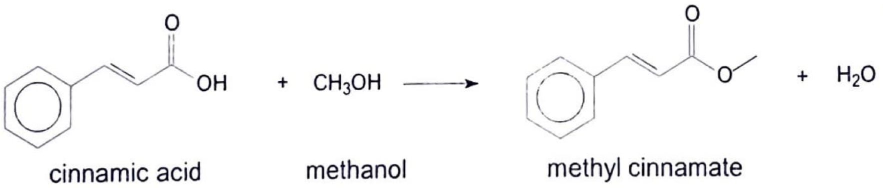
A pure solid will melt over a very small temperature range. If there are impurities present, then the solid will gradually melt over a temperature range (a few degrees Celsius).

Method:
A small sample of the dry solid is placed in a melting point tube and the temperature is raised very gradually. The temperature at which the solid melts, i.e. the temperature when the crystalline solid structure collapses and a meniscus is formed in the sample tube, is recorded as the melting point of the solid.

♦♦ Worked Example 6 ♦♦[Modified 2013 Y6 CT2/B1]

The *Matsutake* mushroom is a delicacy added to many Japanese foods. One of the components isolated from these mushrooms is methyl cinnamate which gives these mushrooms a rich and spicy aroma.

Methyl cinnamate can be prepared from cinnamic acid and methanol.



compound	cinnamic acid	methanol	methyl cinnamate
molar mass / g mol^{-1}	148	32	162
boiling point / °C	300	65	261
melting point / °C	133	–98	38

(a) 10.8 g of cinnamic acid was reacted with 30 cm³ of methanol, which was in excess, together with about 8 to 10 drops of concentrated sulfuric acid. The volume of methanol used was about 10 times more than the actual volume needed as a reactant. The addition of concentrated sulfuric acid to the mixture was highly exothermic.

The reaction mixture was then heated under reflux for about five hours before the unreacted methanol was recovered by distillation.

Techniques used – reflux and distillation

Aim - Prepare methyl cinnamate using cinnamic acid, methanol and concentrated sulfuric acid

(i) You are to plan an experiment to prepare methyl cinnamate.
You may assume that you are provided with:

- two 100 cm³ round bottom flasks,

  1 reaction flask for reflux
  1 more flask to collect methanol in distillation.

- condenser,

  For reflux and for distillation

- heating mantle,

  Heat source

- thermometer,
- the apparatus and chemicals normally found in a school or college laboratory

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,

  - *reflux setup*
  - *distillation setup*
  - *10.8 g of cinnamic acid by mass*
  - *30 cm³ of methanol by volume using measuring cylinder*
  - *Conc H_2SO_4 dropwise*

- how you would ensure that the reaction is conducted under the appropriate conditions.

  "addition of conc H_2SO_4 to mixture is highly exothermic"
  - cool reaction mixture prior to adding
  - stir mixture after during addition to prevent localized heating

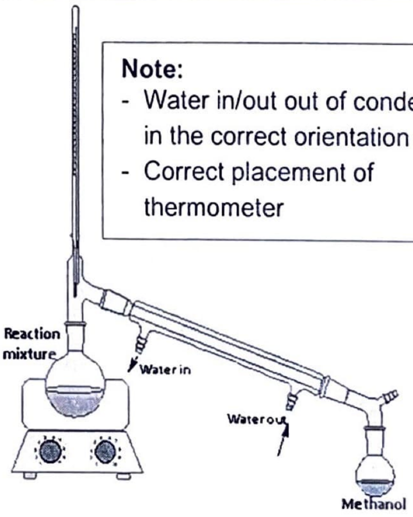
- a fully-labelled diagram of the set-up you would use, to allow the remaining methanol from the reaction mixture to be recovered. Indicate the temperature at which methanol can be collected.

  Only distillation setup diagram required. Heating under reflux not required.

  Check BP of methanol vs the other reagents
  - collect at 65 °C

1. Weigh out accurately 10.8 g of cinnamic acid into a 100 cm³ round bottom flask.
2. Using a 50 cm³ measuring cylinder, add 30 cm³ of methanol into the cinnamic acid in the flask.
3. Place the flask in an ice bath to cool down the reaction mixture as sulfuric acid is added.
4. Using a glass dropper, add 8 – 10 drops of concentrated sulfuric acid to the mixture in the flask.
5. Place the round bottom flask on the heating mantle and heat the reaction mixture using a reflux setup for five hours.
6. Switching off the heating mantle and allow the setup to cool slightly.
7. Dismantle the reflux setup and assemble the distillation setup as shown on the right.
8. Turn on the heating mantle to carry out distillation. Collect the methanol fraction at 65 °C.

Note:
- Water in/out out of condenser in the correct orientation
- Correct placement of thermometer

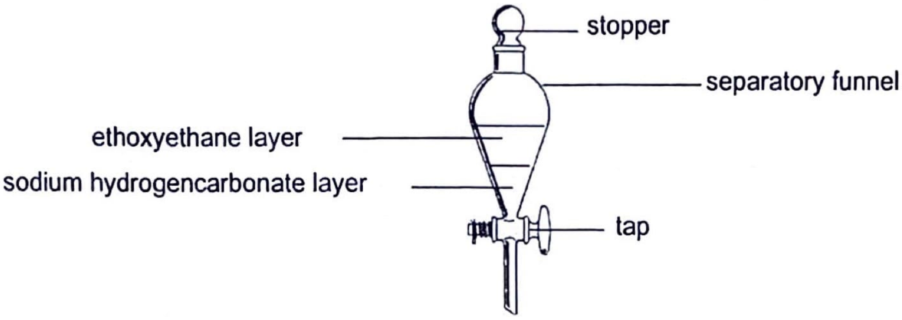


(ii) The excess methanol was used to drive the equilibrium positon to the right. Suggest another reason why methanol was used in excess for this experiment.

Methanol is used as a solvent to dissolve the 10.8 g of cinnamic acid.

(b) The methyl cinnamate was purified according to the following procedure:

1. Transfer the reaction mixture containing methyl cinnamate and unreacted cinnamic acid to a separatory funnel.
2. Add 50 cm^3 of ethoxyethane, $CH_3CH_2OCH_2CH_3$, to the separatory funnel.
3. Add 50 cm^3 of saturated sodium hydrogencarbonate solution to the separatory funnel.
4. Shake the mixture and discard the lower aqueous layer.



5. Repeat Steps **3** and **4** until no more effervescence in the aqueous layer is observed.

Suggest why the mixture must be washed with saturated sodium hydrogencarbonate solution until no more effervescence was observed.

To remove the unreacted cinnamic acid and sulfuric acid catalyst.

(c) The ethoxyethane layer was collected and dried with anhydrous calcium chloride. The ethoxyethane was then evaporated to recover the crude methyl cinnamate, which was subsequently purified by recrystallisation and air-dried.

Two possible solvents, **A** and **B** can be used for the recrystallisation of methyl cinnamate. The table below gives data about the solubility of methyl cinnamate in solvents **A** and **B**.

	Solubility of methyl cinnamate /g per 100 g of solvent	
Temperature / °C	Solvent **A**	Solvent **B**
10	6.0	2.0
70	11.0	9.5

During recrystallisation, 50 g of one of these solvents was saturated with the methyl cinnamate at 70 °C and the solution was then cooled at 10 °C.

(i) Explain why the use of solvent A, rather than solvent B, would lead to a lower yield of recrystallised methyl cinnamate.

(ii) Calculate the final mass of methyl cinnamate that would be obtained if solvent B was used.

(i) The difference in solubilities of methyl cinnamate in solvent **A** is less than that in solvent **B**, thus, less methyl cinnamate will crystallise out of the solvent upon cooling.

(ii) When 50 g of solvent B is used, only 4.75 g of methyl cinnamate would dissolve.
After cooling to 10 °C, 1.0 g of methyl cinnamate will remain dissolved. Hence, mass of methyl cinnamate recovered = 4.75 – 1.0 = 3.75 g

(d) With reference to relevant data from the question, explain how you would check the purity of your product.

To test the purity, collect some crystals and determine its melting point in a melting point tube. If the methyl cinnamate is pure, the melting point would be sharp and it will melt completely between 37 – 39 °C.(or melt completely within 38±1°C)

♦♦ Worked Example 7 ♦♦[N2011/P2/1]

Aspirin was one of the first drugs to be produced synthetically and is one of the most widely used 'over-the-counter' drugs in the world. It is a white solid and is prepared by an acylation reaction between 2-hydroxybenzenecarboxylic acid and ethanoic anhydride.

$HOC_6H_4CO_2H$	$(CH_3CO)_2O$	$CH_3CO_2C_6H_4CO_2H$
2-hydroxybenzenecarboxylic acid	ethanoic anhydride	aspirin

2-Hydroxybenzenecarboxylic acid is a white crystalline solid.
Ethanoic anhydride is a corrosive liquid which has a density of 1.08 g cm^{-3}.
Pure aspirin has a melting point of 135 °C.

- *purify by recrystallization*
- *for precalculations?*
- *check purity using melting point*

Like most organic reactions, the yield of this reaction is less than 100%. Using the procedure described below, a typical yield of pure aspirin is 75%.

- *for precalculations*

Equimolar amounts of 2-hydroxybenzenecarboxylic acid and ethanoic anhydride are used, together with about 8 – 10 drops of 85% phosphoric acid which catalyses the reaction. When mixing the reactants, the initial reaction may be violent.

- *for precalculations*
- ***cool acid and anhydride in ice bath b4 mixing, dropwise addition of phosphoric acid while mixing*

The reaction mixture is then heated under reflux conditions for around fifteen minutes. About 2–3 cm^3 of water is then added to the hot reaction mixture to hydrolyse any unreacted enthanoic anhydride. The addition of this water may cause the mixture to boil.

- ***add water dropwise*

Once the reaction has subsided, the reaction is poured into about 50 cm^3 of cold water. This causes the aspirin to precipitate. The crude aspirin product is purified by recrystallisation from water.

- *solid aspirin is suspended in cold water now – filter to obtain crude aspirin*

(a) Write a balanced equation for the formation of aspirin.

$$\boxed{HOC_6H_4COOH + (CH_3CO)_2O \rightarrow CH_3CO_2C_6H_4CO_2H + CH_3COOH}$$

(b) You are to plan an experiment to prepare 10 g of aspirin.	*Calculate amt of carboxylic acid and anhydride* - *equimolar* - *75% purity*
You may assume that you are provided with: • round bottom flask, • condenser, • heating mantle, • thermometer, • the apparatus and chemicals normally found in a school or college laboratory	*These are for reflux setup* *- reaction flask* *- condenser* *- heat source*
In your plan you should include brief details of:	
• the apparatus you would use,	*Apparatus – reflux setup, electronic balance (mass measurement of carboxylic acid), measuring cylinder (volume measurement of anhydride). beakers. conical flasks for crystallization.*
• the quantities you would use,	*Mass of carboxylic acid from pre-calculation* *Volume of anhydride from pre-calculation*

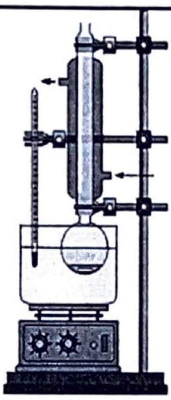
• a fully-labelled diagram of the set-up you would use,	*Reflux setup*
• how you would ensure that the reaction is conducted under the appropriate condition,	*See **points above*
• how you would purify the aspirin and check the purity of your sample.	*- Recrystallisation to purify* *- Check melting point is 135 °C*

Pre-calculations:

Amt of aspirin = 10 / 180 = 0.05556 mol

Amt of 2-hydroxybenzenecarboxylic acid required
= Amt of ethanoic anhydride
= 0.05556 x 100/75
= 0.07408 mol

Mass of 2-hydroxybenzenecarboxylic acid required
= 0.07408 x 138 = 10.2 g (3 s.f.)
Mass of ethanoic anhydride required
= 0.07408 x 102
= 7.56 g (3 s.f.)



Note:
The direction for water in and water out, the open top and a safe way of heating are important marking points!

Procedure:

1) Using an electronic balance, weigh out accurately about 10.2 g of 2-hydroxybenzenecarboxylic acid in a round bottom flask.
2) In a fumehood, measure out 7 cm^3 of ethanoic anhydride using a 10 cm^3 measuring cylinder and add the anhydride to the round bottom flask while stirring with a glass rod. *(Note: As the anhydride is a corrosive liquid, it is not safe to take its mass on a weighing balance. Instead, its volume, which can be determined from its density and the mass calculated, is used.)*
3) Cool the reaction mixture in an ice bath placed inside a fumehood until the mixture is cold.
4) Using a dropper, add 8-10 drops of 85% phosphoric acid to the mixture carefully, swirling the flask after every drop.
5) Set up the apparatus for reflux as shown. Heat the mixture under reflux for 15 minutes.
6) Detach the flask from the set-up. Using a dropper, add 2-3 cm^3 of water dropwise to the mixture, swirling constantly. If the mixture becomes too hot, stop adding water. Cool in an ice bath before further addition of water.
7) When the reaction has subsided, pour the mixture into a beaker containing 50 cm^3 of cold water. Filter the crude product that is precipitated.
8) Transfer the residue into a small beaker. Carefully add hot water dropwise and stir until the aspirin just dissolves. A minimal volume of hot water should be used.
9) Let the mixture cool to room temperature. Crystals will start to grow as the solution cools. Cool the mixture further in an ice bath to ensure all the aspirin has crystallised. Filter and dry the residue to obtain pure aspirin.
10) Weigh the dried aspirin.
11) To test the purity, collect some crystals and determine the melting point. If the aspirin is pure, the melting point should be very close to 135 °C and the melting should be completed within a very small temperature range.

(c) Identify **one** potential safety hazard in this experiment and state how you would minimise this risk.

The anhydride and phosphoric acid are corrosive. Wear gloves and goggles when handling the chemicals / do the experiment in a fumehood. **OR** The solution may boil over when water is added to remove unreacted anhydride. Wear goggles and lab coat when performing this step. **OR** Organic compounds are flammable. Any heating should be done using a water bath and not with a naked flame.