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# H2 CHEMISTRY (9729) CHEMISTRY PRACTICAL

# ESSENTIALS OF PLANNING EXPERIMENTS WORKED EXAMPLES AND PRACTICE QUESTIONS



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# 1 Volumetric Analysis

Volumetric analysis involves the use of a **standard solution (a solution of known concentration)** in **determining the amount of analyte present in the sample**. A **titration** is performed by slowly adding a standard solution from a burette (titrant) to a solution of the analyte in a conical flask (titrand) until the end-point is reached.

Direct titration:The titrand is titrated with a standard solution of the titrant.Back titration:In certain circumstances, the titrand cannot be titrated directly because:

- No suitable indicator is available
- The titration reaction is too slow
- There is no useful direct titration reaction

In these cases, an **excess** of a standard solution of a substance which reacts quantitatively with the titrand is added and the **unreacted** standard solution is titrated with the titrant.

#### **Common Types of Titration**

Type of titration	Titrand and titrant	End-point detection						
		Colour change due to indicator added						
		type of titration marked p			arked pH change	suitable indicator		
		strong acid - stro	ong base		4 – 10	Methyl orange, screened methyl orange, thymolphthalein		
		strong acid – we	ak base	3	8.5 – 6.5	Methyl orange, screene orange	ed methyl	
		weak acid - stro	ng base	7.	.5 – 10.5	Thymolphthalein		
Acid-base	Acid + Base	weak acid – wea	ik base	nc	o marked change	No suitable indicator		
					oolour in			
		Indicator	approxim pH rang	ate e	acid solution	at end-point	alkaline solution	
		methyl orange	3.1 – 4.	.4	red	orange	yellow	
		screened methyl orange	3.1 - 4.4		violet	grey	green	
		thymolphthalein	9.3 – 10.	9.3 – 10.5		light blue (alkaline) colourless (acidic)	blue	
	Reducing agent + Oxidising agent	Colour change due to redox species involved						
		<ul> <li>MnO<sub>4</sub><sup>-</sup> (purple) to Mn<sup>2+</sup> (colourless) in acidic medium</li> </ul>						
Redox		<ul> <li>Cr<sub>2</sub>O<sub>7<sup>2-</sup></sub> (orange) to Cr<sup>3+</sup> (green) in acidic medium</li> </ul>						
		• $I_2$ in the presence of starch indicator (dark blue) to $I^-$						
		(colourless) [lodometric titration]						
Thermometric	Reagents that lead to endo/exo reaction	Maximum/mi	nimum te	emp	<b>perature</b> r	eached		
Complexiometric	Metal cation + Ligand	See page 13 details.	of Chemi	stry	Practical	Planning Handboo	k for	
Precipitation	lons that form a precipitate	See page 13 details.	of Chemi	stry	Practical	Planning Handboo	k for	

### Related Topics and Concepts (this list is non-exhaustive)

- Atoms, molecules and stoichiometry *e.g.* Determine amount of acid/base present in the sample (acid-base titration)
- Redox chemistry e.g. Determine amount of redox species present in the sample (redox titration)
- Chemical Energetics e.g. Determine thermochemical values of the sample (thermometric titration) Note: this will be covered under Section 4: Energetics
- Chemical and Ionic Equilibria *e.g.* Determine amount of reactant/product present in the sample at equilibrium (acid-base / redox titration)

#### Refer to pages 12 to 16 of Chemistry Practical Planning Handbook for more details.

#### 1.1 Acid-Base Titrations

#### Worked Example 1A: Direct Titration

A solid sample contains about 80% by mass of Na<sub>2</sub>CO<sub>3.</sub>

You are to design an experiment in which the percentage purity by mass of Na<sub>2</sub>CO<sub>3</sub> 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<sub>2</sub>CO<sub>3</sub> sample
- Standard titration apparatus
- 0.100 mol dm<sup>-3</sup> dilute HCl

(a) Calculate a suitable mass of sample to be used.

# Pre-calculation:

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

Suppose *m* g of impure Na<sub>2</sub>CO<sub>3</sub> sample is to be dissolved in water and made up to 250 cm<sup>3</sup> in a volumetric flask and 25.0 cm<sup>3</sup> is pipetted, to be titrated against dilute HC*l*.

Let volume of dilute HCl used in the titration be **25.00 cm**<sup>3</sup>. <u>Note:</u>

$$n_{\text{HC}l} = \frac{25.00}{1000} \times 0.100 = 0.00250 \text{ mol}$$
  
 $n_{\text{Na}_2\text{CO}_3} \text{ in } 25.0 \text{ cm}^3 = \frac{1}{2} n_{\text{HC}l} = 1.25 \times 10^{-3} \text{ mol}$ 

$$n_{\text{Na}_2\text{CO}_3}$$
 in 250 cm<sup>3</sup> = 1.25 × 10<sup>-2</sup> mol

$$m_{\text{Na}_{2}\text{CO}_{3}} = 1.25 \times 10^{-2} \times 106.0 = 1.325 \text{ g}$$

mass of impure Na<sub>2</sub>CO<sub>3</sub> to be used,  $\boldsymbol{m} = \frac{1.325}{0.80} = 1.66 \text{ g}$ 

Titre volume to be between 20.00 to 40.00 cm<sup>3</sup> to minimise error associated with the small volume used. Usually volume fixed at **20.00 or 25.00 cm<sup>3</sup>**.

(b) Explain the choice of an appropriate indicator.

Since the **reaction is between a strong acid and weak base**, the region of rapid pH change lies within the pH working range of **methyl orange/ screened methyl orange** which is suitable to be used as an indicator.

(c) Outline a practical sequence for preparation of the  $Na_2CO_3$  solution and titration with dilute HC*l*.

#### Procedure:

- (1. Weigh out about 1.60 1.70 g of the Na<sub>2</sub>CO<sub>3</sub> sample in a clean and dry weighing bottle.
- Preparation of standard  $Na_2CO_3$  solution of solution of standard Na<sub>2</sub>CO<sub>3</sub> solution of standard Na<sub>2</sub>CO<sub>3</sub> solution of solution of solution of standard Na<sub>2</sub>CO<sub>3</sub> solution of solution of standard Na<sub>2</sub>CO<sub>3</sub> solution of solution of solution of standard Na<sub>2</sub>CO<sub>3</sub> solution of solution of solution of solution of solution of standard Na<sub>2</sub>CO<sub>3</sub> solution of soluti

Note: Ensure accurate measurements of mass of solid (to be dissolved) and volumes (for dilution).

- 3. Pipette 25.0 cm<sup>3</sup> into a 250 cm<sup>3</sup> conical flask. Add 2 drops of methyl orange indicator.
- 4. Titrate the solution in the conical flask with standard dilute HC*l* from the burette.



- 6. Repeat the titration until at least two consistent results, within  $\pm 0.10$  cm<sup>3</sup>, are obtained.
- (d) Explain briefly how the results may be used to find the percentage purity of Na<sub>2</sub>CO<sub>3</sub> in the sample.

# Calculations:

Let the average of the consistent volumes of dilute HCl used be  $V dm^3$ .

$$n_{\text{HC}l} = 0.100 V \text{ mol}$$
  
 $n_{\text{Na}_2\text{CO}_3} \text{ in } 25.0 \text{ cm}^3 = \frac{1}{2} \times 0.100 V = 0.0500 V \text{ mol}$   
 $n_{\text{Na}_2\text{CO}_3} \text{ in } 250 \text{ cm}^3 = 0.500 V \text{ mol}$   
 $m_{\text{Na}_2\text{CO}_3} = 0.500 V \times 106.0 = 53.0 V \text{ g}$   
percentage purity by mass of  $\text{Na}_2\text{CO}_3 = \frac{53.0 V}{m} \times 100\%$ 

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

It is assumed that the impurity does not react with dilute HC1.

### Worked Example 1B: Back Titration

A solid sample contains about 80% by mass of Na<sub>2</sub>CO<sub>3</sub>.

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 <u>back titration</u> method.

You may assume that the following are available:

- 3 g of impure Na<sub>2</sub>CO<sub>3</sub> sample
- Standard titration apparatus
- 1.00 mol dm<sup>-3</sup> dilute HCl
- 0.100 mol dm<sup>-3</sup> dilute NaOH
- Methyl orange indicator
- (a) Determine the reagent which should be used in excess and calculate the volume of the reagent required.

#### Pre-calculation:

The reagent to be used in excess is **dilute hydrochloric acid HC**l. This is because it reacts with **sodium carbonate Na<sub>2</sub>CO<sub>3</sub>** and the excess HCl can be titrated against NaOH.

If using 3 g sample of 80% pure  $Na_2CO_3$ ,

$$n_{Na_2CO_3} = \frac{3}{106.0} \times 0.8 = 0.02264 \text{ mol}$$

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

 $n_{HCl}$  to react with Na<sub>2</sub>CO<sub>3</sub> = 2 × 0.2264 = 0.04528 mol

minimum volume of 1.00 mol dm<sup>-3</sup> HC*l* required =  $\frac{0.04528}{1.00}$  = 0.04527 dm<sup>3</sup> = 45.3 cm<sup>3</sup> suitable volume of HC*l* used = <u>46.00 to 50.00 cm<sup>3</sup></u>

(b) Outline the procedure of the experiment. Present your plan as a sequence of numbered steps.

# Procedure:

- 1. Using an analytical balance, weigh accurately about 3.00 g of the impure Na<sub>2</sub>CO<sub>3</sub> into a clean and dry weighing bottle. Record the total mass of weighing bottle and solid.
- 2. Using a burette, measure 48.00 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> HC*l*(aq) into a 250 cm<sup>3</sup> conical flask.

Note: Ensure accurate measurements of mass of solid and volumes.

- 3. Add Na<sub>2</sub>CO<sub>3</sub> from the weighing bottle into the conical flask containing the acid carefully and immediately cover the conical flask with a filter funnel to prevent acid spray from escaping.
- 4. Reweigh the emptied weighing bottle and record its mass. Calculate the mass of Na<sub>2</sub>CO<sub>3</sub> that is added into the conical flask using the two mass readings recorded.
- 5. When effervescence has ceased, rinse the filter funnel with some deionised water so that any acid present in the filter funnel may be washed into the conical flask.

Note: Steps 3 and 5 are important to ensure that all of the acid that is not reacted with Na<sub>2</sub>CO<sub>3</sub> is titrated.

- 6. Add two drops of methyl orange into the solution in the conical flask
- 7. Titrate this solution against 0.100 mol  $dm^{-3}$  NaOH(aq) from the burette.
- 8. Stop the titration when the solution changes from red (pink) to orange.
- 9. Repeat the titration until at least two consistent results, within  $\pm 0.10$  cm<sup>3</sup>, are obtained.
- (c) Show how the experimental results may be used to find the percentage purity of  $Na_2CO_3$  in the sample. Assume that the volume of HC*l* and NaOH used is  $x \text{ cm}^3$  and  $y \text{ cm}^3$  respectively.

# Calculation:

 $Na_2CO_3(s) + 2HC l(aq) \rightarrow 2NaC l(aq) + CO_2(g) + H_2O(l)$ 

 $n_{\text{NaOH}}$  used during titration =  $\frac{y}{1000} \times 0.100 = y \times 10^{-4}$  mol

 $n_{\text{excess HC}l}$  that reacts with NaOH =  $y \times 10^{-4}$  mol

total  $n_{\text{HC}l}$  added to  $\text{Na}_2\text{CO}_3$  initially =  $\frac{x}{1000} \times 1.00 = x \times 10^{-3}$  mol

 $n_{\text{HC}l}$  that reacts with Na<sub>2</sub>CO<sub>3</sub> = ( $x \times 10^{-3} - y \times 10^{-4}$ ) mol

 $n_{\text{Na}_{2}\text{CO}_{3}}$  reacted =  $\frac{1}{2}(x \times 10^{-3} - y \times 10^{-4})$  mol

percentage purity of Na<sub>2</sub>CO<sub>3</sub> in the sample =  $\frac{1}{2}(x \times 10^{-3} - y \times 10^{-4}) \times \frac{106.0}{m_{\text{Na}_2\text{CO}_3}} \text{ used} \times 100\%$ =  $\frac{5300(x \times 10^{-3} - y \times 10^{-4})}{m_{\text{Na}_2\text{CO}_3}} \text{ used}$ 

#### 1.2 Redox Titrations

#### Worked Example 1C: Redox Titration Involving MnO<sub>4</sub><sup>-</sup> (MJC 2018/4/1e)

A saturated aqueous solution of magnesium methanoate, Mg(HCOO)<sub>2</sub>, has a solubility of approximately **150 g dm<sup>-3</sup>** at room temperature. Its exact solubility can be determined by titrating magnesium methanoate against aqueous potassium manganate(VII).

During the titration, methanoate ion,  $HCOO^-$  reacts with manganate(VII) ion,  $MnO_4^-$  in an acidic medium as shown in the equation below.

 $2MnO_4^- + 5HCOO^- + 11H^+ \rightarrow 2Mn^{2+} + 5CO_2 + 8H_2O$ 

You may assume that you are provided with:

- 100 g of solid magnesium methanoate, Mg(HCOO)<sub>2</sub>
- 0.0200 mol dm<sup>-3</sup> aqueous potassium manganate(VII), KMnO<sub>4</sub>
- 1.00 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>
- the apparatus and equipment normally found in a school or college laboratory.

In order to obtain a reliable and feasible titre value, the saturated solution of magnesium methanoate needs to be diluted accurately (~**50 times** dilution) before titration.

(a) Plan an investigation to determine the effect of temperature on the solubility of magnesium methanoate, Mg(HCOO)<sub>2</sub>. Your plan must enable you to plot a graph that includes data from the experiment.

Your plan should include details of:

- the preparation of 50 cm<sup>3</sup> of saturated aqueous solutions of Mg(HCOO)<sub>2</sub> at different temperatures
- the preparation of diluted solutions of Mg(HCOO)<sub>2</sub> for titration
- an outline of how the titration could be carried out
- a sketch of the graph you would expect to obtain
- an outline how the results can be used to determine the effect of temperature on the solubility of Mg(HCOO)<sub>2</sub>

# Pre-calculations and Procedure:

	1.	Weigh approximately 8.0 g of solid $Mg(HCOO)_2$ and transfer the solid to 50 cm <sup>3</sup> of water in a beaker. Stir to ensure even mixing such that the obtained solution is saturated. Ensure solid deposits can be seen in the beaker.
		Note:
		<ul> <li>To determine mass of solid Mg(HCOO)<sub>2</sub> needed: solubility of Mg(HCOO)<sub>2</sub> ≈ 150 g dm<sup>-3</sup></li> </ul>
Preparation of saturated		mass of Mg(HCOO) <sub>2</sub> in 50 cm <sup>3</sup> saturated solution = $150 \times \frac{50}{1000} = 7.5$ g
solution of HCOO <sup>-</sup>		<ul> <li>To ensure that the solution obtained is saturated, Mg(HCOO)<sub>2</sub> should be used in excess. Hence mass to use should be above 7.5 g.</li> <li>Since Mg(HCOO)<sub>2</sub> is being used in excess to produce the saturated solution, the mass of the solid weighed does not need to be very precise.</li> </ul>
	2.	Place this beaker in a thermostatically controlled water bath set at 30 °C and leave it for 1 hour.
	3.	Use a thermometer to measure the temperature of the solution in the beaker. Record the temperature of the solution.
}	4.	Quickly decant the saturated solution into a burette.
	5.	Using the burette, dispense 5.00 cm <sup>3</sup> of the saturated HCOO <sup><math>-</math></sup> solution into a 250 cm <sup>3</sup> volumetric flask.
Preparation		Note:
of diluted solution		• To bring about 50 times dilution, $\frac{5.00}{250}$ cm <sup>3</sup> of HCOO <sup>-</sup> solution needs to be used to make 250 cm <sup>3</sup> of
		<ul> <li>Measurement of volume to be dispensed needs to be accurate.</li> </ul>
ł	6.	Top up to the mark with deionised water, and invert the flask to ensure even mixing to obtain a homogenous solution. Label this as diluted solution at 30 °C.
	7.	Fill another burette with KMnO <sub>4</sub> (aq).
	8.	Pipette 25.0 cm <sup>3</sup> of the diluted HCOO <sup>-</sup> solution into a conical flask and add 20 cm <sup>3</sup> of dilute $H_2SO_4$ using a measuring cylinder.
<b>-</b>		<ul> <li>Note:</li> <li>H<sub>2</sub>SO<sub>4</sub> is added to provide an acidic medium for the redox reaction. HC<i>l</i> and HNO<sub>3</sub> are not suitable acids for this purpose because:</li> <li>○ C<i>l</i><sup>-</sup> from HC<i>l</i> will be oxidised by KMnO<sub>4</sub> to C<i>l</i><sub>2</sub></li> </ul>
l itration 3		<ul> <li>HNO<sub>3</sub> is itself an oxidising agent</li> <li>H<sub>2</sub>SO<sub>4</sub> is added in excess, so measurement of its volume can be done using a less precise appratus such as the measuring cylinder.</li> </ul>
	9.	Note the initial reading of the burette. Titrate with KMnO <sub>4</sub> until a permanent pale pink colour is obtained. Note the final reading of the burette.
		Note: No indicator needed since KmnO <sub>4</sub> produces a distinct colour change
	10.	Carry out accurate titrations to obtain consistent results within $\pm 0.10$ cm <sup>3</sup> . Record vour
l		titration results.
	11.	Repeat Steps 1 to 11 at different temperatures (i.e. 35 °C, 40 °C, 45 °C, 50 °C) by adjusting the temperature of the thermostatically controlled water bath.
	Det	termine the average titre value of KMnO <sub>4</sub> used and determine the amount of MnO <sub>4</sub> <sup>-</sup> used,
	whi	ch can be used to determine the amount of HCOO <sup>-</sup> in the diluted solution and hence
	the	<b>concentration of HCOO</b> <sup>-</sup> in the diluted and saturated solution. This can be correlated

to determine the solubility of Mg(HCOO)<sub>2</sub>.

#### **Calculations and Processing of Data:**

$$n_{MnQ_{4}} = \frac{V_{KMnQ_{4}} \text{ used}}{1000} \times 0.0200 \text{ mol}$$

$$2 \text{ MnQ}_{4} = 5 \text{ HCOO}^{-}$$

$$n_{HCOO^{-}} \text{ in } 25.0 \text{ cm}^{3} \text{ (diluted solution)} = \frac{5}{2} \times \frac{V_{KMnQ_{4}} \text{ used}}{1000} \times 0.0200 \text{ mol}$$

$$n_{HCOO^{-}} \text{ in } 5.00 \text{ cm}^{3} \text{ (saturated solution)} = \frac{250}{25.0} \times \frac{5}{2} \times \frac{V_{KMnQ_{4}} \text{ used}}{1000} \times 0.0200 \text{ mol}$$

$$[HCOO^{-}](\text{saturated}) = \frac{\frac{250}{25.0} \times \frac{5}{2} \times \frac{V_{KMnQ_{4}} \text{ used}}{1000} \times 0.0200}{\frac{5.00}{1000}} \text{ mol dm}^{-3}$$

$$[Mg(HCOO)_{2}](\text{saturated}) = \frac{\frac{250}{25.0} \times \frac{5}{2} \times \frac{V_{KMnQ_{4}} \text{ used}}{1000} \times 0.0200}{\frac{5.00}{1000} \times 2} \text{ mol dm}^{-3}$$

$$\text{solubility of } Mg(HCOO)_{2} \text{ (saturated)} = \frac{\frac{250}{25.0} \times \frac{5}{2} \times \frac{V_{KMnQ_{4}} \text{ used}}{1000} \times 0.0200}{\frac{5.00}{1000} \times 2} \times 114.3 \text{ g dm}^{-3}$$

Repeat the above for each different temperature. **Plot a graph** of **solubility of Mg(HCOO)**<sub>2</sub> **against temperature** to see how temperature affects the solubility of Mg(HCOO)<sub>2</sub>.



(b) A student used the same titration method, this time to measure the concentration of a saturated solution of barium methanoate. Explain why the acidification of the solution with dilute sulfuric acid might make the titration difficult to do.

A precipitate of **BaSO**<sub>4</sub> will be formed thus obstructing an accurate judgement of the end-point of the titration.

# Practice Question 1A: Redox Titration Involving Autocatalytic Reaction (NYJC 2018/4/1g)

Plan an experiment to determine the percentage by mass of sodium ethanedioate,  $C_2O_4Na_2$  in **FB 1**.

Acidified potassium manganate(VII) oxidises ethanedioate ions,  $C_2O_4^{2-}$  ions, as shown below.

 $2MnO_4^{-}(aq) + 5C_2O_4^{2-}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$ 

However, the reaction takes place slowly at first. The rate of the reaction increases as more products are produced. This is because one of the products acts as a catalyst for the reaction. Hence this reaction is an example of 'autocatalysis'.

(a) Identify the product that acts as the catalyst in the reaction.

Mn<sup>2+</sup>(aq)

- (b) Using the information given above, complete the procedures for this additional experiment which is written partially as shown below. Do NOT carry out this experiment.
  - 1. Fill a burette with 0.020 mol dm<sup>-3</sup> of an aqueous solution of potassium manganate(VII).
  - 2. Pipette 10.0 cm<sup>3</sup> of **FB 1** into a 250 cm<sup>3</sup> conical flask.
  - 3. Using a 10 cm<sup>3</sup> measuring cylinder, add in 10 cm<sup>3</sup> of sulfuric acid into the same conical flask.
  - 4. Heat the mixture in the conical flask to about 60/70/80 °C.
  - 5. Titrate the mixture in the conical flask against potassium manganate(VII) until the first permanent ....pale pink... colour remains in the solution.
  - 6. Repeat the titration .as many times necessary to achieve two consistent readings within

±0.10 cm<sup>3</sup>. The average of the two consistent readings will be the volume of potassium

manganate(VII) added to achieve endpoint.

#### Practice Question 1B: Redox Titration Involving I<sub>2</sub> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (JJC 2018/4/3)

The solubility of calcium iodate(V), Ca(IO<sub>3</sub>)<sub>2</sub>, at 20 °C, is approximately 2.4 g dm<sup>-3</sup>.

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

 $Ca(IO_3)_2(s) \implies Ca^{2+}(aq) + 2IO_3^{-}(aq)$ 

The equilibrium constant for the above solubility equilibrium,  $K_{sp}$ , is also known as the solubility product of calcium iodate.

$$K_{sp} = [Ca^{2+}(aq)] [IO_{3}(aq)]^{2}$$

This solubility product can be found by determining the equilibrium concentration of  $IO_3^-$  ions in a saturated solution of calcium iodate.

The exact concentration of  $IO_3^-$  ions is determined by titration. Excess aqueous KI and aqueous H<sup>+</sup> is first added to a sample of saturated calcium iodate solution to liberate iodine.

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate,  $Na_2S_2O_3$  of known concentration.

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

(a) Using the information given above, you are required to write a plan to determine the solubility product,  $K_{sp}$ , of calcium iodate, Ca(IO<sub>3</sub>)<sub>2</sub>, at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals,  $Na_2S_2O_3 \cdot 5H_2O$  ( $M_r = 248.2$ )
- solid calcium iodate, Ca(IO<sub>3</sub>)<sub>2</sub>
- aqueous potassium iodide, KI, of about 0.2 mol dm<sup>-3</sup>
- aqueous hydrochloric acid, HCl, of about 1 mol dm<sup>-3</sup>
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0 cm<sup>3</sup> of 0.075 mol dm<sup>-3</sup> aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>;
- the preparation of about 100 cm<sup>3</sup> of a saturated solution of calcium iodate, Ca(IO<sub>3</sub>)<sub>2</sub> at 20 °C;
- the essential details of the titration process;
- an outline of how you would use your mean titre value to determine the solubility product of Ca(IO<sub>3</sub>)<sub>2</sub>.

In your calculations, you should let  $V \text{ cm}^3$  be your mean titre and express your final mathematical expression in terms of V.

- (b) The solubility of calcium iodate(V), Ca(IO<sub>3</sub>)<sub>2</sub>, at 20 °C, is approximately 2.4 g dm<sup>-3</sup>. Justify, with calculations, that the chosen concentration, 0.075 mol dm<sup>-3</sup>, of aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution is appropriate. [ $M_r$  of Ca(IO<sub>3</sub>)<sub>2</sub> = 389.9]
- (c) The experiment described in your plan in (a) is repeated using 0.1 mol dm<sup>-3</sup> aqueous Ca(NO<sub>3</sub>)<sub>2</sub> solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V).

State and explain how, if at all, the titre values and calculated  $K_{sp}$  would be expected to differ from that obtained in (a).

[Assume that both the experiments were carried out under the same conditions.]

# 2 Gravimetric Analysis

Gravimetric analysis is used to determine the quantity of an analyte through the measurement of mass. The mass measured can either be residue that is formed after a decomposition reaction **(volatilisation gravimetry)** or an insoluble precipitate that is formed as a result of isolating an ion from the aqueous medium **(precipitation gravimetry)**.

#### **General Procedures**

Volatilisation gravimetry:	1.	Weigh	sample	in	clean	and	dry	crucible/boiling	tube	before
		heating	<b>.</b>							

- 2. Heat sample in crucible/boiling tube, gently at first then strongly.
- 3. Heat the solid strongly for at least 10 min to allow sufficient time for decomposition to be complete. There should be only one solid product left after heating.
- 4. Leave the crucible/boiling tube to cool at room temperature (do not use water to cool as the apparatus will crack).
- 5. Weigh sample in crucible/boiling tube after heating and determine the difference in mass.
- 6. Repeat heat-cool-weigh process until 2 consecutive weighings are consistent within 0.01 g.

#### Precipitation gravimetry: 1. Mix reagents together and mix the reaction mixture well.

- 2. Leave mixture to stand for a sufficient length of time so that it reaches equilibrium.
- 3. Filter the mixture using a dry filter paper and filter funnel.
- 4. Wash the residue to remove the impurities
- 5. Transfer the washed residue into a pre-weighed crucible/boiling tube.
- 6. Heat the residue to remove any remaining solvent and volatile impurities.
- 7. Leave the crucible/boiling tube to cool at room temperature (do not use water to cool as the apparatus will crack).
- 8. Weigh sample in crucible/boiling tube after heating and determine the difference in mass.
- 9. Repeat heat-cool-weigh process until 2 consecutive weighings are consistent within 0.01 g.

#### **Related Topics and Concepts**

- Atoms, Molecules and Stoichiometry
- The Periodic Table
- Chemical and Ionic Equilibria

#### Refer to page 17 of Chemistry Practical Planning Handbook for more details.

#### Worked Example 2A: Volatilisation Gravimetry (9259 2008)

Sodium carbonate,  $Na_2CO_3$  does not decompose on heating with a Bunsen burner. Magnesium carbonate,  $MgCO_3$ , decomposes on heating as shown in the equation below.

 $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ 

You are to design an experiment in which the percentage by mass of  $MgCO_3$  in a mixture of  $MgCO_3$  and  $Na_2CO_3$  can be determined by heating and weighing alone. The only apparatus available consists of a boiling-tube and holder, a chemical balance and a Bunsen burner.

You are to show how you would use the results of this experiment to determine the percentage by mass of MgCO<sub>3</sub> in the mixture.

- (a) Outline, step by step, the practical sequence for the method you would use to
  - a. make appropriate weighings,
  - b. decompose the magnesium carbonate in the mixture by heating,
  - c. ensure that decomposition was complete.

#### Procedure:

- 1. Weigh an empty clean and dry boiling tube and record its mass.
- 2. Using a spatula, transfer about 2.00 g of the mixture of Na<sub>2</sub>CO<sub>3</sub> and MgCO<sub>3</sub> provided into the boiling tube. Weigh the boiling tube and the sample and record the total mass.
- 3. Heat the boiling tube with its contents for 10 minutes, gently at first and then gradually strongly using a Bunsen burner.

Note: Heating must be done for a long enough period of time (about 10 min) to ensure that decomposition is complete.

- 4. Allow the boiling tube and its contents to cool. Then weigh the cooled boiling tube and its contents and record the total mass.
- Reheat the boiling tube and its contents for another 10 minutes, then cool and weigh. Repeat this heating-cooling-weighing process until constant mass within 0.01g, is achieved. This indicates that complete decomposition of MgCO<sub>3</sub> has occurred.

Note: All measurements of mass (i.e. Steps 2, 4 and 5) must be as accurate as possible.

(b) Prepare a table to show the masses you would measure and record during the experiment. Include in your table any other masses you would calculate from the experimental results to enable you to determine the percentage by mass of MgCO<sub>3</sub> in the mixture. Insert in your table the letters A, B, C *etc.* to represent each mass. Use these letters to show how your calculated masses are obtained *e.g.* E = B − A.

Mass of empty boiling tube / g	Α
Mass of boiling tube and sample / g	В
Mass of boiling tube and contents after first heating / g	С
Mass of boiling tube and contents after second heating / g	D
Mass of boiling tube and contents after third heating / g	D

Note: Order of recording of masses is important. It should follow a logical flow based on how you have carried out the experiment.

Mass of sample (mixture of  $Na_2CO_3$  and  $MgCO_3$ ) used = (**B** - **A**) g Mass of  $CO_2$  lost = (**B** - **D**) g

(c) Use the letters you have entered in (b) to show how you would process the results to find
 (i) the mass of MgCO<sub>3</sub> in the mixture,

total 
$$n_{CO_2}$$
 lost =  $\frac{\mathbf{B} - \mathbf{D}}{44.0}$  mol

 $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ 

 $n_{MgCO_3}$  decomposed =  $n_{CO_2}$  lost =  $\frac{\mathbf{B} - \mathbf{D}}{44.0}$  mol

hence, mass of MgCO<sub>3</sub> in the mixture =  $\frac{\mathbf{B} - \mathbf{D}}{44.0} \times 84.3 \text{ g}$ 

(ii) the percentage by mass of  $MgCO_3$  in the mixture.

percentage by mass of MgCO<sub>3</sub> in the mixture =  $\frac{\frac{\mathbf{B} - \mathbf{D}}{44.0} \times 84.3}{\mathbf{B} - \mathbf{A}} \times 100\%$ 

(d) Suggest a possible source of error in this experiment.

Uneven or inconsistent heating resulting in some of the mixture not decomposed.

- (e) List some safety aspects to consider when performing the experiment.
  - Handle the boiling tube with a **test tube holder** all the times.
  - Point the boiling tube away from self and others.
  - Do not cool down heated apparatus with water to prevent shattering of the apparatus.

### Practice Question 2A: Volatilisation Gravimetry Involving CuSO4.nH2O

A sample of hydrated copper(II) sulfate has a formula of CuSO<sub>4</sub>·nH<sub>2</sub>O

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 CuSO₄·*n*H₂O
- Crucible
- Weighing balance
- Bunsen burner
- (a) Outline a step by step procedure, in such a way that another student could follow your instructions, 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<sub>4</sub>·nH<sub>2</sub>O.

#### Practice Question 2B: Volatilisation Gravimetry Involving Carbonates (SAJC 2018/4/1g)

- (a) Unlike Group 2 carbonates, solid sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, does not decompose on heating with a Bunsen burner. However, for solid sodium hydrogencarbonate, NaHCO<sub>3</sub>, it will form sodium carbonate, steam and carbon dioxide when heated.
  - (i) Write an equation, with state symbols, to represent the thermal decomposition of sodium hydrogen carbonate.
  - (ii) Given the above information, you are to devise a plan to determine the percentage by mass of NaHCO<sub>3</sub> in a solid mixture of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>.

You may assume you are provided with

- a boiling tube
- a pair of tongs
- 10 g of NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solid mixture
- a heat resistant mat
- equipment normally found in a school or college laboratory

In your plan, you should include details of:

- procedure you would follow, including the apparatus you would use and the safety precautions to take,
- measurements you would take,
- a brief outline of how the results can be used to determine the percentage by mass of NaHCO<sub>3</sub> in the mixture. You may make assumptions for the masses involved and use appropriate molar mass values to solve this.

### Practice Question 2C: Precipitation Gravimetry (ACJC 2019/4/1g)

The technique of gravimetry includes all analytical methods in which the analytical property is a measurement of mass or a change in mass. This technique can also be used in determining the solubility product of magnesium carbonate.

One of the possible approaches is to determine the mass of precipitate formed after mixing two solutions of known concentration. After preparing a mixture of saturated solution containing the precipitate, it can be passed through a pre-weighed filter paper that retains the precipitate. Residual moisture can be removed by drying the filter paper and the precipitate. The amount of precipitate can be determined, from which the concentration of ions in the saturated solution and hence solubility product can be determined.

(a) Plan an investigation to determine the solubility product of magnesium carbonate using the approach outlined above.

You are provided with the following:

- 0.400 mol dm<sup>-3</sup> sodium carbonate solution
- 0.400 mol dm<sup>-3</sup> magnesium nitrate solution
- apparatus and equipment normally found in a school 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 you would make to allow for gravimetric analysis.
- (b) Show how the measurements recorded in (a) can be used to calculate the concentration of Mg<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, in mol dm<sup>-3</sup>, in the saturated solution.

# **3 Gas Collection Experiments**

Some chemical reactions give off a gaseous product. By measuring the volume of the gas evolved when an excess of reagent is added to the sample, quantitative information can be obtained to determine the amount of the sample that is present.

### **Common Experimental Set-ups**

You will need to know to draw labelled diagrams for different gas collection experiments. Here are some common set-ups:

#### 1. Gas collection via downward displacement of water using a measuring cylinder



2. Gas collection via a graduated gas syringe



3. Gas collection via a graduated gas syringe and use of an pressure-equalising dropping funnel



#### **Related Topics and Concepts**

- Atoms, Molecules and Stoichiometry
- The Gaseous State
- Reaction Kinetics

#### Refer to page 9 of Chemistry Practical Planning Handbook for more details.

#### Worked Example 3A (DHS 2018/4/2a)

An ideal gas is a theoretical idea – a gas in which there are no attractive forces between the molecules, and in which the molecules take up no space. The ideal gas law is usually stated as pV = nRT, where

- *p* is the pressure
- V is the volume
- *n* is the number of moles
- T is the temperature in K of the gas, and
- *R* is the ideal gas constant.

The value of R is determined experimentally by measuring the other variables in the equation, and solving mathematically to get the value of the constant. R is the same for all gases – provided the gas has ideal behaviour.

In this experiment you will determine the ideal gas constant using  $H_2$  gas. The  $H_2$  will be generated using the reaction between magnesium and hydrochloric acid.

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

You may assume you are provided with:

- a two-necked round bottom flask,
- a rubber tubing,
- a water tub,
- 0.1 mol dm<sup>-3</sup> hydrochloric acid,
- thermometer,
- barometer (instrument used to measure pressure),
- one piece of magnesium ribbon strip of about 0.06 g,
- · apparatus normally found in a school laboratory

Your plan should contain the following:

- the procedure that you would follow and the measurements that you would take
- a tabulation of the experimental data to be collected
- the reactants and conditions that you would use
- the mass of magnesium that you would use and the volume of hydrochloric acid that you would measure. Assume that the molar volume of gas under experimental conditions is 24.0 dm<sup>3</sup> mol<sup>-1</sup>. [A<sub>r</sub>: Mg, 24.3]

# Pre-Calculations:



If 0.06 g of Mg was used,

$$n_{\rm Mg} = \frac{0.06}{24.3} = 2.469 \times 10^{-3} \text{ mol}$$

 $n_{\rm HCl}$  required = 2.469 × 10<sup>-3</sup> × 2 = 4.938 × 10<sup>-3</sup> mol

volume of HCl required =  $\frac{4.938 \times 10^{-3}}{0.1} \times 1000 = 49.38 \text{ cm}^3$ 

volume of H<sub>2</sub> evolved (assuming r.t.p.) =  $2.469 \times 10^{-3} \times 24000 = 59.3 \text{ cm}^{-3}$ 

To calculate maximum mass of Mg allowed to evolve **50 cm<sup>3</sup>** of H<sub>2</sub>:

Note:	This calculation is for the use of a <b>50.00 cm<sup>3</sup></b> burette to collect the gas produced.	

$$n_{\rm Mg} = n_{\rm H_2} = \frac{50}{24000} = 2.083 \times 10^{-3} \text{ mol}$$

 $m_{\rm Mg} = 2.083 \times 10^{-3} \times 24.3 = 0.0506 \text{ g}$ 

minimum volume of HCl required =  $\frac{2.083 \times 10^{-3} \times 2}{0.1} = 0.0417 \text{ dm}^3 = 41.7 \text{ cm}^3$ 

# Procedure:



1. Cut the magnesium strip to three roughly equal pieces. Using a weighing balance, weigh each piece of magnesium strip in a weighing bottle. Each strip should weigh about 0.02 g.

Note: Accurate measurements of mass of magnesium strip is needed to calculate the actual amount of metal used.

- 2. Place one piece of cut magnesium strip into the two-necked round bottom flask.
- 3. Secure the two-necked round bottom flask with a retort stand.
- 4. Using a 50 cm<sup>3</sup> measuring cylinder, measure out 25 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> hydrochloric acid. Transfer the 25 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> hydrochloric acid to a pressure-equalising dropping funnel and stopper the funnel.

Note: Acid is to be used in excess to ensure that all the magnesium used is reacted. For a 0.02 g piece of magnesium strip to fully react, the minimum volume of HCl needed =  $49.38 \div 3 = 16.5$  cm<sup>3</sup>.

- 5. Connect the pressure-equalising dropping funnel to one of the necks of the two-necked round bottom flask.
- 6. Fill the water tub with tap water.
- 7. Submerge the mouth of an inverted 50.00 cm<sup>3</sup> burette (filled with water) in the water tub and secure the burette with a second retort stand. Adjust the water level in the burette until it is between 48.00 cm<sup>3</sup> and 50.00 cm<sup>3</sup>. Note and record the initial reading of the burette.

- 8. Connect one end of a rubber tubing (with stopper) to the other neck of the two-necked round bottom flask and place the other end inside the inverted burette.
- 9. Measure and record the ambient temperature using the thermometer.
- 10. Measure and record the pressure of the room using the barometer.
- 11. Open the tap of the dropping funnel fully and gently swirl the two-necked round bottom flask.
- 12. Note the final reading of the burette when all effervescence has ceased.
- 13. Repeat Steps 2 to 12 with the other two pieces of magnesium.
- 14. Determine *R* using the pressure of the room, volume of gas produced, temperature at which the measurement was taken and the amount of Mg that had reacted.

#### Side Note:

The gas collection method yields results fast, but it is not so accurate because:

- Swirling of the conical flask is variable, which will vary the volume of gas collected in the burette.
- Air and the gas evolved are both compressible, and heat of reaction may cause fluctuation in gas volumes due to expansion.

# Tabulation of Data:

expt	mass of empty weighing bottle / g	mass of weighing bottle and Mg strip / g	mass of Mg strip used / g	final burette reading / cm <sup>3</sup>	initial burette reading / cm <sup>3</sup>	volume of H <sub>2</sub> produce / cm <sup>3</sup>	temperature / °C	barometer reading / kPa
1								
2								
3								

# Practice Question 3A (TJC 2018/4/1c)

You are required to write a plan for determining the exact percentage by mass of anhydrous sodium carbonate in the impure sample by collecting and measuring the volume of carbon dioxide gas evolved from its reaction with hydrochloric acid.

You may assume that you are provided with:

- impure solid anhydrous sodium carbonate,
- 0.10 mol dm<sup>-3</sup> hydrochloric acid,
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:

- practical details, including a well-labelled diagram of the set-up, of how you would carry out the gas collection when 0.30 g of carbonate was reacted with 80 cm<sup>3</sup> of hydrochloric acid;
- brief, but specific details of how the results would then be used to determine the exact percentage by mass of anhydrous sodium carbonate.

# 4 Chemical Energetics

Enthalpy Change	Symbol	Definition
Standard enthalpy change of reaction	$\Delta H_{\rm r}^{\ominus}$	The energy change when molar quantities of reactants as specified by the chemical equation react to form products, with all reactants and products in their standard states, at a specified temperature, usually 298 K.
Standard enthalpy change of combustion	$\Delta H_{c}^{\ominus}$	The energy released when 1 mole of a substance is completely burnt in excess oxygen, with all reactants and products in their standard states, at a specified temperature, usually 298 K.
Standard enthalpy change of neutralisation	$\Delta H_{n}^{\ominus}$	The energy released when 1 mole of water is formed in the neutralisation reaction between an acid and a base, all in their standard states, at a specified temperature, usually 298 K.
Standard enthalpy change of solution	$\Delta H_{ m sol}^{\ominus}$	The energy change when 1 mole of substance in its standard state is completely dissolved in a solvent to give a solution of infinite dilution, at a specified temperature, usually 298 K.

# Common Enthalpy Changes to Calculate from Experiments

# **Calculations**

•  $q = mc \Delta T$  OR  $q = C \Delta T$ 

q = amount of **heat released** or **absorbed** by reaction (unit: J)

[Note: no sign since heat released or absorbed has indicated the direction. If q refers to heat change, a sign is required and the formula  $q = -mc\Delta T$  will be used instead.]

- m = mass of solution (unit: g)
- c = specific heat capacity of water (unit: J g<sup>-1</sup> K<sup>-1</sup>)
- C = heat capacity of substance e.g. calorimeter (unit: J K<sup>-1</sup>)
- $\Delta T$  = change in temperature (unit: K or °C)

$$\Delta H_{\rm r} = \pm \frac{q}{n} = \pm \frac{mc\Delta T}{n}$$

n = amount of limiting reagent or amount of reagent based on  $\Delta H$  definition (see table above)

- Positive ΔH<sub>r</sub>: Endothermic reaction
   Negative ΔH<sub>r</sub>: Exothermic reaction
- Energy cycles may need to be drawn to help compute the desired enthalpy change of reaction from experimental data using **Hess' Law**.

# 4.1 Calorimetry

Common Experimental Set-ups (drawing of labelled diagrams required)

1. To find enthalpy change of reaction of reaction mixture in Styrofoam cup calorimeter



2. To find enthalpy change of combustion of fuel



# **Collection and Processing of Data**

For reactions that are completed almost instantaneously e.g. the reaction between NaOH and HC*l*, the temperature reaches a maximum (or minimum) almost immediately upon the mixing of the reactants. For such reactions, heat loss to (or gain from) the surroundings can be considered to be minimal. Hence, to find the temperature change,  $\Delta T$ , the initial and final temperatures can be read off the thermometer directly.

However, for **slow reactions**, it takes a while for the system to reach the maximum (or minimum) temperature. This leads to significant heat loss to (or gain from) the surroundings. To account for this, a series of temperatures can be recorded before and after the mixing to give a **temperature-time graph**.



#### Possible Sources of Errors and Suggested Improvements

Possible Sources of Errors	Suggested Improvements			
Heat loss to the surrounding air	Carry out experiment in draught-free room OR Cover calorimeter with insulating lid			
Heat loss to the calorimeter	Calibrate the calorimeter used by first conducting the experiment using the calorimeter with a reaction of known $\Delta H$			
The temperature measurement is not precise enough e.g. 1 °C interval thermometer which measures to the nearest 0.5 °C	Use thermometer of a higher precision e.g. 0.2 °C interval thermometer which measures to the nearest 0.1 °C			
Thermometer used has slow response time e.g. due to large bulb	Use a thermocouple/data logger with temperature probe which allows fast and easy measurement of the actual temperature			
Incomplete combustion of fuel (for combustion experiments)	Increase oxygen content of surroundings (e.g. placing beaker of $H_2O_2$ solution with MnO <sub>2</sub> )			
Rapid loss of mass of fuel due to evaporation. (for combustion experiments)	Cover the wick with a cap when spirit lamp is not in use			

#### Refer to pages 18 to 22 of Chemistry Practical Planning Handbook for more details.

#### Worked Example 4A: Finding Enthalpy Change of Solution

Ammonium salts are commonly used in instant cold packs. The cold pack contains water, and in the water is another pouch containing the ammonium salt. When the pack is squeezed, this inner pouch is broken, releasing the salt, which quickly dissolves and lowers the temperature.

To determine whether ammonium chloride or ammonium nitrate is more effective as the ingredient in the cold pack, a student decided to conduct an experiment to find out the enthalpy change of solution of the two salts, starting with ammonium chloride.

He added ammonium chloride to water and found the temperature change by plotting a suitable graph to correct for surrounding heat transfer.

Solubility of ammonium chloride at 25  $^{\circ}$ C = 6.95 mol dm<sup>-3</sup> 4.3 J is required to raise the temperature of 1.0 cm<sup>3</sup> of any solution by 1  $^{\circ}$ C.

In a preliminary investigation, the enthalpy change of solution of ammonium chloride was found to be approximately +15 kJ mol<sup>-1</sup>.

(a) Draw a labelled diagram to show the set-up you could use in a school laboratory to carry out the experiment.



(b) (i) By considering the apparatus chosen in your diagram, state a volume of water you could use in the experiment.

Volume of water to be used =  $100 \text{ cm}^3$ 

Note: Any volume between 25 cm<sup>3</sup> to 100 cm<sup>3</sup> (max volume that can be contained in Styrofoam cup for the experiment) is acceptable

(ii) Calculate the **maximum** mass of ammonium chloride that can be added to the volume of water stated in (b)(i).

Maximum mass that can dissolve in 100 cm<sup>3</sup> of water =  $6.95 \times \frac{100}{1000} \times 53.5 = 37.2g$ 

(c) Suggest a **minimum** mass of ammonium chloride that could be used. Justify your choice with relevant calculations, stating any assumptions you made.

Assuming a temperature change of 5 °C to be measured and no heat loss to surroundings,

$$\Delta H_{\text{solution}} = +\frac{q}{n} = +\frac{mc\Delta T}{n_{\text{salt}}}$$
$$n_{\text{salt}} \times 15 \times 10^3 = 100 \times 4.3 \times 5$$

 $n_{\rm salt} = 0.1433 \, {\rm mol}$ 

minimum mass to use =  $0.1433 \times 53.5 = 7.67 \ g$ 

1

Note: In planning this experiment, some **pre-calculations** have to be done to determine the quantity of reactants to use. Parts (**b**) and (**c**) are examples of necessary pre-calculations.

To decide on a suitable mass of  $NH_4Cl$  to use, first decide the volume of water to be used. This decision will have to be made **based on the chemicals and apparatus provided**. From there, you have to make use of your knowledge of stoichiometry to calculate the mass of  $NH_4Cl$  to be used. In your pre-calculations, do remember to state any assumptions made.

### (d) Describe the procedure to find the enthalpy change of solution of ammonium chloride. In your plan, you should:

- allow for the plotting of a suitable graph.
- include appropriate apparatus, masses and volumes of reagents, using your answers in parts (a), (b) and (c), and draw table(s) with headings to show the measurements you would make.

Knowledge of the calculations required to find the enthalpy change of solution is necessary to answer this part of the question. Since  $\Delta H_{\text{solution}} = +\frac{q}{n} = +\frac{mc\Delta T}{n_{\text{salt}}}$ , the following need to be measured and recorded in the procedures: • Change in temperature upon dissolving of salt  $\Rightarrow$  initial and final (lowest) temperatures

- Change in temperature upon dissolving of sait ⇒ initial and final (lowest) temperatures
   Mass of water used (can be calculated from the volume of water used using the density of water, 1.00 g cm<sup>-3</sup>)
- Amount of salt used (can be calculated from the volume of water used usin)
- Amount of sait used (can be calculated from the mass of sait used)

#### Procedure:

- 1. Weigh accurately 8.00 g of ammonium chloride in a clean and dry weighing bottle, using a weighing balance.
- 2. Using a 100 cm<sup>3</sup> measuring cylinder, add 100 cm<sup>3</sup> of water into a dry Styrofoam cup calorimeter. Place the Styrofoam cup inside a second Styrofoam cup which is held in a 250 cm<sup>3</sup> glass beaker to prevent it tipping over.
- 3. Cover with a lid and insert a thermometer through the lid.
- 4. Stir the water gently using the thermometer. Record the temperature of the solution in the Styrofoam cup and start the stopwatch.
- 5. Record the temperature of the water in the Styrofoam cup using a 0.2 °C interval thermometer, every 30 s until 2.5 min.
- 6. At exactly 3 min, pour the ammonium chloride into the water. Stir the mixture but do not measure the temperature at this time.

- 7. Stir the solution gently and record the temperature of the solution at 3.5 min. Continue to stir and record the temperature at 30 s intervals until the temperature of the mixture starts to rise steadily for 5 consecutive readings.
- 8. Reweigh the emptied weighing bottle.

#### **Recording of data:**

Mass of empty weighing bottle / g	$m_0$
Mass of weighing bottle and salt / g	<i>m</i> 1
Mass of emptied weighing bottle / g	<i>m</i> <sub>2</sub>
Mass of salt used / g	$m_1 - m_2$

Time / min	Temperature of solution / °C
0.0	
0.5	
1.0	
1.5	
2.0	
2.5	
3.0	
3.5	
i	

(e) Draw a sketch of the graph that you expect to obtain in the experiment. Indicate clearly on the graph the initial and final temperatures that you would read.



(f) In the student's experiment, he dissolved m g of ammonium chloride in v cm<sup>3</sup> of water, and obtained a temperature change of T °C. Outline how you would use his results to calculate a value for the enthalpy change of solution of ammonium chloride.

$$\Delta H_{\text{solution}} = + \frac{\mathbf{v} \times 1.00 \times 4.3 \times \mathbf{T}}{\left(\frac{\mathbf{m}}{53.5}\right)} \text{ J mol}^{-1}$$

(g) The student repeats the same procedure for ammonium nitrate. How might he conclude which of the two salts is more effective as the ingredient in the cold pack?

The salt with the **more endothermic** enthalpy change of solution **OR** gives the **fastest drop in temperature** will be the more effective ingredient.

# Worked Example 4B: Finding Enthalpy Change of Combustion

Alkynes, which contain C=C triple 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 is exemplified by the following:

$$CH_{3}CH_{2}CH_{2}CH_{2}C \equiv CCH_{2}CH_{2}CH_{2}CH_{3} + H_{2} \xrightarrow{\text{Lindlar catalyst}} H_{3}C(H_{2}C)_{3} (CH_{2})_{3}CH_{3}$$

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,  $\Delta H_1$ , via Hess' Law.

(a) Given that the standard enthalpy change of combustion for H<sub>2</sub> is -286 kJ mol<sup>-1</sup>. State the enthalpy changes that are necessary in order to calculate  $\Delta H_1$ .

Note: You need to understand of **Hess's Law** and know how to draw the **energy cycle** or know the **formula** linking  $\Delta H_r$  and the  $\Delta H_c$  of all the reactants and products *i.e.*  $\Delta H_r = \Sigma \Delta H_c$  (reactants)  $-\Sigma \Delta H_c$  (products) before you can come up with this answer.



By Hess's Law,

$$\Delta H_1 = \Delta H_c$$
(5-decyne) – 286 –  $\Delta H_c$ (*cis*-dec-5-ene)

Alternatively, you can make use of the **formula**:  $\Delta H_r = \Sigma \Delta H_c$  (reactants) –  $\Sigma \Delta H_c$  (products)

- (b) 5-decyne and *cis*-dec-5-ene are both liquids at standard conditions. Describe the procedure to obtain the value of <u>one</u> of the enthalpy change that you have stated in your answer to (a). In your plan, include:
  - a labelled diagram of the experimental set-up
  - table(s) with headings to show the measurements you would make.

Knowledge of the calculations required to find the enthalpy change of combustion is necessary to answer this

part of the question. Since  $\Delta H_{c} = -\frac{q}{n} = -\frac{C\Delta T}{n_{fuel}}$ , the following need to be measured and recorded:

- Heat capacity of the calorimeter (including the water), *C* : to calibrate with a fuel of known enthalpy change of combustion e.g. ethanol
- Temperatures of water in calorimeter before and after combustion,  $T_i$  and  $T_f$
- Mass of spirit lamp and fuel before and after combustion,  $m_1$  and  $m_2$

#### Procedure:

Calibration of metal calorimeter (with water)

1. Set up the apparatus as shown in the diagram below.



2. Fill the calorimeter with 100 cm<sup>3</sup> of water.

Note: Put in sufficient water to cover the bulb of the thermometer. The volume of water need not be accurately known as the whole calorimeter (including the water) is calibrated with a fuel of known  $\Delta H_c$ , *e.g.* ethanol in this case.

3. Fill the spirit lamp with the ethanol and cap the spirit lamp. Using a weighing balance, weigh and record the mass of the spirit burner with ethanol,  $m_1$ .

Note: Capping the spirit lamp reduces the loss of fuel via evaporation

- 4. Stir the water in the calorimeter and take note of its initial temperature,  $T_1$ , using a 0.1 °C thermometer.
- 5. Uncap the spirit lamp, place it under the calorimeter and light the wick.
- 6. Gently stir the water in the calorimeter until there is a rise in temperature of about 5 °C.

- Note: Choose temperature range that can be measured with instrument used without incurring significant error, and enables results to be obtained within a sensible time frame.
  - Keep in mind too that the temperature range chosen should also lead to large enough loss in mass of the fuel such that the percentage error is kept small. If the enthalpy change of combustion is provided (not applicable for this question), you will be able to do pre-calculations to determined the rise in temperature you will want to look out for.
- 7. Cap the spirit burner to extinguish the flame. Immediately record the final temperature of the water,  $T_2$ .
- 8. Cool the spirit lamp and reweigh the cooled lamp,  $m_2$ .

#### Determination of $\Delta H_c$ of 5-decyne or *cis*-dec-5-ene

- 9. Fill an identical clean spirit lamp with the fuel (5-decyne or *cis*-dec-5-ene) and cap the spirit lamp. Using a weighing balance, weigh and record the mass of the spirit burner with the fuel,  $m_3$ .
- 10. Stir the water in the calorimeter and take note of its initial temperature,  $T_3$ , using a 0.2 °C interval thermometer.
- 11. Uncap the spirit lamp, place it under the calorimeter and light the wick.
- 12. Gently stir the water in the calorimeter until there is a rise in temperature of about 5 °C.
- 13. Cap the spirit burner to extinguish the flame. Immediately record the final temperature of the water,  $T_{4}$ .
- 14. Cool the spirit lamp and reweigh the cooled lamp,  $m_4$ .

#### Recording of data:

mass of spirit lamp + ethanol before combustion / g	<i>m</i> 1
mass of spirit lamp + ethanol after combustion / g	<i>m</i> <sub>2</sub>
temperature of water before combustion of ethanol / °C	<i>T</i> <sub>1</sub>
temperature of water after combustion of ethanol / °C	<i>T</i> <sub>2</sub>
mass of spirit lamp + fuel before combustion / g	<i>m</i> 3
mass of spirit lamp + fuel after combustion / g	$m_4$
temperature of water before combustion of fuel / °C	<i>T</i> <sub>3</sub>
temperature of water after combustion of fuel / °C	<i>T</i> <sub>4</sub>

(c) How would you use these measurements to obtain the value of the enthalpy change chosen?

#### Calibration of calorimeter

$$q = -C\Delta T$$

$$\Delta H_{c} \text{ (ethanol)} \times n_{\text{ethanol}} = -C(T_{2} - T_{1})$$

$$\Delta H_{c} \text{ (ethanol)} \times \frac{m_{1} - m_{2}}{12.0 \times 2 + 1.0 \times 6 + 16.0} = -C(T_{2} - T_{1})$$

$$C = \frac{-\Delta H_{c} \text{ (ethanol)}}{T_{2} - T_{1}} \times \frac{m_{1} - m_{2}}{46.0}$$

 $\Delta H_{\rm c}$  of fuel

$$q = -C\Delta T$$
  

$$\Delta H_{c} (fuel) \times n_{fuel} = -C(T_{4} - T_{3})$$
  

$$\Delta H_{c} (fuel) \times \frac{m_{3} - m_{4}}{M(fuel)} = -C(T_{4} - T_{3})$$
  

$$\Delta H_{c} (fuel) = -\Delta H_{c} (ethanol) \times \frac{m_{1} - m_{2}}{m_{3} - m_{4}} \times \frac{T_{4} - T_{3}}{T_{2} - T_{1}} \times \frac{M(fuel)}{46.0}$$

# Practice Question 4A (CJC 2018/4/2)

You are provided with 150 cm<sup>3</sup> of each of three solutions, **FA 6**, **FA 7** and **FA 8**. You are to identify which of these solutions correspond to the following solutions:

1 mol dm<sup>-3</sup> sodium hydroxide, NaOH 2 mol dm<sup>-3</sup> hydrochloric acid, HC*l* 1 mol dm<sup>-3</sup> hydrochloric acid, HC*l* 

You are also provided with the following apparatus: a thermometer, a Styrofoam cup, 2 measuring cylinders.

You are to plan a simple experiment which will allow an identification of the three solutions to be made, using only the apparatus and materials listed above and deionised water. (Note that you are **not** provided with any pH indicator).

You are **not** required to carry out the plan but you have to present your results in an appropriate manner based on your plan so that the identification can be made.

# Practice Question 4B (HCI 2018/4/3)

You are tasked to determine the enthalpy change of reaction of copper and hydrochloric acid,  $\Delta H_r$ , as shown in the equation below.

$$Cu(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2(g) \qquad \Delta H_r$$

However, copper metal and hydrochloric acid do **not** react together under normal conditions.  $\Delta H_r$  must therefore be determined by an **indirect** method involving two other reactions and a metal.

One of these reactions is the displacement of copper from aqueous copper(II) chloride, and the other is an acid-metal reaction.

(a) Information of some metals is shown in Table 3.1 below.

element	relative atomic mass	electrode reaction	E⇔/V
Ag	107.9	Ag⁺ + e⁻ ⇔ Ag	+0.80
Cu	63.5	$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+0.34
Mg	24.3	$Mg^{2+} + 2e^{-} \rightleftharpoons Mg$	-2.38
Na	23.0	Na⁺ + e⁻ <del>⇔</del> Na	-2.71
Pb	207.2	$Pb^{2+} + 2e^{-} \rightleftharpoons Pb$	-0.13

Table 3.1

Choose a suitable metal from Table 3.1 to be used in the task.

- (b) Using the metal you have chosen in (a), construct an energy cycle to show how  $\Delta H_r$  can be calculated from the enthalpy change of the displacement of copper from aqueous copper(II) chloride,  $\Delta H_1$ , and the enthalpy change for the acid-metal reaction,  $\Delta H_2$ .
- (c) Plan and describe a practical procedure, which would enable you to determine  $\Delta H_2$ , which is exothermic. Your plan must enable you to plot a graph that includes data from the experiment.

You may assume that you are provided with:

- 1.0 mol dm<sup>-3</sup> hydrochloric acid,
- the metal you have chosen in powder form,
- a stopwatch,
- chemicals and apparatus normally found in a school laboratory.

In your plan, you should include:

- apparatus and chemicals needed,
- a detailed method which provides full instruction, including any calculations you used to work out suitable quantities of the chemicals used,
- a sketch of the graph you expect to obtain,
- an outline of the calculations you would perform to calculate  $\Delta H_2$ .

You may assume the density of all aqueous solutions are 1.0 g cm<sup>-3</sup> and the specific heat capacity of the mixture is 4.18 J g<sup>-1</sup> K<sup>-1</sup>.

# YOU ARE NOT REQUIRED TO CARRY OUT THIS EXPERIMENT.

#### 4.2 Thermometric Titrations

Thermometric titration is a quantitative analysis method in which one reactant (the titrant) is added to another reactant in a calorimeter. The enthalpy change of the reaction causes a temperature change which, when plotted against the volume of titrant, may be used to find the titration endpoint.

#### **Collection and Processing of Data**



When a maximum (or minimum) temperature is reached, the corresponding volume of reagent added is the volume required to fully react with the titrant.

Refer to page 20 of Chemistry Practical Planning Handbook for more details.

Scan the QR code to access the SLS lesson package for detailed analysis on the different shapes of graph to determine enthalpy change of reaction.


#### Worked Example 4C (CJC 2019/4/3)

The reaction between an acid and a metal hydroxide is exothermic. It is possible to make use of this fact to determine the equivalence-point of a neutralisation reaction without the use of an indicator. This process is known as thermometric titration and can be used to calculate the concentration of an acid solution. Portions of acid are progressively added to the hydroxide solution until the equivalence-point is reached and passed. The temperature is monitored throughout the experiment.

The data obtained is plotted and two best-fit graph lines are drawn. One line is drawn using data before the equivalence-point and the second line using the remaining data. These lines are then extrapolated (extended) until they cross.

(a) Aqueous barium hydroxide is neutralised by the addition of nitric acid. The enthalpy change of neutralisation has the symbol  $\Delta H_{neu}$ .

Write an ionic equation for the reaction for which the enthalpy change is  $\Delta H_{neu}$ . You should include state symbols in your equation.

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

(b) Using the information given above, you are required to write a plan for a thermometric titration in which nitric acid is added to aqueous barium hydroxide.

You are also required to explain how the data you obtain from this experiment may be used to determine the concentration of the nitric acid, and the value of  $\Delta H_{neu}$  for this neutralisation reaction.

You may assume that the original solutions are at room temperature and that the maximum temperature rise obtained in this experiment is between 10 °C and 12 °C.

You may also assume that you are provided with:

- 1.00 mol dm<sup>-3</sup> aqueous Ba(OH)<sub>2;</sub>
- HNO<sub>3</sub> of approximate concentration 1.5 mol dm<sup>-3</sup>;
- graph paper;
- the equipment normally found in a school or college laboratory.

Your plan should include:

- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- how you would recognise that the equivalence-point had been passed;
- on the grid provided, a sketch of the graph you would expect to obtain;
- an explanation of the shape of your graph;
- how the data obtained from the graph would be used to determine the
  - concentration of the nitric acid
  - value of  $\Delta H_{neu}$  for this reaction.

#### Pre-calculations:

$$Ba(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

Let the volume of Ba(OH)<sub>2</sub> used be  $x \text{ cm}^3$ amount of Ba(OH)<sub>2</sub> =  $\frac{x}{1000} \times 1.00 = x \times 10^{-3} \text{ mol}$ amount of HNO<sub>3</sub> required =  $2 \times x \times 10^{-3} = 2x \times 10^{-3} \text{ mol}$ approximate equivalence volume of HNO<sub>3</sub> =  $\frac{2x \times 10^{-3}}{1.5} = 1.33x \times 10^{-3} \text{ dm}^3 = 1.33x \text{ cm}^3$ 

Given that the maximum temperature rise is 12 °C,

$$\Delta H_{\text{neu}} = -\frac{mc\Delta T}{n_{\text{H}_2\text{O}}}$$
$$= -\frac{(x+1.33x) \times 4.18 \times 12}{2x \times 10^{-3}}$$
$$= -58.5 \text{ kJ mol}^{-1}$$

As this value is close to the theoretical value for enthalpy change of neutralisation involving a strong acid and strong base (-57 kJ mol<sup>-1</sup>), this confirms that using  $x \text{ cm}^3$  of Ba(OH)<sub>2</sub> with an equivalence volume of about 1.33 $x \text{ cm}^3$  of HNO<sub>3</sub> can bring about the expected temperature rise of about 12 °C.

#### Procedure:

- 1. Fill a burette with 1.5 mol  $dm^{-3}$  aqueous HNO<sub>3</sub>.
- 2. Using a pipette, transfer 25.0 cm<sup>3</sup> of  $Ba(OH)_2$  into a Styrofoam cup.

Note: Volume of  $Ba(OH)_2$ , *x*, is fixed at 25 cm<sup>3</sup> so that the bulb of the thermometer can be completely immersed into the solution when measuring the initial temperature in a Styrofoam cup.

- 3. Place the polystyrene cup inside a second polystyrene cup which is held in a 250 cm<sup>3</sup> glass beaker to prevent it tipping over.
- 4. Stir the solution in the Styrofoam cup with a 0.2 °C interval thermometer. Record the temperature of the solution.
- 5. From a burette, add 5.00 cm<sup>3</sup> of HNO<sub>3</sub> to the Styrofoam cup. Stir the mixture with the thermometer and record the maximum temperature reached.

Note: Choose a volume that is not too large (will take a long time to be transferred, resulting in significant heat loss) or too small (will lead to high percentage error). A volume between 2.00 to 10.00 is appropriate.

6. Repeat Step 5 until a total of 60.00 cm<sup>3</sup> of HNO<sub>3</sub> has been added. After each addition, record the maximum temperature reached and the total volume of HNO<sub>3</sub> added up to that point.

Note: Choose a total volume that allows for sufficient number of data points to be measured after the equivalence point such that the line-of-best-fit can be drawn.

## Processing of data:

- 7. A graph of maximum temperature against volume of  $HNO_3$  is plotted.
- 8. Draw a line-of-best-fit for the points where the temperature is rising.
- 9. Draw a second line-of-best-fit for the points where the temperature is falling.
- 10. Extrapolate both lines until they cross.
- 11. Read from the graph the intersection of the lines-of-best-fit. This is the volume of HNO<sub>3</sub> required to completely react with 25.0 cm<sup>3</sup> of Ba(OH)<sub>2</sub> (*i.e.* equivalence volume), and the maximum temperature reached.



Note: The two lines are *not straight* lines as the total volume of the reaction mixture is changing as titration proceeds, hence *m* in  $q = mc\Delta T$  is changing as well as *q*.

## **Calculations:**

Let the equivalence volume be  $V_{eq}$  cm<sup>3</sup>. Let the maximum temperature at equivalence point be  $T_{max}$  °C, and the initial temperature be  $T_{initial}$  °C.

$$[HNO_{3}] = \frac{2n_{Ba(OH)_{2}}}{V_{eq}} = \frac{2 \times \frac{25.0}{1000} \times 1.00}{\frac{V_{eq}}{1000}} = \frac{50}{V_{eq}} \mod dm^{-3}$$
$$\Delta H_{neu} = -\frac{q}{n_{H_{2}O}} = -\frac{mc\Delta T}{n_{H_{2}O}}$$
$$= -\frac{(25 + V_{eq}) \times 4.18 \times (T_{max} - T_{initial})}{0.0500} \text{ J mol}^{-1}$$

(c) How, if at all, will the maximum temperature rise vary if you use double the volumes of the original acid and metal hydroxide solutions? Explain your answer.

No change. Even though amount of  $H_2O$  produced is doubled, the total volume of the solution is also doubled.

## Worked Example 4D (NYJC 2018/4/1h)

The volume of aqueous sodium hydroxide needed to completely neutralise all the ethanedioic acid,  $C_2O_4H_2$  present in **FB 1** can be obtained by carrying out a thermometric titration.

The reaction between an acid and an alkali is exothermic. It is possible to make use of this fact to determine the equivalence-point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration* and can be used to calculate the concentration of an acid solution and the value of the enthalpy change of neutralisation,  $\Delta H_n$ .

The concentration of an acid solution can be determined by adding various volumes of acid and alkali and measure the change in temperature. A series of about six experiments were conducted, where different volumes of alkali were added to a fixed volume (for example 25.0 cm<sup>3</sup>) of acid while keeping the total volume of the solution constant by adding appropriate volumes of water.

The data obtained is plotted and two best-fit graph lines are drawn. One line is drawn using data before the equivalence-point and the second line using the remaining data. These lines are then extrapolated (extended) until they cross.

Using the information given above, you are required to write a plan for a thermometric titration in which a known concentration of an aqueous solution of sodium hydroxide is added to FB 1. You are to determine the volume of aqueous sodium hydroxide required to completely neutralise the ethanedioic acid present in FB 1.

You may also assume that you are provided with:

- **FB 1** which is a mixture of approximately 0.01 mol dm<sup>-3</sup> aqueous sodium ethanedioate, C<sub>2</sub>O<sub>4</sub>Na<sub>2</sub>, and approximately 0.1 mol dm<sup>-3</sup> ethanedioic acid, C<sub>2</sub>O<sub>4</sub>H<sub>2</sub>.
- 0.35 mol dm<sup>-3</sup> sodium hydroxide, NaOH
- the equipment normally found in a school or college laboratory.

Your plan should include:

- calculation of the approximate volume of aqueous sodium hydroxide required to completely neutralise the ethanedioic acid present in **FB 1**;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a table containing the volumes of each reagent to be added;
- how you would recognise that the equivalence-point had been passed;
- a sketch of the graph you would expect to obtain;
- an explanation of the shape of your graph.

#### **Pre-calculations:**

For 25 cm<sup>3</sup> of **FB 1**,

Note: Volume of acid is fixed at 25 cm<sup>3</sup> so that the bulb of the thermometer can be completely immersed into the solution when measuring the initial temperature in a Styrofoam cup.

Amount of  $C_2O_4H_2 = \frac{25}{1000} \times 0.1 = 0.00250 \text{ mol}$ 

Amount of NaOH required for neutralisation =  $0.00250 \times 2 = 0.00500$  mol Approximate volume of NaOH required =  $\frac{0.00500}{2.25} \times 1000 = 14.29$  cm<sup>3</sup>

## Procedure:

- 1. Using a burette, transfer 25.00 cm<sup>3</sup> of **FB 1** into a Styrofoam cup. Place the cup in a 250 cm<sup>3</sup> beaker to prevent it tipping over.
- 2. Using a second burette, measure the required volume of water as shown in the table below and add it to the **FB 1** in the Styrofoam cup. Use 0.2 °C interval thermometer to stir the mixture gently.
- 3. Record the initial temperature of the **FB 1** and water mixture using the thermometer.
- 4. From a third burette, measure the required volume of NaOH as shown in the table below into a 100 cm<sup>3</sup> beaker. Record the initial temperature of the NaOH using a 0.2 °C interval thermometer
- 5. Add the NaOH to the **FB 1** and water mixture in the Styrofoam cup. Use the thermometer to stir the mixture gently.

Note: Do not add NaOH to the Styrofoam from the burette as it takes a long time for the required volume to be transferred, which results in more heat loss, making the temperature rise measured more inaccurate.

- 6. Record the highest temperature reached.
- 7. Wash and carefully dry the Styrofoam cup and 100 cm<sup>3</sup> beaker.
- 8. Repeat steps 1 to 7 by varying the volumes of water and NaOH added to **FB 1** as shown in the table below. Record all measurements of volume, temperature, weighted initial temperature and temperature change,  $\Delta T$ .

expt	vol of FB 1/ cm <sup>3</sup>	vol of water/ cm <sup>3</sup>	initial temp of <b>FB 1</b> and water/ ºC	vol of NaOH/ cm <sup>3</sup>	initial temp of NaOH/ ºC	weighted initial temp/ ºC	highest temp/ °C	∆ <i>T</i> / °C
1	25.00	22.00		8.00				
2	25.00	18.00		12.00				
3	25.00	16.00		14.00				
4	25.00	14.00		16.00				
5	25.00	12.00		18.00				
6	25.00	10.00		20.00				

Note:

- Keep volume of FB 1 constant and vary volume of NaOH. Volumes of NaOH chosen should have three volumes lower than 14.29 cm<sup>3</sup> (max volume of NaOH required calculated in pre-calculations), and three volumes higher than 14.29 cm<sup>3</sup>.
- Keep total volume of mixture constant by topping up with the appropriate volumes of deionised water. Total volume should be kept to within 100 cm<sup>3</sup> taking into account the maximum volume of the Styrofoam cup used and to prevent spillage upon mixing.

## Processing of data:

- 9. Plot a graph of the  $\Delta T$  against the volume of NaOH added.
- 10. Draw a line-of-best-fit for the points before the maximum temperature change.
- 11. Draw a second line-of-best-fit for the points after the maximum temperature change.
- 12. Extrapolate both lines until they meet.
- 13. Read from the graph the maximum temperature change,  $\Delta T_{max}$  and the volume of NaOH needed to obtain this value. This is the equivalence point.



• Before equivalence point, the limiting reagent is NaOH. As more NaOH is added, the amount of water formed increases. Since  $\Delta H_n = -\frac{m \times c \times \Delta T}{n_{H_2O}}$ ,  $\Delta T$  is directly proportional to

the amount of water formed in the neutralisation reaction. Since the amount of water increases with increasing volume of NaOH,  $\Delta T$  increases.

- After the equivalence point, the limiting reagent is the ethanedioic acid in FB 1. The amount of water formed depends on the amount of acid reacted instead. As a fixed volume of FB 1 is used, the amount of acid present is unchanged. Hence, Δ*T* remains constant.
- (ii) In another experiment, hydrochloric acid is used instead of FB 1. If the hydrochloric acid has the same concentration as the ethanedioic acid present in FB 1, draw on your graph in (i) another pair of lines to show the results you would expect to obtain. Explain your answer.

For hydrochloric acid which is a strong monobasic acid,, the first line-of-best-fit has a **steeper** gradient and intersects the second line-of-best-fit at a lower  $\Delta T_{max}$  and at half V<sub>eq</sub>.

A monobasic acid will require half the volume of NaOH for complete neutralisation  $\Rightarrow$  half V<sub>eq</sub> and also produce half the amount of water at complete neutralisation. Hence total heat released from reaction will be lower than that with ethanedioic acid  $\Rightarrow$  lower  $\Delta T_{max}$ 

However, HCI is a **strong** acid, the **neutralisation reaction is more exothermic** as compared to weak acids (as some energy is absorbed during neutralisation to dissociate the undissociated weak acid). Hence rate of temperature change i.e. **gradient will be steeper.** 

Note: It may be useful to also visualise how the graph for a strong dibasic acid looks like as compared to a weak dibasic acid.

#### Practice Question 4C (PJC 2018/4/1g – modified)

The reaction between an acid and a metal hydroxide is exothermic.

A thermometric titration can be done to calculate the basicity of an acid by performing several experiments in which varied volumes of acid and base are mixed together, keeping the total volume constant. The highest temperature for each experiment is then recorded.

The data obtained can then be used to plot a graph of  $\Delta T$  against volume of NaOH used to determine the basicity of an acid.

Using the information above, plan an investigation to determine the basicity of an unknown acid  $H_nA$  of concentration 2.00 mol dm<sup>-3</sup> (where n = 1 or 2).

You may assume that you are provided with

- 2.00 mol dm<sup>-3</sup> sodium hydroxide, NaOH
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the volumes of reactants that you would use,
- the apparatus that you would use,
- the procedure that you would follow and the measurements that you would take,
- how you would determine the basicity of the unknown acid, H<sub>n</sub>A via sketches of the graphs you would expect to obtain.

## 5 Reaction Kinetics

The rate of a chemical reaction may be studied by **monitoring the composition of the reacting mixture as the reaction progresses or when reaction stops**. This can be done using either the **discontinuous** or **continuous** (or real time analysis) methods.

**Discontinuous method:** The rate of reaction is studied by repeating the experiment many times using different reaction mixtures. (i.e. clock reaction)

Continuous method: Composition of the reaction mixture is analysed while the reaction is in progress.

The composition of a reaction mixture may be followed by tracking any **chemical** or **physical** changes as the reaction proceeds.

characteristic of reaction	property to track
leads to change in number of gaseous particles in system	pressure
leads to the production of gaseous product from non-gaseous reactants	mass or volume
leads to change in number of ions in system	conductivity
leads to consumption/production of coloured species	absorbance <i>via</i> colourimetry
leads to consumption/production of acidic/basic species	concentration or titre volume <i>via</i> titration (acid- base)
leads to consumption/production of oxidising/reducing species	Concentration or titre volume <i>via</i> titration (redox)

With the experimental data obtained from the monitoring of the composition of the reacting mixture, there are two common methods that can be used to **determine the reaction orders** with respect to each reactant, and therefore the **rate equation** – the **initial rates method (non-graphical method)** and the **graphical method**.

Refer to pages 23 to 28 of Chemistry Practical Planning Handbook for more details.

#### 5.1 Overview of a Kinetic Study



## 5.2 Discontinuous Method

There are certain reactions that are accompanied by prominent visual changes. The rate of such reactions can be studied by carrying out the reaction multiple times with different concentrations of the reactants, measuring the time taken for the visual change to occur each time.

From the data collected, order of reactions is deduced via non-graphical or graphical method.

## 5.2.1 Initial Rate Method (non-graphical method)

In this method of studying kinetics, the determination of the initial rate involves measuring the change in concentration of one of the reactants or products which occurs in the first small time interval after the reagents are mixed.

In other words, the **initial rate of the reaction is actually approximated by the average rate of the reaction**. The approximation is a good one provided the reaction has only proceeded to a **small extent**.

In practice, we measure the average rate of reacting a fixed concentration of a reactant or forming a fixed concentration of product.

Consider the reaction  $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{D}$ , which has the rate equation, rate =  $k[\mathbf{A}]^m[\mathbf{B}]^n$ .

## To find m with respect to reactant A:

• Prepare reaction mixture 1 by mixing reactants **A** and **B** of concentrations as specified in the table below.

reaction mixture	initial [ <b>A</b> ] /mol dm <sup>-3</sup>	initial [ <b>B</b> ] /mol dm <sup>-3</sup>	time taken/s	initial rate of reaction ( <i>i.e.</i> $\frac{d[\mathbf{D}]}{dt}$ at $t = 0$ ) / mol dm <sup>-3</sup> s <sup>-1</sup>
1	р	q	<i>t</i> 1	$\frac{d}{t_1}$
2	2р	q	$t_2$	$\frac{d}{t_2}$

- Upon mixing the reactants, measure the **time taken for the concentration of product D to increase from zero to** *d* **mol** dm<sup>-3</sup> by using a suitable experimental technique.
- Repeat the measurement using Reaction Mixture 2.
- For each mixture, determine the initial rate of the reaction (*i.e.*  $\frac{d[\mathbf{D}]}{dt}$  at time t = 0) by

calculating the average rate of the reaction (i.e.  $\frac{d[D]}{dt} \approx \frac{\Delta[D]}{\Delta t} = \frac{d}{\text{time taken}}$ ).

• Since for the two mixtures, the only variable is the initial [A], the experimentally determined initial rates should vary with the initial [A] raised to the power of *m*. The value of *m* is deduced accordingly. Order of reaction is deduced using initial rate data.

#### To find n with respect to reactant B:

• The above procedure is repeated with the initial [A] kept constant but the initial [B] varied.

## Worked Example 5A: Discontinuous Method (Deduction via Initial Rate Method)

 $S_2O_8^{2-}$  ions are reduced in the presence of I<sup>-</sup> ions. You are to design an experiment to determine the order of reaction with respect to  $S_2O_8^{2-}$  by an <u>initial rate method</u>.

You may assume the following are available:

- 0.200 mol dm<sup>-3</sup> aqueous KI
- 0.100 mol dm<sup>-3</sup> aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>
- 0.00500 mol dm<sup>-3</sup> aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- starch indicator
- stopwatch
- white tile
- standard laboratory apparatus
- 100 cm<sup>3</sup> beaker
- deionised water
- (a) Write balanced equations for the two reactions involved.

 $S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$  $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ 

- (b) Taking into consideration the reactions involved in (a) and the apparatus and reagents given, describe an experimental procedure that would allow you to determine the order of reaction with respect to  $S_2O_8^{2-}$  by an initial rate method.
  - 1. Using two different 50 cm<sup>3</sup> measuring cylinders, add 20.0 cm<sup>3</sup> of KI and 10.0 cm<sup>3</sup> of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to a clean and dry 100 cm<sup>3</sup> beaker.
  - 2. Using a 10 cm<sup>3</sup> measuring cylinder, add 5.0 cm<sup>3</sup> of starch to the same beaker.
  - 3. Using a 100 cm<sup>3</sup> measuring cylinder, add 45.0 cm<sup>3</sup> of deionised water to the same beaker.
  - 4. Mix the contents thoroughly by swirling the beaker and place the beaker on a white tile.
  - 5. Measure out 20.0 cm<sup>3</sup> of  $Na_2S_2O_8$  using a 50 cm<sup>3</sup> measuring cylinder.

Note: Measuring cylinder chosen should be appropriate for the volume to be measured. It should not be too big in comparison to the volume measured to minimise error incurred, but should not be too small such that it has to be filled multiple times to measure the required volume.

- 6. Pour the Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution rapidly into the beaker. Start the stopwatch when about half of the Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> has been added. Swirl the beaker again.
- 7. Stop the stopwatch when the dark blue colour first appears and record the time elapsed, t to 0.1 s.
- 8. Repeat Steps 1 to 5 for Experiments 2 to 5 with varying volumes of deionised water and  $Na_2S_2O_8$  according to the table below:

## WORKED EXAMPLES AND PRACTICE QUESTIONS

Expt	volume of KI / cm <sup>3</sup>	volume of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> / cm <sup>3</sup>	volume of H <sub>2</sub> O / cm <sup>3</sup>	volume of Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , V / cm <sup>3</sup>	time elapsed, <i>t</i> / s	$\frac{1}{t}/s^{-1}$
1	20.0	10.0	45.0	20.0		
2	20.0	10.0	50.0	15.0		
3	20.0	10.0	55.0	10.0		
4	20.0	10.0	40.0	25.0		
5	20.0	10.0	35.0	30.0		

Note:

• Total volume of solution must be kept constant so that the volume of each reagent used will be directly proportional to the initial concentration of the reagent.

 Volumes of KI, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> should be kept constant such that any changes in the initial rates of reaction is solely due to the changes in the concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, such that the order of reaction wrt Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> can be determined.

- Initial rate of reaction can be regarded to be directly proportional to  $\frac{1}{4}$ .
- To plot a graph (for **(c)**), there should be at least 5 data points.
- (c) Explain briefly how the results of the experimental procedure can be used to determine the order of reaction with respect to  $S_2O_8^{2-}$ .

#### 1. By inspection

Assuming rate of reaction  $\propto \frac{1}{t}$  and the [S<sub>2</sub>O<sub>8</sub><sup>2–</sup>]  $\propto$  volume of S<sub>2</sub>O<sub>8</sub><sup>2–</sup>, compare experiments

1 and 3.

When volume of  $S_2O_8^{2-}$  is **doubled**, if  $\frac{1}{t}$  is

- the same, reaction is  $\underline{\text{zero}}$  order w.r.t.  $S_2O_8^{2-}$
- doubled, reaction is first order w.r.t. S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.
- quadrupled, reaction is second order w.r.t. S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.
- 2. By graphing

Since rate of reaction  $\propto \frac{1}{t}$  and the  $[S_2O_8^{2-}] \propto$  volume of  $S_2O_8^{2-}$ , plotting a graph of  $\frac{1}{t}$ against volume of  $S_2O_8^{2-}$  is equivalent to plotting a graph of <u>rate against  $[S_2O_8^{2-}]$ </u>.

If the reaction is <u>zero order</u> w.r.t.  $S_2O_8^{2-}$ , a <u>horizontal straight line graph with the</u> <u>same</u>  $\frac{1}{t}$  will be obtained.

If the reaction is <u>first order</u> w.r.t.  $S_2O_8^{2-}$ , a <u>straight line graph (with a positive</u> gradient) starting from the origin will be obtained.

If the reaction is <u>second order</u> w.r.t.  $S_2O_8^{2-}$ , a <u>parabola starting from the origin</u> will be obtained.

## Worked Example 5B: Discontinuous Method (Deduction via Graphical Method)

You are to investigate the effect of <u>varying the concentration of an acid</u> on the rate of reaction between magnesium and hydrochloric acid at room temperature by a graphical method.

You are provided with the following

- approximately 20 cm of magnesium ribbon (2.5 g, *A*<sub>r</sub> 24.3)
- 2.0 mol dm<sup>-3</sup> hydrochloric acid
- deionised water
- two burettes
- stopwatch
- small beakers
- glass rod
- ruler calibrated in cm
- a pair of scissors

Using the items provided, plan an experiment by which you can study the effect of varying the concentration of hydrochloric acid on the rate of its reaction with magnesium.

(a) Calculate the minimum volume of 2.0 mol dm<sup>-3</sup> HC*l* required to completely react with 3 cm of Mg ribbon used in each experiment.

## Pre-calculation:

Amount of Mg in 3 cm of the ribbon =  $\frac{3}{20} \times 2.5 \div 24.3 = 0.0154$  mol

Amount of HCl needed =  $2 \times 0.0154 = 0.0309$  mol

Minimum volume of 2.0 mol dm<sup>-3</sup> HC*l* used in each expt =  $\frac{0.0309}{2.0}$  = 0.01545 dm<sup>3</sup> = **15.45 cm<sup>3</sup>** 

(b) By considering your answer to (a), complete the following table by suggesting suitable volumes of HCl and water for all 5 experiments.

Experiment	1	2	3	4	5
Volume of $HC1/ cm^3$					50.00
Volume of water / cm <sup>3</sup>					0.00

Note:

- Volume of HCl used must be more than 15.45 cm<sup>3</sup> to fully react with the 3 cm Mg ribbon used.
- Total volume of each experiment must be kept constant so that volume of HC*l* used ∞ concentration of HC*l* used

Experiment	1	2	3	4	5
Volume of HC1 / cm <sup>3</sup>	20.00	25.00	30.00	40.00	50.00
Volume of water / cm <sup>3</sup>	30.00	25.00	20.00	10.00	0.00

## (c) Using the information from (a) and (b), outline the procedure of your method of investigation. <u>Procedure:</u>

- 1. Cut the magnesium ribbon provided into lengths of 3.0 cm.
- 2. Fill one burette with deionised water and another with 2.0 mol  $dm^{-3} HCl$ .

Note: Volumes of water and acid must be accurately measured to allow for accurate calculations of concentrations.

- 3. Add 50.00 cm<sup>3</sup> of HCl into a small beaker.
- 4. Place one 3.0 cm magnesium ribbon into the beaker starting a stopwatch at the same time. Stir the mixture with a glass rod.
- 5. Measure and record the time needed for the magnesium ribbon to completely dissolve.
- Repeat Steps 2 to 5 with the volumes of HCl and water as stated in the table in (b) for Experiments 1 to 4. In each experiment, stir the HCl and water mixture before adding in the magnesium ribbon in Step 4 to ensure homogeneity.
- (d) Why is the length of Mg ribbon used constant for each experiment?

This is to ensure that the <u>only variable is [HC1]</u> in each experiment, so that the effect of change in [HC1] on the rate of the reaction can be monitored.

(e) Suggest the type of graph which you would plot. Explain how the order of reaction with respect to HC*l* may be determined from your graph.

Since total volume of HC*l* and water is kept constant,  $[HCl] \propto V_{HCl}$ . Since length of Mg ribbon used in experiment is constant,  $\frac{rate \propto 1}{t}$ .

Hence, a graph of  $\frac{1}{t}$  against  $V_{HCI}$  is similar to that of rate against [HCI].

If the  $\frac{1}{t}$  against  $V_{HCl}$  graph is a <u>horizontal line</u>, the reaction is <u>zero</u> order with respect to HCl.

If the  $\frac{1}{t}$  against  $V_{HCl}$  graph is a <u>straight line that passes through the origin</u>, the reaction is <u>first</u> order with respect to HC*l*.

If the  $\frac{1}{t}$  against  $V_{\text{HC}l}$  graph is a <u>parabola that passes through the origin</u>, the reaction could be <u>second</u> order with respect to HC*l*.

## Practice Question 5A: Discontinuous Method (EJC 2018/4/3b)

Calcium carbonate that reacts with hydrochloric acid in an acid-carbonate reaction as shown below.

$$CaCO_{3}(s) + 2HCl(aq) \rightarrow CaCl_{2}(aq) + H_{2}O(l) + CO_{2}(g)$$

Besides using the continuous measurement method in **3(a)** to determine the order of reaction of a reactant, the <u>initial rates method</u> can also be used.

Plan an investigation, which **does not** involve graph plotting, to determine the order of reaction with respect to hydrochloric acid, HC*l*, using the initial rates method.

You are provided the following chemicals and apparatus:

- same apparatus used in the experimental setup in 3(a),
- 2.00 mol dm<sup>-3</sup> HCl solution
- FA 5 powdered CaCO<sub>3</sub>
- stopwatch

In your plan, you should include details of:

- the different concentrations of the reactants used and the conditions of the experiment,
- the procedure you would follow, including the end-point of the experiment
- the measurements you would take,
- an outline of how you would use your results to determine the order of reaction with respect to HC*l*.

You may use the space below to draw a table indicating the headers of the measurements and calculations you would be performing.

#### Practice Question 5B: Discontinuous Method (Changing Temperature) (IJC 2018/4/2f-g)

(f) Sodium thiosulfate reacts with acid to produce a pale yellow precipitate of sulfur.

 $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l)$ 

A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction. Plan an investigation to determine the effect of temperature on the rate of reaction.

You may assume that you are provided with

- 0.10 moldm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.
- 1.00 moldm<sup>-3</sup> hydrochloric acid, HCl
- the equipment normally found in a school or college laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- a suitable number of experiments you would do, and a reasonable temperature range (minimum and maximum temperatures),
- the procedure that you would follow and the measurements that you would take.
- (g) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

## 5.3 Continuous Method

Continuous method studies the rate of reaction in a single reaction mixture without disturbing the reacting system. The change being monitored is related to the change in concentration of either the reactant or the product.

## 5.3.1 Sampling method

This method is used for reactions in aqueous solutions. An aliquot is drawn out of the reaction mixture at regular time intervals. The **reaction in the aliquot is then quenched** (stopped or slowed down drastically) so that the reaction composition can be analysed at leisure.

Quenching may be done by:

- Sudden cooling
- Adding a large amount of solvent
- Rapid neutralisation of an acid reagent
- Removal of a catalyst
- Addition of a quencher

The composition of the remaining reaction mixture can then be determined by carrying out titration.

Order of reaction is then deduced via a graphical method (plotting of graph), either through the shape of the graph, or by determining the initial rates from the concentration-time graphs (initial rate method).

#### 5.2.2 Graphical Method

Consider the reaction  $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} + \mathbf{D}$ , which has the rate equation, rate =  $k[\mathbf{A}]^m[\mathbf{B}]^n$ .

#### To find m with respect to reactant A:

- Prepare a reaction mixture of A and B with initial [B] > initial [A] such that at all times in the reaction mixture, [B] ≈ initial [B] ≈ constant.
   Hence the rate equation becomes rate = k'[A]<sup>m</sup>, where k' = k[B]<sup>n</sup>.
- Follow the change in [A] with time using a suitable experimental technique (sampling or continuous measurement).
- From the experimental data obtained, plot a graph of [A] against time.



## To find n with respect to reactant B:

- Method 1: Same as above method in determining the value of *m*, except to use initial [A] > initial [B].
- Method 2: 1. Repeat the experiment used to find m (see above) using a different initial [B] but still ensure that initial [B] > initial [A].
  - 2. Using the second set of data obtained, plot another graph of [A] against time.
  - 3. For each of the two graphs plotted, determine the initial rate of the reaction by finding the gradient of the tangent to the curve at time t = 0.
  - 4. By comparing the change in the value of initial [B] with the change in the initial rate of the reaction (*i.e.* change in gradient of tangent), the value of *n* can be determined as done in the initial rates method (see Section 5.1).

## Worked Example 5C: Sampling Method (Deduction via Graphical Method)

You are to investigate the order of reaction with respect to  $H_2O_2$  using a sampling method. Hydrogen peroxide decomposes catalytically according to the following equation:

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

You are provided with the following:

٠	aqueous hydrogen peroxide	٠	50 cm <sup>3</sup> burette
٠	aqueous sodium hydroxide	٠	25 cm <sup>3</sup> pipettes
•	aqueous iron(III) chloride	٠	250 cm <sup>3</sup> beakers
٠	dilute cold sulfuric acid	٠	250 cm <sup>3</sup> conical flasks
٠	0.02 mol dm <sup>-3</sup> aqueous potassium manganate(VII)	٠	stopwatch
•	50 cm <sup>3</sup> measuring cylinders	٠	glass rod

When mixed, sodium hydroxide and iron(III) chloride reacts together to produce a catalyst which catalyses the decomposition of hydrogen peroxide.

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

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

[O]:  $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ [R]:  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ Overall:  $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ 

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

The acid completely reacts with sodium hydroxide, <u>removing the catalyst</u> for the decomposition of  $H_2O_2$ , <u>quenching</u> the reaction. The <u>low temperature</u> also significantly <u>reduces the rate of decomposition</u>.

- (c) Taking into consideration the information in (a) and (b), and the apparatus and reagents given, describe an experimental procedure that would allow you to determine the order of reaction with respect to H<sub>2</sub>O<sub>2</sub> using a sampling method. The first three steps of the experiment are outlined as follows:
  - 1. Using a pipette, transfer 50.0 cm<sup>3</sup> of hydrogen peroxide into a 250 cm<sup>3</sup> beaker. To the same beaker, add 25 cm<sup>3</sup> of sodium hydroxide using a measuring cylinder.
  - 2. Place 50 cm<sup>3</sup> of iron(III) chloride into a second measuring cylinder.
  - 3. Add the solution of iron(III) chloride into the same beaker (in step 1) and start the stopwatch immediately. Stir the mixture using a glass rod to ensure even mixing.
  - 4. Using a pipette, withdraw 25.0 cm<sup>3</sup> of the reaction mixture into a 250 cm<sup>3</sup> conical flask. At time **2 min**, add 20 cm<sup>3</sup> of cold dilute sulfuric acid into the conical flask.
  - Take further 25.0 cm<sup>3</sup> samples from the reaction mixture and transfer them into separate conical flasks, and add cold dilute sulfuric acid (as in step 4) at four, six, eight, ten, twelve and fourteen minutes respectively, after the initial mixing.

Note: Need at least 5 readings to plot the graph for analysis

- 6. Titrate the hydrogen peroxide present in each of the conical flasks obtained against aqueous potassium manganate(VII) placed in a 50.00 cm<sup>3</sup> burette.
- 7. Record the titration results in a suitable table.
- 8. Pipette 10.0 cm<sup>3</sup> of hydrogen peroxide into a 250 cm<sup>3</sup> conical flask.
- 9. Add 20 cm<sup>3</sup> of dilute sulfuric acid into the conical flask and titrate against aqueous potassium manganate(VII). This is the volume of KMnO<sub>4</sub> at t = 0,  $V_0$ .
- (d) Draw the suitable tables to record the experimental data.

Time from initial mixing / min	0	2	4	6	8	10	12	14
Final burette reading / cm <sup>3</sup>								
Initial burette reading / cm <sup>3</sup>								
Volume of <u>KMnO<sub>4</sub></u> / cm <sup>3</sup>	V <sub>0</sub>	<b>V</b> 1	V <sub>2</sub>	V <sub>3</sub>	<b>V</b> 4	<b>V</b> 5	<b>V</b> 6	<b>V</b> 7

(e) Suggest the type of graph which you would plot. Explain how the order of reaction with respect  $H_2O_2$  may be determined from your graph.

Volume of KMnO<sub>4</sub> used  $\infty$  amount of KMnO<sub>4</sub> reacted  $\infty$  amount of H<sub>2</sub>O<sub>2</sub> in conical flask.

As volumes of aliquots withdrawn were constant at 25.0 cm<sup>3</sup>,

Amount of  $H_2O_2$  in conical flask  $\propto [H_2O_2]$  in conical flask

Hence, to monitor the change in concentration of  $H_2O_2$  against time, sketch the graph of volume of KMnO<sub>4</sub> used against time.

If the graph obtained is a <u>straight downward sloping line</u>,  $\frac{d[H_2O_2]}{dt}$  = constant. Reaction is

<u>zero</u> order w.r.t. H<sub>2</sub>O<sub>2</sub>.

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

If the graph obtained is a <u>downward sloping curve</u> with an <u>increasing half-life</u>, reaction is <u>second</u> (or above) order w.r.t.  $H_2O_2$ .



## Practice Question 5C: Continuous Method (modified 2017 A level P4/2c)

The decomposition of hydrogen peroxide, can be catalysed by the enzyme catalase, present in liver.

Equation 1  $2H_2O_2 \rightarrow 2H_2O + O_2$ 

The rate equation for this decomposition is shown.

rate =  $k[H_2O_2][catalase]$ 

If the concentration of the catalase is kept constant, the rate equation becomes

rate = 
$$k'[H_2O_2]$$

where k' = k[catalase].

The sampling method can be used to investigate the effect of temperature, T, on the rate of decomposition of  $H_2O_2$ .

Plan an investigation to determine the effect of temperature, T, on the rate of decomposition of H<sub>2</sub>O<sub>2</sub> with catalase.

You may assume that you are provided with

- 500 cm<sup>3</sup> of 0.170 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>
- a piece of liver
- a scalpel (knife)
- 0.0200 mol dm<sup>-3</sup> KMnO<sub>4</sub>(aq)
- 0.2 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>(aq)
- common college laboratory apparatus

In your plan, you should include brief details of

- the reactants and conditions that you would use,
- the apparatus that you would use,
- the procedure that you would follow and the measurements that you would take,
- how you would determine the initial rate for each experiment
- how you would deduce the effect of temperature on rate of reaction.

## 6 Qualitative Analysis

## 6.1 Inorganic Qualitative Analysis

Inorganic Qualitative Analysis (QA) involves the identification of ions present in a sample. There are generally two types of tests: **dry reactions** which involve **solid** samples, and **wet reactions** which involve **solutions**.

## **Dry Reactions**

**Dry reactions** usually involve heating of the solid samples and testing for any gas that may be evolved from the heating.

The confirmatory tests for gases are as follows:

Gas	Test	Observation
H <sub>2</sub> (neutral)	lighted splint or burning splint	Gas evolved extinguishes lighted/ burning splint with a 'pop' sound.
$O_2$ (neutral) (usually accompanied by other gas, <i>e.g.</i> Solid NO <sub>3</sub> <sup>-</sup> salt gives NO <sub>2</sub> and O <sub>2</sub> gas Solid XO <sub>3</sub> <sup>-</sup> salt gives X <sub>2</sub> and O <sub>2</sub> gas (X is C <i>l</i> , Br, I)	glowing splint	Gas evolved rekindles the glowing splint.
CO <sub>2</sub> (acidic)	aqueous Ca(OH) <sub>2</sub> (do not use too much, add just enough Ca(OH) <sub>2</sub> to cover the tip of the delivery tube)	Gas evolved forms a white ppt with Ca(OH) <sub>2</sub> . (White ppt dissolves with excess CO <sub>2</sub> .)
NH <sub>3</sub> (alkaline)	moist red litmus paper	Gas evolved turns moist red litmus paper blue.
SO₂ (acidic)	acidified potassium manganate(VII) (Add dil. H <sub>2</sub> SO <sub>4</sub> to acidify KMnO <sub>4</sub> , then use filter paper strip dipped into acidified KMnO <sub>4</sub> )	Gas evolved decolourises purple KMnO4.
NO₂ (brown gas; acidic)	FeSO <sub>4</sub> solution	Gas evolved turns green FeSO <sub>4</sub> black.
Cl <sub>2</sub> (pale greenish yellow; pungent)	moist blue litmus paper	Pale greenish yellow gas evolved turns moist blue litmus paper red and then bleached it.
Br₂ (reddish brown vapour)	moist blue litmus paper	Reddish brown gas evolved turns moist blue litmus paper red and then bleached it.
$I_2$ (violet vapour, condenses to a black crystals)	starch iodide paper	Violet gas evolved turns starch iodide paper blue-black.

## Wet Reactions

Wet reactions usually involve one of the following changes:

- by the formation of a **precipitate**,
- by the evolution of a **gas**, or
- by a change in **colour**.

The majority of the reactions carried out in QA are wet reactions.

To predict and understand the formation of precipitates in QA, it is useful to know the **solubilities of common salts and hydroxides**:

- All sodium, potassium and ammonium compounds are soluble.
- All nitrates are soluble.
- All chlorides, bromides and iodides are soluble except those of silver and lead. Silver halides may be further differentiated by their colour and solubility in excess aq NH<sub>3</sub>.
- All sulfates are soluble except barium and lead(II) sulfate.
- All carbonates and sulfites are insoluble except those of sodium, potassium and ammonium.
- All hydroxides are insoluble except Group 1 and Group 2 (excluding Mg<sup>2+</sup>) hydroxides. Hydroxides of lead, aluminium, zinc and chromium are soluble in excess aq NaOH

All relevant QA tests and their positive descriptions can be found in the Data Booklet provided. These tests can be grouped to make it easier for understanding:

## Identification of cations

- Addition of NaOH dropwise
  - Observe for formation coloured precipitate (Cu<sup>2+</sup>, Fe<sup>2+</sup> etc.) or white precipitate
  - Observe whether precipitate dissolves upon addition of excess NaOH
  - Observe for evolution of ammonia gas upon heating (indicates presence of NH4<sup>+</sup> ions)
- Addition of  $\mathbf{NH}_3$  dropwise
  - Observe for formation coloured precipitate (Cu<sup>2+</sup>, Fe<sup>2+</sup> etc.) or white precipitate
  - Observe whether precipitate dissolves upon addition of excess NH<sub>3</sub>

Identification of anions

- Test for halides: Addition of AgNO<sub>3</sub>, followed by aqueous NH<sub>3</sub>.
- Test for **SO**<sub>4</sub><sup>2-</sup> and **SO**<sub>3</sub><sup>2-</sup>: Addition of **Ba**<sup>2+</sup>, followed by **dilute acid**
- Test for  $NO_3^-$  and  $NO_2^-$ : Addition of A*l* and heating (followed by test for  $NH_3$  gas)
- Test for CO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup> or SO<sub>3</sub><sup>2-</sup>: Addition of an acid. Does the gas liberated form a white ppt in Ca(OH)<sub>2</sub> (*i.e.* CO<sub>3</sub><sup>2-</sup> present)? Is brown NO<sub>2</sub> gas liberated (*i.e.* NO<sub>2</sub><sup>-</sup> present)? Does it turn purple acidified KMnO<sub>4</sub> colourless (*i.e.* SO<sub>3</sub><sup>2-</sup> present)?

## In your procedure,

- Show sense of **coherence** and provide detailed **sequence** of plan
- Choose appropriate **procedures**, **apparatus** and **materials** with essential details (e.g. **specific amounts** of all materials used at each stage)

## Refer to pages 30 to 33 of Chemistry Practical Planning Handbook for more details.

#### Questions annotated with asterisk (\*) will be covered during lecture.

#### Worked Example 6A

You are provided with two solutions, FA 1 and FA 2.

Br<sup>-</sup>, C*t*<sup>-</sup>, Mg<sup>2+</sup> and A $l^{\beta+}$  could be present in these solutions. Each of these solutions contain one cation and one anion.

By reference to the Qualitative Analysis Notes, outline a sequence of chemical tests by which you could identify each of ions present each of the solutions.

Procedure	Expected observations	Ion identified
Place 1 cm depth of <b>FA 1</b> in a test-tube.		
Add AgNO <sub>3</sub> solution dropwise followed by excess aqueous ammonia.	White ppt, soluble in excess NH <sub>3</sub> OR Cream ppt, insoluble in excess	C <i>t</i> - Br⁻
Repeat using <b>FA 2</b> .		
Place 1 cm depth of <b>FA 1</b> in a test-tube.		
Add aqueous NaOH solution until in excess.	White ppt, insoluble in excess aq NaOH OR	Mg <sup>2+</sup>
Repeat using <b>FA 2</b> .	White ppt, soluble in excess aq NaOH to give colourless solution	Aℓ³+
Place 1 cm depth of <b>FA 1</b> in a test-tube.		
Add aqueous ammonia solution until in excess.	White ppt formed, insoluble in excess NH <sub>3</sub> (aq) OR	Mg <sup>2+</sup>
Repeat using <b>FA 2</b> .	White ppt formed, insoluble in excess NH <sub>3</sub> (aq)	Aℓ³+

#### \* Worked Example 6B

You are provided with a solution containing the anions I<sup>-</sup> and Cl, labeled **FA 3**.

You are provided with the reagents NaOH(aq),  $NH_3(aq)$ ,  $HNO_3(aq)$ , HC/(aq),  $AgNO_3(aq)$  and deionised water, together with test-tubes, a filter funnel and filter paper.

You are to devise a sequence of steps by which, using only these materials, but not necessarily all of them, the two anions in **FA 3** could be separated so that each anion is present in a separate precipitate. Give a description of your proposed sequence of steps, numbering each step.

Procedure	Expected Observation
<ol> <li>Add excess aqueous AgNO<sub>3</sub> to 1 cm<sup>3</sup> of the mixture in a test tube.</li> </ol>	White and yellow ppt formed.Reaction: $Ag^+(aq) + X^-(aq) \rightleftharpoons AgX(s)$
2. Add <b>excess</b> aqueous NH <sub>3</sub> to the resulting mixture.	<ul> <li>White ppt dissolved, leaving yellow ppt.</li> <li>Reaction: Ag<sup>+</sup>(aq) + X<sup>-</sup>(aq) ⇒ AgX(s)</li> <li>For AgC<i>l</i>, the addition of dilute NH<sub>3</sub> is sufficient to lower [Ag<sup>+</sup>] such that the ionic product becomes smaller than K<sub>sp</sub> of AgC<i>l</i>. Hence, the AgC<i>l</i> precipitate dissolves completely in dilute NH<sub>3</sub>.</li> <li>For AgI, the value of K<sub>sp</sub> is extremely low. Thus, regardless of the concentration of NH<sub>3</sub> added, the ionic product of AgI remains greater than its K<sub>sp</sub>. Hence the AgI precipitate remains when dilute or concentrated NH<sub>3</sub> is added.</li> </ul>
3. Filter the mixture into a test-tube and wash the residue with deionised water. Keep filtrate for Step 4.	Yellow ppt (AgI) is collected.
<ol> <li>Using a dropper, add dropwise aqueous HNO<sub>3</sub> to the test-tube containing the filtrate from Step 3.</li> </ol>	<ul> <li>White ppt is formed.</li> <li>Reaction: Ag<sup>+</sup>(aq) + 2NH<sub>3</sub>(aq) ⇒ [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>(aq)</li> <li>Addition of HNO<sub>3</sub> removes NH<sub>3</sub>, shifting position of the above equilibrium to the left to form more Ag<sup>+</sup>. Due to the increase in [Ag<sup>+</sup>], the ionic product of AgCl is now greater than its greater than its K<sub>sp</sub>. Hence the AgCl precipitate is reformed.</li> </ul>
5. <b>Filter</b> out the ppt and wash the residue with deionised water.	White ppt (AgCI) is collected.

#### Practice Question 6A: Inorganic QA (PJC 2018/4/3d)

**FA 7** is a solution that contains  $Fe^{2+}$  and  $Al^{3+}$  ions.

Plan a sequence of steps by which the two ions could be separated so that each ion is present in a separate precipitate. For each of the steps, you are to specify the location of the ions and their formulae.

You are also required to specify the amount (dropwise or excess) of reagents that you add.

You may assume that the usual bench reagents and apparatus are available for use.

#### Practice Question 6B: Inorganic QA (TJC 2018/4/3e)

There are four solutions labelled **FB 1**, **FB 2**, **FB 3**, and **FB 4**. Each solution contains one of the following:

- dilute hydrochloric acid
- aqueous sodium carbonate
- aqueous barium nitrate
- aqueous aluminium chloride

The solution names and **FB** codes are not in order.

- (i) Without any indicators and using these solutions alone, plan the steps which will enable you to identify these solutions. Write your plan in the space below, showing how you would record your observations in a table.
- (ii) Describe, with reference to the reactions occurring, how you would use the observations to confirm the identities of FB 1, FB 2, FB 3, and FB 4.

## 6.2 Organic Qualitative Analysis

|--|

Reagent / Test	Reagent / Test Observation		
	Orange Br <sub>2</sub> (aq) decolourised	C=C	
<b>Br₂(aq)</b> , r.t.	Orange Br <sub>2</sub> (aq) decolourised; white ppt	OH , NH <sub>2</sub>	
Brady's reagent, r.t.; 2,4-DNPH; 2,4-dinitrophenylhydrazine; $O_2N$ $NO_2$ $NH-NH_2$	Orange ppt		
Neutral FeC <i>l</i> ₃(aq)	Purple colouration	OH	
Fehling's reagent; $Cu(C_4H_4O_6)_2^{2-}(aq), OH^{-}(aq);$ $Cu^{2+}(aq), OH^{-}(aq);$ Warm the mixture in a beaker of hot water.	Brick-red ppt (of Cu <sub>2</sub> O)	aliphatic O only	
HC <i>l</i> , HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> (aq)	Dissolves	amines	
<b>Iodoform test</b> ; <b>I</b> <sub>2</sub> (aq), NaOH(aq) Place 5 drops of the compound in a test-tube. Add about 1 cm depth of aqueous I <sub>2</sub> . Add NaOH(aq) a drop at a time, with shaking, until the brown colour <i>just disappears</i> . Warm the mixture in a beaker of hot water.	Yellow ppt (of CHI <sub>3</sub> )	$O$ $OH$ $CH_3$ $CH_3$	
<b>KMnO₄(aq), H₂SO₄(aq)</b> , warm the mixture in a beaker of hot water.	Purple KMnO4 decolourised	C=C, 1°, 2° alcohol, O $CH_3$	
<b>KMnO₄(aq), NaOH(aq)</b> , warm the mixture in a beaker of hot water.	Purple KMnO4 decolourised; Brown MnO2 ppt	R H, O	
K₂Cr₂O⁊(aq), H₂SO₄(aq)	Orange K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> turns green	1º, 2º alcohol, R H	
Na metal, r.t.	Effervescence of H <sub>2</sub> which gives a 'pop' sound with a lighted splint	RCO <sub>2</sub> H, OH	

Reagent / Test	Observation	Functional Group	
NaHCO₃(aq)/(s), r.t.	Effervescence of $CO_2$ which gives a white ppt with $Ca(OH)_2$	RCO <sub>2</sub> H	
	Effervescence of CO <sub>2</sub> which gives a white ppt with Ca(OH) <sub>2</sub>	RCO₂H	
Na₂CO₃(aq)/(s), r.t.	Dissolves without CO <sub>2</sub> gas	OH	
NaOH(aq), r.t.	Dissolves	RCO <sub>2</sub> H, OH	
PC <i>1</i> 5, r.t.	White fumes of acidic HC1	ROH, RCO <sub>2</sub> H	
Tollen's reagent; [Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> , OH <sup>-</sup> (aq); Add 30 drops of AgNO <sub>3</sub> (aq) into a test- tube followed by 5 drops of NaOH(aq). Then add dilute NH <sub>3</sub> (aq) drop-by-drop until the brown Ag <sub>2</sub> O(s) is <i>just</i> <i>dissolved</i> . Warm the mixture in a beaker of hot water.	Silver mirror	aliphatic and aromatic O R H	
RCO <sub>2</sub> H, conc. H <sub>2</sub> SO <sub>4</sub> , warm	Sweet smell (ester)	ROH	
ROH, conc H <sub>2</sub> SO <sub>4</sub> , warm		RCO₂H	

## Refer to page 34 of Chemistry Practical Planning Handbook for more details.

## \* Worked Example 6C

You are given 3 unlabelled bottles and each bottle contains one of the following organic compounds:

- Ethanol, CH<sub>3</sub>CH<sub>2</sub>OH
- Propanal, CH<sub>3</sub>CH<sub>2</sub>CHO
- Ethanoic acid, CH<sub>3</sub>CO<sub>2</sub>H

Outline a sequence of simple chemical tests by which you could identify each of the above organic substances. You are not allowed to identify the substances by elimination.

Chemicals and apparatus provided:

- 3 unlabelled bottles each containing one organic compound
- Any other common laboratory chemical reagent and apparatus, if necessary

	Procedure	Expected observations	Compound identified
1.	Using a dropper, add 1 cm depth of each of unknown samples into 3 separate test tubes.		
	Then to each test-tube, add <b>2 cm</b> <b>depth of Na<sub>2</sub>CO<sub>3</sub>(aq)</b> solution dropwise and shake gently. Bubble any gas evolved into freshly prepared Ca(OH) <sub>2</sub> (aq) using a delivery tube.	Effervescence of CO <sub>2</sub> (g) which gives a white precipitate when bubbled into Ca(OH) <sub>2</sub> (aq)	Ethanoic acid
2.	Using a dropper, place 1 cm depth of the remaining unknowns into 2 different test-tube.		
	Add <b>2 drops of freshly prepared</b> <b>Tollens' reagent</b> and <b>warm</b> the mixture in a water bath.	Silver mirror is observed.	Propanal
3.	Using a dropper, place 1 cm depth of the remaining unknown into a test-tube.		
	Add <b>2 drops of I</b> <sub>2</sub> followed <b>by 2 cm</b> <b>depth of NaOH(aq)</b> and <b>warm</b> .	Yellow ppt is observed.	Ethanol

Note: Many organic compounds are potentially **flammable**. Heating should be done in a **water bath** which is heated using a hot plate. **No naked flame** (e.g. Bunsen burner) should be used.

#### Worked Example 6D (HCI 2018/4/4d)

Consider the following organic compounds: 3-hydroxybenzaldehyde, phenol, 2-phenylethanal

Plan an investigation, using test-tube reactions involving reagents containing **transition elements other** than KMnO<sub>4</sub>, which would allow you to identify each of these three organic compounds.

You are provided with either pure liquid samples of these compounds or samples containing the compounds dissolved in an inert organic solvent.

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

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

The plan should include the following:

- Selection of reagents and conditions that would unambiguously identify all 3 compounds with positive tests for each **or** Selection reagents and conditions that would unambiguously identify 2 compounds with positive tests for each
- Logical sequence/order of testing; does not test compounds already identified
- Clearly and unambiguously links the testing sequence with the compounds to be identified

Reagents containing transition elements that can be used are:

- Fehling's solution
- Tollens' reagent.
- Neutral iron(III) chloride FeCl<sub>3</sub>
- Potassium dichromate(VI), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, in the presence of dilute H<sub>2</sub>SO<sub>4</sub>

#### Procedure:

All tests should be carried out in a **separate** test-tubes, and **fresh samples** of the organic compound should be used each time.

- 1. To 1 cm<sup>3</sup> of each organic compound, add 1 cm<sup>3</sup> of Tollens' reagent and warm in a water bath. The test-tubes showing the formation of silver mirror would be either 3-hydroxybenzaldehyde or 2-phenylethanal. The test-tube that does not give the silver mirror would contain phenol.
- 2. To 1 cm<sup>3</sup> of the compound that does not give a positive test in step 1, add **a few drops of neutral FeC***l*<sub>3</sub>. The formation of violet colouration would confirm the identity of **phenol**.
- To 1 cm<sup>3</sup> of separate samples of the organic compounds that give silver mirror in Step 1, add 1 cm<sup>3</sup> of Fehling's solution and heat in a water bath. The test-tube that shows the formation of brick-red ppt would contain 2-phenylethanal while the one with no brick-red ppt would contain 3-hydroxybenzaldehyde.

## Worked Example 6E: Inorganic and Organic QA (RI 2018/4/3c)

The labels of four bottles of solutions in your school chemistry laboratory are found to be missing. They are aqueous solutions of Na<sub>2</sub>CO<sub>3</sub>,  $Al_2(SO_4)_3$ , CH<sub>3</sub>COOH and CH<sub>3</sub>CH<sub>2</sub>CHO.

To identify the solutions in the unlabelled bottles, the following reagents are provided:

- FA 2 which is an aqueous solution of CuSO<sub>4</sub>,
- solution **X** which contains alkaline tartrate ions (a component of Fehling's Reagent).

Fehling's solution can be prepared by mixing equal volumes of solution X and FA 2.

Using only the four unlabelled solutions, **FA 2** and solution **X**, you are to describe a detailed sequence of steps to identify each of the four solutions. Each of the solutions should be identified by at least one positive test.

Your plan should also state the expected observations, identities of any gas and/or precipitate formed and solutions identified at each step.

## Procedure:

- 1. Add **FA 2** to the four unknown solutions separately. The solution that produces a **bluish green ppt** of **CuCO**<sub>3</sub> is **Na**<sub>2</sub>**CO**<sub>3</sub>.
- 2. To the three remaining solutions that did not give a blue–green ppt, add an **equal volume of Solution X and warm**.
- 3. The solution that produces a **reddish brown ppt of Cu<sub>2</sub>O** is CH<sub>3</sub>CH<sub>2</sub>CHO.
- 4. To the two remaining solutions, add the unknown that was identified as Na<sub>2</sub>CO<sub>3</sub>.
- 5. The solution that **produces effervescence of CO**<sub>2</sub> **only** is **CH**<sub>3</sub>**COOH**. The solution that **produces effervescence of CO**<sub>2</sub> and a white ppt of  $Al(OH)_3$  is  $Al_2(SO_4)_3$ .

#### Practice Question 6C: Organic QA (RI 2017/4/3b)

Consider the following organic compounds.







ethanamide

pentan-3-one

propanal

You are provided with aqueous solutions of the three organic compounds above.

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

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

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

#### Practice Question 6D: Organic QA (NYJC 2017/4/3i)

You are provided with four bottles of solutions **without labels**, each bottle contains one of the following compounds

butanal phenylpropan-2-ol propanol propanone

Using only the following chemicals, suggest minimum number of tests you would choose to identify the four unknown solutions. You may use positive or negative results to deduce the identity of your compounds.

Record your choices in the table provided and tick the column where you expect to obtain a positive result for the test you have chosen. Draw a line after each test.

- Sodium
- Fehling's solution
- Tollens' reagent
- Aqueous bromine, Br<sub>2</sub>(aq)
- 2,4-dinitrophenylhydrazine (2,4–DNPH)
- Aqueous iodine, I<sub>2</sub>(aq), and sodium hydroxide, NaOH(aq)
- Acidified potassium manganate(VII) solution, KMnO<sub>4</sub>

test no.	reagent added	butanal	phenyl propan–2–ol	propanol	propanone

You are to plan how the four unknown solutions can be identified using the tests that you have chosen in the table above. Your plan should include details of

- each test is to be carried out,
- how you deduce the identities of the unknown solutions.

# 7 Organic Synthesis

Organic synthesis is a special branch of chemical synthesis and is concerned with the construction of **organic compounds** *via* **organic reactions**. Each step of a synthesis involves a chemical reaction, and **reagents** and **conditions** for each of these reactions need to be chosen to give a *good yield* and a *pure product*. There are **four critical stages** in organic synthesis:

	7.1		7.2		7.3		7.4
	Synthesis		Isolation		Purification	Ch	aracterisation
7.1.1	Inert atmosphere	7.2.1	Extraction &	7.3.1	Extraction &	7.4.1	Melting & boiling
7.1.2	Measuring &		washing		washing		range
	weighing		<ul> <li>liquid-liquid</li> </ul>	7.3.2	Distillation	7.4.2	Polarimetry
7.1.3	Mixing & stirring	7.2.2	Filtration	7.3.3	Sublimation &	7.4.3	Chemical tests
7.1.4	Slow addition		✓ gravity		deposition	7.4.4	Mass (% yield)
7.1.5	Reflux & heating		✓ vacuum	7.3.4	Recrystallisation	7.4.5	Chromatography
7.1.6	Thin-Layer		✓ hot	7.3.5	Chromatography		√ Rf
	Chromatography	7.2.3	Drying agent		(Prep TLC)	7.4.6	Spectroscopy
	(TLC)	7.2.4	Distillation		,		
7.1.7	Quenching		✓ simple				
	0		✓ fractional				
			✓ vacuum				
		7.2.5	Crystallisation				

## 7.1 Synthesis

- 1. Decide on a reaction to accomplish the synthesis.
- 2. Calculate the reactant and reagent quantities.
- 3. Calculate the total volume of solution, and use a flask with at least twice that capacity.
- 4. If the reaction is moisture or air sensitive (*e.g.* LiA*l*H<sub>4</sub> reduction), oven-dry the flask and prepare to run the experiment under an inert atmosphere.
- 5. Weigh your reactants, into your reaction flask, onto weighing paper, or into a separate flask. Do not mix anything yet, and do not weigh sensitive reagents (*e.g.* NaBH<sub>4</sub>) until just before use.
- 6. Save a small sample of each reactant in a vial, for TLC comparison.
- 7. Take a TLC of the reaction as soon as addition is complete. **Co-spot with the reactant** sample(s).
- 8. **TLC the reaction at regular intervals**. The appropriate interval to employ will depend on the reaction rate (*e.g.* every 10 minutes, or 30 minutes, or every hour). When one of the reactants has been consumed, **quench** the reaction immediately.
- 7.1.1 Inert atmosphere
  - ✓ It is sometimes necessary (*e.g.* in reactions involving LiA*l*H₄ or in certain Grignard preparations) to carry out a reaction in *an atmosphere of an inert gas*, such as N₂. A suitable set-up is shown in Eg 25 on page 37<sup>1</sup> of the *Chemistry Practical Planning Handbook*<sup>1</sup>.

## 7.1.2 Measuring & weighing

(see A: Balances and Weighing<sup>1</sup> on page 6 and B: Working with Liquids on page 6)

✓ Large excess of reagents is avoided to prevent wastage and possible undesirable further side reactions.

<sup>&</sup>lt;sup>1</sup> Note that the *section*, *example* and *page number* are referenced to the *Chemistry Practical Planning Handbook*, where more details can be found, unless otherwise stated.

- o Usually at most **1.1 equivalent** of the reagent is used, with respect to the substrate.
- ✓ Catalysts are usually employed in small amounts, at most **10 mol%** (*i.e.* 0.1 equivalent) with respect to the substrate.

## 7.1.3 Mixing & stirring

- ✓ Even and consistent stirring is achieved by means of a magnetic stirrer with magnetic stirring bar (see "Hot plates and stirrer hot plates" in G: Heating on page 8).
- 7.1.4 Slow addition
  - ✓ In the addition of a solid reactant to a liquid reactant, take special caution in the order of mixing to avoid **overheating** as most reactions are exothermic.
  - ✓ In the addition of a liquid reactant to another liquid, ensure that the liquid is introduced via a graduated syringe or dropping funnel (see "Reflux with addition of chemicals" in E: Reflux on page 11) to ensure smooth flow and no spillage.



## 7.1.5 Reflux & heating

- ✓ Although many reactions are exothermic. However, organic reactions are usually associated with significant **activation energies** due to the breaking and forming of covalent bonds. Hence, heating if often necessary for the reaction to complete in a reasonable period of time.
- ✓ Direct heating using a Bunsen burner should be *avoided* as most organic compounds are highly flammable.
- ✓ Heating (see G: Heating on page 8) is commonly done using a sand bath, water bath or oil bath in conjunction with a hot plate.
  - Sand bath: >250°C, Oil bath: <250°C, Water bath: <100°C</li>
  - If without magnetic stirring, boiling / antibumping chips are usually added to ensure smooth boiling (see "Bumping" in G: Heating on page 8).
- Refluxing (see E: Reflux on page 11) is carried out when prolonged heating of a reaction mixture is required. No loss of reaction mixture as vapour is immediately condensed in the condenser during the process.



7.1.6 Thin-Layer Chromatography (TLC)

- ✓ Thin-layer chromatography (TLC) is used for identifying compounds and determining their purity. (see page 36)
  - $\circ~$  The most common adsorbent used is silica gel (SiO\_2) on a glass slide.
  - A fluorescent powder is put into the adsorbent to help with visualisation, which glows a bright green when exposed to 254-nm wavelength ultraviolet light.
- ✓ The steps in performing a TLC involve
  - **Spotting** the compounds on the TLC plate

- **Developing** the plate by running an *eluent* through the adsorbent
- Visualising the spots by examining the plate.



- ✓ Interpretation of a TLC plate involves
  - Measuring the distance from the solvent front to the baseline.
  - Measuring the distance from where the spot stopped to the baseline. Measure to the *centre of the spot*, rather than to one edge. If there are more than one spot, get a distance for each.



- $\circ$  Divide the distance the solvent moved into the distance the spot(s) moved. The resulting ratio is called the *R*<sub>f</sub> value.
- In identical circumstances, this value would always be the same for a single compound, all the time.
- 7.1.7 Quenching
  - ✓ Once TLC indicates that the reaction is complete, **quench** the reaction mixture.
    - Commonly involves adding water (or aqueous solution such as brine, saturated NH<sub>4</sub>C*l*, *etc*.) to the reaction mixture.
    - $\circ~$  If quenching the reaction is exothermic, cool the flask with an ice bath.
    - Otherwise, if a gas is evolved during the quench, watch the reaction carefully to be sure it is under control.
  - ✓ If possible, workup the reaction immediately after quenching it, to isolate the crude product.

#### 7.2 Isolation

For an aqueous workup of most organic reactions this involve:

- 1. Diluting the reaction mixture with a solvent for workup (this is the organic layer).
- 2. **Washing** the organic layer with various aqueous solutions. Some of the by-products generated during the reaction will be neutralised or removed by dissolving in the aqueous layer. Ideally, the two layers will be clearly visible.
- 3. Drying the organic layer with one of the drying agents (see K: Drying Liquids on page 9).
- 4. Filtering off the drying agent (see F: Filtration on page 8).
- 5. Rotoevaporation (see F: Evaporation on page 12) to remove the solvent.

## 7.2.1 Extraction & washing

- ✓ After quenching with water, the organic compounds are **extracted** into a suitable organic solvent and the organic layer **washed** with various aqueous solutions.
- ✓ Washing is performed *via* liquid-liquid extraction of the organic layer (see C: Liquid-liquid extraction on page 10). The function of different aqueous wash solution is as follows:
  - $\circ$  saturated NH<sub>4</sub>Cl (pH 5–6) : to neutralise bases
  - $\circ$  1 mol dm<sup>-3</sup> HCl (pH 1) : to neutralise bases; to acidify mixture
  - o saturated NaHCO<sub>3</sub> (pH 9) : to neutralise acids
  - o 1 mol dm<sup>-3</sup> NaOH (pH 14) : to neutralise acids; to basify mixture
  - o 1 mol dm<sup>-3</sup> NH<sub>3</sub> (pH 11) : to neutralise acids; to basify mixture
  - brine (saturated NaCl)
- : to remove residual water from organic layer
  - 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>
- : to remove  $Br_2$  or  $I_2$
- ✓ E.g. Separation of a mixture of carboxylic acid and an alkane, using a polar solvent
  - 1. Dissolve the mixture in a clean, dry beaker in dichloromethane.
  - 2. Clean and dry the tap of a separatory funnel and set up as shown below.





- 3. Make sure that the tap is closed and then add the solution containing the mixture, using a stemmed funnel.
- 4. Add NaOH(aq) to the separatory funnel, place the stopper in the separatory funnel and gently invert it and hold it as shown.
- 5. Open the tap, to release any pressure caused by the heat of reaction.
- 6. Close the tap, shake the mixture once and open the tap to release any pressure.
- 7. Repeat step 6 until no more vapour is expelled via the tap.
- 8. Close the tap, and replace the separatory funnel in the ring or clamp.
- 9. Take out the stopper and allow the solvent layers to separate.
- 10. When the liquids have stopped swirling, open the tap gently and slowly run the dichloromethane lower layer into a clean conical flask.
- 11. Run the remaining aqueous layer into a clean, dry conical flask.
- 12. Return the dichloromethane layer to the separatory funnel and extract it with another portion of sodium hydroxide.
- 13. Repeat the extraction process another two more times, collecting all the sodium hydroxide extracts in the same flask.
- 14. Finally, extract the dichloromethane with water, to remove any traces of sodium hydroxide and add these 'washings' to the sodium hydroxide layer flask.
- 15. You now have a solution of the hydrocarbon in dichloromethane and a solution of the sodium salt of the carboxylic acid in sodium hydroxide, ready for further processing.

# 7.2.2 Filtration

# (see F: Filtration on page 8)

- $\checkmark$  There are two scenarios where filtration may be required:
  - The product is insoluble and crashes out from the reaction mixture either directly or upon quenching. The crude product can then be isolated by *gravity* or *suction/vacuum* filtration, pending on the particle size.



- There are insoluble by-products which must first be removed before liquid-liquid extraction can be performed.
- ✓ In either case, should either the desired product or the by-product(s) have higher solubility at elevated temperature, *hot filtration* (using a stemless filter funnel) may also be required to maximise the differences in solubilities of the different components to increase the effectiveness of separation.

# 7.2.3 Drying agent

# (see K: Drying Liquids on page 9)

✓ Even after extraction with brine, there will still be substantial amount of water left in the organic layer. The residual water in the liquid can be removed by treating it with a suitable drying agent, before removal of the solvent and purification.

Drying agent	Capacity	Speed	Efficiency
MgSO <sub>4</sub>	High	Fast	Good
CaCl <sub>2</sub>	High	Slow	Poor

# 7.2.4 Distillation

- ✓ In some cases, the reaction need not be quenched and the (crude) product may be isolated by either simple or fractional distillation (see D: Distillation on page 11).
  - o Separation is the result of the differing boiling points of the individual constituents
- ✓ There are several types of distillation process each applicable to different situations depending on the chemicals to be separated or purified:
  - simple distillation : used for separating liquids, boiling below 200 °C at atmospheric pressure, from other compounds. For effective separation, there should be a difference in the boiling points of the components of at least 25 °C.
  - fractional distillation : used for separating components of liquid mixtures, which have boiling points differing by less than 25 °C, at temperatures *below* 200 °C.

vacuum or reduced-pressure distillation : used for separating liquids boiling above 200 °C, when decomposition may occur at the high temperature. The effect of distilling at reduced pressure is to lower the boiling point of a liquid.



✓ An example is the synthesis of aldehyde via the dichromate oxidation of a primary alcohol. (see Eg 27 on page 38)

# 7.2.5 Crystallisation

- ✓ In some cases, the product formed is soluble when the reaction mixture is hot due to the heating, but will crystallise out when the mixture is allowed to cool after the reaction is complete.
- ✓ The crude crystalline product can then be isolated by filtration (see F: Filtration on page 8) and further purified.
- ✓ An example where crystallisation is used to isolate the crude product is found in the synthesis of aspirin from salicylic acid. (see Eg 29 on page 39)

# 7.3 Purification

If the crude product isolated upon aqueous workup is not sufficiently pure for whatever purpose of the synthesis, further purification can be performed.

# 7.3.1 Extraction & washing

✓ If the crude product proved to be still contaminated with impurities that can be removed by washing with suitable aqueous solution (see "Extraction & washing" on page 72 above), the procedure can be repeated to better the purity of the product.

# 7.3.2 Distillation

(see D: Distillation on page 11)

✓ A crude *liquid* product obtained after rotoevaporation (see F: Evaporation on page 12) of the organic solvent from an organic extract, can be further purified by either simple or fractional distillation, pending on the boiling point differences.



- ✓ If the relative molecular mass of the product is above 350, usually the boiling point is too high for distillation at normal pressure and the compound could decompose before boiling occurs. Distillation under *reduced pressure* (see "*Vacuum or reduced-pressure distillation*" in **D: Distillation** on page 11) may be considered for such cases.
- 7.3.3 Sublimation & deposition
  - ✓ Only for compounds which sublimes (*i.e.* from solid to gaseous phase, without going through (see page 40)
- 7.3.4 Recrystallisation
  - ✓ Solid crude product isolated after aqueous workup can be purified by recrystallisation (see B: Recrystallisation on page 10), which involves dissolving the impure material in a hot solvent and then cooling the solution to produce crystals.
  - ✓ Purification by recrystallisation is based on the theory of saturated solutions and a suitable recrystallisation solvent is one in which the chemical to be purified is *insoluble* in the *cold solvent* and *soluble* in the *hot solvent*.
  - ✓ E.g.
    - 1. Weigh the crude sample.
    - 2. Transfer the solid into a clean, dry conical flask.
    - 3. Add cold solvent and a glass rod as an anti-bumping device to the flask and then heat the mixture on a hot plate. Add more solvent if necessary, until the compound has just dissolved completely.
    - 4. Remove the flask from the heat and allow it to cool for 2 minutes.
    - 5. Add a small amount of decolourising charcoal to the solution, and heat the mixture gently for 5 minutes.
    - 6. Filter the recrystallisation solution through a stemless funnel and fluted filter paper. At the same time, keep the recrystallisation solution hot during the filtration by putting it back onto the hot plate.
    - 7. When filtration is complete, remove collection flask from heat, take out the glass rod and clamp the flask in an ice-water bath.\*
    - 8. When the solution is cold (about 5 °C), collect the solid by suction filtration.
    - 9. Rinse the compound on the filter using a little ice-cold solvent and continue suction, to make the crystals as dry as possible.



- 10. Transfer the crystals to a clock-glass using a spatula and spread them in a thin layer.
- 11. Dry the compound by pressing between pieces of filter paper.
- 12. Air dry the compound.
- \* If no crystals appear on cooling, a supersaturated solution has been formed. To induce precipitation of the solute, sites for nucleation and crystal growth must be provided:
  - 1. Seeding the solution by adding a few crystals ('dust') of the crude compound, or
  - 2. Scratching the inside of the flask at the surface of the liquid using a glass rod

#### 7.3.5 Chromatography (Prep TLC)

- ✓ When an analytical technique (like TLC) is used to *isolate compounds*, it is often called a preparative (prep) technique. So TLC becomes "prep TLC".
- ✓ The same method is used, only on a larger scale.
  - Instead of a microscope slide, prep TLC uses a 30 × 30 cm glass plate coated with a thick layer of the adsorbent (0.5–2.0 mm).
  - Rather than just looking at the bands, the adsorbent holding the different bands is scraped into different flasks.
  - The adsorbents are then treated with appropriate solvents to **leach out** the compounds.
  - $\circ\,$  The adsorbent is filtered off and the solvent evaporated to recover the separate compounds.

#### 7.4 Characterisation

#### 7.4.1 Melting & boiling range

(see A: Melting points on page 10)

- A melting point is the temperature at which the first crystal just starts to melt until the temperature at which the last crystal just disappears. Thus the melting point is actually a melting range.
- ✓ The melting point of a solid can be determined using the Thiele tube.
- ✓ Boiling point can be approximated by the temperature range where a liquid is collected during distillation (see D: Distillation on page 11).



✓ Generally, a melting or boiling range greater than 2°C usually indicates an *impure* compound.

#### 7.4.2 Polarimetry

(see F: Polarimetry on page 29)

- ✓ Similar to melting and boiling point, the **specific rotation**,  $[\alpha]_{\lambda}^{\tau}$ , of a **chiral** compound is characteristic of the compound, at temperature  $T^{\circ}C$ , in a specific solvent.
- ✓ If a synthesis is stereoselective, then one of the enantiomers will be produced in greater amount over the other (*i.e.* not racemic). The **optical purity** of the product should also be determined.

### 7.4.3 Chemical tests

(see "Organic QA" in G: Qualitative Analysis (QA) on page 34)

- Chemical test can be performed to show the presence or absence of certain functional group(s).
- ✓ An example is seen in Eg 29 on page 39, where neutral FeCl<sub>3</sub> can be used to ascertain if the crude aspirin contains unreacted salicylic acid *via* the phenolic group.

7.4.4 Mass (% yield)

✓ The percentage yield of an organic synthesis should always be reported as this will allow determination of the amount of starting material to use.

#### 7.4.5 Chromatography

(see "Thin-Layer Chromatography (TLC)" under *Synthesis* on page 36)

- ✓ The  $R_f$  value for the product should always be reported, together with the solvent system used to develop the TLC.
- ✓ There are other more sophisticated chromatography methods, *e.g.* gas chromatography (GC), high-performance liquid chromatography (HPLC), *etc.* which allows for the analysis of the components of a mixture.

# 7.4.6 Spectroscopy

- ✓ Powerful spectroscopy methods are available which allows for the confirmation of the identity of the desired product in a synthesis. These data should also be reported.
- ✓ *E.g.* infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry

### Worked Example 7A (Nov 2010/2/2)

1-Bromobutane may be made by reacting together butan-1-ol, sodium bromide and concentrated sulfuric acid in the presence of water, as described below.

compound	boiling point / °C	density / g cm <sup>-3</sup>	Mr	solubility in water
1-bromobutane	102	1.35	137	insoluble
butan-1-ol	118	0.81	74	moderate
sodium bromide	1390	3.20	103	soluble
concentrated sulfuric acid	330	1.84	98	soluble
water	100	1.00	18	_

Data about these four compounds and 1-bromobutane are given in the table.

#### Preparation of impure 1-bromobutane

- 1. Place 35 g of powdered sodium bromide, 30 cm<sup>3</sup> of water and 25 cm<sup>3</sup> of butan-1-ol in a 250 cm<sup>3</sup> two-necked flask. In one neck is placed a tap funnel and in the other neck is placed a reflux condenser.
- 2. Place 25 cm<sup>3</sup> of concentrated sulfuric acid in the tap funnel and then add the acid drop by drop to the reagents in the flask. Keep the contents well shaken and cool occasionally in an ice-water bath.
- 3. When all the acid has been added, gently boil the mixture for about 45 minutes, shaking the flask gently from time to time.
- 4. Rearrange the apparatus for distillation. Distil off the impure 1-bromobutane (about 30 cm<sup>3</sup>).
- (a) The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.
   Write an equation for each of these stages.

stage I  $NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$ 

stage II  $CH_3(CH_2)_3OH + HBr \rightarrow CH_3(CH_2)_3Br + H_2O$ 

(b) By using the amounts given above, one of the reagents, butan-1-ol or sodium bromide, will be present in an excess in this preparation.

Use the data above to determine, by calculation, which reagent is in an excess.

$$n_{\text{butan-1-ol}} = \frac{25 \times 0.81}{74} = 0.274 \text{ mol}$$
  
 $n_{\text{NaBr}} = \frac{35}{103} = 0.340 \text{ mol}$ 

Since they react in a 1:1 ratio, hence <u>NaBr</u> is in excess.

- (c) When the concentrated sulfuric acid is added to the reaction mixture (step 2), cooling is necessary. Two by-products, one inorganic and one organic, may be produced if the temperature is not controlled carefully.
  - (i) Suggest the main cause of heat being produced at this stage.

The dilution of concentrated sulfuric acid is highly exothermic.

(ii) What by-products may be formed? In **each** case, identify the by-product and write an equation showing its formation.

inorganic by-product	Br <sub>2</sub>
equation	$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2$
organic by-product	CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub>
equation	$CH_{3}CH_{2}CH_{2}CH_{2}OH \rightarrow CH_{3}CH_{2}CH=CH_{2} + H_{2}O$

(d) The reaction mixture is heated for 45 minutes (step 3).Why is this process necessary for the preparation of many covalent organic compounds? Explain your answer.

Even if the reaction is exothermic, due to the need to break and form covalent bonds,

organic reactions are usually associated with high activation energy, hence the need to

heat.

(e) When the mixture is distilled (step 4), the main product is 1-bromobutane. Two other compounds are also present as impurities in the distillate.Use the data in the table to suggest the identities of these two compounds and a reason for their presence.

compounds are ..... butan-1-ol and .... water

reason. Their boiling points (118°C and 100°C) are close to that of 1-bromobutane (102°C).

The preparation of organic compounds usually produces a mixture of the required compound and other impurities. Obtaining the required compound in a pure state involves the application of chemical knowledge and principles.

The purification of crude 1-bromobutane is described below.

Purification of impure 1-bromobutane

- 5. Shake the distillate with water in a separating funnel and separate the aqueous layer from the 1bromobutane. Reject the aqueous layer.
- 6. Return the 1-bromobutane to the funnel, add about half its volume of concentrated hydrochloric acid, and shake. Separate and discard the layer of acid.
- 7. Shake the 1-bromobutane cautiously with dilute aqueous sodium carbonate in the separating funnel, releasing the pressure at intervals.
- 8. Transfer the 1-bromobutane into a conical flask and add some granular anhydrous calcium chloride. Swirl the mixture until the liquid is clear.
- 9. Filter the 1-bromobutane into a clean, dry round-bottomed flask and distil it. Collect the fraction by boiling over a suitable range.
- (f) After distillation from the reaction mixture, the impure 1-bromobutane is shaken with water (step 9) and the two layers are allowed to separate.

Will the 1-bromobutane be the upper or lower layer? ......

Explain your answer.

The density of 1-bromobutane (1.35 g cm<sup>-3</sup>) is higher than that of water (1.00 g cm<sup>-3</sup>)

(g) After separating the 1-bromobutane from the water there will still be a very small amount of one of the original reactants present as an impurity. To remove this, the 1-bromobutane is shaken (step 6) with concentrated hydrochloric acid – a strong acid.

A reaction occurs with the impurity present in the 1-bromobutane, making it more soluble in water.

(i) Suggest with which of the original reactants the concentrated hydrochloric acid reacts.

Butan-1-ol
(ii) By using structural formulae, construct an equation for this reaction.

 $CH_{3}CH_{2}CH_{2}CH_{2}OH + HCl \rightarrow CH_{3}CH_{2}CH_{2}OH_{2}^{+}Cl^{-}$ 

(iii) Suggest why the product in (ii) is more soluble in water than the original reactant.

Due to the stronger ion-dipole interaction of the charged product compared to hydrogen

bonding in butan-1-ol itself.

(h) What impurity will be removed when the 1-bromobutane is then treated with dilute aqueous sodium carbonate (step 7)? Write an equation for this reaction.

impurity ......HCl

equation  $2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$ 

(i) Suggest what is removed when the impure 1-bromobutane is treated with anhydrous calcium chloride (step 8).

water

(j) The final step in the process of purification is distillation of the pure product (step 9). Suggest a suitable range of temperature for the collection of the required fraction.

from ...... 101 °C to ..... 103 °C

# Worked Example 7B (Nov 2011/2/1)

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. The other product of this reaction is ethanoic acid.

HOC <sub>6</sub> H₄CO <sub>2</sub> H	(CH₃CO)₂O	CH <sub>3</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H
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<sup>-3</sup>. Pure aspirin has a melting point of 135 °C.

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%.

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.

The reaction mixture is then heated under reflux conditions for around fifteen minutes.

About 2–3 cm<sup>3</sup> of water is then added to the hot reaction mixture to hydrolyse any unreacted ethanoic anhydride. The addition of this water may cause the mixture to boil.

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

- (a) Using the information given above:
  - (i) Write a balanced equation for the formation of aspirin

$$(CH_3CO)_2O + OH \rightarrow OCOCH_3 + CH_3CO_2H$$

- (ii) Calculate the masses of reactants you would use to prepare 10 g of pure aspirin amount of aspirin formed =  $\frac{10}{180.0}$  = 0.05556 mol amount of HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H formed = 0.05556 ×  $\frac{100}{75}$  = 0.07407 mol mass of HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H required = 0.07407 × 138.0 = **10.2 g** amount of ethanoic anhydride required = 0.07407 mol mass of ethanoic anhydride required = 0.07407 × 102.0 = **7.56 g**
- (b) Write a plan for the preparation of 10 g of pure aspirin.

In your plan you should:

- Draw a diagram of the assembled apparatus you would use when heating the reaction mixture;
- Give a full description of the procedures you would use to prepare and purify the aspirin;
- Explain how you would check the purity of your sample.

# Experimental set-up:



Pre-calculations:
As ethanoic anhydride is a liquid with a density of 1.08 g cm <sup><math>-3</math></sup> ,
volume of ethanoic anhydride to be used = $\frac{7.56}{1.08}$ = 7 cm <sup>3</sup> .
1.00
Procedure:
Preparation of aspirin
1. Accurately weigh 10.2 g of 2-hydroxybenzenecarboxylic acid on a weighing balance
in a 50 cm <sup>3</sup> round bottomed flask.
2. Place a magnetic stirrer into the round bottomed flask and clamp the flask in a silicone
oil bath, which is placed on a magnetic hot plate stirrer as shown in the diagram above.
The set-up must be placed in a <b>fume cupboard</b> .
3. Start the stirring and by means of a 10 cm <sup>3</sup> syringe, carefully add 7 cm <sup>3</sup> of ethanoic
anhydride into the 50 cm <sup>3</sup> round bottom flask.
4. Using a dropper, carefully add 10 drops of 85% phosphoric acid catalyst to the mixture
in the round bottomed flask.
5. Connect the <b>condenser</b> to the flask, fitted with a calcium chloride <b>guard tube</b> .
6. Heat the reaction mixture under reflux for around <b>15 minutes</b> .
7. Stop the heating and remove the condenser. Still with stirring, add 3 cm <sup>3</sup> of deionised
water dropwise using a dropping pipette. Take note of the boiling of the water and if
necessary, slow down the addition of water into the reaction mixture.
8. Once reaction has stopped and cooled, remove the round bottomed flask from the setup
and pour the reaction mixture into 50 cm <sup>3</sup> of cold water in a 100 cm <sup>3</sup> beaker.
9. Once crystals of aspirin are formed, separate the crystals by filtering using filter paper and
filter funnel. (Alternatively, a Buchner funnel may be used with suction filtration.)

10. Wash the crystals of crude aspirin with cold deionised water to remove any impurities.
11. Dry the crystals in a dessicator.
Purification of aspirin (recrystallisation of crude product):
12. Dissolve the crude aspirin in a <b>minimal amount</b> of <b>boiling</b> deionised water in a clean, dry
conical flask.
13. Filter the hot solution using filter paper and a pre-heated stemless filter funnel into another
clean, dry conical flask.
14. Allow the solution to cool and crystals of aspirin will form. This may be done in an ice bath.
15. Collect the crystals via suction filtration using a <b>Buchner funnel</b> . Rinse the conical flask
with a small amount of cold water to ensure complete transfer.
16. Wash the crystals of crude aspirin with small amount of cold deionised water to remove
any impurities
17. Dry the crystals in a <b>dessicator</b> .
Check for purity of product:
Determine the melting point of the aspirin produced and compare it with its actual melting
point (135 °C). This can be done by placing a small amount of sample of aspirin into a melting
point capillary tube and determine its melting point using a melting point apparatus.

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

Ethanoic anhydride is corrosive; wear gloves and/or safety goggles when handling it. or

Organic substances are flammable. All heating must be done using a hotplate with an oil

bath and do not use naked flame around organic substances

#### Practice Question 7A

The Grignard reagent, R<sup>1</sup>-MgBr, can be made by reaction between alkyl bromide and magnesium. In a Grignard reaction, the Grignard reagent may be added to a carbonyl compound for the formation of an alcohol. This reaction is useful for the formation of carbon–carbon bonds.



- (a) The above reaction between the Grignard reagent and ketone can give a yield of about 80%. You are required to prepare 5 g of 2-methylbutan-2-ol.
  - (i) Identify a *symmetrical* ketone and the alkyl bromide required to synthesise 2-methylbutan-2-ol.
  - (ii) Assuming that the alkyl bromide can be completely converted into the Grignard reagent, determine the mass of each reactant in (a)(i) needed to prepare the desired amount of the pure organic product
  - (iii) Similar to the lithium aluminium hydride, the Grignard reagent is rapidly destroyed by water and air.Give a suitable solvent and the condition required for the solvent in the synthesis of the Grignard reagent.
- (b) The Grignard reagent was first prepared by adding an appropriate mass of magnesium to an appropriate mass of alkyl bromide dissolved in an appropriate volume of solvent. The mixture was then heated under reflux for about 30 minutes.

After cooling the reaction mixture which now contains the prepared Grignard reagent, a fixed amount of ketone was then slowly added dropwise to it with intermittent swirling and warming.

- (i) You are provided with the following apparatus: two-necked round bottom flask, condenser, heating mantle and dropping funnel.
   Draw a suitable set-up using the glassware provided for conducting the above experiment.
- (ii) Write a step-by-step procedure on how you would prepare 4 g of the pure 2-methylbutan-2-ol using provided magnesium as well as the suggested alkyl bromide and ketone from your answers in (a)(i) bearing in mind that the yield in such a procedure is about 80 %.

The following data will be useful: Density of alkyl bromide =  $1.46 \text{ g cm}^{-3}$ Density of ketone =  $0.786 \text{ g cm}^{-3}$  Your plan should:

- Show how the quantities of reactants calculated in (a)(ii) are used;
- Show that the mass of magnesium used is in excess for complete conversion of the alkyl bromide to the Grignard reagent;
- Use appropriate volume of the solvent from your answer in (a)(iii);
- Ensure that the reactions are conducted under the appropriate condition.
- Assume that product is a solid, soluble in hot water but not in cold water.

# Practice Question 7B (AJC 2018/4/3c)

2,4-dinitrophenylhydrazine can be synthesised from benzene by a 3–step synthesis with bromobenzene and 2,4-dinitrobromobenzene as intermediates. The preparation of organic compounds usually produces a mixture of the required compound and other impurities.

The synthesis of bromobenzene is described below. When excess bromine is used in the synthesis of bromobenzene, 1,4-dibromobenzene is formed as a by-product.

#### Preparation and purification of bromobenzene

20.0 cm<sup>3</sup> of benzene, 6.0 cm<sup>3</sup> of bromine are mixed with an iron tack to catalyse the reaction. The mixture is warmed at 50–55 °C. During the reaction, acidic fumes of hydrogen bromide is evolved. After about 15 min when the reaction subsides, the reaction mixture is removed from the water bath.

The mixture is then heated to drive off unreacted bromine and cooled before doing solvent extraction. 25 cm<sup>3</sup> of ether is added to dissolve the mixture before shaking the ether solution with two 5 cm<sup>3</sup> portions of sodium hydroxide and one 10 cm<sup>3</sup> portion of water, keeping only the ether layer each time and disposing the aqueous layer. A spatula full of anhydrous magnesium sulfate is added to dry the ether layer for a few minutes before it is filtered away. Fractional distillation is done and only the bromobenzene fraction is collected.

The procedure above, when excess benzene was used, achieved a yield of 75%. A student would like to investigate if increasing the proportion of bromine used, by reducing amount of benzene in the reaction mixture, can raise the yield of bromobenzene.

Some relevant data are given in Table 7.1.

compound	boiling point / °C	density / g cm <sup>-3</sup>	Mr
bromine	59	3.12	159.8
benzene	80	0.88	78.0
bromobenzene	156	1.50	156.9
1,4-dibromobenzene	220	1.84	235.8

#### Table 7.1

- (a) Write a balanced equation for the formation of bromobenzene from benzene.
- (b) It is also found from literature that when the amount of bromine used is twice the amount of benzene, 1,4-dibromobenzene is formed as the major product instead.

Calculate the volume of benzene that you would use to react with 6.0 cm<sup>3</sup> of bromine such that the amount of bromine is twice that of benzene.

(c) The optimum ratio of bromine to benzene can be determined by repeating the experiment several times using different initial ratios of reactants each time.

Using the information given and your answer to **(b)**, suggest the different volumes of reactants to be used in each experiment and complete Table 7.2.

experiment number	volume of benzene used / $\rm cm^3$	volume of bromine used / $\rm cm^3$
1	20.0	6.0
2		
3		

Table 7.2

(d) You are required to write a plan to determine the optimum ratio of bromine to benzene to achieve the highest possible yield of bromobenzene.

Your plan should include the following:

- give a full description of the procedure that you would use to prepare and purify bromobenzene using the three different reaction mixtures in (c),
- an outline of how percentage yield (with reference to amount of benzene used) would be obtained from each of the three different reaction mixtures,
- any safety precaution that you consider important.
- (e) The bromobenzene obtained is then converted to 2,4-dinitrophenylhydrazine as shown in the following reaction scheme.



Name the types of reaction that occur during each of the steps.

# **Suggested Solutions to Practice Questions**

# Practice Question 1A: Redox Titration Involving Autocatalytic Reaction (NYJC 2018/4/1g)

# (i) Mn<sup>2+</sup>(aq)

- (ii) 1. Fill a burette with 0.020 mol  $dm^{-3}$  of an aqueous solution of potassium manganate(VII).
  - 2. Pipette 10.0 cm<sup>3</sup> of **FB 1** into a 250 cm<sup>3</sup> conical flask.
  - 3. Using a 10 cm<sup>3</sup> measuring cylinder, add in 10 cm<sup>3</sup> of sulfuric acid into the same conical flask.
  - 4. Heat the mixture in the conical flask to about 60/70/80 °C.
  - 5. Titrate the mixture in the conical flask against potassium manganate(VII) until the first permanent .....pale pink... colour remains in the solution.
  - Repeat the titration ...as many times necessary to achieve two consistent readings within ±0.10 cm<sup>3</sup>. The average of the two consistent readings will be the volume of potassium manganate(VII) added to achieve endpoint.

# Practice Question 1B: Redox Titration Involving I<sub>2</sub> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (JJC 2018/4/3)

# (a) <u>Pre-calculations and Procedure:</u>

(i) To prepare 250.0 cm<sup>3</sup> of 0.075 mol dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq):

Mass of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O required =  $\frac{250}{1000} \times 0.075 \times 248.2 = 4.65$  g

- 1. Weigh accurately 4.65 g of solid  $Na_2S_2O_3.5H_2O$  into a weighing bottle using an electronic weighing balance.
- 2. Transfer all the weighed solid into a small beaker and dissolve the solid completely with about 50 cm<sup>3</sup> deionised water.
- Using a filter funnel, carefully transfer the solution and all washings into a 250.0 cm<sup>3</sup> graduated flask. Make up to the graduated mark with deionised water. Stopper and shake the flask well to obtain a homogeneous solution.

# (ii) To prepare 100 cm<sup>3</sup> of Ca(IO<sub>3</sub>)<sub>2</sub> saturated solution at 20 $^{\circ}$ C:

- 1. Use a 100 cm<sup>3</sup> measuring cylinder to transfer 100 cm<sup>3</sup> of deionised water into a 250 cm<sup>3</sup> conical flask.
- 2. Using a spatula, add a few tips of solid Ca(IO<sub>3</sub>)<sub>2</sub> into the conical flask. Stopper the flask and shake the flask for a few minutes. Keep adding more solid Ca(IO<sub>3</sub>)<sub>2</sub>, with shaking after each addition, until some Ca(IO<sub>3</sub>)<sub>2</sub> solids are left undissolved.
- 3. To ensure that the solution is saturated, shake the flask at intervals and leave the conical flask in a thermostat controlled water bath set at 20 °C for some time. There must be some solids left undissolved.
- 4. To remove undissolved solids, filter the saturated solution into a clean, dry conical flask using a dry filter funnel and a piece of dry filter paper.

# (iii) Titration:

- 1. Fill a burette with 0.075 mol dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq).
- 2. Pipette 25.0 cm<sup>3</sup> of the saturated solution into a conical flask.
- 3. Use a 10 cm<sup>3</sup> measuring cylinder to add to the flask 5 cm<sup>3</sup> of HC*l*(aq) and 10 cm<sup>3</sup> of KI(aq).
- 4. Titrate the liberated I<sub>2</sub> in the mixture with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq) from the burette until the solution turns pale yellow. Then add about 1 cm<sup>3</sup> of starch indicator and continue the titration until the dark blue-black colour just disappears/turns colourless at the end-point.
- 5. Repeat the titration to obtain two consistent titres within 0.10 cm<sup>3</sup> in difference.

# **Calculations:**

Amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> required =  $\frac{V}{1000} \times 0.075 = 7.5 \times 10^{-5} V$  mol Amount of IO<sub>3</sub><sup>-</sup> in 25.0 cm<sup>3</sup> saturated solution =  $\frac{1}{6} \times 7.5 \times 10^{-5} V = 1.25 \times 10^{-5} V$  mol [IO<sub>3</sub><sup>-</sup>] in saturated solution =  $1.25 \times 10^{-5} V \times \frac{1000}{25.0} = 5 \times 10^{-4} V$  mol dm<sup>-3</sup> Ca(IO<sub>3</sub>)<sub>2</sub> (s)  $\implies$  Ca<sup>2+</sup> (aq) + 2IO<sub>3</sub><sup>-</sup> (aq) eqm conc. -  $2.5 \times 10^{-4} V$   $5 \times 10^{-4} V$   $K_{sp} (Ca(IO_3)_2) = [Ca^{2+}(aq)] [IO_3^{-}(aq)]^2$ =  $(2.5 \times 10^{-4} V)(5 \times 10^{-4} V)^2 = 6.25 \times 10^{-11} V^3 mol^3 dm^{-9}$ (b) Expected [IO<sub>3</sub><sup>-</sup>] in the saturated solution =  $\frac{2.4}{389.9} \times 2 = 0.0123 mol dm^{-3}$ Amount of IO<sub>3</sub><sup>-</sup> in 25.0 cm<sup>3</sup> =  $\frac{25.0}{1000} \times 0.0123 = 3.08 \times 10^{-4} mol$ Amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> required =  $3.08 \times 10^{-4} \times 6 = 1.85 \times 10^{-3} mol$ 

Expected titre when 0.075 mol dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is used  
= 
$$\frac{1.85 \times 10^{-3}}{0.075}$$
 = 0.0246 dm<sup>3</sup> = 24.6 cm<sup>3</sup> which is **within the capacity of a burette**.

(c) Ca(IO<sub>3</sub>)<sub>2</sub> (s) ⇐ Ca<sup>2+</sup> (aq) + 2IO<sub>3</sub><sup>-</sup> (aq)-----(1)
 Presence of common ion Ca<sup>2+</sup> from Ca(NO<sub>3</sub>)<sub>2</sub> causes the position of equilibrium (1) to shift left (or the solubility of Ca(NO<sub>3</sub>)<sub>2</sub> in 0.10 mol dm<sup>-3</sup> Ca(NO<sub>3</sub>)<sub>2</sub> is lower) and hence the titre values will be smaller due to lower [IO<sub>3</sub><sup>-</sup>] in saturated solution.
 However, since the temperature is kept constant, the calculated K<sub>sp</sub> value would remain the unchanged.

### Practice Question 2A: Volatilisation Gravimetry Involving CuSO<sub>4</sub>.nH<sub>2</sub>O

#### (a) <u>Procedure:</u>

- 1. Using an analytical/weighing balance, weigh and record the mass of a clean, empty and dry crucible.
- 2. Weigh out accurately about 5.00 g of solid CuSO₄⋅*n*H₂O into the crucible. Record the total mass of the crucible and the solid CuSO₄⋅*n*H₂O.
- 3. Using a Bunsen burner, heat the crucible and its content 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 consistent results are obtained.

(b)	Mass of empty crucible / g	Α
	Mass of crucible and CuSO <sub>4</sub> . <i>n</i> H <sub>2</sub> O / g	В
	Mass of crucible and its contents after first heating / g	С
	after second heating / g	D
	after third heating / g	D

(c) Mass of CuSO<sub>4</sub> left after heating =  $(\mathbf{D} - \mathbf{A})$  g Molar mass of CuSO<sub>4</sub> = 159.6 g mol<sup>-1</sup> Amount of CuSO<sub>4</sub> =  $(\mathbf{D} - \mathbf{A}) \div 159.6$  mol

Mass of H<sub>2</sub>O driven off =  $(\mathbf{B} - \mathbf{D})$  g Amount of H<sub>2</sub>O driven off =  $(\mathbf{B} - \mathbf{D}) \div 18.0$  mol

 $CuSO_{4.}nH_{2}O(s) \rightarrow CuSO_{4}(s) + nH_{2}O(g)$  $n = \frac{amount \text{ of } H_{2}O}{amount \text{ of } CuSO_{4}} = \frac{\mathbf{B} - \mathbf{D}}{18.0} \div \frac{\mathbf{D} - \mathbf{A}}{159.6} = \frac{159.6}{18.0} \times \frac{\mathbf{B} - \mathbf{D}}{\mathbf{D} - \mathbf{A}}$ 

# Practice Question 2B: Volatilisation Gravimetry Involving Carbonates (SAJC 2018/4/1g)

- (a) (i) 2 NaHCO<sub>3</sub>(s)  $\rightarrow$  Na<sub>2</sub>CO<sub>3</sub>(s) + H<sub>2</sub>O(g) + CO<sub>2</sub>(g)
  - (ii) <u>Procedure</u>
    - 1. Weigh the clean and dry empty boiling tube using a weighing balance.
    - 2. Place 10.00 g (or any mass as defined) of sample powder in the boiling tube and weigh again. Record the mass reading.
    - 3. Using the tongs provided, gently heat the boiling tube with the sample using a Bunsen burner for about 2–3 minutes, before strongly heating the tube for another 5 minutes.
    - 4. Cool the boiling tube on a heat resistant mat before weighing the tube and sample. Record the mass reading.
    - 5. Repeat the heat-cool-weigh process till constant mass within 0.01g is obtained.

# Treatment of results:

Let the final mass (of Na<sub>2</sub>CO<sub>3</sub>) obtained be *y* g. Mass of H<sub>2</sub>O and CO<sub>2</sub> = (10 - y) g Mass of 1 mol of H<sub>2</sub>O and 1 mol of CO<sub>2</sub> = 18.0 + 44.0 = 62.0 g Amount of H<sub>2</sub>O and CO<sub>2</sub> evolved =  $\frac{2(10-y)}{62.0}$  mol = amount of NaHCO<sub>3</sub> Mass of NaHCO<sub>3</sub> =  $\frac{2(10-y)}{62.0} \times 84.0$  g % by mass =  $\frac{\frac{2(10-y)}{62.0} \times 84.0}{10.00} \times 100\%$ 

### Practice Question 2C: Precipitation Gravimetry (ACJC 2019/4/1g)

#### (a) <u>Procedure:</u>

- 1. Measure 50.00 cm<sup>3</sup> of sodium carbonate solution and 50.00 cm<sup>3</sup> magnesium nitrate solution using two separate 50.00 cm<sup>3</sup> burettes into a 250 cm<sup>3</sup> beaker (and place the beaker in a temperature controlled water bath).
- 2. Stir the mixture and leave to stand for some time.
- 3. Filter the mixture using a pre-weighed filter paper (with mass  $M_1$  g).
- 4. Dry precipitated MgCO<sub>3</sub> together with filter paper.
- 5. Weigh the dried precipitated MgCO<sub>3</sub> together with the filter paper and record the mass (M<sub>2</sub> g).
- **(b)** Amount of ppt =  $\frac{M_2 M_1}{M_r \text{ of } MgCO_3}$

= Amount of  $Mg^{2+}$  not dissolved = Amount of  $CO_3^{2-}$  not dissolved

Amount of Mg<sup>2+</sup> dissolved = Amount of CO<sub>3</sub><sup>2-</sup> dissolved =  $0.400 \times \frac{50.0}{1000} - \frac{M_2 - M_1}{M_r}$  of MgCO<sub>3</sub> Concentration of Mg<sup>2+</sup> = Concentration of CO<sub>3</sub><sup>2-</sup> =  $\left(0.400 \times \frac{50.0}{1000} - \frac{M_2 - M_1}{M_r}\right) \div \frac{100.0}{1000}$ 

# Practice Question 3A (TJC 2018/4/1c)

#### Procedure:

- 1. Using a weighing balance, weigh 0.30 g of anhydrous sodium carbonate into a small test tube.
- 2. Using a 100 cm<sup>3</sup> measuring cylinder, measure 80.0 cm<sup>3</sup> of HC*l* and transfer it to a 250 cm<sup>3</sup> conical flask.
- 3. Assemble the set-up as shown in the diagram below.



- 4. Record the initial volume reading of the 100 cm<sup>3</sup> gas syringe before removing the string to start the reaction.
- 5. Record the final volume reading of the gas syringe 20 minutes after the reaction has completed and there is no movement observed of the plunger in the syringe (to allow the temperature and pressure to equilibrate with the surroundings).

# Calculation:

Let  $y \text{ cm}^3$  be the volume of carbon dioxide evolved.

Amount of carbon dioxide =  $\frac{y}{24000}$  mol

Amounts of Na<sub>2</sub>CO<sub>3</sub> present =  $\frac{y}{24000}$  mol

Mass of anhydrous sodium carbonate present =  $\frac{y \times 106}{24000} = \frac{53y}{12000}g$ 

% by mass of anhydrous sodium carbonate =  $\frac{53y \times 100}{12000 \times 0.30} = \frac{53y}{36}$ %

# Practice Question 4A (CJC 2018/4/2)

#### Procedure:

- 1. Using a measuring cylinder, pour 30 cm<sup>3</sup> of **FA 6** into the Styrofoam cup provided and record its temperature using the thermometer. Rinse the thermometer with deionised water and dry with a paper towel.
- 2. Using another measuring cylinder to measure 30 cm<sup>3</sup> of **FA 7** and add it to **FA 6** in the Styrofoam cup. Stir, using the thermometer and record the highest temperature rise.
- 3. Thoroughly rinse out the Styrofoam cup with deionised water and dry it.
- 4. Repeat Steps 1 and 2 using the volumes of FA 6, FA 7 and FA 8 as shown in the table below.

Experiment	1	2	3
V <sub>FA 6</sub> / cm <sup>3</sup>	30	30	0
V <sub>FA 7</sub> / cm <sup>3</sup>	30	0	30
V <sub>FA 8</sub> / cm <sup>3</sup>	0	30	30
∆ <b>7 / °C</b>	<i>T</i> <sub>1</sub>	<i>T</i> <sub>2</sub>	<i>T</i> <sub>3</sub>

- 5. From Experiments 1 to 3, identify the solution that causes a rise in temperature when mixed with either of the two remaining solutions.
- 6. Repeat Steps 1 and 2 to carry out two further experiments with 30 cm<sup>3</sup> of that solution, and 15 cm<sup>3</sup> of each of the other solutions. For example, if **FA 6** lead to increases in temperature when reacted with both **FA 7** and **FA 8**:

Experiment	4	5
V <sub>FA 6</sub> / cm <sup>3</sup>	30	30
V <sub>FA 7</sub> / cm <sup>3</sup>	15	0
V <sub>FA 8</sub> / cm <sup>3</sup>	0	15
∆7/°C	<i>T</i> <sub>4</sub>	<i>T</i> <sub>5</sub>

Note:		

• Specific volumes used must be mentioned, and the permutations of the different solutions must allow for identification of the different species. For Experiments 4 and 5, volumes of the acid used must be chosen such that the 1 mol dm<sup>-3</sup> acid is a limiting reagent, which will give rise to a different temperature increase from the other experiment.

Experiment 4: **FA 6** 2 mol dm<sup>-3</sup> NaOH(aq) HCl(aq) NaCl(aq)  $H_2O(l)$ 0.0300 0.0300 0.0300 mol FA 6 1 mol dm<sup>-3</sup> Experiment 5: NaCl(aq) NaOH(aq) HCl(aq)  $H_2O(l)$ + 0.0300 0.0150 0.0150 mol Total volume used for each solution cannot exceed the 150 cm<sup>3</sup> given.

#### Analysis of Results:

- From Experiments 1, 2 and 3, identify the pair of solutions that **do not lead to a temperature rise upon mixing**. This shows that the solutions in this pair are both acids, and the remaining solution is the **base**, NaOH. For example, if there was no increase in temperature in Experiment 3, **FA 6** is NaOH.
- From Experiments 4 and 5, identify the pair of solutions that lead to a larger increase in temperature. The acid involved in that experiment is the acid with a higher concentration. For example, if the temperature rise is greater in Experiment 4 compared to Experiment 5, FA 7 is 2 mol dm<sup>-3</sup> hydrochloric acid, HC1.

#### Practice Question 4B (HCI 2018/4/3)

(a) Magnesium



From the energy cycle,  $\Delta H_{\rm r} = \Delta H_2 - \Delta H_1$ 

(c) Pre-calculations:

Let the volume of HCl used be 100 cm<sup>3</sup>.

Amount of HC
$$l = \frac{100}{1000} \times 1.0 = 0.100$$
 mol

Amount of Mg required for complete reaction = $\frac{0.100}{2}$				
Maximum mass of Mg that can be used = $\frac{0.100}{2} \times 24.3 = 1.215$ g				
ote: One of the reagents should be used in excess to ensure the other reagent completely reac either have Mg in excess of HC1 in excess.	ts. You can			

# Procedure:

- 1. Weigh accurately 1.00 g of magnesium powder in a clean and dry weighing bottle, using a weighing balance.
- Using a 100 cm<sup>3</sup> measuring cylinder, add 100 cm<sup>3</sup> of HC*l*(aq) into a dry Styrofoam cup calorimeter. Place the Styrofoam cup inside a second Styrofoam cup which is held in a 250 cm<sup>3</sup> glass beaker to prevent it tipping over.
- 3. Cover with a lid and insert a 0.1 °C thermometer through the lid.
- 4. Stir the water gently using the thermometer. Record the temperature of the solution in the Styrofoam cup and start the stopwatch.
- 5. Record the temperature of the solution in the Styrofoam cup using the thermometer, at 30 s intervals until 2.5 min.
- 6. At exactly 3 min, pour the magnesium powder into the water. Stir the mixture but do not measure the temperature at this time.
- 7. Stir the solution gently and record the temperature of the solution at 3.5 min. Continue to stir and record the temperature at 30 s intervals until the temperature of the mixture starts to decrease steadily for 5 consecutive readings.
- 8. Reweigh the emptied weighing bottle.

# Processing of data

- 9. Plot a graph of temperature against time.
- 10. Draw a best-fit straight line taking into account all of the points before t = 3.0 min.
- 11. Draw another best-fit straight line taking into account all of the points after the maximum temperature is reached.
- 12. Extrapolate both lines to t = 3.0 min



13. From the graph, read the minimum temperature,  $T_{min}$  and the maximum temperature,  $T_{max}$  at t = 3.0 min.

#### Practice Question 4C (PJC 2018/4/1g - modified)

# Procedure:

- 1. Fill up one 50 cm<sup>3</sup> burette with the unknown acid, and another burette with 2.00 mol dm<sup>-3</sup>NaOH.
- 2. Using a burette, measure 10.00 cm<sup>3</sup> of acid into a Styrofoam cup labelled acid. Place the cup inside a second Styrofoam cup which is placed in a 250 cm<sup>3</sup> beaker to support it.
- 3. Using another burette, measure out 50.00 cm<sup>3</sup> of NaOH into another Styrofoam cup labelled FA 2.
- 4. Record the initial temperature of acid solution, and record the initial temperature of NaOH solution separately with a thermometer of 0.2 °C interval.
- 5. Add the NaOH(aq) from the cup containing NaOH, into the Styrofoam cup containing the acid and cover with a plastic lid.
- 6. Stir gently the mixture with the thermometer and record the highest temperature reached.
- 7. Wash the cups and dry them carefully with paper.
- 8. Repeat steps 2 to 7 for 15.00, 30.00, 40.00 and 50.00 cm<sup>3</sup> of acid and varying volumes of NaOH(aq) to make the total volume of mixture constant at 60.00 cm<sup>3</sup>.

#### Processing of data:

- 9. A graph of  $\Delta T$  against volume of NaOH is plotted.
- 10. Draw a line-of-best-fit for the points where  $\Delta T$  is rising.
- 11. Draw a second line-of-best-fit for the points where  $\Delta T$  is falling.
- 12. Extrapolate both lines until they cross.

If the acid is monobasic, the following graph will be obtained:



To produce  $\Delta T_{max}$ , an equimolar mixture of NaOH and acid is needed. This happens when 30 cm<sup>3</sup> of NaOH and 30 cm<sup>3</sup> of acid are reacted.

If the acid is dibasic, the following graph will be obtained:



To produce  $\Delta T_{max}$ , the ratio of NaOH : acid must be 2 : 1. This happens when 40 cm<sup>3</sup> of NaOH and 60 – 40 = 20 cm<sup>3</sup> of acid are reacted.

### Practice Question 5A: Initial Rates Method (EJC 2018/4/3b)

#### Procedure:

1. Set up the apparatus as shown below.



- 2. Adjust the water level in the burette until it is between 48.0 cm<sup>3</sup> and 50.0 cm<sup>3</sup>.
- 3. Measure 0.200 g of solid **FA 5** using a weighing bottle and transfer it into a dry and clean 250 cm<sup>3</sup> conical flask.
- 4. Using a 50 cm<sup>3</sup> measuring cylinder, measure 50 cm<sup>3</sup> of HCl.
- 5. Transfer HC*l* into the conical flask containing **FA 5** and insert the bung into the conical flask.
- 6. Hold the flask by its neck and **gently swirl** it continuously.
- 7. When burette reading has changed by  $5 \text{ cm}^3$ , record the time taken **t**, for it to reach this point.
- 8. Using a 50 cm<sup>3</sup> measuring cylinder, measure 25 cm<sup>3</sup> of HC*l* and top up the solution to 50 cm<sup>3</sup> using deionised water.
- 9. Repeat steps 5 7 using the solution in step 8.

#### Processing of data:

For each concentration of HC*l* used (2.00 and 1.00 mol dm<sup>-3</sup> respectively), calculate for **1/t**. As 1/t is **proportional** to the rate, 1/t can be used in place of rate.

By inspection, when concentration is **doubled**, if the rate **does not change**, it is a **zero** order of reaction w.r.t HC*l*. If the rate is **doubled**, it is a **first** order of reaction w.r.t. HC*l*. If the rate is **quadrupled**, it is a **second** order of reaction w.r.t HC*l*.

### Practice Question 5B: Initial Rates Method (Changing Temperature) (IJC 2018/4/2f-g)

#### (f) <u>Procedure:</u>

- 1. Use a 50 cm<sup>3</sup> measuring cylinder to transfer 40 cm<sup>3</sup> of  $Na_2S_2O_3$  into the 100 cm<sup>3</sup> beaker.
- 2. Use a 50 cm<sup>3</sup> measuring cylinder to measure 25 cm<sup>3</sup> of HC*l* into another 100 cm<sup>3</sup> beaker.
- 3. Place both beakers in a water bath set at 30 °C.
- 4. Ensure that both solutions have reached 30 °C by using a thermometer to measure their initial temperatures.
- 5. Pour the HCl into the beaker containing  $Na_2S_2O_3$  and start timing immediately.
- 6. Stir the mixture in the beaker once and place the beaker on top of a piece of paper marked with a cross.
- 7. Look down through the solution in the beaker at the cross on the paper.
- 8. Stop timing when the solution first becomes opaque, obscuring the cross.
- 9. Record the time taken to the nearest 0.1 s.
- 10. Repeat Steps 1 to 9 with the **same** volumes of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and HC*l* used but at temperatures 35 °C, 40 °C, 45 °C, 50 °C and 55 °C.

Note:

- Need at least 5 readings to plot the graph for analysis
- Experiments cover at least a 25 °C temperature range, with maximum temperature not exceeding 100 °C.
- (g) Sulfur dioxide gas is evolved in this reaction, which is mildly toxic. Conduct experiment in fume cupboard to minimise inhalation of the gas. OR Apparatus may be hot after heating in the water bath. Use heat proof gloves or tongs to handle apparatus that becomes too hot to touch.

# Practice Question 5C: Continuous Method (modified 2017 A level P4/2c)

# Method:

The initial rates of the reaction between  $H_2O_2$  and catalase will be determined from graphs of V<sub>FA3</sub> against time, *t*. From the comparison of the initial rates for the five specific temperature conditions (25, 35, 45, 55, 65 °C), the effect of temperature on rate of decomposition of  $H_2O_2$  in the presence of catalase can be determined. Each reaction will be carried out via sampling method. In addition, the temperature of each reaction has to be kept constant using a water bath and the concentration of  $H_2O_2$  and  $H_2SO_4$ , and the volume(mass) of the liver will be kept constant for all five temperatures.

# Procedure:

- 1. Fill a 50 cm<sup>3</sup> burette with KMnO<sub>4</sub>.
- 2. Prepare the water bath and set the temperature to 25 °C.
- 3. Using a 100 cm<sup>3</sup> measuring cylinder, add 100.0 cm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> into a 250 cm<sup>3</sup> conical flask labelled reaction mixture. Place this conical flask into the water bath and allow it to equilibrate to the set temperature.
- 4. Using a 100 cm<sup>3</sup> measuring cylinder, add 50.0 cm<sup>3</sup> of  $H_2SO_4$  to a second conical flask.
- 5. Using a scalpel, cut a 1 cm × 1 cm × 1 cm piece of liver (OR weigh 1.00 g of liver using a mass balance) and add it to the conical flask labelled reaction mixture. Start the stopwatch and swirl the mixture thoroughly to mix its content.
- 6. Transfer a 10.0 cm<sup>3</sup> aliquot of the reaction mixture to a 10 cm<sup>3</sup> measuring cylinder (or boiling tube) using a 10 cm<sup>3</sup> dropping pipette.

- 7. At time, t = 2.0 min, immediately transfer this aliquot into the second conical flask and swirl the mixture vigorously.
- 8. Titrate the H<sub>2</sub>O<sub>2</sub> in the second conical flask with KMnO<sub>4</sub> immediately. The end-point is reached when a permanent pale pink colour is obtained. Record the titration results.
- 9. Wash out the second conical flask with water.
- 10. Repeat steps 6 to 9 for t = 5.0, 8.0, 11.0 and 14.0 min respectively, recording their results.
- 11. Repeat steps 1 to 11, changing the temperature of the water bath to 35, 45, 55 and 65 °C respectively.

Analysis:

- 1. Using the titration results, determine the volume of KMnO<sub>4</sub> used at each time interval.
- 2. Plot graph(s) of V<sub>FA3</sub> against time for all five temperature conditions.
- 3. By drawing a tangent at t = 0.0 min, determine the initial rates for rate of decomposition between catalase and H<sub>2</sub>O<sub>2</sub> for each temperature condition using the gradient of the tangent.
- 4. By comparing the initial rates for all the experiments, conclude how temperature will affect the rate of reaction.

# Practice Question 6A: Inorganic QA (PJC 2018/4/3d)

#### Procedure:

- 12. Add excess NaOH (aq) to FA 7.
- 13. Filter the mixture from Step 1. The residue is Fe(OH)<sub>2</sub>(s) while the filtrate is Al(OH)<sub>4</sub>-(aq).
- 14. To the filtrate, Add **HC***l* dropwise.
- 15. Filter the mixture from Step 3. The residue is A*t*(OH)<sub>2</sub>(s).

#### Practice Question 6B: Inorganic QA (TJC 2018/4/3e)

- (i) Add **FB 1** separately to 1 cm<sup>3</sup> solutions of **FB 2**, **FB 3** and **FB 4** in a test-tube each.
  - 1. Record your observations in the table below.
  - 2. Repeat Steps 1 and 2 using solutions **FB 2**, **FB 3** and **FB 4** separately, **adding each** solution in turn to all the other solutions.

FB	1	2	3	4
1				
2				
3				
4				

(ii)

FB	HC1	Na <sub>2</sub> CO <sub>3</sub>	BaNO₃	A <i>1</i> C <i>1</i> <sub>3</sub>
HC1				
Na₂CO₃	CO <sub>2</sub> evolved			
BaNO₃	No reaction	White ppt		
A <i>1</i> C <i>1</i> <sub>3</sub>	No reaction	White ppt + CO <sub>2</sub> evolved	No reaction	

- The solution that forms a white ppt with one other solution is aqueous Ba(NO<sub>3</sub>)<sub>2</sub>, as Ba<sup>2+</sup> will form a precipitate with carbonate.
- The solution that produces effervescence with one other solution is dilute HC*l* as HC*l* will liberate CO<sub>2</sub> from Na<sub>2</sub>CO<sub>3</sub>.
- The solution that forms a white ppt with effervescence with one other solution is aqueous A*l*C*l*<sub>3</sub> as A*l*C*l*<sub>3</sub> is acidic (refer to Periodic Table lecture notes) and will react with Na<sub>2</sub>CO<sub>3</sub> to form a precipitate and liberate CO<sub>2</sub>.
- The solution that forms only a white ppt with one solution, effervescence with another solution, and with the last solution, white ppt with effervescence is Na<sub>2</sub>CO<sub>3</sub>.

# Practice Question 6C: Organic QA (RI 2017/4/3b)

#### Procedure:

- Using a dropper, place 1 cm<sup>3</sup> of the three unknown organic compounds in separate test-tubes. Then add 1 cm depth of Tollen's reagent and warm the reaction mixture in a hot water bath. Result: Only propanal would react with Tollen's reagent to form a silver mirror and hence can be identified.
- Using a dropper, place 1 cm<sup>3</sup> of the two remaining unknown organic compound in separate test-tubes. Then add a few drops of 2,4-dinitrophenylhydrazine. Result: Only pentan-3-one would react with 2,4-dinitrophenylhydrazine to form an orange precipitate and hence can be identified.
- Using a dropper, place 1 cm<sup>3</sup> of the remaining unknown organic compound in a boiling tube. Add 3 cm<sup>3</sup> of aqueous NaOH and heat. Result: Ethanamide will undergo hydrolysis to form NH<sub>3</sub>(g) which turns damp red litmus paper blue and hence can be identified.

test no.	reagent added	butanal	phenylpropan-2-ol	propanol	propanone		
1	2,4-DNPH	$\checkmark$			~		
2	aq I <sub>2</sub> , NaOH		$\checkmark$		~		
Other po	Other possible tests						
3	Fehling's	$\checkmark$					
4	Sodium		~	$\checkmark$			
5	Tollens'	$\checkmark$					
6	KMnO <sub>4</sub> / H <sup>+</sup>	$\checkmark$	$\checkmark$	$\checkmark$			

# Practice Question 6D: Organic QA (NYJC 2017/4/3i)

# Procedure:

- 1. To 4 separate test-tubes, place 1 cm depth of each unknown solution followed by **2,4-DNPH** and shake the mixture. Record the observations.
- To another set of 4 test-tubes, add 1 cm depth of each unknown solution followed by 1 cm depth of aq I<sub>2</sub>. Add NaOH(aq) dropwise to each test-tube till the yellow colour is almost discharged. Warm the test-tubes. Record the observations.

### **Deductions:**

- Solution that gives orange ppt with 2,4-DNPH and yellow ppt with alkaline aq I<sub>2</sub> is methyl propapone.
- Solution that gives orange ppt with 2,4-DNPH but does not give yellow ppt with alkaline aq I<sub>2</sub> is butanal.
- Solution that gives **yellow ppt** with alkaline aq I<sub>2</sub> but **does not give orange ppt** with 2,4–DNPH is **phenylpropan-2-ol**.
- Solution that **does not give orange ppt** with 2,4-DNPH **nor yellow ppt** with alkaline aq I<sub>2</sub> is **propanol**.

#### Practice Question 7A

- (a) (i) Propanone and bromoethane
  - (ii) mass of product assuming 80% yield =  $\frac{100}{80} \times 5 = 6.25$  g amount of product =  $\frac{6.25}{12.0 \times 5 + 1.0 \times 12 + 16.0} = 0.07102$  mol assuming both are limiting reagents, mass of bromoethane =  $0.07102 \times (12.0 \times 2 + 1.0 \times 5 + 79.9) = 7.734$  g  $\approx 7.73$  g mass of propanone =  $0.07102 \times (12.0 \times 3 + 1.0 \times 6 + 16.0) = 4.119$  g  $\approx 4.12$  g
  - (iii) Anhydrous / dry ether



Note:

- A two-necked round bottomed flask is normally used when corrosive liquids are to be added to the reaction mixture bit by bit.
- A dropping funnel with stopper is used as organic compounds, which are volatile, may escape to the environment.

### (ii) <u>Pre-calculation:</u>

mass of Mg required assuming 1.1 equivalent =  $1.1 \times 0.07102 \times 24.3 = 1.90$  g

volume of bromoethane required =  $\frac{7.734}{1.46}$  = 5.30 cm<sup>3</sup> volume of propanone required =  $\frac{4.119}{0.786}$  = 5.24 cm<sup>3</sup> ≈ 5.25 cm<sup>3</sup>

#### Procedure:

#### Preparation of 2-methylbutan-2-ol

- 1. Using a **weighing balance**, accurately weigh **1.90 g of magnesium** into **a two-neck round bottom flask**.
- 2. Using a **10 cm<sup>3</sup> syringe**, add **5.30 cm<sup>3</sup> of bromoethane** into the flask.
- 3. Using a 50.0 cm<sup>3</sup> measuring cylinder, place **50 cm<sup>3</sup> of anhydrous ether** into the flask.
- 4. Using a 25.0 cm<sup>3</sup> measuring cylinder, place **25 cm<sup>3</sup> of anhydrous ether** into the dropping funnel.
- 5. Using a **10** cm<sup>3</sup> syringe, add **5.25** cm<sup>3</sup> of propanone into the dropping funnel. Stopper the dropping funnel and swirl to ensure mixing.
- 6. Place a magnetic stirrer into the two-neck round bottom flask, connect the condenser and dropping funnel, and place the setup on a heating mantle as shown in the diagram above. Clamp the flask and the condenser using a retort stand.
- Start the stirring and heat the reaction mixture and allow the mixture to reflux gently for 30 min. Cool the reaction mixture to room temperature.
- 8. Remove the stopper and add the solution of propanone in dry ether in the dropping funnel **dropwise** to the Grignard reagent at room temperature. **Warm** the mixture using the heating mantle.
- Once reaction has stopped and cooled, remove the round bottomed flask from the setup. Filter using filter paper and filter funnel to remove the excess magnesium and pour the filtrate into some / 50 cm<sup>3</sup> of cold/ice water with 10 cm<sup>3</sup> 1 mol dm<sup>-3</sup> sulfuric acid in a beaker.
- 10. Once product crystals are formed, separate the crystals by filtering using filter paper and filter funnel. (Alternatively, a Buchner funnel may be used with suction filtration.)
- 11. Wash the crystals of crude product with small amount of cold deionised water to remove any impurities.
- 12. Dry the crystals in a dessicator (optional).

#### Purification of 2-methylbutan-2-ol:

- 13. Dissolve the crude product in a minimal amount of hot deionised water in a clean, dry conical flask.
- 14. Filter the hot solution using filter paper and a pre-heated stemless filter funnel into another clean, dry conical flask.

- 15. Allow the solution to cool and crystals of 2-methylbutan-2-ol will form. This may be done in an ice bath.
- 16. Filter the solution using a Buchner funnel. Rinse the conical flask with a small amount of cold deionised water to ensure complete transfer.
- 17. Wash the crystals with small amount of cold deionised water to remove any impurities.
- 18. Dry the crystals in a dessicator.

Note:

- Volume of solvent used is approximately 5 times the total mass of reagents used. However, the volume
  of solvent to be used also depends on the capacity of the flask. The volume of a two-necked round
  bottomed flask is usually 100 250 cm<sup>3</sup>.
- The purpose of the sulfuric acid in step 9 is to destroy any remaining unreacted Grignard reagent.

#### Practice Question 7B (AJC 2018/4/3c)

- (a)  $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

mount of benzene = 
$$\frac{0.1171}{2}$$
 = 0.05857 mc

mass of benzene =  $0.05857 \times 78.0 = 4.568$  g

volume of benzene = 
$$\frac{4.568}{0.88}$$
 = 5.19 cm<sup>3</sup>

(c)	experiment number	volume of benzene used $/  \mathrm{cm}^3$	volume of bromine used $/ \text{ cm}^3$
	1	20.0	6.0
	2	10.0	6.0
	3	7.0	6.0

Explanation:

<i>n</i> (benzene) : <i>n</i> (Br <sub>2</sub> )	<i>n</i> (benzene) / mol	<i>n</i> (Br <sub>2</sub> ) / mol	V(benzene) / cm <sup>3</sup>	V(Br <sub>2</sub> ) / cm <sup>3</sup>
1:1	0.1171	0.1171	10.0	6.0
1 : 1.5	0.007806	0.1171	7.0	6.0

#### (d) Procedure:

- Using a 20 cm<sup>3</sup> measuring cylinder, measure 20.0 cm<sup>3</sup> (0.226 mol) of benzene, and a 10 cm<sup>3</sup> measuring cylinder to measure 6.0 cm<sup>3</sup> (0.117 mol) of bromine. Add both into a 50 cm<sup>3</sup> round-bottomed flask.
- 2. Add an iron tack to the reaction mixture.
- 3. Using a water bath, gently heat the flask fitted with a reflux condenser at 50–55 °C for about 15 minutes. Reaction should be done in a fume cupboard to remove the acidic fumes of hydrogen bromide evolved.

- 4. After about 15 min when the reaction subsides, remove the reaction mixture from the water bath.
- 5. The mixture is then transferred into a 100 cm<sup>3</sup> conical flask heated over a hot plate to drive off unreacted bromine until the bromine vapour above the liquid disappears (or solution turns from brown/orange to colourless). This should be done in the fume cupboard to collect the bromine gas evolved.
- 6. Allow the mixture to stand and cool before doing solvent extraction.
- 7. Using a 25 cm<sup>3</sup> measuring cylinder, add 25.0 cm<sup>3</sup> of ether to dissolve the cooled reaction mixture. Open the cover to release the pressure build-up.
- 8. Using a 10 cm<sup>3</sup> measuring cylinder, add 5 cm<sup>3</sup> of sodium hydroxide to the ether solution before shaking the mixture in a 100 cm<sup>3</sup> separatory funnel. Open the tap to release the aqueous layer.
- 9. Repeat step 8.
- 10. Using a 10 cm<sup>3</sup> measuring cylinder, add 10 cm<sup>3</sup> portion of water to the ether solution before shaking the mixture in the separatory funnel. Open the tap to release the aqueous layer.
- 11. Add a spatula full of magnesium sulfate to the ether layer, swirl and stand for a few minutes to dry the ether layer before it is filtered away.
- 12. Perform fractional distillation and collect the fraction between 140–160 °C for bromobenzene.
- 13. Weigh the bromobenzene collected.
- 14. Calculate the percentage yield of bromobenzene based on benzene. This is the yield.
- 15. Repeat the experiment with the sets of reagents in (c) and determine the yield for these reaction mixtures.
- (e) Step 2: electrophilic substitution Step 3: nucleophilic substitution