



Teachers' Version

CATHOLIC JUNIOR COLLEGE H2 CHEMISTRY 9729

2020 JC2 PRACTICAL HANDBOOK – Book 5 (Part 1)

Contents	Page
1 Volumetric Analysis	
Q1 Stoichiometry (Acid-Base Titration) [ACJC Prelim 2010]	8-12
Q2 % Composition (Back Titration) [CJC Prelim 2010]	8-15
Q3 Solubility Product (Acid-Base Titration) [JJJC Prelim 2011]	8-17
Q4 Partition (Acid-base Titration) [ACJC Prelim 2011]	8-20
Q5 Formulae (Redox Titration) [IJC Prelim 2010]	8-23
Q6 Concentration (Redox Titration) [Assignment] [HCI Prelim 2017]	8-25
Q7 Preparation of barium chloride solution (Titration) [ASRJJC Prelim 2019]	8-27
2 Gravimetric Analysis	
Q8 Percentage Composition [VJC Prelim 2017]	8-29
Q9 Percentage Purity [EJC Prelim 2019]	8-31
Q10 Chemical Formula of Compound (assignment) [TPJC Prelim 2017]	8-35
Q11 Percentage of Cu (assignment) [RI Prelim 2017]	8-38
Q12 Solubility Product (K_{sp}) of $MgCO_3$ [ACJC Prelim 2019]	8-40
3 Chemical Energetics	
Q13 Basicity [SAJC Prelim 2010]	8-42
Q14 Neutralisation [IJC Prelim 2011]	8-45
Q15 Concentration of Acid [SAJC Prelim 2011]	8-48
Q16 Dissolution [NJC Prelim 2011]	8-50
Q17 Dissolution [HCI Prelim 2011]	8-52
Q18 Combustion (+ QA) [TJC Prelim 2010]	8-55
Q19 Thermometry [SAJC Prelim 2019]	8-58
Q20 Enthalpy Change of Reaction [MJC Prelim 2017]	8-60
Q21 Identification of Unknown Compounds [NJC Prelim 2017]	8-63
Q22 Calculation of enthalpy change (assignment) [TJC Prelim 2017]	8-65

Introduction

Watch the video <https://goo.gl/p4XXf7> (Duration: 7:00 min) for an e-lecture of this introduction.



PLANNING (P)

Planning is one of the components of SPA which is tested as one of the questions in Paper 2 (Structured Qs, Written Paper), comprising 12 marks out of a total of 72 marks. Therefore, it is a significant portion of the paper.

You should have in mind the **general strategy/plan (the big picture)** providing the theoretical background using appropriate scientific knowledge and understanding, based on sound chemistry principles and the treatment of results.

In planning, your plan should include the following:

1 A **detailed procedure/sequence within the plan (the detailed picture)**

- (i) Provide a clear and logical account, with a sense of coherence of the experiment to be followed. This should include:
- correct choice of apparatus (e.g. beakers, test-tubes, conical flasks, standard flasks, pipettes, burettes etc., and their capacities, e.g. 25.0 cm^3 , 250 cm^3 , 50 cm^3 etc.);
 - chemicals and their concentrations where appropriate (e.g. 0.100 mol dm^{-3} NaOH, $0.0200\text{ mol dm}^{-3}$ KMnO_4 etc.) and
 - quantities or amounts used (e.g. 2.00 g of iron, 4.00 g of CaCO_3 etc.).
- (ii) **Justification** of specific concentrations of solutions must be worked out.

Dilution of solutions may have to be carried out in order to make the experiment sensible.

- 2 You should describe how the data is used in order to reach a conclusion. In other words, **calculations** where appropriate, may be necessary, if the experiment demands it.
- 3 The risks involved in the experiment should be assessed and **precautions** to keep these risks to a minimum should be described; i.e. consideration of **safety matters** must be noted.

Planning At A Glance

	VOLUMETRIC ANALYSIS	CHEMICAL ENERGETICS	GAS COLLECTION	KINETICS	GRAVIMETRIC ANALYSIS	QUALITATIVE ANALYSIS
Appropriate Method	Clue from question: "titrimetric analysis" - determine purity of substance - find concentration of unknown	Clue from question: "find enthalpy of" - combustion of organic compound - neutralisation (acid-base) OR "determine basicity of an acid"	Clue from question: "by collecting gas..." - find molar gas R - find amount of gas products formed (e.g. decomposition)	Clue from question: "...find how one variables affect RATE..." - use concentration w.r.t. time OR - use initial rate w.r.t. concentration	Clue from question: "...thermal decomposition of..." "using precipitation method..."	Clue from question: "describe procedures of simple chemical tests by which you could identify each of the cations / anions / organic substances"
Big Picture	Acid-base reaction OR Redox reaction (usually KMnO_4 involved - burette)	Need known m , c , ΔT and appropriate no. of mol of substance	Use of ideal gas equation $pV = nRT$ (assumed at r.t.p.)	Concentration-time expt OR 'clock reaction' (requires visible change to stop clock)	Thermal decomposition - measure gas produced or - measure mass loss Precipitation method - weigh ppt formed (AMS)	Use Distinguishing Tests to confirm presence of organic functional groups
Calculations	From titration, obtain vol of <i>consistent</i> titre. Use AMS (mole concept) to solve.	From expt, find ΔT Using $Q = mc\Delta T$ & n , find ΔH . <u>Note:</u> • if aq. sol, assume c of water = $4.2 \text{ J mol}^{-1} \text{ K}^{-1}$ • m can be mass or volume of TOTAL solution added	Gas collected can be used for: - ideal gas calculation - order of reaction (kinetics) - decomposition (AMS) (So, use appropriate concept for analysis of results)	To find ORDER of RXN: ▪ plot graph of concentration vs. time – determine half-life OR ▪ study how rate change w.r.t. concentration	Find mass loss after CONSTANT MASS is achieved after heating. Use equation & AMS <u>Precipitation method:</u> Weigh mass of ppt after drying	NO CALCULATION Make deductions based on expected observations – e.g. "The compound which produces white ppt is ..."
Details	<u>Typical Apparatus:</u> ▪ 50 cm^3 burette ▪ 25.0 cm^3 pipette ▪ 250 cm^3 conical flask ▪ 250 cm^3 volumetric flask <u>State appropriate:</u> ▪ mass or volume used to prepare standard solution, if applicable ▪ concentration of known reagent (need to calculate - assume 25 cm^3 titre and 25 cm^3 pipetted) ▪ indicator (and colour change at end-point)	<u>Typical Apparatus:</u> ▪ thermometer ▪ Styrofoam cup (supported in 250 cm^3 beaker) <u>State appropriate:</u> ▪ volumes to be added [total vol. must not be too small - min. 30 cm^3] ▪ mass of solid added, if applicable ▪ limiting reagent ▪ initial & highest (or lowest) temperature reached <u>Note:</u> Heat capacity of container may need to be found.	<u>Typical Apparatus:</u> ▪ WELL-GREASED syringe ▪ measuring cylinder / burette (for collection by displacement of water) In some reactions - Gas may need to be passed through solutions (e.g. KOH) for further reaction, or dried (using conc. H_2SO_4 or CaCl_2 granules) - Use of U-tube for such experiments. (see planning handbook pg. 40)	<u>Typical Apparatus:</u> ▪ STOP WATCH <u>State appropriate:</u> ▪ Fixed vol. (10 cm^3) taken to determine concentration (e.g. titration, colorimetry, gas collection, etc) at FIXED TIME interval OR ▪ Measure TIME TAKEN when observable change seen (e.g. deep-blue colour of starch-iodine complex appears/disappears; 'X' sign just obscured, etc) @ different concentrations <u>Note: Keep TOTAL VOL CONSTANT by adding H_2O</u>	<u>Typical Apparatus:</u> ▪ boiling tube / crucible ▪ weighing balance <u>General procedure:</u> ▪ Mass of empty container ▪ Starting Mass (min 1g) of compound ▪ High heating for abt 5 mins ▪ Weigh mass of compound after cooling. ▪ Repeat heating, cooling and reweighing until mass is CONSTANT <u>Precipitation Method:</u> • Filter ppt formed • Dry until constant ppt mass obtained	<u>Typical Apparatus:</u> ▪ boiling tube / test-tube ▪ delivery tube ▪ water bath (if needed) <u>Typical procedure:</u> ▪ Add 1 cm^3 of each compound into separate boiling tubes ... ▪ Add ... (specify amounts to be added) [Use elimination method. i.e. add reagents to remaining compounds to confirm identity]

	VOLUMETRIC ANALYSIS	CHEMICAL ENERGETICS	GAS COLLECTION	KINETICS	GRAVIMETRIC ANALYSIS	QUALITATIVE ANALYSIS
Safety	<ul style="list-style-type: none"> Use pipette filler to avoid accidental swallowing of chemicals. 	<ul style="list-style-type: none"> Wear gloves if reagents used are corrosive. 	<ul style="list-style-type: none"> keep flammable gas (e.g. H₂) away from naked flame. 	<p>Appropriate safety precautions: e.g. wear gloves if corrosive acid used; wear goggles if heating is required.</p>	<p>Wear goggles when heating.</p>	<ul style="list-style-type: none"> wear goggles when heating wear gloves if compd is corrosive carry out expt in fume cupboard if reactant / product is toxic. keep flammable gas (e.g. H₂) away from naked flame. use water bath rather than direct heating if reactant / product is volatile, flammable.
Precautions	<ul style="list-style-type: none"> Fill burette below eye-level to avoid spillage and accidents. 					
Accuracy	<ul style="list-style-type: none"> Add titrant drop-wise towards the end-point (to avoid end-point being over-shot). <p><u>Reliability:</u></p> <ul style="list-style-type: none"> Repeat titration to obtain <i>consistent</i> titres (within 0.10 cm³ of each other) 	<ul style="list-style-type: none"> Minimise heat loss/gained to the surrounding (which reduces accuracy of T_f measured). <p>e.g. carry out experiment in draught-free environment (switch off all fans); add cover/lid to cup.</p> <ul style="list-style-type: none"> use thermometer of higher precision. transfer solutions carefully without spillage. <p><u>Reliability:</u></p> <ul style="list-style-type: none"> Repeat experiment for consistent readings (say, $\frac{\Delta T}{m_s} < 0.1$) 	<p>Vol of gas collected may be reduced by:</p> <ol style="list-style-type: none"> solubility of gas in water, e.g. CO₂, O₂ Hence, saturate water with the gas to be collected or use gas syringe. gas loss when reaction is started. 	<p>Keep constant all other variables (e.g. reaction temperature, etc) – only one variable changed at any one time</p>	<p>Avoid heating too strongly to prevent further decomposition of compound (e.g. when heating to find water of crystallisation)</p> <p><u>Precipitation Method:</u> Ppt should be as dry as possible to reduce weighing water solvent.</p>	<p>Presence of impurities may affect observation - e.g. presence of water in boiling tube produces H₂(g) with Na(s)</p>

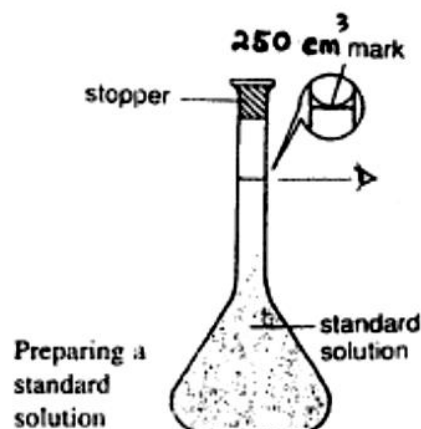
1. Volumetric Analysis

Volumetric analysis (or titrimetric analysis) is the *quantitative* technique involving *titration* to determine the amount of a particular substance in a solution of unknown concentration.

Acid-base Titration				Redox Titration		Iodometric Titration											
<ul style="list-style-type: none"> 2-3 drops of indicator required. Common indicators: 				<ol style="list-style-type: none"> Using <u>acidified potassium manganate(VII)</u>, KMnO_4 (usually placed in burette). <ul style="list-style-type: none"> acidified by adding equal volume of dil H_2SO_4 to the solution in the conical flask. <u>no indicator</u> needed because KMnO_4 acts as its own indicator. <u>end-point</u>: first permanent pink colour on adding one excess drop of KMnO_4. <p>[In some cases, end-point colour is <u>not</u> pink due to interference from the presence of coloured products; e.g. yellow Fe^{3+} makes the end-point colour appears orange.]</p> <p>e.g.</p> $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$ $2\text{MnO}_4^- + 5\text{SO}_3^{2-} + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}$ $2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$ $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$ $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$ Using <u>acidified potassium dichromate(VI)</u>, $\text{K}_2\text{Cr}_2\text{O}_7$ (usually placed in burette). <ul style="list-style-type: none"> acidified by adding equal volume of dil H_2SO_4 to the solution in the conical flask. <u>Indicator</u>: N-phenylanthranilic acid. <u>end-point</u>: from deep-green to violet. <p>e.g.</p> $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$ $\text{Cr}_2\text{O}_7^{2-} + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 7\text{H}_2\text{O}$ $\text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{O}_4^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{CO}_2 + 7\text{H}_2\text{O}$ $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$ 		<ul style="list-style-type: none"> Iodine titrated with sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$ (placed in burette). $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ <u>Indicator</u>: starch solution added near the end-point (when solution is pale yellow) to give deep-blue colour of starch-iodine complex. [- to ensure reliability of results; minimal amount of I_2 'locked' in complex formed.] <u>end-point</u>: deep-blue to colourless. Iodine is normally obtained <u>indirectly</u>, say, by the action of oxidising agent on I^- ions. <p>e.g.</p> $\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$ <p>Then, $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ so, $\text{Cr}_2\text{O}_7^{2-} \equiv 3\text{I}_2 \equiv 6\text{S}_2\text{O}_3^{2-}$ therefore: $\text{Cr}_2\text{O}_7^{2-} \equiv 6\text{S}_2\text{O}_3^{2-}$</p> <p>e.g.</p> $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$ <p>Then, $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ so, $\text{IO}_3^- \equiv 3\text{I}_2 \equiv 6\text{S}_2\text{O}_3^{2-}$ therefore: $\text{IO}_3^- \equiv 6\text{S}_2\text{O}_3^{2-}$</p>											
<ul style="list-style-type: none"> Choice of indicator: <table border="1"> <thead> <tr> <th>Acid / Base</th> <th>Suitable indicator</th> </tr> </thead> <tbody> <tr> <td>Strong acid - strong base</td> <td>methyl orange, screened methyl orange or phenolphthalein</td> </tr> <tr> <td>Strong acid - weak base</td> <td>methyl orange or screened methyl orange</td> </tr> <tr> <td>Weak acid - strong base</td> <td>phenolphthalein</td> </tr> <tr> <td>Weak acid - weak base</td> <td>no suitable indicator</td> </tr> </tbody> </table> <p>e.g. titration of Na_2CO_3 with dil HCl</p> <ul style="list-style-type: none"> with phenolphthalein indicator $\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{NaHCO}_3$ <p>so, $\text{Na}_2\text{CO}_3 \equiv \text{HCl}$</p> with methyl orange indicator $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$ <p>so, $\text{Na}_2\text{CO}_3 \equiv 2\text{HCl}$</p> <p>[Phenolphthalein – now classified as 'carcinogen' and is no longer used in school lab work.]</p>				Acid / Base	Suitable indicator	Strong acid - strong base	methyl orange, screened methyl orange or phenolphthalein	Strong acid - weak base	methyl orange or screened methyl orange	Weak acid - strong base	phenolphthalein	Weak acid - weak base	no suitable indicator				
Acid / Base	Suitable indicator																
Strong acid - strong base	methyl orange, screened methyl orange or phenolphthalein																
Strong acid - weak base	methyl orange or screened methyl orange																
Weak acid - strong base	phenolphthalein																
Weak acid - weak base	no suitable indicator																

1.1 Sequence of steps

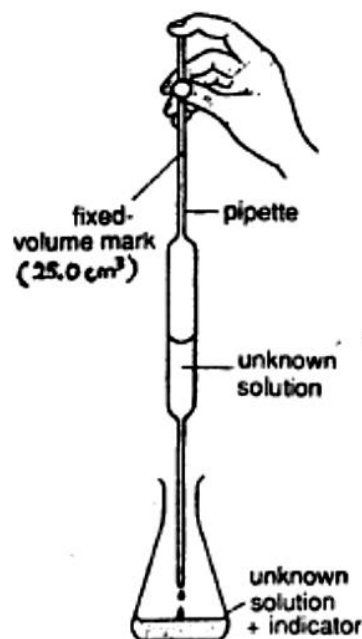
1. Prepare a *standard solution* of the *analyte* using a 250 cm^3 volumetric flask.



- State volume used for dilution; or state mass of substance dissolved.
- State identity of *solvent* used; e.g. make up to the mark with distilled water.
- Shake well to obtain homogeneous solution.

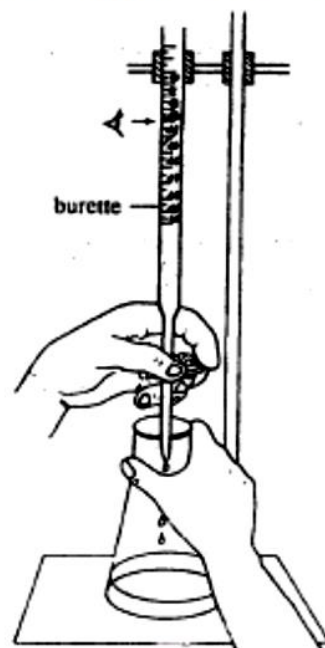
[*analyte* – solution of unknown concentration which is being analysed.]

2. Pipette 25.0 cm^3 of analyte into a 250 cm^3 conical flask.



- Add *indicator*, if required; e.g. add 2-3 drops of methyl orange indicator.
- Add equal volume of dilute sulfuric acid, if acidification required; e.g. KMnO_4 titration.

3. *Titrate* with appropriate *titrant*.



- Justify choice of concentration of titrant.
- State expected colour change at end-point.
- *Repeat titration* until 2 consistent titres (within $\pm 0.10\text{ cm}^3$) are obtained.
[- to ensure reliability of results]

1.2 Safety Precautions

- use pipette filler to avoid accidental swallowing of chemicals;
- fill burette below eye level to avoid spillage;
- ensure no naked flame around (if there are volatile liquids or flammable gas);
- perform experiment in fume cupboard (if there are toxic or corrosive chemicals).

[volatile liquids, e.g. alcohols; flammable gas, e.g. H_2 ;
toxic gas, e.g. NO_2 ; corrosive chemicals, e.g. conc. Acids]

1.3 Choice of concentration of titrant

- To avoid too small a titre volume which has a high error or an unnecessarily large titre volume, the concentration of the ... (titrant) ... is chosen such that

titre volume \approx volume of ... (analyte) ... titrated

1.4 Procedure and Recording of data

1. To weigh a solid.

Procedure:

1. Weigh a dry, empty weighing bottle.
2. Place about g of solid into the weighing bottle and reweigh.

Recording of data:

Mass of empty weighing bottle / g	A
Mass of weighing bottle + solid / g	B
Mass of solid / g	B - A

Note:

- Record data as 'mass' and not 'weight'
- Indicate units as (g) or /g or written after mass reading.
- If solid cannot be completely transferred (e.g. in energetics experiment), re-weigh.

Mass of empty weighing bottle / g	A
Mass of weighing bottle + solid / g	B
Mass of weighing bottle + residue / g	C
Mass of solid used / g	B - C

To ensure reliability of results:

- Weigh in a draught-free environment; i.e. switch off fans near weighing balances.
- Ensure no spillage of chemicals on balance pan; i.e. transfer chemicals into weighing bottle outside the balance.

2. To prepare standard solution.

Procedure:

• from solid

1. Dissolve weighed solid in distilled water in a clean 250 cm³ beaker. Rinse the weighing bottle with distilled water and pour the washing into the beaker (to ensure complete transfer of solid).
2. Transfer the concentrated solution from the beaker into a clean 250 cm³ volumetric (or graduated or standard) flask. Rinse the beaker with distilled water and pour the washing into the volumetric flask (to ensure complete transfer of solution).
3. Make up to the mark with distilled water. Shake well to obtain a homogeneous solution.

To ensure reliability of results:

- Filter off any undissolved solid (impurities).
- Ensure complete transfer of chemicals by repeated washing of vessel.

• by dilution from a conc. solution X

1. Using a burette (or pipette), place cm³ of X into a 250 cm³ volumetric (or graduated or standard) flask.
2. Make up to the mark with distilled water. Shake well to obtain a homogeneous solution.

3. Titration

Procedure:

1. Pipette 25.0 cm³ of (analyte) into a 250 cm³ conical flask.
2. Add 2-3 drops of indicator [for acid-base titration] OR add equal volume of dil sulfuric acid using a measuring cylinder [for redox titration]
3. Titrate (analyte) against mol dm⁻³ (titrant) placed in a 50 cm³ burette until the colour of solution in the conical flask changed from to on adding one excess drop of (titrant)
4. Repeat the titration until 2 consistent readings (titres within ± 0.10 cm³) are obtained.

Recording of data:

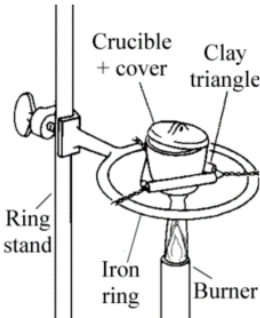
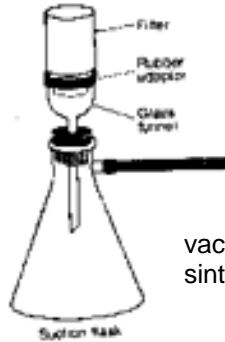
	1	2
Final burette reading / cm ³	A	C
Initial burette reading / cm ³	B	D
Volume of (titrant) used / cm ³	A - B	C - D

To ensure reliability of results:

- Rinse pipette with the solution to be pipetted.
- Rinse burette with a small volume of titrant.
- Ensure no air bubbles are trapped in the burette, particularly in the jet near the tap.
- Repeat titrations to obtain 2 consistent titres (within ± 0.10 cm³).

2. Gravimetric Analysis [Given in 2019 Practical Handbook 2]

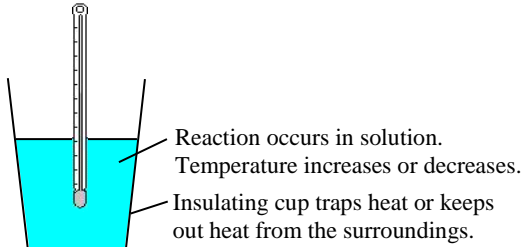
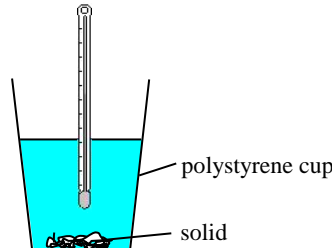
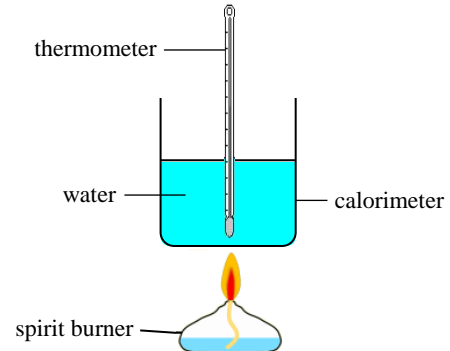
Gravimetric analysis is the *quantitative* isolation of a substance by *heating* (or *precipitation*) and the *weighing* of the residue (or precipitate).

By heating	By precipitation												
<ul style="list-style-type: none">sample heated until <u>constant mass</u> is obtained.sample may be heated in a <u>crucible</u> or <u>test-tube</u> or <u>boiling-tube</u>. <div></div> <p><u>Measures to ensure reliability of results:</u></p> <ul style="list-style-type: none">if a <u>crucible</u> is used, the sample should be heated gently first – to prevent loss of solid through “spattering”.<u>repeat</u> the process of <u>heating, cooling and reweighing</u> until constant mass is obtained. <p>e.g. The value of n in Epsom salts, $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$, determined by heating a known mass (m_1) of the salt to constant mass (m_2) – to remove all the water of crystallisation.</p> $\text{MgSO}_4 \cdot n\text{H}_2\text{O}(\text{s}) \rightarrow \text{MgSO}_4(\text{s}) + n\text{H}_2\text{O}(\text{g})$ <p>mass lost = mass of water of crystallisation = $(m_1 - m_2) \text{ g}$</p> <p>mass of residue = $m_2 \text{ g}$</p> $n = \frac{\text{mol of water}}{\text{mol of residue}}$	<p><u>Procedure:</u></p> <ol style="list-style-type: none">1. Weigh a <u>dry</u>, empty boiling-tube/crucible.2. Place $m \text{ g}$ of (substance) into boiling-tube and reweigh. [<i>usually about 3 g</i>]3. Heat (substance) in boiling-tube <i>strongly</i> for about 5 mins using a Bunsen burner.4. Allow boiling-tube and contents to cool on a heat-proof mat. Reweigh when cool.5. <u>Repeat heating, cooling and reweighing</u> until there is no further loss in mass (i.e. final mass within 0.05 g). <p>This is to ensure that</p> <ul style="list-style-type: none">all the water of crystallisation has been driven from the crystals; orall the (substance) has decomposed; orall the metal is converted to the oxide. <p>[<i>depending on the task given.</i>]</p> <p><u>Recording of results:</u></p> <table><tr><td>Mass of boiling-tube and (substance) / g</td><td>B</td></tr><tr><td>Mass of empty boiling-tube / g</td><td>A</td></tr><tr><td>Mass of (substance) / g</td><td>B – A</td></tr><tr><td>Mass of boiling-tube and residue after 1st heating / g after 2nd heating / g</td><td>C C</td></tr><tr><td>Final mass of residue /g</td><td>C – A</td></tr><tr><td>Loss in mass / g</td><td>B – C</td></tr></table>	Mass of boiling-tube and (substance) / g	B	Mass of empty boiling-tube / g	A	Mass of (substance) / g	B – A	Mass of boiling-tube and residue after 1 st heating / g after 2 nd heating / g	C C	Final mass of residue /g	C – A	Loss in mass / g	B – C
Mass of boiling-tube and (substance) / g	B												
Mass of empty boiling-tube / g	A												
Mass of (substance) / g	B – A												
Mass of boiling-tube and residue after 1 st heating / g after 2 nd heating / g	C C												
Final mass of residue /g	C – A												
Loss in mass / g	B – C												
	<ul style="list-style-type: none">precipitate dried until <u>constant mass</u> is obtained.precipitate may be separated by vacuum filtration using a sintered glass crucible. <div></div> <p>vacuum filtration using sintered glass crucible</p> <p><u>Measures to ensure reliability of results:</u></p> <ul style="list-style-type: none">test filtrate to ensure that precipitation is complete (by adding a few drops of precipitating agent).<u>repeat</u> the process of <u>drying and reweighing</u> until constant mass is obtained. <p>e.g. Percentage of Cu in a sample of copper wire determined by digesting the sample in hot concentrated sulfuric acid and then precipitate the Cu^{2+} ions completely as copper iodide by adding $\text{KI}(\text{aq})$.</p>												

3. Energetics (by Calorimetry) [Given in 2019 Practical Handbook 2]

Calorimetry is used to determine the heat released or absorbed in a chemical reaction. It involves the measurement of *temperature* using a calorimeter. The simplest calorimeter is the *coffee cup calorimeter* which is essentially a polystyrene (Styrofoam) cup. The change in temperature, ΔT , is obtained by measuring the initial temperature, T_1 , of the reactants, and the final temperature, T_2 , of the contents of the calorimeter.

$$\Delta T = T_2 - T_1$$

Reaction involving two solutions	Reaction involving solid and solution	Burning of fuel
 <ul style="list-style-type: none"> record <i>highest</i> temperature reached (for <i>exothermic</i> reaction); or record <i>lowest</i> temperature reached (for <i>endothermic</i> reaction). heat evolved/absorbed = $mc\Delta T$ where m numerically equals <i>sum of volume of the solutions</i>. <p><u>To ensure reliability of results:</u></p> <ul style="list-style-type: none"> use <u>dry</u> calorimeter (dry polystyrene cup). accurate measurement of volume (using pipette or burette). use thermometer of higher precision. transfer solutions carefully without spillage. minimise heat loss to (or gained from) the surrounding <ul style="list-style-type: none"> work in a draught-free environment (switch off fans); place polystyrene cup in plastic beaker for additional insulation and add a lid. 	 <ul style="list-style-type: none"> reweigh weighing bottle and residual solid (to determine actual mass of solid reacted). record <i>highest</i> temperature reached (for <i>exothermic</i> reaction); or record <i>lowest</i> temperature reached (for <i>endothermic</i> reaction). heat evolved/absorbed = $mc\Delta T$ where m numerically equals <i>volume of the solution (ignore mass of solid used)</i>. <p>[Polystyrene cup is a good insulator and has negligible heat capacity.]</p> <p><u>To ensure reliability of results:</u></p> <ul style="list-style-type: none"> Add solid X to solution without spillage. Repeat experiment for consistent readings <p>(i.e. $\frac{\Delta T}{m_s} < 0.1 \text{ } ^\circ\text{C g}^{-1}$ where m_s = mass of solid).</p>	 <ul style="list-style-type: none"> cool spirit burner before reweighing to determine actual mass of fuel burned. heat released by fuel = heat absorbed by calorimeter and water. <p>Note:</p> <p>When comparing different fuels, the following should be kept constant:</p> <ul style="list-style-type: none"> mass (or volume) of water used; initial temperature of the water; temperature increase, ΔT; distance of flame from calorimeter. <p>The best fuel would be the one that gives the most energy per gram of fuel.</p> <p>energy per gram of fuel = $\frac{\text{heat released to water (J)}}{\text{mass of fuel burned (g)}}$</p>

3.1 Calibration of calorimeter

A calorimeter should first be calibrated before use to determine its *heat capacity*; i.e. its ability to absorb/release heat.

This is done by carrying out a process in it that gives off a known quantity of heat and measure the temperature change to see how much of that heat is absorbed by the solution and how much is absorbed by the calorimeter.

e.g. Mix warm water (mass m_w) at T_{iw} to cold water (mass m_c) at T_{ic} in a calorimeter (heat capacity c_c) and record the equilibrium temperature T_f .

In this process, the warm water cools down to T_f while the calorimeter and its water warm up to T_f ; i.e.

heat loss by warm water = heat gained by calorimeter and cold water

$$m_w \times 4.18 \times (T_f - T_{iw}) = c_c \times (T_f - T_{ic}) + m_c \times 4.18 \times (T_f - T_{ic})$$

$$m_w \times 4.18 \times (T_f - T_{iw}) = (T_f - T_{ic}) (c_c + 4.18 m_c)$$

Procedure:

1. Weigh an empty dry calorimeter. Using a measuring cylinder, place 30 cm³ of cold water at 10 – 15 °C into the calorimeter. Adjust the temperature of the water by adding ice. Weigh the calorimeter and cold water.
2. Weigh another empty dry calorimeter. Using a measuring cylinder, place 30 cm³ of warm water at 40 – 45 °C into this calorimeter. Reweigh the calorimeter and warm water.
3. Record the initial temperature of cold water and the initial temperature of warm water.
4. Quickly, without splashing, add the warm water to the cold water in the calorimeter and stir gently with the thermometer.
5. Record the equilibrium temperature of the water mixture.

Recording of data:

Mass of empty calorimeter 1 / g	A
Mass of calorimeter 1 + cold water / g	B
Mass of cold water / g	B – A
Mass of empty calorimeter 2 / g	C
Mass of calorimeter 2 + warm water / g	D
Initial temperature of cold water / °C	T_1
Initial temperature of warm water / °C	T_2
Equilibrium temperature / °C	T_3
Temperature change of calorimeter and cold water / °C	$T_3 - T_1$
Temperature change of warm water / °C	$T_3 - T_2$

Processing of results:

heat loss by warm water = $mc\Delta T$

$$= (D - C) \times 4.18 \times (T_3 - T_2)$$

$$= 4.18 (D - C)(T_3 - T_2) \text{ J}$$

heat gained by calorimeter and cold water

$$= mc\Delta T$$

$$= c_c \times (T_3 - T_1) + (B - A) \times 4.18 \times (T_3 - T_1)$$

$$= (T_3 - T_1) [c_c + 4.18 (B - A)] \text{ J}$$

where c_c is the heat capacity of calorimeter.

Since heat loss by warm water = heat gained by calorimeter and cold water

$$4.18 (D - C)(T_3 - T_2) = (T_3 - T_1) [c_c + 4.18 (B - A)]$$

$$\therefore c_c = \frac{4.18(D-C)(T_3-T_2)}{(T_3-T_1)} - 4.18 (B-A)$$

$$= 4.18 \left[\frac{(D-C)(T_3-T_2)}{(T_3-T_1)} - (B-A) \right] \text{ J K}^{-1}$$

3.2 Procedure and Recording of data

Reaction involving two solutions	Reaction involving solid and solution	Burning of fuel																																
<p><u>Procedure:</u></p> <ol style="list-style-type: none">Using a measuring cylinder/pipette/burette, place cm³ of solution A into a dry polystyrene cup. Record the initial temperature of solution A.Measure cm³ of solution B in another measuring cylinder. Record the initial temperature of solution B.Add solution B to solution A in the polystyrene cup and stir the mixture gently.Record the highest/lowest temperature reached. <p><u>Recording of data:</u></p> <table><tr><td>Initial temperature of A / °C</td><td>T_1</td></tr><tr><td>Initial temperature of B / °C</td><td>T_2</td></tr><tr><td>Average Initial temperature / °C</td><td>$\frac{(T_1 + T_2)}{2}$</td></tr><tr><td>Highest/lowest temperature reached / °C</td><td>T_3</td></tr><tr><td>Temperature rise/fall, ΔT / °C</td><td>$\frac{T_3 - (T_1 + T_2)}{2}$</td></tr></table>	Initial temperature of A / °C	T_1	Initial temperature of B / °C	T_2	Average Initial temperature / °C	$\frac{(T_1 + T_2)}{2}$	Highest/lowest temperature reached / °C	T_3	Temperature rise/fall, ΔT / °C	$\frac{T_3 - (T_1 + T_2)}{2}$	<p><u>Procedure:</u></p> <ol style="list-style-type: none">Weigh accurately g of solid X.Using a pipette/burette, place cm³ of solution Y into a dry polystyrene cup. Record the initial temperature of solution Y.Add solid X to solution Y in the polystyrene cup and stir the mixture gently.Record the highest/lowest temperature reached.Reweigh the weighing bottle and residue. <p><u>Recording of data:</u></p> <table><tr><td>Mass of empty weighing bottle / g</td><td>A</td></tr><tr><td>Mass of weighing bottle + solid X / g</td><td>B</td></tr><tr><td>Mass of weighing bottle + residue / g</td><td>C</td></tr><tr><td>Initial temperature of Y / °C</td><td>T_1</td></tr><tr><td>Highest/lowest temp. reached / °C</td><td>T_2</td></tr><tr><td>Temperature change, ΔT / °C</td><td>$T_2 - T_1$</td></tr></table> <p><u>To ensure reliability of results:</u></p> <ul style="list-style-type: none">Repeat experiment for consistent readings (i.e. $\frac{\Delta T}{m_s} < 0.1 \text{ } ^\circ\text{C g}^{-1}$).	Mass of empty weighing bottle / g	A	Mass of weighing bottle + solid X / g	B	Mass of weighing bottle + residue / g	C	Initial temperature of Y / °C	T_1	Highest/lowest temp. reached / °C	T_2	Temperature change, ΔT / °C	$T_2 - T_1$	<p><u>Procedure:</u></p> <ol style="list-style-type: none">Weigh the spirit burner containing the fuel.Using a pipette/burette, place 100 cm³ of water into a copper calorimeter. Record the initial temperature of the water.Heat the water using the flame from the burning fuel. Stir the water gently until a 10–20 °C temperature rise is noted. Record this temperature.Cool the spirit burner to room temperature. When cooled, reweigh the burner and remaining fuel. <p><u>Recording of data:</u></p> <table><tr><td>Initial mass of spirit burner and fuel / g</td><td>A</td></tr><tr><td>Final mass of spirit burner and fuel / g</td><td>B</td></tr><tr><td>Initial temperature of water / °C</td><td>T_1</td></tr><tr><td>Final temperature of water / °C</td><td>T_2</td></tr><tr><td>Temperature rise, ΔT / °C</td><td>$T_2 - T_1$</td></tr></table> <p><u>To ensure reliability of results:</u></p> <ul style="list-style-type: none">Repeat experiment to obtain average values.	Initial mass of spirit burner and fuel / g	A	Final mass of spirit burner and fuel / g	B	Initial temperature of water / °C	T_1	Final temperature of water / °C	T_2	Temperature rise, ΔT / °C	$T_2 - T_1$
Initial temperature of A / °C	T_1																																	
Initial temperature of B / °C	T_2																																	
Average Initial temperature / °C	$\frac{(T_1 + T_2)}{2}$																																	
Highest/lowest temperature reached / °C	T_3																																	
Temperature rise/fall, ΔT / °C	$\frac{T_3 - (T_1 + T_2)}{2}$																																	
Mass of empty weighing bottle / g	A																																	
Mass of weighing bottle + solid X / g	B																																	
Mass of weighing bottle + residue / g	C																																	
Initial temperature of Y / °C	T_1																																	
Highest/lowest temp. reached / °C	T_2																																	
Temperature change, ΔT / °C	$T_2 - T_1$																																	
Initial mass of spirit burner and fuel / g	A																																	
Final mass of spirit burner and fuel / g	B																																	
Initial temperature of water / °C	T_1																																	
Final temperature of water / °C	T_2																																	
Temperature rise, ΔT / °C	$T_2 - T_1$																																	

Volumetric Analysis

Q1 Stoichiometry (Acid-base Titration)

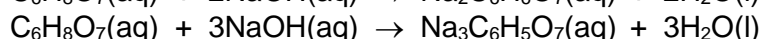
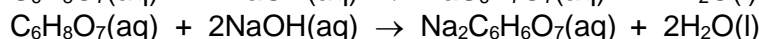
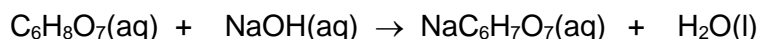
[ACJC Prelim 2010]

Task: To determine the stoichiometric equation for reaction of citric acid with NaOH.

Weak organic acids such as tartaric acid, malic acid, lactic acid, acetic acid and citric acid, are significant constituents in determining the sensory properties of wines and beverages. Soft drinks often contain varying quantities of several acids, which give sodas their tart flavour. Acids can be classified as monobasic, dibasic, or tribasic, depending on how many protons donated to the base during neutralisation.

In sodas, such as Sprite and 7-Up, the acids are carbonic acid (from carbonated water) and citric acid.

Citric acid, $\text{C}_6\text{H}_8\text{O}_7$, reacts with $\text{NaOH}(\text{aq})$ in one of the following ways:



Note experimental method to use.

You are to plan a **titration** to determine which of the above equations correctly represents the neutralisation between citric acid and NaOH.

You are provided with a can (330 cm^3) of 7-Up which has been opened so that it is decarbonated and you can assume that the **only acid present is citric acid** and its concentration is **$0.0420 \text{ mol dm}^{-3}$** ; **solid NaOH**; **deionised water**. **Note chemicals given.**

You are also provided with the **standard apparatus** present in the laboratory.

- (a) A standard aqueous NaOH solution may be prepared using solid NaOH so that it can be titrated with citric acid. Suggest an appropriate concentration of the standard aqueous NaOH solution to be prepared. Show your working.

[You are to assume that the pipette provided has a capacity of 25.0 cm^3 and that $10.00 \text{ cm}^3 \leq \text{titre values} \leq 35.00 \text{ cm}^3$] [2]

min [NaOH] : determined by max titre = 35.00 cm^3 for citric acid being tribasic.

Since citric acid $\equiv 3\text{NaOH}$,

mol of NaOH in $35.00 \text{ cm}^3 = 3 \times \text{mol of citric acid}$

$$= 3 \times 0.0420 \times \frac{25.0}{1000} = 3.15 \times 10^{-3} \text{ mol}$$

$$\therefore \text{minimum [NaOH]} = \frac{1000}{35.00} \times 3.15 \times 10^{-3} = 0.0900 \text{ mol dm}^{-3}$$

max [NaOH] : determined by min titre = 10.00 cm^3 for citric acid being monobasic.

Since citric acid $\equiv \text{NaOH}$,

mol of NaOH in $10.00 \text{ cm}^3 = \text{mol of citric acid}$

$$= 0.0420 \times \frac{25.0}{1000} = 1.05 \times 10^{-3} \text{ mol}$$

$$\therefore \text{maximum [NaOH]} = \frac{1000}{10.00} \times 1.05 \times 10^{-3} = 0.105 \text{ mol dm}^{-3}$$

Hence, a suitable [NaOH] is $0.100 \text{ mol dm}^{-3}$.

[Any answers between 0.09 mol dm^{-3} and $0.105 \text{ mol dm}^{-3}$ is acceptable.]

- (b) Outline, step-by-step, how you would prepare, in a graduated flask, 250 cm³ of an aqueous solution of NaOH with exactly the concentration you have given in (a).

[Ar: Na,23.0; H,1.0; O,16.0]

[4]

Assume [NaOH] to prepare is 0.100 mol dm⁻³

$$\text{mol of NaOH in 250 cm}^3 = \frac{250}{1000} \times 0.100 = 0.0250 \text{ mol}$$

$$\begin{aligned} \text{mass of NaOH in 250 cm}^3 &= 0.0250 \times (23.0 + 16.0 + 1.0) \\ &= 0.0250 \times 40.0 = 1.00 \text{ g} \end{aligned}$$

[Justify mass of NaOH used.]

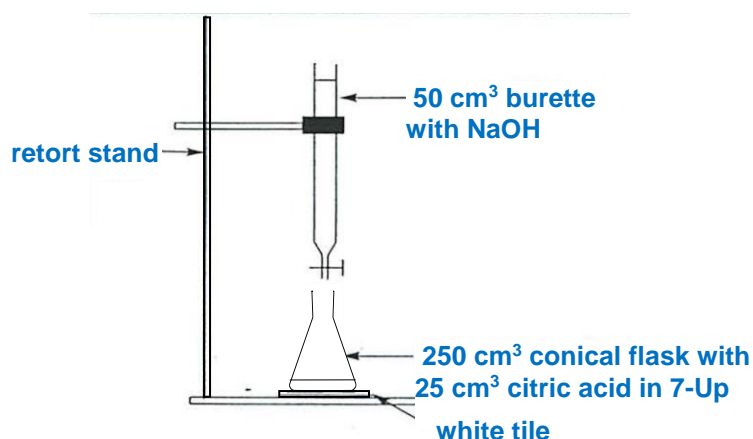
1. Weigh accurately 1.00 g of NaOH in a dry weighing bottle using a weighing balance.
2. Dissolve the NaOH in about 100 cm³ deionised water in a 250 cm³ beaker.
3. Using a filter funnel and glass rod, transfer the solution into a 250 cm³ graduated flask. Rinse the beaker, glass rod and filter funnel with deionised water and add washings into the graduated flask.
4. Make up to the 250 cm³ mark using deionised water. Stopper and shake well to get a homogenous solution.

[Include capacity of apparatus and quantity of chemicals used.]

- (c) Draw a labelled diagram of the apparatus you would use to titrate the citric acid in 7-Up with the standard aqueous NaOH solution which you have prepared. The following details should be included in your labels:

- the volume of citric acid used
- name and capacity of apparatus used.

[1]



**[show graduation markings on burette;
no sharp corners for conical flask.]**

- (d) Suggest a suitable indicator to be used during this titration and state the colour change observed at end-point of the titration. [1]

Indicator – Phenolphthalein

end-point colour change – from colourless to pink

[Note: citric acid is in conical flask, while NaOH is in burette]

- (e) Draw up tables with appropriate headings to show the data you would record in (b) and (c). [1]

mass of weighing bottle + NaOH / g	
mass of empty weighing bottle / g	
mass of NaOH / g	

final burette reading / cm ³		
initial burette reading / cm ³		
volume of NaOH used / cm ³		

[Tables with appropriate headers and units]

- (f) Assuming that the average titre of NaOH used is y cm³, show how you would process the results to find the correct equation for the neutralisation reaction between citric acid and NaOH. [1]

$$\text{mol of NaOH in } y \text{ cm}^3 = \frac{y}{1000} \times 0.100 = y \times 10^{-4} \text{ mol}$$

$$\text{mol of citric acid in } 25.0 \text{ cm}^3 = \frac{25}{1000} \times 0.042 = 1.05 \times 10^{-3} \text{ mol}$$

$$\text{basicity of citric acid} = \frac{n(\text{NaOH})}{n(\text{acid})} = \frac{y \times 10^{-4}}{1.05 \times 10^{-3}} = 0.0952y$$

if $0.0952y = 1$, then equation is $\text{C}_6\text{H}_8\text{O}_7 + \text{NaOH} \rightarrow \text{NaC}_6\text{H}_7\text{O}_7 + \text{H}_2\text{O}$

if $0.0952y = 2$, then equation is $\text{C}_6\text{H}_8\text{O}_7 + 2\text{NaOH} \rightarrow \text{Na}_2\text{C}_6\text{H}_7\text{O}_7 + 2\text{H}_2\text{O}$

if $0.0952y = 3$, then equation is $\text{C}_6\text{H}_8\text{O}_7 + 3\text{NaOH} \rightarrow \text{Na}_3\text{C}_6\text{H}_7\text{O}_7 + 3\text{H}_2\text{O}$

- (g) If the result shows that citric acid is tribasic and given the following informations:

- citric acid is a tertiary alcohol,
- citric acid is optically inactive,

draw a possible structural formula of citric acid.

[1]



[tertiary alcohol \Rightarrow 3 R groups attached to C with –OH group.]

[optically inactive \Rightarrow no chiral carbons (i.e. at least two same groups)]

- (h) Identify a safety risk in the experiment and explain how you would minimise it when carrying out the experiment. [1]

Solid NaOH is corrosive;

hence, wear gloves when handling NaOH(s).

[Total: 12]

Task: To determine the % by mass of CaCO_3 in mussel shells.

New Zealand green-lipped mussels are rich in omega-3 fatty acids. Freeze-dried tissues of such mussels are sold in many countries as nutritional supplement to relieve arthritic symptoms.

Mussel shells are a good source of calcium carbonate and may be used as 'fertilisers' to regulate soil acidity. When hydrochloric acid is added to mussel shells, the following reaction occurs.



You are to determine the percentage of calcium carbonate in a 1.0 g sample of mussel shell fragments by a **back titration method**. *Note experimental method.*

The shell fragments are first treated with an excess of hydrochloric acid and the unreacted acid is then determined by titration with standard sodium hydroxide solution.

- (a) Calculate the **minimum volume** of 1 mol dm^{-3} hydrochloric acid that must be added to the 1.0 g sample of mussel shell fragments for **complete reaction** to occur. [2]

$$M_r \text{ of } \text{CaCO}_3 = 40.0 + 12.0 + 3(16.0) = 100$$

Assuming that shell contains 100 % CaCO_3 ,

$$\text{mol of } \text{CaCO}_3 = \frac{m}{M_r} = \frac{1.0}{100} = 0.0100 \text{ mol}$$

$$\text{mol of HCl} = 2 \times \text{mol of } \text{CaCO}_3 = 2 \times 0.0100 = 0.0200 \text{ mol}$$

$$\therefore \text{ vol of HCl} = \frac{n}{c} = \frac{0.020}{1} \times 1000 = \underline{20.0 \text{ cm}^3}$$

- (b) Upon complete reaction of the calcium carbonate in a 1.0 g sample of mussel shell fragments, the excess unreacted hydrochloric acid was diluted to prepare a 250 cm^3 standard solution for titration with 0.10 mol dm^{-3} sodium hydroxide solution.

- (i) If 25.0 cm^3 of sodium hydroxide solution was required to react with 25.0 cm^3 of the standard solution of hydrochloric acid solution prepared, calculate the number of moles of HCl present in the 250 cm^3 standard solution prepared.

$$\text{mol of NaOH} = \frac{25.0}{1000} \times 0.10 = 2.50 \times 10^{-3} \text{ mol}$$

$$\text{mol of HCl in } 25.0 \text{ cm}^3 \text{ std solution} = \text{mol of NaOH} = 2.50 \times 10^{-3} \text{ mol}$$

$$\text{mol of HCl in } 250 \text{ cm}^3 \text{ std solution} = \frac{250}{25.0} \times 2.50 \times 10^{-3} = \underline{0.0250 \text{ mol}}$$

- (ii) If 40.0 cm^3 of the original 1.0 mol dm^{-3} hydrochloric acid was added to the 1 g sample of mussel shell fragments, calculate the number of moles of CaCO_3 present in the sample of mussel shell fragments and hence determine the percentage of CaCO_3 in the mussel shells. [4]

$$\text{initial mol of HCl added} = \frac{40.0}{1000} \times 1.0 = 0.0400 \text{ mol}$$

$$\text{mol of HCl reacted with CaCO}_3 = 0.0400 - 0.0250 = 0.0150 \text{ mol}$$

$$\begin{aligned} \text{mol of CaCO}_3 \text{ in 1.0 g shell fragments} &= \frac{1}{2} \times \text{mol of HCl} \\ &= \frac{1}{2} \times 0.0150 = 7.50 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{mass of CaCO}_3 \text{ in 1.0 g shell fragments} = 7.50 \times 10^{-3} \times 100 = 0.750 \text{ g}$$

$$\% \text{ of CaCO}_3 \text{ in shell fragments} = \frac{0.750}{1.0} \times 100\% = \underline{75.0\%}$$

- (c) Outline the **procedure** you would carry out in the back titration method. In your description, you should include **details of the apparatus and chemicals** used and measure(s) taken to ensure **reliability of results**. [4]

1. Using a **burette**, run **40.00 cm³** of **1 mol dm⁻³ HCl** into a **100 cm³ beaker** containing the **1.0 g** sample of mussel shell fragments. Reaction is complete when there is **no more effervescence** of **CO₂(g)**.

[add excess acid; ensure complete reaction]

2. Filter with a filter funnel and filter paper to remove any impurities.

3. Transfer the filtrate and washings into a **250 cm³ volumetric flask** and make up to the mark with **distilled water**. Shake well to obtain a homogeneous solution.

[dilution of acid to 250 cm³ using standard flask]

4. **Pipette 25.0 cm³** of diluted HCl (from the volumetric flask) into a **250 cm³ conical flask**. Add 2 drops of **phenolphthalein indicator**.

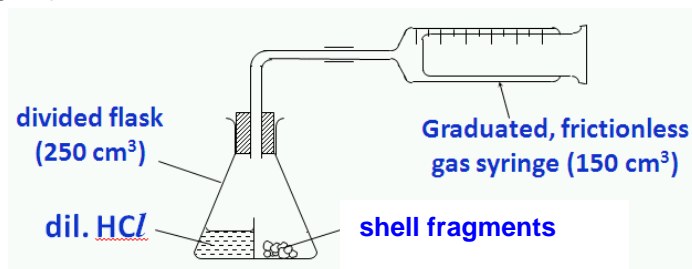
[indicator + end-pt colour change]

5. **Titrate** with **0.10 mol dm⁻³ sodium hydroxide** (placed in a **50 cm³ burette**) until the solution in the conical flask changed from **colourless to pink**.

6. Repeat the titration (steps 4 and 5) until **consistent** results (two titres within **±0.10 cm³** of each other) are obtained.

[repeat titration to ensure reliability of results]

- (d) An alternate method to determine the percentage of calcium carbonate in mussel shells involves measuring the volume of carbon dioxide gas evolved when an excess of hydrochloric acid is added. Draw a **labelled diagram** of the apparatus (set-up) that could be used to collect and measure, as accurately as possible, the volume of carbon dioxide gas produced. [2]



- minimise gas lost – use divided flask; i.e. start with ‘closed’ system, yet keeping the two reagents apart.*
- accurate measurement of gas volume*
- use graduated (frictionless) gas syringe / collect in inverted burette over water saturated with CO₂(g)*

[Total: 12]

Task: To determine the solubility product of calcium hydroxide.

You are to plan an experiment to determine the *solubility* of calcium hydroxide, Ca(OH)_2 , in $0.100 \text{ mol dm}^{-3} \text{ CaCl}_2$ and hence the *solubility product* of calcium hydroxide at the laboratory temperature.

In addition to the standard apparatus present in the laboratory, you are provided with the following materials:

solid calcium hydroxide, Ca(OH)_2
 150 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous calcium chloride, CaCl_2
 150 cm^3 of $0.200 \text{ mol dm}^{-3}$ aqueous hydrochloric acid, HCl
acid-base indicators
de-ionised water

- (a) The pH of a saturated solution of Ca(OH)_2 in $0.100 \text{ mol dm}^{-3} \text{ CaCl}_2$ measured using a pH meter was found to be 12.4.

Calculate the concentration of the OH^- ions, in mol dm^{-3} , in the saturated solution, assuming the laboratory temperature is 25°C . [1]

K_w of water at 25°C is $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

$$\text{pOH} = (14 - 12.4) = 1.6$$

$$[\text{OH}^-] = 10^{-1.6} = 0.0251 \text{ mol dm}^{-3}$$

- (b) The concentration of OH^- ions in the saturated solution can also be determined from an acid-base titration.

- (i) Using the hydrochloric acid provided and your answer in (a), calculate the volume of HCl needed to prepare 250 cm^3 of a diluted HCl solution such that 24.50 cm^3 of the diluted HCl reacts with 25.0 cm^3 of the saturated solution in the titration.

Since $\text{H}^+ \equiv \text{OH}^-$

$$\text{mol of HCl in } 24.50 \text{ cm}^3 = \text{mol of OH}^- = 0.0251 \times \frac{25.0}{1000} = 6.275 \times 10^{-4} \text{ mol}$$

$$[\text{H}^+]_{\text{diluted}} = \frac{1000}{24.50} \times 6.275 \times 10^{-4} = 0.0256 \text{ mol dm}^{-3}$$

Since mol of HCl before dilution = mol of HCl after dilution,

$$\text{Volume of HCl required} = 250 \times 0.0256 / 0.200 = 32.0 \text{ cm}^3$$

[use volumetric/graduated flask for dilution]

- (ii) Briefly describe how you would carry out the dilution to prepare the diluted HCl solution using your answer in b(i). [2]

1. Using a 50.00 cm^3 burette, run 32.00 cm^3 of $0.200 \text{ mol dm}^{-3} \text{ HCl}$ into a 250 cm^3 graduated flask.
2. Add de-ionised water and make up to the mark using deionised water.
3. Stopper the graduated flask and shake well to obtain a homogeneous solution.

[Include capacity of apparatus and quantity of chemicals used.]

- (c) Using volumetric analysis, write a plan to determine the *solubility* of calcium hydroxide, Ca(OH)_2 in $0.100 \text{ mol dm}^{-3} \text{ CaCl}_2$ and hence the *solubility product* of Ca(OH)_2 at the laboratory temperature.

Your plan should include

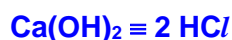
- preparation of the saturated solution;
- **detailed procedure** (including apparatus, appropriate concentration of chemical(s), quantity of chemical, etc);
- measures taken to ensure reliability of result. [5]

Preparation of saturated solution:

1. Using a 100 cm^3 **measuring cylinder**, place 150 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ CaCl}_2$ into a 250 cm^3 **dry** beaker.
2. Using a spatula, add a large spatula of solid Ca(OH)_2 into the beaker and stir with a glass rod. Continue to add more solid and stir, until some Ca(OH)_2 **remains undissolved** to **ensure a saturated solution** is obtained. Let the solution **stand for a few hours** (to establish equilibrium).
[must allow solution to attain equilibrium]
3. **Filter** the saturated solution using a **dry** filter funnel and dry filter paper into a **dry** conical flask/beaker to **ensure the saturated solution is not diluted**.

Titration of saturated Ca(OH)_2 solution with standard HCl :

1. Pipette **25.0 cm^3** of saturated Ca(OH)_2 solution into a 250 cm^3 conical flask.
 2. Add 1-2 drops of **methyl orange indicator** into the conical flask.
[specify indicator]
 3. Titrate with the diluted HCl (placed in a 50 cm^3 burette) until the solution in the conical flask turns from **yellow to orange**.
[colour change at end-point]
 4. Repeat the titration until consistent results (two titres within $\pm 0.10 \text{ cm}^3$ of each other) are obtained.
[repeat titration to ensure reliability of results]
- (d) Assuming that the concentration of the diluted HCl used is $0.0245 \text{ mol dm}^{-3}$ and 22.75 cm^3 of HCl reacted with 25.0 cm^3 of saturated Ca(OH)_2 in the above titration, calculate:
- (i) the *solubility* of Ca(OH)_2 , in mol dm^{-3} , in $0.100 \text{ mol dm}^{-3} \text{ CaCl}_2$ at the laboratory temperature.



$$\text{mol of Ca(OH)}_2 \text{ in } 25.0 \text{ cm}^3 = \frac{1}{2} \times \text{mol of HCl}$$

$$= \frac{1}{2} \times 0.0245 \times \frac{22.75}{1000}$$

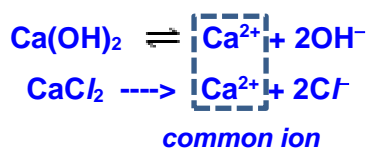
$$= 2.79 \times 10^{-4} \text{ mol}$$

$$\text{mol of Ca(OH)}_2 \text{ in } 1 \text{ dm}^3 = \frac{1000}{25.0} \times 2.79 \times 10^{-4} = 0.0112 \text{ mol}$$

$$\text{Solubility of Ca(OH)}_2 \text{ in } 0.100 \text{ mol dm}^{-3} \text{ CaCl}_2 \text{ at the laboratory temperature} \\ = \underline{\underline{0.0112 \text{ mol dm}^{-3}}}$$

- (ii) the *solubility product* of Ca(OH)_2 at the laboratory temperature, stating the units clearly.

[3]



$$\begin{aligned} [\text{Ca}^{2+}] &= [\text{Ca}^{2+}] \text{ from CaCl}_2 + [\text{Ca}^{2+}] \text{ from saturated Ca(OH)}_2 \\ &= 0.1 + 0.0112 \\ &= 0.1112 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{OH}^-] &= 2 \times [\text{Ca(OH)}_2] \\ &= 2 \times 0.0112 \\ &= 0.0224 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{OH}^-]^2 \\ &= (0.1112)(0.0224)^2 \\ &= \underline{5.58 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}} \end{aligned}$$

- (e) Identify one potential safety hazard in this experiment and suggest how you would minimise this risk. [1]

Solid Ca(OH)_2 is corrosive / dilute hydrochloric acid causes irritation to skin.

Thus, to minimise risk, wear gloves & laboratory coat to avoid direct contact.

[Total: 12]

Q4 Partition (Acid-base titration)

[ACJC Prelim 2011]

Task: To determine the partition coefficient for ethanoic acid between water and cyclohexane.

When a solute is added to two solvents, A and B, which do not mix, some of the solute dissolves in each of the solvents and an equilibrium is set up between the two solvents. It has been shown that for dilute solutions, at equilibrium the ratio of the two concentrations is a constant known as the **Partition Coefficient**, K , and it will remain a constant if the solute remains in the same molecular state in the two solvents.

$$\frac{\text{Concentration of solute in solvent A}}{\text{Concentration of solute in solvent B}} = K$$

An experiment was conducted to verify the above observation. Ethanoic acid (solute) was shaken with two immiscible solvents (water and cyclohexane, C_6H_{12}), so that the solute distributed itself between the two solvents. The concentrations of the two solutions were then determined so that the ratio $[\text{CH}_3\text{CO}_2\text{H}]_{\text{aq}} / [\text{CH}_3\text{CO}_2\text{H}]_{\text{s}}$ known as the **Partition Coefficient**, K can be calculated at a given temperature.

Using apparatus which are found as standard items in a school laboratory, an experiment was carried out to determine the **Partition Coefficient**, K for ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, between water and cyclohexane, C_6H_{12} . $\Rightarrow [\text{acid}]_{\text{water}} / [\text{acid}]_{\text{cyclohexane}}$

The following steps were carried out:

1. 5.0 g of the sample was first dissolved in 50 cm³ of water in a beaker and the aqueous solution was then transferred into a separating funnel.
 2. 50 cm³ of cyclohexane was then poured into the separating funnel containing the aqueous solution, stoppered and shaken intermittently.
 3. The concentration of ethanoic acid in the two layers was then determined by titration with 0.05 mol dm⁻³ NaOH.
- a) i) Outline how a fixed volume of the sample of the aqueous layer can be removed from the mixture in the separating funnel for titrimetric analysis. (Note: The organic layer is less dense compared with the aqueous layer.) [2]

- Place a finger on the open end of a 10.0 cm³ pipette and insert it into the bottom aqueous layer.
- Gently blow lightly into the pipette to dispel any organic layer that may have entered the pipette before withdrawing the required amount of sample.

OR

- Drain the aqueous layer into one dry beaker and the organic layer into another. Pipette 10.0 cm³ of the aqueous layer into a conical flask.

[demonstrate how to use a separating funnel (with actual apparatus)]

- shake and release pressure every now and then;
- show how to drain lower aqueous layer into conical flask.]

ii) Outline stepwise how the removed sample could be analysed by titration to determine the concentration of the solute that had dissolved in that layer. [2]

1. Pipette 25.0 cm³ of the aqueous solution into a 250 cm³ conical flask.
2. Add 1-2 drops of phenolphthalein indicator into the conical flask.
3. Titrate with 0.05 mol dm⁻³ aqueous NaOH (placed in a 50 cm³ burette) until the solution in the conical flask turns from colourless to pink.
4. Repeat the titration until consistent results (two titres within ± 0.10 cm³ of each other) are obtained. **[repeat titration to ensure reliability of results]**

b) When analysing the organic layer, a fixed volume of water (about twice the volume) is added to the pipetted volume of cyclohexane solution in the conical flask and shaken vigorously, prior to the titration. Explain the purpose of this action. [2]

- NaOH(aq) cannot neutralise the ethanoic acid in the organic layer (immiscible).
- The ethanoic acid must first be extracted into the water for complete neutralisation by the alkali during titration.

c) Based on your procedure, state and explain one significant error or limitation that could be encountered in determining an accurate value for the distribution ratio. [1]

- **Short equilibration time for partitioning**
- **Some organic layer could have been sucked up the pipette when collecting aqueous layer for analysis (if student withdrew sample directly from separating funnel)**
- **Titre reading for organic layer may be lesser than expected due to limited or partial partitioning of acid into water; i.e. not all ethanoic acid extracted into the water.**

d) Suggest one possible modification that would minimise the error or limitation that you have stated in (c). Explain how this modification leads to an improvement in the accuracy and reliability of the results. [1]

- **Allow a longer time for partitioning / distribution of acid between the two solvents**
- **Add / use more water to extract acid quantitatively into aqueous layer before titration or use a fixed volume of standard alkali for extraction and determine solute by back titration with standard acid.**

[Any one]

- e) A student did the above experiment but carried out only one titration using a fixed aliquot of the aqueous layer and then proceeded to use the titre value to calculate a value for K. Assuming the student obtained a titre value of $y \text{ cm}^3$ of $M \text{ mol dm}^{-3}$ NaOH (aq) when 10.0 cm^3 of the aqueous layer was titrated, outline how the student could have used the result to determine a value for K. [3]

mol of $\text{CH}_3\text{CO}_2\text{H}$ in 10 cm^3 of aqueous layer = mol of NaOH reacted

$$= M \times \frac{y}{1000} \text{ mol}$$

mol of $\text{CH}_3\text{CO}_2\text{H}$ in 50 cm^3 of aqueous layer = $(5 \times M \times \frac{y}{1000}) \text{ mol}$

$$\text{Thus } [\text{CH}_3\text{CO}_2\text{H}]_{\text{aq}} = \frac{1000}{50} \times (5 \times M \times \frac{y}{1000}) = \frac{My}{10} \text{ mol dm}^{-3}$$

Since mass of $\text{CH}_3\text{CO}_2\text{H}$ dissolved = 5.0 g ,

$$\text{Total mol of } \text{CH}_3\text{CO}_2\text{H} \text{ used} = \frac{m}{M_r} = \frac{5.0}{60.0} \text{ mol}$$

mol of $\text{CH}_3\text{CO}_2\text{H}$ in 50 cm^3 of organic layer = total mol – mol in aq layer

$$= \left(\frac{5.0}{60.0} - 5 \frac{My}{1000} \right) \text{ mol}$$

$$\begin{aligned} \text{Thus, } [\text{CH}_3\text{CO}_2\text{H}]_s &= \frac{1000}{50} \times \left(\frac{5.0}{60.0} - 5 \frac{My}{1000} \right) \text{ mol dm}^{-3} \\ &= \left(\frac{5}{3} - \frac{My}{10} \right) \text{ mol dm}^{-3} \end{aligned}$$

Partition coefficient $K = [\text{CH}_3\text{CO}_2\text{H}]_{\text{aq}} / [\text{CH}_3\text{CO}_2\text{H}]_s$

$$\begin{aligned} &= \frac{My}{10} / \left(\frac{5}{3} - \frac{My}{10} \right) \\ &= \frac{(0.1)My}{1.67 - (0.1)My} \end{aligned}$$

- f) When a solute is distributed between the two immiscible solvents, it is important to ensure that the resulting solutions are dilute for the distribution to occur and the partition coefficient to remain constant. Suggest why this is critical in this experiment. [1]

- Ethanoic acid may dimerise (via hydrogen bonding) in the organic layer when it is concentrated and thus affect the distribution ratio.

[Total: 12]

Task: To determine the value of x in iron(II) ammonium sulfate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$.

Iron(II) sulfate and ammonium sulfate combine to form the double salt, iron(II) ammonium sulfate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$.

- (a) Describe how a titration method involving Fe^{2+} may be used to determine the value of x in a sample of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ (details of calculations are not required). You may assume all the apparatus used are clean and dry. [4]

Preparation of Fe^{2+} solution:

1. Weigh accurately m g of sample using a weighing balance.
2. Dissolve in about 100 cm^3 of 1.0 mol dm^{-3} sulfuric acid in a 250 cm^3 beaker.
[Dissolving the iron(II) salt in acid prevents oxidation of Fe^{2+} to Fe^{3+} .]
3. Using a filter funnel and glass rod, transfer the solution into a 250 cm^3 graduated flask. Rinse the beaker, glass rod and filter funnel with deionised water and add washings into the graduated flask.
4. Make up to the 250 cm^3 mark using de-ionised water. Stopper and shake well to get a homogenous solution.

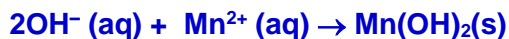
Titration of Fe^{2+} solution with acidified standard KMnO_4 :

1. Pipette 25.0 cm^3 of the Fe^{2+} solution into a 250 cm^3 conical flask.
2. Add 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid using a measuring cylinder.
3. Titrate with standard KMnO_4 (of known concentration, and placed in a 50 cm^3 burette) until the solution in the conical flask turns from colourless to first permanent pink.
[or add a few drops of ferroin indicator; titrate with standard $\text{K}_2\text{Cr}_2\text{O}_7$ from the burette until the indicator turns from red to blue.]
4. Repeat the titration until consistent results (two titres within $\pm 0.10 \text{ cm}^3$ of each other) are obtained.
[repeat titration to ensure reliability of results]

(b)(i) Write an overall ionic equation for the above titration.



(ii) An excess of sodium hydroxide solution was added to the titration flask after the titration was complete. Write **two** equations with state symbols for the reactions taking place.



(iii) State and explain whether a back titration method using aqueous NaOH would be suitable in determining the value of **x** in the double salt. [4]

Iron(II) ions will form precipitate of iron(II) hydroxide / react with aq NaOH, thus it is not possible / not a suitable method to use NaOH(aq) to determine value of x.

(c) An impure sample of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ was contaminated with sulfite ions, SO_3^{2-} . Describe one test to distinguish between sulfite and sulfate ions. [4]

Test :

- 1. add aq. BaCl_2 / $\text{Ba}(\text{NO}_3)_2$ to the solution sample.**
- 2. then add dilute HCl / HNO_3 and test any gas evolved with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper.**

Observation:

For SO_4^{2-} : white ppt is insoluble in excess dilute acids

For SO_3^{2-} : white ppt dissolves in excess dilute acids & SO_2 gas is evolved, which turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper from orange to (pale) green.

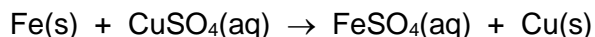
[Total: 12]

Q6 Concentration (Redox Titration) [Assignment] [HCI Prelim 2017]

Task: To determine the concentration of a copper(II) sulfate solution after its reaction with excess iron powder

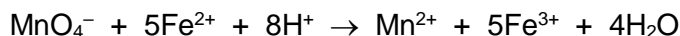
To determine the concentration of a copper(II) sulfate solution, excess iron powder was added to 40.00 cm³ of the copper(II) sulfate solution, **FA5**, and the heat given out was measured and compared against the known enthalpy change of the reaction.

The reaction involved is:



The concentration of copper(II) sulfate may also be determined by titration of the reaction mixture obtained after the above reaction. In this titration, the iron and copper solids in the reaction mixture are first filtered off, and the filtrate is then diluted to obtain a solution suitable for titration with aqueous potassium manganate(VII) of known concentration, in the presence of acid.

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



- (a) Determine a suitable concentration of aqueous potassium manganate(VII) to use in this titration. The concentration of manganate(VII) should not exceed 0.0500 mol dm⁻³.

You are to assume that the concentration of copper(II) sulfate in **FA 5** is 0.800 mol dm⁻³. (Note that this is not the actual value.)

Show clearly your calculations and any assumptions.

$n(\text{Cu}^{2+})$ in 40.00 cm³ of **FA 5**
= $0.800 \times 40/1000 = 0.032 \text{ mol} = n(\text{Fe}^{2+})$ produced in mixture [1]

Assume pipette 25 cm³ (out of 40 cm³) of Fe²⁺ and dilute to 250 cm³, then draw out 25 cm³ for titration,

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

$n(\text{MnO}_4^-)$ needed for titration = $0.0020 / 5 = 0.00040 \text{ mol}$ [1]

Assume titre to be 25 cm³,
[KMnO₄] = $0.00040 / (25/1000) = 0.0160 \text{ mol dm}^{-3}$ [1]

[3]

- (b) Plan an experiment to determine the concentration of copper(II) sulfate in **FA 5**, starting with the reaction mixture formed after the reaction of excess iron powder **FA 5**, and using the titration method described above.

In your plan, you should include details of:

- the quantities of chemicals you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take.

1. Filter the reaction mixture into a dry conical flask, using dry filter funnel and dry filter paper.

2. Pipette 25.0 cm³ of the filtrate into a 250 cm³ volumetric flask. Top up to the mark with deionised water. Stopper and shake to ensure a homogeneous solution.

3. Fill a burette with 0.0160 mol dm⁻³ aqueous KMnO₄ solution. Record the initial burette reading.

4. Pipette 25.0 cm³ of the diluted solution into a conical flask.

5. Add 10 cm³ of 1.0 mol dm⁻³ H₂SO₄ solution into the conical flask.

6. Titrate the solution in the conical flask with KMnO₄ until the end-point where the solution turns from yellow to orange/pink. Record the final burette reading.

7. Repeat steps 4-6 until consistent results within +/-0.10 cm³ are obtained.

Filters reaction mixture into volumetric flask and ensure quantitative transfer of all Fe²⁺

OR: Filters reaction mixture using dry filter funnel, dry filter paper and dry conical flask into beaker/conical flask and draws out suitable volume of filtrate using pipette for dilution [1]

Proposes correct dilution steps and apparatus [1]

Proposes correct titration steps and apparatus [1]

Adds excess dilute H₂SO₄ into conical flask before titration [1]

Gives correct colour change at end-point (yellow to orange/pink) [1]

[5]

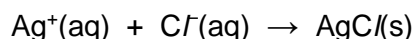
[Total: 8]

Q7 Preparation of barium chloride solution (Titration)

Task: To determine the concentration dissolved chloride ions

When solid hydrated barium chloride, $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$, dissolves in water, $\text{Ba}^{2+}(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions are formed.

The concentration of dissolved chloride ions in a solution can be determined by titration with aqueous silver nitrate of known concentration.



Potassium chromate(VI), $\text{K}_2\text{CrO}_4(\text{aq})$, can be used as the indicator for the reaction. At the end-point of the titration, it forms a red precipitate in the presence of excess silver ions.

The solubilities, in mol dm^{-3} , of the various ionic solids at 20°C are given in the table below.

cation	anion		
	Cl^-	CrO_4^{2-}	SO_4^{2-}
Ag^+	1.32×10^{-5}	6.63×10^{-5}	0.940
Ba^{2+}	1.72	1.10×10^{-5}	1.05×10^{-5}

Sulfuric acid must be added to the solution to prevent the $\text{Ba}^{2+}(\text{aq})$ ions from interfering with the action of the potassium chromate(VI) indicator.

- (i) How would $\text{Ba}^{2+}(\text{aq})$ ions interfere with the action of this indicator? [1]

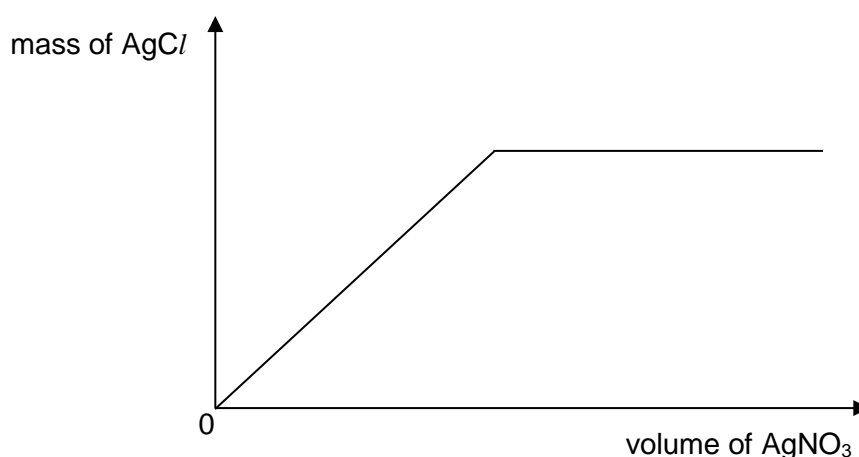
Insoluble barium chromate will be formed. [1]

- (ii) How does the addition of sulfuric acid prevent $\text{Ba}^{2+}(\text{aq})$ ions from interfering with the action of this indicator? [1]

The formation of insoluble barium sulfate will ensure that insoluble barium chromate is not formed during titration. [1]

- (iii) In an initial rough titration, excess silver nitrate solution is added so that the end-point is exceeded.

Draw a sketch graph to show how the mass of silver chloride varies with the volume of silver nitrate added. [1]



Straight line pass through origin **and** reaches a plateau **[1]**

You are provided with the apparatus normally used in a school laboratory and the following materials:

3.00g of hydrated barium chloride, $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$
0.050 mol dm^{-3} aqueous silver nitrate
1.0 mol dm^{-3} potassium chromate(VI) solution
1.0 mol dm^{-3} sulfuric acid

(iv) Describe how you would prepare a solution of barium chloride that is suitable for use in your titration. You should give details of any apparatus used. [2]

1. Weigh accurately about 3.00 g of $\text{BaCl}_2 \cdot x\text{H}_2\text{O}$ in a pre-weighed weighing bottle, using a weighing balance (or electronic balance)
2. Dissolve this solid in a beaker with 30 cm^3 of water.
3. Transfer the solution and washings into a 250 cm^3 graduated flask and make up to the mark with deionised water
4. Shake the solution to obtain a homogeneous solution.
5. Reweigh the emptied weighing bottle.

[1]: Sound procedure for standard solution preparation (weigh solid, dissolve in water, transfer, make up to the mark)

[1]: Ensures accuracy and reliability for preparation of standard solution (use of graduated flask, transfer washings, shake, reweigh if solid not completely transferred to graduated flask)

(v) A known volume of the barium chloride solution you have prepared in (iv) is transferred to a conical flask. [1]

In what order should the other three solutions then be added to the flask?

First: sulfuric acid

Second: potassium chromate(VI)

Third: silver nitrate

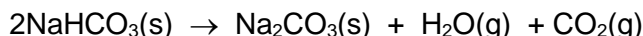
Gravimetric Analysis

Q8 Percentage Composition

[VJC Prelim 2017]

Task: To determine the percentage by mass of sodium hydrogencarbonate in a mixture of sodium carbonate and sodium hydrogencarbonate.

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



You are to design an experiment in which the percentage by mass of NaHCO_3 in a mixture of NaHCO_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
a Bunsen burner
a heat proof mat

You are to show how you would use the results of this experiment to determine the percentage by mass of NaHCO_3 in the mixture.

(i) Outline, step by step, the practical sequence for the method you would use to:

- make appropriate weighings,
- decompose the sodium hydrogencarbonate in the mixture by heating,
- ensure that the decomposition was complete.

1. Weigh the clean and dry boiling tube.
2. Add all the sample into the boiling tube. Weigh the mass of the boiling tube with the sample.
3. Heat the boiling tube gently at first (~1 min) and then strongly (~5 min) to decompose the sodium hydrogencarbonate. Heat the whole length of the tube to ensure even heating of the mixture and to prevent condensation.
4. Cool the boiling tube on a heat proof mat, and weigh the mass of the boiling tube and its residue.
5. Repeat heating, cooling and weighing steps [steps 3 and 4] until constant mass is achieved (OR consecutive mass difference within $\pm 0.050 \text{ g}$ is achieved) to ensure complete decomposition. Record all masses.

weigh empty boiling tube, sample and boiling tube before and after heating
give details such as dry boiling tube, heat strongly, heat whole length of tube, use of heat proof mat for cooling
heat until constant mass (OR within $\pm 0.050 \text{ g}$) to ensure complete decomposition

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

The crucible has a wider surface area for the volatile substances such as water vapour and carbon dioxide to escape more readily which lowers the risk of breakage due to condensation.

[1]

- (iii) 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 NaHCO_3 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. **B – A**.

Mass of empty boiling tube / g	A
Mass of boiling tube and sample before heating / g	B
Mass of boiling tube and residue after heating / g	C
Mass of sample used / g	B – A
Mass loss due to H_2O and CO_2 / g	B – C

Tabulation with headers and units as well as raw data recorded (first 3 rows)

Processed data of mass of sample used and mass loss due to heating (last 2 rows)

[2]

- (iv) Use the letters you have entered in (c)(iii) to show how you would process the results to find:

- the mass of NaHCO_3 in the mixture,

[Ar: C, 12.0; H, 1.0; O, 16.0; Na, 23.0]

Mass of NaHCO_3 in the mixture
 $= (B - C) \times \frac{168.0}{62.0} \text{ g} = R \text{ g}$

- the percentage by mass of NaHCO_3 in the mixture.

Percentage of NaHCO_3 in the mixture = $[R / (B - A)] \times 100 \%$

[2]

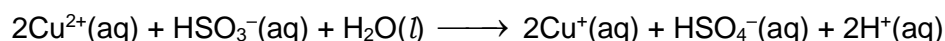
[Total: 8]

Task: To determine the percentage purity of copper(II) nitrate in a sample.

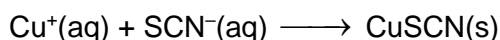
The amount of Cu^{2+} in a sample can be determined by gravimetric method involving precipitation of copper(I) thiocyanate, CuSCN .

The essential experimental conditions are:

1. *slight acidity* of the solution with respect to hydrochloric acid, since the solubility of the precipitate increases appreciably with decreasing pH;
2. *boiling* with ammonium hydrogensulfite, NH_4HSO_3 , a *reducing agent*, to first reduce copper(II) to copper(I);



3. precipitation using a *slight excess of ammonium thiocyanate*, NH_4SCN , since a large excess increases the solubility of the copper(I) thiocyanate due to the formation of a thiocyanate complex.



Isolation of the precipitate is achieved by filtering through a sintered-glass crucible shown in Fig. 4.1, which does not require the use of filter paper. At the same time, the crucible serves as a *container* to hold the precipitate during weighing and drying.

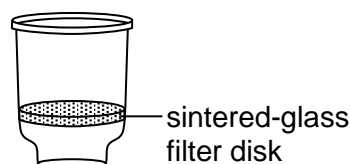


Fig. 4.1

The precipitate is washed with dilute NH_4SCN solution, containing a little NH_4HSO_3 to prevent any oxidation of the copper(I) salt. This is followed by washing with ethanol.

The precipitate (in the crucible) is dried by heating in a hot air oven at 110–120 °C.

In the question, you are to plan a procedure that would allow you to determine the percentage purity of a sample of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

You can assume that you are provided with:

- 3.00 g of solid copper(II) nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (solubility : 267 g / 100 cm^3 of water),
- 10 cm^3 of 1.00 mol dm^{-3} hydrochloric acid, HCl ,
- 150 cm^3 of 0.10 mol dm^{-3} ammonium hydrogensulfite, NH_4HSO_3 ,
- 150 cm^3 of 0.25 mol dm^{-3} ammonium thiocyanate, NH_4SCN ,
- 50 cm^3 of ethanol,
- sintered-glass crucible,
- the equipment normally found in a school or college laboratory.

- (a) Assuming that 2.50 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is used. Determine the minimum volume of 0.10 mol dm^{-3} ammonium hydrogensulfite, NH_4HSO_3 , that is needed to convert all the $\text{Cu}^{2+}(\text{aq})$ into $\text{Cu}^+(\text{aq})$.

[Ar: Cu, 63.5; O, 16.0; N, 14.0; H, 1.0]

$$n_{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}} = \frac{2.50}{63.5 + 2(14.0 + 16.0 \times 3) + 3(1.0 \times 2 + 16.0)} = \frac{2.50}{241.5} = 0.01035 \text{ mol}$$

$$\text{minimum } n_{\text{HSO}_3^-} \text{ required} = \frac{1}{2} \times n_{\text{Cu}^{2+}} = \frac{1}{2} \times 0.01035 = 0.005176 \text{ mol}$$

$$\text{minimum } V_{\text{NH}_4\text{HSO}_3} \text{ required} = \frac{0.005176}{0.10} = 0.05176 \text{ dm}^3 \approx 51.80 \text{ cm}^3$$

minimum volume of 0.10 mol dm^{-3} NH_4HSO_3 needed = **51.80 cm³** [1]

- (b) Determine the minimum volume of 0.25 mol dm^{-3} ammonium thiocyanate, NH_4SCN , needed to precipitate all the $\text{Cu}^+(\text{aq})$ produced in **4(a)**.

$$n_{\text{Cu}^+} = n_{\text{Cu}^{2+}} = 0.01035 \text{ mol}$$

$$\text{minimum } n_{\text{SCN}^-} = n_{\text{Cu}^+} = 0.01035 \text{ mol}$$

$$\text{minimum } V_{\text{NH}_4\text{SCN}} \text{ required} = \frac{0.01035}{0.25} = 0.04141 \text{ dm}^3 = 41.50 \text{ cm}^3$$

minimum volume of 0.25 mol dm^{-3} NH_4SCN needed = **41.50 cm³** [1]

- (c) Plan an investigation to determine the percentage purity of a 2.50 g sample of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ based on the gravimetric method described above.

In your plan, you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow.

Procedure:

1. Weigh out **accurately about 2.50 g** of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ into a clean and dry **weighing bottle** using an **analytical balance**.
2. Dissolve the solid in **50 cm³ of deionised water** in a **250 cm³ beaker**.
3. Add **1 cm³ of 1.00 mol dm⁻³ HCl** by means of a **10 cm³ measuring cylinder**.
4. Add in **70 cm³ of 0.10 mol dm⁻³ NH₄HSO₃** by means of a **100 cm³ measuring cylinder**.
5. Bring the solution to **boil over a Bunsen flame** for 5 minutes.
6. Turn off the Bunsen burner.
7. Add in **42 cm³ of 0.25 mol dm⁻³ NH₄SCN slowly** to the mixture using a **50 cm³ measuring cylinder**, stirring with a glass rod.
8. Allow the mixture to stand for 30 minutes at room temperature.
9. **Weigh and record the mass of a clean and dry sintered-glass crucible**.
10. Filter the mixture through the sintered-glass funnel, and **wash the precipitate 3 times** with a mixture consisting of **10 cm³ of 0.25 mol dm⁻³ NH₄SCN** and **1 cm³ of 0.10 mol dm⁻³ NH₄HSO₃**.
11. **Wash the precipitate 3 times with 10 cm³ portions of cold ethanol**.
12. **Heat the crucible and precipitate in a hot air oven at 110–120 °C for 1 hour**.

.....

13. Cool the crucible in a dessicator. Weigh and record the mass of the cooled crucible with the precipitate.

.....

14. Repeat step 12 and 13 until constant mass of the crucible with precipitate is obtained within $\pm 0.01\text{g}$.

.....

.....

.....

.....

.....

.....

.....

.....

.....

[10]

(d) Assuming that m g of CuSCN is obtained from 2.50 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ sample in 4(c). Express the percentage purity of the sample in terms of m .

[A_r : Cu, 63.5; S, 32.1; O, 16.0; N, 14.0; C, 12.0; H, 1.0]

$$n_{\text{CuSCN}} = \frac{m}{63.5 + 32.1 + 12.0 + 14.0} = \frac{m}{121.6} \text{ mol}$$

$$n_{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}} = n_{\text{CuSCN}} = \frac{m}{121.6} \text{ mol}$$

$$\begin{aligned} m_{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}} &= n_{\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}} \times [63.5 + 2(14.0 + 16.0 \times 3) + 3(1.0 \times 2 + 16.0)] \\ &= \frac{m}{121.6} \times 241.5 \text{ g} \end{aligned}$$

$$\text{percentage purity} = \frac{\frac{m}{121.6} \times 241.5}{2.50} \times 100\% = \underline{79.4m\%}$$

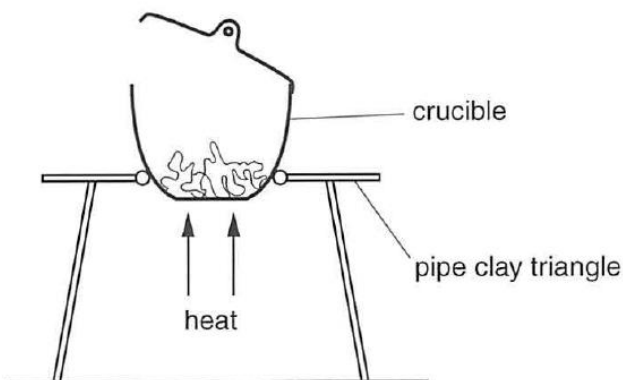
[2]

[Total : 14]

Q10 Chemical Formula of Compound [Assignment] [TPJC Prelim 2017]

Task: To determine the chemical formula of magnesium oxide.

The formula of magnesium oxide can be determined experimentally by the direct combination of magnesium metal with oxygen in the air.

**Method**

- The weighed crucible and magnesium are heated strongly to start the reaction.
- The lid is lifted regularly to allow more air to enter the crucible. The magnesium oxide forms as a fine white powder which may be lost as smoke. Therefore the lid is rapidly replaced to prevent any loss of magnesium oxide.
- When the reaction appears to be complete, the lid is removed and the contents of the crucible are heated strongly for 2-3 minutes.
- After cooling, the crucible and lid are reweighed.
- The mass of magnesium oxide formed and the mass of oxygen combined with the magnesium are calculated from the experimental results.

A number of students perform the experiment, each starting with a different mass of magnesium.

The mass of oxygen is plotted against the mass of magnesium for each student's experiment.

The students expect to obtain a straight-line graph passing through the origin.

The experimental results for each student are given in the table below.

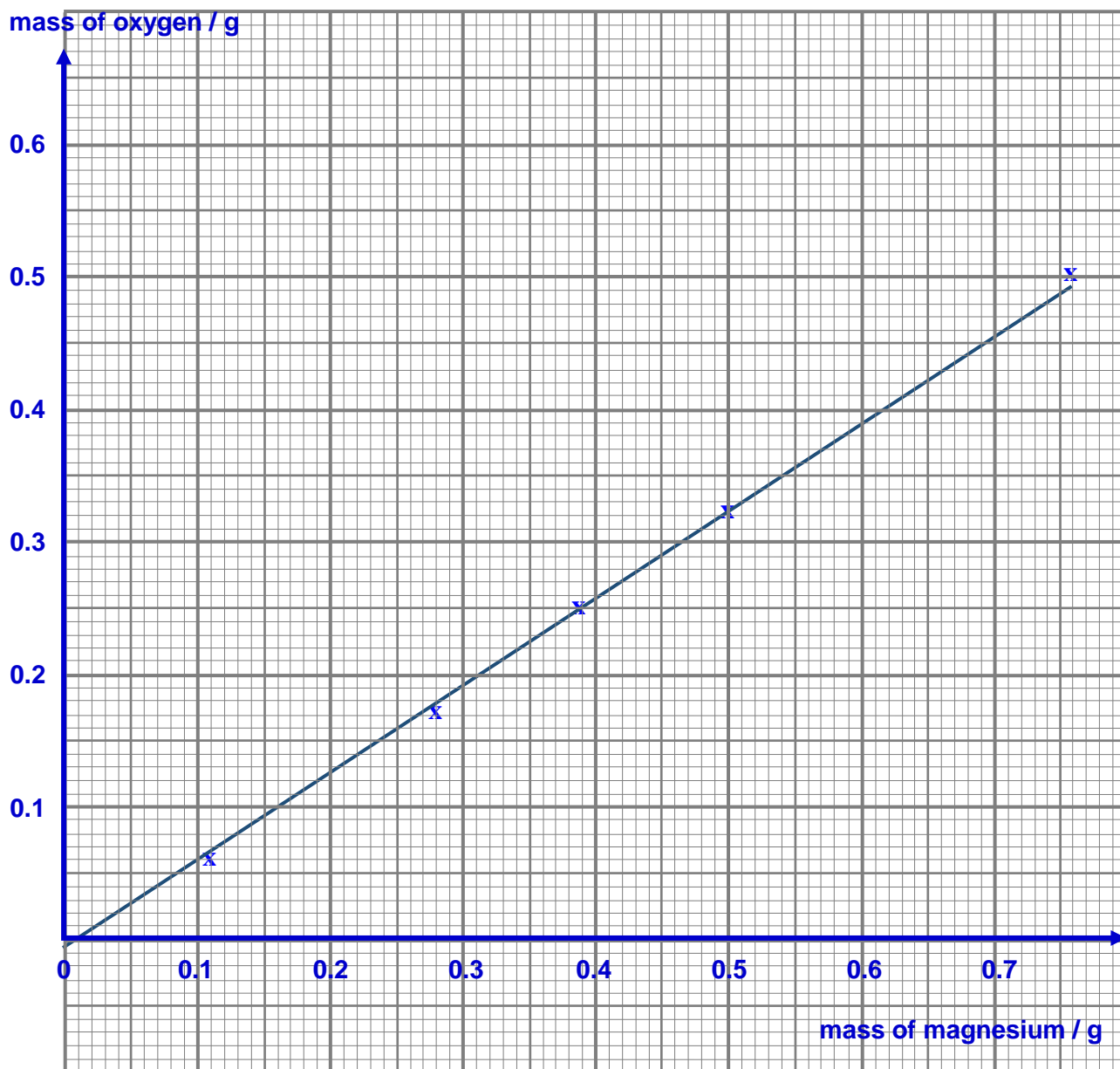
student	mass of crucible + lid / g	mass of crucible + lid + magnesium / g	mass of crucible + lid + magnesium oxide / g	mass of magnesium / g	mass of oxygen / g
1	23.15	23.26	23.33	0.11	0.07
2	21.74	22.02	22.20	0.28	0.18
3	22.53	22.92	23.18	0.39	0.26
4	23.20	23.70	24.03	0.50	0.33
5	23.66	24.42	24.93	0.76	0.51
6	22.08	22.28	16.28		

- (a) For each of the students **1 to 5**, calculate the masses of magnesium and oxygen that react together and complete the above table. Give your answers to **two** decimal places.

You may assume that, in each case, all the magnesium used has been reacted.

[2]

- (b) For students 1 to 5 only, plot the mass of oxygen against mass of magnesium. Draw the best-fit straight line through your plotted points and the origin of the graph.



[2]

- (c) Explain why the students would have expected to obtain a straight line graph.

The ratio of magnesium to oxygen present is fixed in the oxide. This means that the mass of magnesium is directly proportional to the mass of oxygen.

- (d) By considering his experimental results, suggest the most likely error **student 6** could have made.

The student could have forgotten to weigh the crucible together with the lid, resulting in the mass of (crucible + lid + MgO) to be even lower than that of the empty (crucible + lid).

..... [1]

- (e) A student extends the investigation by heating larger masses of magnesium in the same apparatus.

It is found that the ratio $\frac{\text{mass of oxygen}}{\text{mass of magnesium}}$ in these experiments is less than that shown by the straight line you have drawn.

By referring to the description of the experimental method, suggest a possible reason for this observation.

Any one of the following reasons:

- too large a mass of magnesium meant that not all the magnesium was able to react with oxygen to form the oxide due
 - either (1) to the layer of magnesium oxide formed prevent the magnesium from contact with oxygen as the same crucible is being use
 - or (2) heated strongly for 2-3 minutes is insufficient for larger mass to react.
- the crucible lid had to be lifted more often in order to allow more air to enter, resulting in greater loss of magnesium oxide as smoke. [1]

- (f) When a few drops of distilled water are added to the cooled white solid formed in the experiment, a reaction takes place and some ammonia gas, NH_3 , is released.

Suggest a reaction that must have taken place during the experiment resulting in the formation of ammonia when water is added to the cooled white solid.

Magnesium reacted with nitrogen in the air to form a compound (magnesium nitride) which reacts with water to give NH_3 .

..... [1]

[Total: 8]

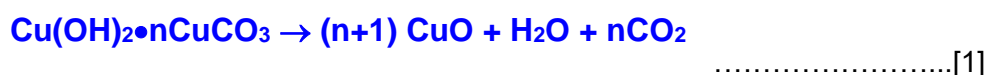
Task: To determine the percentage by mass of copper in $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$

When aqueous solutions of copper(II) sulfate and sodium carbonate are combined, a solid known as basic copper(II) carbonate, $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$, precipitates from solution.

$\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$ decomposes to copper(II) oxide when heated by a Bunsen flame.

The percentage by mass of copper in this basic copper(II) carbonate can be determined in the laboratory using a gravimetric technique.

- (i) Write a chemical equation for the thermal decomposition of $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$.



- (ii) Outline, step by step, the practical sequence for the method you would use to

- carry out the weighing of a sample of $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$ solid,
- decompose this sample by heating, and
- ensure that the decomposition is complete.

You may assume that the following are available:

- 5 g of $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$
 - crucible
 - pipe-clay triangle
 - weighing balance
 - Bunsen burner
 - all other common lab apparatus
-
- Using an **analytical/weighing balance**, **weigh** and **record the mass of a clean, empty and dry crucible**.
 - Weigh out accurately about **5.00 g** of solid $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$ into the crucible. Record the **total mass** of the crucible and the solid $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$.
 - Place the crucible on a **pipe-clay triangle**. Using a **Bunsen burner**, **heat** the crucible and its contents **gently** at first, and then heat **strongly** for 10 minutes.
 - **Cool** and **weigh** the crucible and its contents.
 - **Repeat the heating-cooling-weighing process** until **consistent results** are obtained. (i.e. when two consecutive mass readings have a difference less than 0.01 g).

.....

.....

.....

.....

.....

.....

.....[4]

- (iii) Prepare a table in the space below 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 copper in the mixture. Insert in your table the letters **A**, **B**, **C**, etc. to represent each mass.

Tabulation of results

Mass of empty crucible / g	A
Mass of crucible and $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$ / g	B
Mass of crucible and its contents	
after first heating / g	C
after second heating / g	D
after third heating / g	D

[2]

- (iv) Use the letters you have written in (iii) to show how you would process the results to find the percentage by mass of copper in $\text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3$.
[A_r : Cu, 63.5; O, 16.0; C, 12.0; H, 1.0]

$$\text{Amount of CuO obtained} = \frac{D-A}{63.5+16.0} = \frac{D-A}{79.5} \text{ mol}$$

$$\text{Amount of Cu in } \text{Cu}(\text{OH})_2 \cdot n\text{CuCO}_3 = \text{amount of CuO obtained}$$

$$\% \text{ by mass of Cu} = \frac{63.5 \times (D-A)}{79.5 \times (B-A)} \times 100\%$$

[2]

[Total: 9]

Task: To determine the solubility product, K_{sp} , of magnesium carbonate.

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.

- (i) 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⁻³ sodium carbonate solution
- 0.400 mol dm⁻³ 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.
-
- **Measure 50.00 cm³ of sodium carbonate solution and 50.00 cm³ magnesium nitrate solution using two separate 50.00 cm³ burettes into a 250 cm³ beaker (and place the beaker in a temperature controlled water bath)**
 - **Stir the mixture and leave to stand for some time.**
 - **Filter the mixture using a pre-weighed filter paper (M1 g)**
 - **Dry precipitated $MgCO_3$ together with filter paper**
 - **Weigh the dried precipitated $MgCO_3$ together with the filter paper (M2 g).**

.....

.....

.....

.....

Chemical Energetics

Q13 Basicity

[SAJC Prelim 2010]

Task: To determine the identity of the **acid** present in solution FA 1.

Acid **A** is $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CH}(\text{Cl})\text{CO}_2\text{H}$ (M_r : 194.5)

Acid **B** is $\text{HO}_2\text{C}(\text{CH}_2)_3\text{COCH}_2\text{CO}_2\text{H}$ (M_r : 174)

Acid **C** is $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{H}$ (M_r : 158)

(a) **FA 1** is a solution containing one of the acids **A – C** with concentration **10.0 g dm^{-3}** .

Given solid potassium hydroxide pellets and all standard laboratory apparatus, design a **titrimetric experiment** to determine which acid is present in **FA 1**.

\Rightarrow **titration of acid using standard KOH solution**

In your plan, describe clearly the steps you would carry out and justify the amounts of chemicals you would use.

Show clearly how you would determine the identity of the acid.

[8]

$$[\text{acid A}] = \frac{10.0}{194.5} = 0.0514 \text{ mol dm}^{-3}$$

$$[\text{acid B}] = \frac{10.0}{174} = 0.0575 \text{ mol dm}^{-3}$$

$$[\text{acid C}] = \frac{10.0}{158} = 0.0633 \text{ mol dm}^{-3}$$

Plan:

1. Find [acid] in mol dm^{-3} by titration with **standard KOH solution**.
2. [KOH] chosen such that vol of titre \approx vol of analyte
3. choose **appropriate indicator** for weak acid/strong base titration.

Justification of amounts

In a titration, the concentrations of the reactants are usually made such that the volume of titre = volume of aliquot used.

Since the acids are all **dibasic**, $\text{mol of KOH} = 2 \times \text{mol of acid}$

or $[\text{KOH}] = 2 \times [\text{acid}]$

since [acid] ranges from **0.0514 to $0.0633 \text{ mol dm}^{-3}$** ,

\Rightarrow $[\text{KOH}]$ ranges from **0.1028 to $0.1266 \text{ mol dm}^{-3}$** .

Hence, to prepare 250 cm^3 standard solution of KOH of **0.10 mol dm^{-3}** ,

$$\text{mol of KOH} = 0.10 \times \frac{250}{1000} = 0.0250 \text{ mol}$$

$$\begin{aligned} \therefore \text{mass of KOH used} &= 0.0250 \times (39.1 + 16.0 + 1.0) \\ &= 0.0250 \times 56.1 = \underline{1.40 \text{ g}} \end{aligned}$$

Procedure

Preparation of standard KOH solution (1.0 mol dm⁻³)

1. Weigh accurately about **1.40 g** of KOH into a **dry weighing bottle**.
2. Dissolve the solid using some distilled water, in a beaker.
3. Transfer the solution and all washings into a **250 cm³ volumetric flask**.
Top up the solution with distilled water to the 250 cm³ mark.
Shake well to obtain a homogeneous solution.

Titration of acid FA1 with standard KOH solution

1. Pipette 25.0 cm³ of the acid solution, **FA1**, into a 250 cm³ conical flask.
Add 1-2 drops of **phenolphthalein** indicator.
2. Fill a 50 cm³ burette with the standard KOH solution prepared.
3. Titrate the acid solution, **FA1**, with standard KOH solution until the first permanent **pink colour** is obtained.
4. Repeat the titration until consistent results (within **±0.10 cm³**) are obtained.

** Allow solution in burette and conical flask to be reversed, colour change of indicator must be changed accordingly.*

Determination of identity of FA1

Let average titre of dilute KOH used = V cm³

$$\text{Mol of KOH used} = 0.10 \times \frac{V}{1000} = (0.1 V \times 10^{-3}) \text{ mol}$$



$$\begin{aligned}\text{Mol of acid in } 25.0 \text{ cm}^3 &= \frac{1}{2} \times \text{mol of KOH} \\ &= \frac{1}{2} (0.1 V \times 10^{-3}) \text{ mol}\end{aligned}$$

$$[\text{Acid}] = \frac{1000}{25.0} \times \frac{1}{2} (0.1 V \times 10^{-3}) = (2 V \times 10^{-3}) \text{ mol dm}^{-3}$$

$$\text{Given } [\text{Acid}] = 10.0 \text{ g dm}^{-3}$$

$$\therefore [\text{Acid}] = \frac{10.0}{M_r \text{ of acid}} = 2 V \times 10^{-3}$$

$$\therefore M_r \text{ of acid} = \frac{10}{2 V \times 10^{-3}}$$

$$\text{So, if } \frac{10}{2 V \times 10^{-3}} = \mathbf{194.5}, \text{ then FA 1 contains acid A.}$$

$$\text{if } \frac{10}{2 V \times 10^{-3}} = \mathbf{174}, \text{ then FA 1 contains acid B.}$$

$$\text{if } \frac{10}{2 V \times 10^{-3}} = \mathbf{158}, \text{ then FA 1 contains acid C.}$$

- (b) **FA 2** is a solution containing 1 mol dm^{-3} of either **acid C** or $\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$.

In an attempt to identify the acid present in **FA 2**, a student decided to mix different volumes of **FA 2** and aqueous KOH in two separate experiments. The temperature rise for each experiment was measured.

- (i) Given the concentration of aqueous KOH used in the experiments is 1 mol dm^{-3} , complete the following table.

Experiment	Vol of KOH / cm^3	Vol of FA 2 / cm^3	Temperature rise / $^\circ\text{C}$
1	25	50	T_1
2	50	25	T_2

[2]

- (ii) Explain how the student can make use of the data collected in (b)(i) to identify the acid in **FA 2**. State whether it is **monobasic** or **dibasic**. [2]

Since $[\text{Acid}] = [\text{KOH}]$,



Expt 1: 0.025 0.025 0.025 mol acid is in excess

Expt 2: 0.025 0.025 0.025 mol base is in excess



Expt 1: 0.0125 0.025 0.025 mol acid is in excess

Expt 2: 0.025 0.05 0.05 mol

If $T_1 = T_2$, then acid is $\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$; i.e. acid is **monobasic**.

If $T_2 = 2T_1$, then acid is **C**; i.e. acid is **dibasic**.

This is because for a dibasic acid, the amount of water formed in Expt 2 is **twice** that formed in Expt 1

Task: To investigate the variation in enthalpy change of neutralisation when different acids reacts with aqueous NaOH.

You are given a number of different acids to investigate how the enthalpy change of neutralisation, $\Delta H_{\text{neutralisation}}$, varies when the acids are neutralised with aqueous sodium hydroxide, NaOH.

- (a) (i) Hydrochloric acid, nitric acid and sulfuric acid are all strong acids.

Predict how $\Delta H_{\text{neutralisation}}$ values for these acids would compare with each other.

The three acids should have the same $\Delta H_{\text{neutralisation}}$ values.

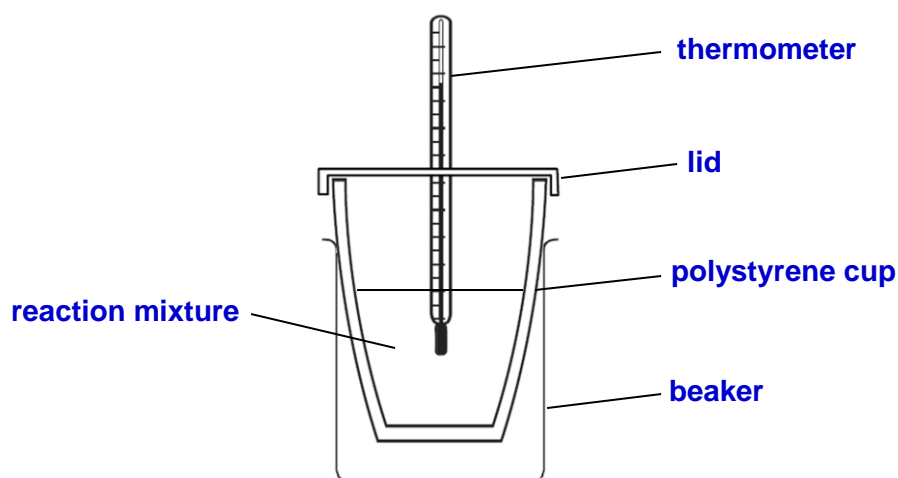
This is because all strong acids dissociate fully in water and $\Delta H_{\text{neutralisation}}$ is the heat evolved when one mole of water is produced during acid-base reaction; i.e. $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ $\Delta H_{\text{neutralisation}}$

- (ii) Predict and explain how the expected $\Delta H_{\text{neutralisation}}$ for a weak acid, such as ethanoic acid or ethanedioic acid, compares with that for hydrochloric acid. [2]

$\Delta H_{\text{neutralisation}}$ for a weak acid should be less exothermic than a strong acid because weak acids are only partially ionised and some of the energy is absorbed when the weak acid dissociates into ions.

- (b) (i) Draw and label a diagram of the apparatus you would use to determine the temperature change, ΔT , when each of the acids reacts with 30.0 cm^3 of 2.0 mol dm^{-3} aqueous sodium hydroxide.

Any experimental method that is normally carried out in a college laboratory may be used.



- (ii) Identify **one** possible source of error in the experiment and state how you would minimise the effect. [3]

S/N	Source of error	Improvement
1	Heat is lost to the surroundings.	Use <u>wind-shield</u> . [If a lid is not used in the set-up above, a <u>lid</u> can be used to cover the cup to reduce heat loss (due to convection).] [If a beaker is not used in the set-up above, a <u>beaker</u> can be used to contain the cup to reduce heat loss (due to convection).]
2	The thermometer used may be of low precision.	Use thermometer of <u>higher precision</u> to allow temperature to be read to a greater degree of precision.
3	There could be some loss of material if the solution overflows or sprays out.	Use a <u>larger</u> cup/container. (If a lid is not used in the set-up above, a <u>lid</u> can be used to minimise spray.)

Any one.

- (c) In each experiment, 30.0 cm³ of 2.0 mol dm⁻³ aqueous NaOH is to be used. Suggest appropriate volumes for each of the acids to be used in the individual experiments. [1]

acid		volume/ cm ³	concentration/ mol dm ⁻³
hydrochloric	HCl	30	2.0
ethanedioic	(CO ₂ H) ₂	15	1.0

- (d) Ethanedioic acid is a hydrated crystalline solid, (CO₂H)₂·2H₂O.
 ⇒ use volumetric flask of 100 cm³ capacity
 Outline how you would prepare 100 cm³ of 1 mol dm⁻³ solution of ethanedioic acid. In your answer, you should show how you determine the initial mass of ethanedioic acid to be used. [Ar: C, 12.0; H, 1.0; O, 16.0] [4]

Justification of amount:

$$\text{mol of ethanedioic acid} = 1.0 \times \frac{100}{1000} = 0.100 \text{ mol}$$

$$\begin{aligned} \text{mass of ethanedioic acid} &= 0.100 \times [2(12.0) + 4(16.0) + 2(1.0) + 2(18.0)] \\ &= 0.100 \times 126 = 12.6 \text{ g} \end{aligned}$$

Preparation of solution of ethanedioic acid (1.0 mol dm⁻³)

1. Weigh accurately about 12.60 g of ethanedioic acid into a dry weighing bottle.
2. Transfer the solid into a 50 cm³ beaker and dissolve the solid using some distilled water.
3. Transfer the solution and all washings into a 100 cm³ volumetric flask. Top up the solution with distilled water to the 100 cm³ mark. Shake well to obtain a homogenous solution.

- (e) Using the volume and concentration from (c) and ΔT to represent the temperature change, derive a mathematical expression for the enthalpy change of neutralisation of **sodium hydroxide with hydrochloric acid**.

[4.3 J of heat energy raise the temperature of 1 cm³ of any solution by 1 °C]

[1]

$$\text{heat evolved} = mc\Delta T$$

$$= (\text{vol of HCl} + \text{vol of NaOH}) \times 4.3 \times \text{temp rise}$$

$$= (30.0 + 30.0) \times 4.3 \times \Delta T$$

$$= (258 \times \Delta T) \text{ J}$$



$$\text{mol of water} = \text{mol of HCl}$$

$$= 2.0 \times \frac{30}{1000}$$

$$= 0.0600 \text{ mol}$$

$$\Delta H_{\text{neutralisation}} = \frac{\text{heat evolved}}{\text{mol of water}}$$

$$= -\frac{258\Delta T}{0.0600}$$

$$= (-4300\Delta T) \text{ J mol}^{-1} = \underline{\underline{(-4.3\Delta T) \text{ kJ mol}^{-1}}}$$

- (f) Suggest what modification you could make to your experimental procedure to ensure **complete neutralisation** of the acid. [1]

The number of moles of acid used can be made slightly lesser than the number of moles of NaOH used so that the acid is the limiting reagent.

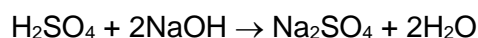
[Total: 12]

Task: To determine the concentration of sulfuric acid.

FA 1 is a solution of sulfuric acid, H_2SO_4 , of concentration approximately 1 mol dm^{-3} .

FA 2 is a solution of 1.50 mol dm^{-3} sodium hydroxide, NaOH

When sulphuric acid neutralises sodium hydroxide, water is produced.



The neutralisation process is exothermic, that is, gives out heat, and the amount of heat produced changes with the amount of water produced. From the temperature rise in various experiments, the actual concentration of H_2SO_4 in **FA 1** can be determined.

- (a) Calculate the approximate temperature rise, ΔT , when 10 cm^3 of **FA 1** and 40 cm^3 of **FA 2** were mixed. In your calculations, you are to assume

specific heat capacity of the mixture = $4.18 \text{ J cm}^{-3} \text{ K}^{-1}$

$\Delta H_{\text{neutralisation}}$ (per mole of water) = $-57.4 \text{ kJ mol}^{-1}$ [3]

$$\text{mol of H}_2\text{SO}_4 = 1 \times \frac{10}{1000} = 0.0100 \text{ mol}$$

$$\text{mol of NaOH} = 1.50 \times \frac{40}{1000} = 0.0600 \text{ (excess)}$$

$$\text{mol of H}_2\text{O formed} = 2 \times \text{mol of H}_2\text{SO}_4 = 0.0200 \text{ mol}$$

Given $\Delta H_{\text{neutralisation}}$ (per mole of water) = $-57.4 \text{ kJ mol}^{-1}$

$$\therefore \text{amount of heat produced} = (0.0200 \times 57.4 \times 10^3) = 1148 \text{ J}$$

Since amount of heat = $mc \Delta T$

$$\therefore \Delta T = \frac{\text{heat produced}}{mc} = \frac{1148}{(10+40) \times 4.18} = 5.5^\circ\text{C}$$

- (b) Fill in the table below, the approximate temperature rise when various volumes of **FA 1** and **FA 2** were mixed. In each case, the total volume of mixture is 50 cm^3 . [2]

Volume of FA 1 / cm^3	10	20	30	40
Volume of FA 2 / cm^3	40	30	20	10
Temperature rise, $\Delta T / ^\circ\text{C}$	5.5	11.0	8.2 / 8.3	4.1 / 4.2

[Since mol of water = $2 \times \text{mol of sulfuric acid} \Rightarrow \Delta T \propto \text{vol of FA 1}$]

- (c) With the help of (b), describe the steps you would carry out to determine the exact concentration of H_2SO_4 in **FA 1**. [3]

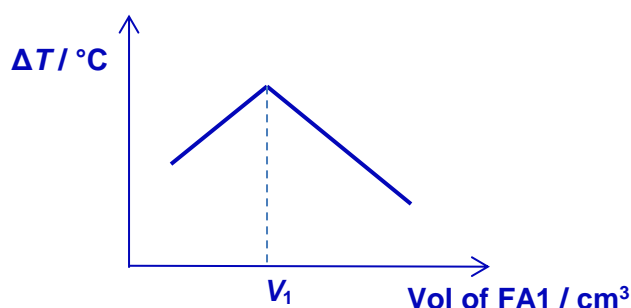
- Measure 10.0 cm^3 of **FA 1** (using a 20 cm^3 measuring cylinder) into a Styrofoam cup. Measure the temperature of **FA 1** in the cup using a thermometer.
- Measure 40.0 cm^3 of **FA 2** using another 50 cm^3 measuring cylinder. Measure the temperature of **FA 2**.
- Take the average of the temperatures of **FA 1** and **FA 2** as the initial temperature.
- Pour the **FA 2** into the Styrofoam cup containing **FA 1** and stir using the thermometer. Record the highest temperature reached.
- Repeat steps 1 to 4 using the various volumes of **FA 1** and **FA 2** shown in the table in (b).

- (d) Identify one source of error in your procedure and explain how you would minimise the error. [2]

Source of error	Improvement
Heat absorbed by the calorimeter	Calibrate calorimeter to account for heat absorbed
Heat is lost to the surroundings.	Use a <u>wind-shield</u> OR Provide lagging on the body of the calorimeter OR Use a lid to cover the calorimeter
Measuring cylinders not precise in measuring volumes of FA 1 and FA 2.	Use a <u>burette</u> to measure accurately the volumes of FA 1 and FA 2.

Any one.

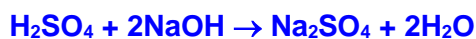
- (e) From the graph of temperature rise against volume of **FA 1**, show how you would treat the data in order to determine the actual concentration of H_2SO_4 in **FA 1**. [2]



From the graph, find the point of intersection of the two lines, which indicates the point of maximum temperature rise.

Let vol of H_2SO_4 in FA 1 = $V_1 \text{ cm}^3$ at point of intersection

\therefore vol of NaOH (FA 2) = $(50 - V_1) \text{ cm}^3$



mol of $\text{H}_2\text{SO}_4 = \frac{1}{2} \times \text{mol of NaOH}$

$$[\text{H}_2\text{SO}_4] \times \frac{V_1}{1000} = \frac{1}{2} \times 1.50 \times \frac{(50 - V_1)}{1000}$$

$$\therefore [\text{H}_2\text{SO}_4] = \left(0.75 \times \frac{(50 - V_1)}{V_1} \right) \text{ mol dm}^{-3}$$

[Total: 12]

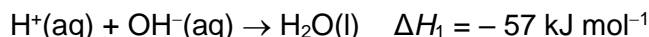
Task: To determine the enthalpy change of solution of Mg(OH)_2 in water.

You are to design an experiment to determine the enthalpy change of solution of Mg(OH)_2 in water.



You are provided with the following data and a list of apparatus and reagents:

Data:



Reagents:

- 2.0 mol dm^{-3} of HCl
- Mg(OH)_2 solid

Apparatus:

- a thermometer with 0.2°C division
- a 100 cm^3 Styrofoam cup with a lid
- two 50 cm^3 measuring cylinders

- (a) Suggest a reason why ΔH_{soln} of solid Mg(OH)_2 cannot be determined by measuring temperature change when a certain amount of solid Mg(OH)_2 is dissolved in water. [1]

Mg(OH)_2 is not soluble in water therefore ΔH_{soln} cannot be determined directly.

- (b) Given that the enthalpy change of reaction between solid Mg(OH)_2 and hydrochloric acid is **approximately** $-30.0 \text{ kJ mol}^{-1}$,

- (i) give the thermochemical equation of the reaction between solid Mg(OH)_2 and hydrochloric acid. [1]



[Thermochemical eqn must be accompanied with the associated enthalpy change, indicating whether it is endo- or exo- when there is no ambiguity.]

- (ii) prove with calculations whether 50.0 cm^3 of 2.0 mol dm^{-3} HCl and 1.17 g of Mg(OH)_2 are suitable quantities to work with. [1]

$$M_r \text{ of } \text{Mg(OH)}_2 = 24.3 + 2(16.0 + 1.0) = 58.3$$

$$\text{amt of } \text{Mg(OH)}_2 = \frac{1.17}{58.3} = 0.02007 \text{ mol}$$

$$\text{amt of } \text{HCl} = 2.0 \times \frac{50.0}{1000} = 0.100 \text{ mol}$$

Since 0.02007 mol of Mg(OH)_2 needs 0.04 mol of HCl for reaction, therefore Mg(OH)_2 is limiting.

Heat released by reaction = heat absorbed by solution

$$30.0 \times 10^3 \times 0.02007 = 50 \times 4.18 \times \Delta T$$

$$\Delta T = 2.9^\circ\text{C}$$

\therefore amt of solid Mg(OH)_2 not suitable as ΔT is not within $5 - 10^\circ\text{C}$.

[For energetics, the data you are collecting is change in temperature and it must be of this range: $5^\circ\text{C} < \Delta T < 10^\circ\text{C}$.

Therefore the easiest method to increase ΔT it to use

(i) more solid Mg(OH)_2 or (ii) use half the volume of HCl solution – but if vol is too small, depth of solution may be too shallow to cover bulb of thermometer

- (iii) Hence give a detailed procedure to determine the enthalpy change of reaction between solid $\text{Mg}(\text{OH})_2$ and HCl solution accurately. [5]

Use double the mass of $\text{Mg}(\text{OH})_2$ solid so that ΔT is doubled to become 5.8°C and dil HCl is still present in excess.

Procedure:

1. Weigh accurately about 2.34 g of $\text{Mg}(\text{OH})_2$ in a weighing bottle.
 2. Using a 50 cm^3 measuring cylinder, measure 50 cm^3 of HCl into a styrofoam cup supported in 250 cm^3 beaker.
 3. Measure initial temperature of HCl .
 4. Add solid $\text{Mg}(\text{OH})_2$ into the styrofoam cup, **taking care to replace the lid immediately.**
 5. **Stir** with thermometer and measure the **highest temperature reached.**
 6. **Weigh mass of weighing bottle and residual solid and calculate the actual mass (m) of $\text{Mg}(\text{OH})_2$ used.**
 7. Wash the styrofoam cup and dry it thoroughly before the next experiment.
 8. Repeat experiment until $\Delta T/m$ is within 5 % difference.
- (c) Given the following data, show how the enthalpy change of reaction between solid $\text{Mg}(\text{OH})_2$ and hydrochloric acid can be determined accurately.

	Expt
Mass of weighing bottle and solid sample / g	a
Mass of weighing bottle and residual solid / g	b
Initial temperature of 50.0 cm^3 of hydrochloric acid / $^\circ\text{C}$	T_1
Final constant temperature of hydrochloric acid / $^\circ\text{C}$	T_2 where $T_2 > T_1$

$$\text{mass of } \text{Mg}(\text{OH})_2 = (a - b) \text{ g}$$

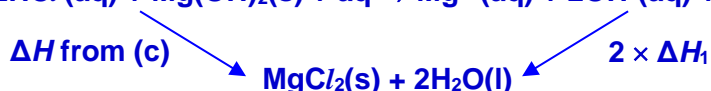
$$\text{mol of } \text{Mg}(\text{OH})_2 = \frac{(a - b)}{58.3} \text{ mol}$$

$$\text{heat evolved} = mc \Delta T = 50 \times 4.18 \times (T_2 - T_1)$$

$$\therefore \Delta H = \frac{\text{heat evolved}}{\text{mol of limiting reagent}} = - \frac{50 \times 4.18 \times (T_2 - T_1)}{(a - b)/58.3} = -12185 \frac{(T_2 - T_1)}{(a - b)} \text{ J mol}^{-1}$$

[1]

- (d) By considering the data given and your answer to part (c), construct a suitable energy cycle that will enable you to determine the enthalpy change of solution of $\text{Mg}(\text{OH})_2$. [2]



$$\therefore \Delta H_{\text{solution}} = \Delta H(\text{c}) - 2 \times \Delta H_1$$

- (e) Suggest and explain a safety precaution for this experiment. [1]

Wear gloves to avoid direct contact with HCl as it is of high concentration (corrosive).

[Total: 12]

Task: To determine the enthalpy change of solution of ammonium chloride and ammonium nitrate.

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 pack's 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.

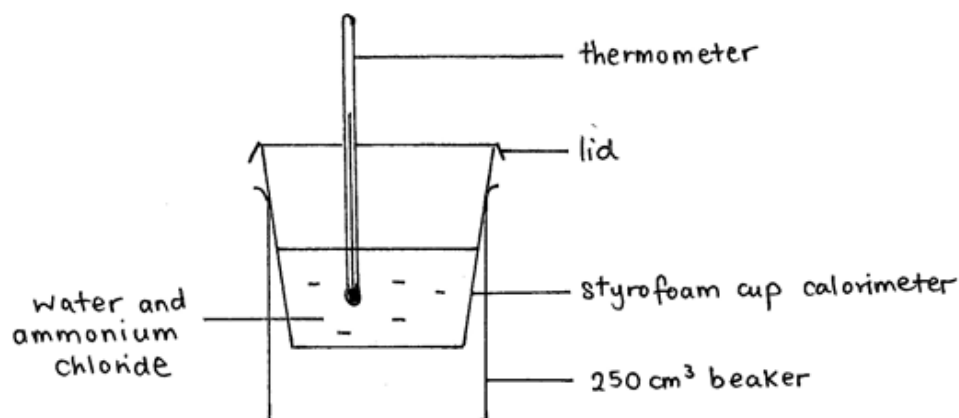
He added ammonium chloride to water and found the temperature change by plotting a suitable graph to correct for surrounding heat transfer.

Solubility of ammonium chloride at 25 °C = 6.95 mol dm⁻³

4.3 J are required to raise the temperature of 1.0 cm³ of any solution by 1°C.

In a preliminary investigation, the enthalpy change of solution of ammonium chloride was found to be approximately +15 kJ mol⁻¹.

- (a) Draw a **labelled diagram** to show the apparatus you could use in a school laboratory to carry out the experiment. [1]



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

100 cm³ [accept 10 cm³ to 200 cm³]

- (ii) Calculate the maximum mass of ammonium chloride that can be added to the volume of water stated in (b)(i). [2]

Given: solubility of ammonium chloride = 6.95 mol dm⁻³

M_r of NH₄Cl = 14.0 + 4(1.0) + 35.5 = 53.5

∴ maximum mass of NH₄Cl that can dissolve in 100 cm³ of water

$$= \left(\frac{100}{1000} \times 6.95 \right) \times 53.5 = 37.2 \text{ g}$$

- (c) Suggest a minimum mass of ammonium chloride that could be used. Justify your choice with relevant calculations, stating any assumptions you made. [2]

Given: ΔH_{sol} of NH_4Cl = +15 kJ mol⁻¹

Let $\Delta T = 5^\circ\text{C}$, and assume no heat loss to surroundings,

$$\text{heat absorbed} = (n_{\text{salt}} \times 15 \times 10^3) \text{ J}$$

Since heat absorbed = $mc\Delta T = (100 \times 4.3 \times 5) \text{ J}$

$$\Rightarrow n_{\text{salt}} \times 15 \times 10^3 = (100 \times 4.3 \times 5)$$

$$\therefore n_{\text{salt}} = 0.143 \text{ mol}$$

$$\therefore \text{minimum mass of salt to use} = 0.143 \times 53.5 = 7.65 \text{ g}$$

- (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 \Rightarrow mass of NH_4Cl between 7.65 g and 37.2 g
- draw table(s) with headings to show the measurements you would make.

[4]

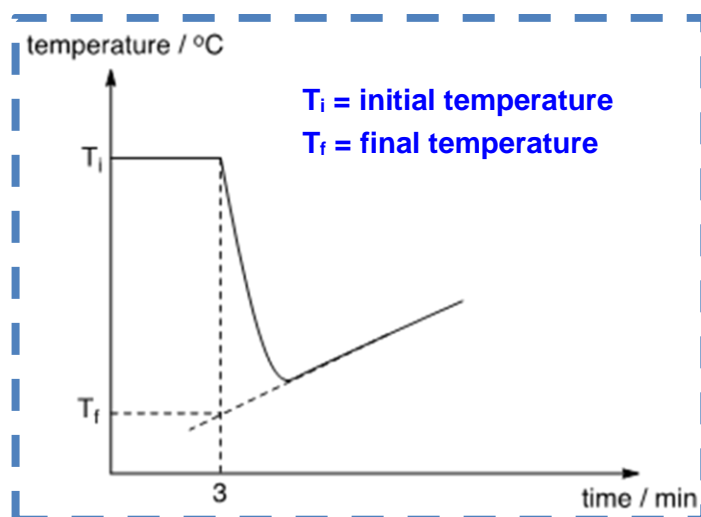
- Weigh accurately 8.00 g of ammonium chloride in a weighing bottle, using a weighing balance.
- Using a 100 cm³ measuring cylinder, add 100 cm³ of water into a dry styrofoam cup calorimeter. Support the styrofoam cup on a 250 cm³ beaker. Stir the water gently using the thermometer.
- Start the stopwatch.
- Record the temperature of water in the styrofoam cup using a 0.1 °C thermometer, at 30 s intervals (accept 1 min) until 2.5 min.
- At exactly 3 min (accept 1–5 min), tip the ammonium chloride into the water. Do not measure the temperature at this time.
- 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 solution returns to room temperature.
- Reweigh the weighing bottle.

Table with headings:

mass of weighing bottle and salt, NH_4Cl / g	m_1
mass of weighing bottle after experiment / g	m_2
mass of salt, NH_4Cl , 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	
.	

- (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. [1]



- (f) In the student's experiment, he dissolved m g of ammonium chloride in V cm³ 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. [1]

$$\Delta H_{\text{solution}} = \frac{\text{heat absorbed}}{\text{mol of NH}_4\text{Cl}} = + \frac{V \times 4.3 \times T}{\frac{m}{53.5}} \text{ J mol}^{-1}$$

$$= +230 \frac{VT}{m} \text{ J mol}^{-1} \text{ [Always simplify answer.]}$$

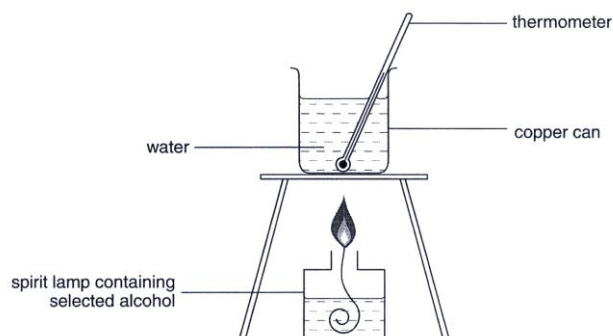
- (g) The student repeats the same procedure for ammonium nitrate. How might he conclude which of the two salts is more effective as the ingredient in the cold pack? [1]

The salt with the more endothermic enthalpy change of solution (or gives the fastest drop in temperature) will be the more effective ingredient in the cold pack.

[Total: 12]

Task: To determine the enthalpy change of combustion of ethanol.

- (a) The enthalpy change of combustion of ethanol, ΔH_c can be determined experimentally under laboratory conditions using the following apparatus.



- (i) Using the apparatus shown above and any other apparatus required that is normally found in a school laboratory, **plan** a step-by-step method to determine the enthalpy change of combustion of ethanol, ΔH_c .

Plan [find mass of ethanol needed to raise temp of 50 cm³ water by 5 °C]

1. Fill the copper can with 50.0 cm³ water and set up the apparatus as in the diagram. Measure and record the initial temperature of the water.
2. Weigh and record the mass of the entire spirit lamp.
3. Light up the spirit lamp. Stir the contents of the copper can until there is a 5 °C rise in temperature. Blow to extinguish the flame and record the temperature in the table
4. Reweigh the entire spirit lamp when cooled.

Show how you would tabulate your results. All necessary measurements should be shown in the table. You may use letters to represent each reading obtained e.g. T_1 , T_2 .. to represent temperature readings, M_1 , M_2 .. to represent mass readings etc.

Mass of spirit lamp + ethanol before combustion / g	M_1
Mass of spirit lamp + ethanol after combustion / g	M_2
Mass of ethanol burnt / g	$M_1 - M_2$
Initial temperature of water / °C	T_1
Final temperature of water / °C	T_2
Temperature rise of water / °C	$T_2 - T_1$

Using the lettered symbols in your table, show how you would process your results to find the enthalpy change of combustion of ethanol, ΔH_c .

[4.2 J of heat energy raise the temperature of 1 cm³ of water by 1 °C]

$$\begin{aligned}\text{Heat evolved during combustion} &= \text{heat gained by water in copper can} \\ &= 50.0 \times 4.2 \times (T_2 - T_1) \text{ J}\end{aligned}$$

$$\text{Number of moles of ethanol burnt} = (M_1 - M_2) / 46 \text{ mol}$$

$$\begin{aligned}\Delta H_c &= \frac{\text{heat evolved}}{\text{mol of ethanol}} = - \frac{50.0 \times 4.2 \times (T_2 - T_1)}{\frac{(M_1 - M_2)}{46.0}} \text{ J mol}^{-1} \\ &= -9.66 \frac{(T_2 - T_1)}{(M_1 - M_2)} \text{ kJ mol}^{-1}\end{aligned}$$

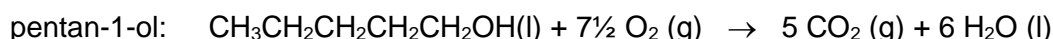
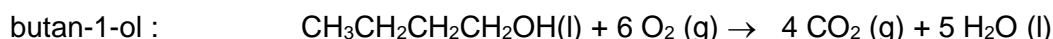
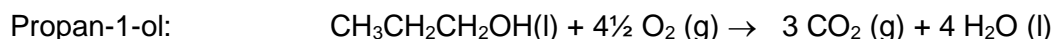
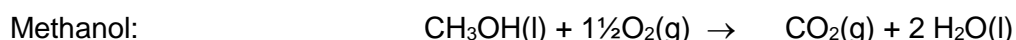
- (ii) The apparatus shown in the above diagram and used in the experiment you have described is inefficient as much of the energy released from the burning ethanol is lost to the atmosphere.

Suggest **one simple improvement** to the apparatus shown on page 2 that will reduce the loss of heat energy to the atmosphere. The suggested improvement should be supported by an appropriate reason.

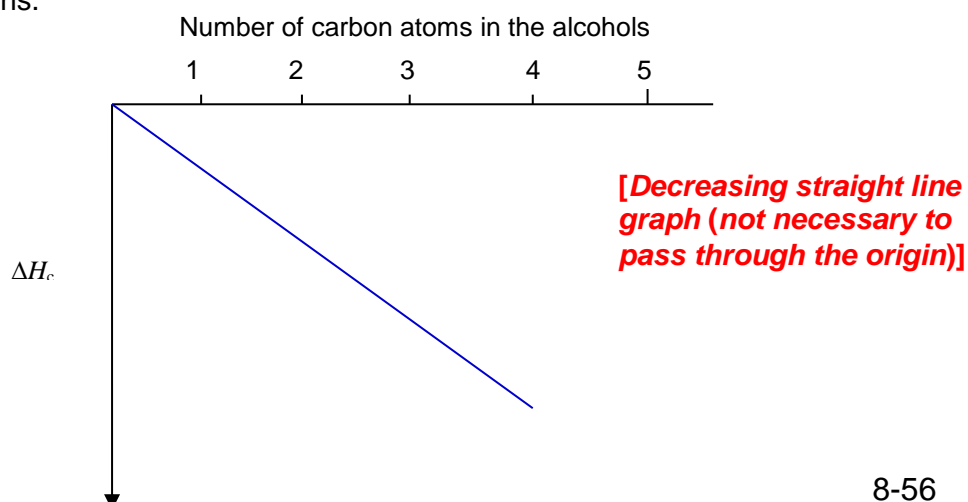
Any one of the following:

- Provide lagging or insulation on sides but not bottom of can to prevent heat loss through the sides of the can by conduction.
- Put a lid on the copper can to prevent heat loss from the top of can by convection.
- Reduce distance between base of can and the spirit lamp to avoid loss of heat by convection.
- Use a wind-shield to exclude draughts to minimise heat lost to surrounding.

- (iii) The equations for the complete combustion of the first five members of the alcohol homologous series are shown below.



There is a trend in ΔH_c for these five alcohols. Sketch the trend indicated by the equations.



- (b) Labels have come off three bottles each containing an aqueous solution of the following chemicals: **aluminium nitrate**

lead nitrate

zinc nitrate

You are provided with the reagents **NaOH(aq)**, **NH₃(aq)**, Na₂CO₃(aq), dil H₂SO₄ and dilute HCl.

Using only the above reagents, but not necessarily all of them, you are to plan a method to identify each of the solutions. Maximum credit will be given for the minimum number of tests to positively identify each of the solutions. Marks will be deducted for additional or unnecessary tests.

Record your expected results in the table below.

	Experiment	Expected observation with each solution tested and deductions from these observations
1	<ul style="list-style-type: none"> Add dil HCl or dil H₂SO₄ to separate samples of the three solutions. 	<ul style="list-style-type: none"> Pb(NO₃)₂ : White precipitate (PbCl₂ or PbSO₄) Al(NO₃)₃: No precipitate Zn(NO₃)₂: No precipitate
2	<ul style="list-style-type: none"> Add NH₃(aq) to the two solutions where no precipitate is formed with the first reagent. 	<ul style="list-style-type: none"> Zn(NO₃)₂: White precipitate (Zn(OH)₂) soluble in excess ammonia [Zn(NH₃)₄]²⁺ Al(NO₃)₃: White precipitate (Al(OH)₃) insoluble in excess ammonia

OR

1	<ul style="list-style-type: none"> Add NH₃(aq) to separate samples of the three solutions. 	<ul style="list-style-type: none"> Zn(NO₃)₂: White precipitate soluble in excess ammonia. Pb(NO₃)₂ : White precipitate (Pb(OH)₂), insoluble in excess ammonia. Al(NO₃)₃: White precipitate (Al(OH)₃), insoluble in excess ammonia.
2	<ul style="list-style-type: none"> Add dil HCl or dil H₂SO₄ to the two solutions where the ppt formed was insoluble in excess NH₃(aq). 	<ul style="list-style-type: none"> Pb(NO₃)₂: White precipitate (PbCl₂ or PbSO₄) Al(NO₃)₃: No precipitate

OR

1	<ul style="list-style-type: none"> Add Na₂CO₃ to separate samples of the three solutions. 	<ul style="list-style-type: none"> Al(NO₃)₃: White precipitate (Al(OH)₃), with effervescence or CO₂ or gas which forms white ppt with lime water. Zn(NO₃)₂: White precipitate (ZnCO₃). Pb(NO₃)₂ : White precipitate (PbCO₃)..
2	<ul style="list-style-type: none"> Add NH₃(aq) to the two solutions where no effervescence was seen with the first reagent. 	<ul style="list-style-type: none"> Pb(NO₃)₂ : White precipitate, insoluble in excess ammonia. Zn(NO₃)₂: White precipitate, soluble in excess ammonia.

[4]

[Total: 12]

Task: Determination of the formula of an unknown metal complex ion

You are provided the following reagents.

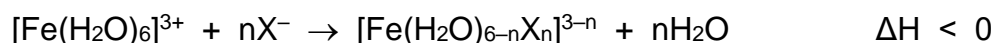
FA1 is 0.03 mol dm⁻³ of FeCl₃ solution

FA4 is 6% volume H₂O₂

FA5 is 0.00215 mol dm⁻³ of X⁻ solution

Thermometry is sometimes used to determine the number of ligands attached to the central metal atom or ion. One of such monodentate ligand is X⁻ present in **FA5**.

A student performed an experiment to determine the structural formula of the hexa-coordinated complex.



He used varying volumes of **FA1** and **FA5** only, while keeping the total volume of the mixture at 80 cm³. He recorded the change in temperature.

(i) Outline how you would:

- determine the effect of changing the volumes of **FA1** and **FA5** on the temperature change of the experiment and hence,
- vary the volumes of **FA1** and **FA5** to form the needed hexa-coordinated complex, $[\text{Fe}(\text{H}_2\text{O})_{6-n}\text{X}_n]^{3-n}$.

There is no need to perform the experiment.

No details regarding the use of specific apparatus are required. [3]

For experiment 1

A 10 cm³ portion of **FA1** was added to 70 cm³ of **FA5**. The mixture was mixed thoroughly and the highest temperature reached was noted down.

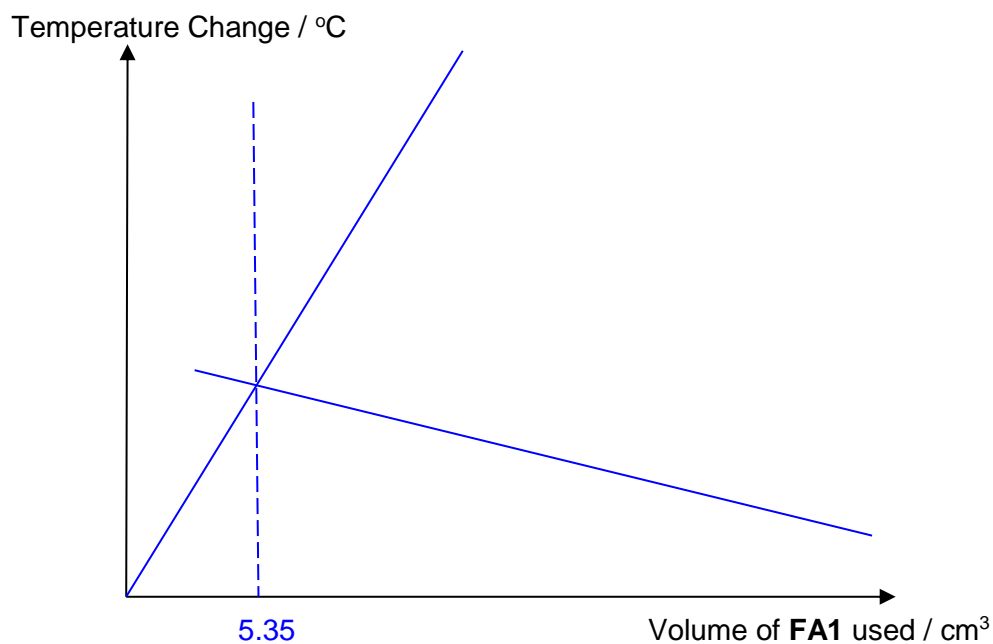
The procedure was repeated for experiments 2 to 7 (minimum 5), with the following changes in the volume of **FA1** and **FA5** as stated in the table below.

Experiment	Volume of FA1 / cm ³	Volume of FA5 / cm ³	ΔT / °C
1	10	70	
2	20	60	
3	30	50	
4	40	40	
5	50	30	
6	60	20	
7	70	10	

(ii) The student plotted a graph and concluded that n=1 in the structural formula of $[\text{Fe}(\text{H}_2\text{O})_{6-n}\text{X}_n]^{3-n}$. On the axes of **Figure 3.1**, sketch a graph that the student would

obtain from your experiment in (i) to draw this conclusion. Indicate the volume of **FA1** that the student would use to reach this conclusion on the x-axis of the graph.

[2]



Two straight lines drawn

Concentration of **FA1** = 0.03 mol dm^{-3}

Concentration of X^- = $0.00215 \text{ mol dm}^{-3}$

Let the intersection occur at $y \text{ cm}^3$ of **FA1**

Amount of **FA1** used = $\frac{y}{1000} \times 0.03 = 3 \times 10^{-5} y \text{ mol}$

Amount of X^- used = $\frac{80-y}{1000} \times 0.00215 = (1.72 \times 10^{-4} - 2.15 \times 10^{-6} y) \text{ mol}$

Since ratio of $\text{Fe}^{3+} : \text{X}^-$ is 1 : 1;

$3 \times 10^{-5} y = 1.72 \times 10^{-4} - 2.15 \times 10^{-6} y$

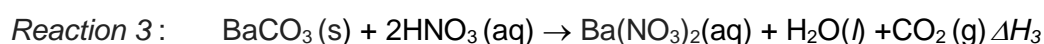
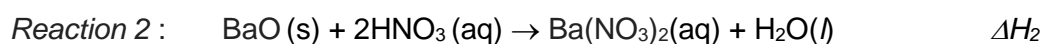
Intersection occurred at 5.35 cm^3 of **FA1**

Task: To determine enthalpy change of reaction via Hess' Law

Barium carbonate, BaCO_3 , is widely used in the ceramics industry as an ingredient in glazes. BaCO_3 can be formed from the reaction between barium oxide and carbon dioxide as shown in *Reaction 1*.

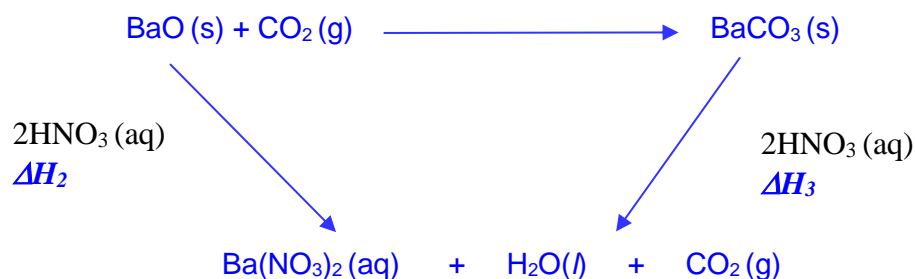


Experimentally, it is difficult to measure the enthalpy change of reaction, ΔH_1 directly. Instead, Hess's Law can be used to calculate ΔH_1 using experimentally determined values of ΔH_2 and ΔH_3 for the following reactions as shown below.



- (i) Construct an energy cycle using the information in the question to show how the enthalpy change of reaction, ΔH_1 , can be calculated from ΔH_2 and ΔH_3 .

[1]



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

- (ii) You are to plan an experiment that will allow you to determine the enthalpy change of *Reaction 2*, ΔH_2 . Your plan must enable you to plot a graph that includes data from the experiment. You may assume that all solutions have a density of 1 g cm^{-3} and the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

You may also assume that the following are provided:

- 3 g solid barium oxide
- 120 cm^3 of $0.500 \text{ mol dm}^{-3}$ aqueous nitric acid, HNO_3
- Styrofoam cup
- stop-watch
- thermometer
- apparatus and materials normally found in a school laboratory.

YOU ARE NOT REQUIRED TO PERFORM THIS EXPERIMENT.

In your plan, you should include details of:

- calculations of suitable quantities of reagents used;
- an outline of all essential experimental procedures;
- a sketch of the graph you expect to obtain and
- an outline of the calculations you would perform to find ΔH_2 in kJ mol^{-1} .

Pre-calculations

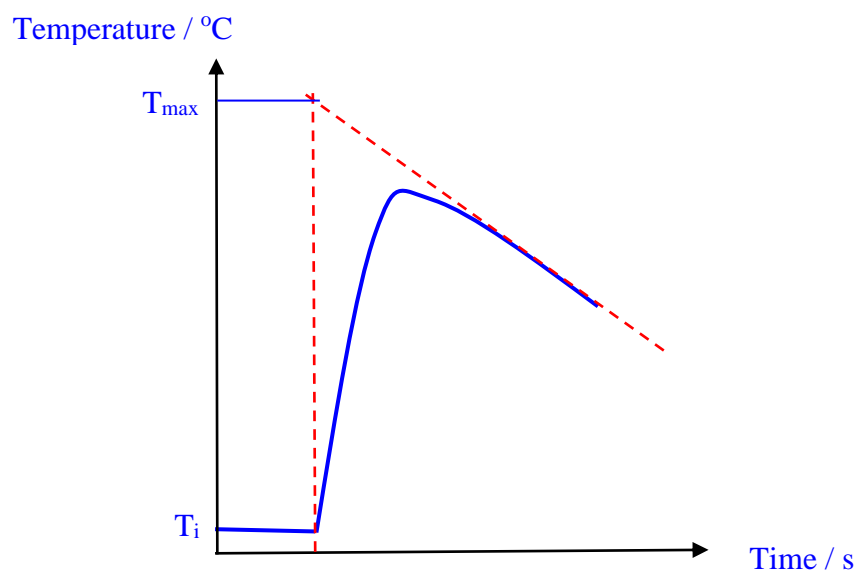
If mass of BaO used is 1.00 g, amount of BaO = $\frac{1.00}{137.0+16.0} = 0.006536 \text{ mol}$

Amount of $\text{HNO}_3 = 2 \times 0.006536 = 0.01307 \text{ mol}$

Minimum volume of HNO_3 required to dissolve the BaO solid = $\frac{0.01307}{0.500} = 26.14 \text{ cm}^3$

Experimental Procedure

1. Weigh out about 1 g of BaO into a dry weighing bottle. Record the mass readings in a table.
2. Using a 50 cm^3 measuring cylinder, transfer 40 cm^3 of HNO_3 into the styrofoam cup supported in a glass beaker.
3. Measure and record the initial temperature of the HNO_3 . Start the stop-watch and stir the solution gently with the thermometer. Record the temperature of the solution every 30 seconds for 2.0 minutes.
4. At 2.0 minutes, transfer the BaO solid into the styrofoam cup. Continuously stir the mixture thoroughly, and read the temperature at 2.5 minutes. Following this, record the temperature every 30 seconds from 3.0 minutes to 8.0 minutes.
5. At the end of the experiment, reweigh the weighing bottle and record the actual mass of BaO used.
6. Plot a graph of temperature against time to obtain a cooling curve. Obtain the maximum temperature change by extrapolation.



To calculate ΔH_2

Quantity of heat absorbed by solution, $Q = (V_{\text{HNO}_3}) \times 4.18 \times (T_i - T_{\text{max}})$
 $= x \text{ J}$

$$\Delta H_2 = -x \div \frac{1.00}{137.0 + 16.0} / 1000$$

$$= -y \text{ kJ mol}^{-1}$$

Other methods possible: *Fixed volume of HNO_3 and change mass of BaO*
OR *Fixed mass of BaO and change volume of HNO_3*

Task: To identify three unknown compounds

You are to plan an experiment to determine the identities of 3 unknown solutions using experimental techniques from thermochemistry.

You are provided with the following:

- solutions of **FB 1**, **FB 2** and **FB 3**, which can be any of the following:
 - 1 mol dm⁻³ aqueous ammonia
 - 1 mol dm⁻³ potassium hydroxide
 - 2 mol dm⁻³ hydrochloric acid
- the apparatus normally found in a school laboratory

In your plan, you should include

- appropriate quantities of solution used,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- an outline of how you would use your results to identify the 3 solutions.

(Note: the use of indicator and litmus paper is not allowed)

Suggested solution:**Procedure:**

1. Using three **10.0 cm³ measuring cylinders**, measure 5.0 cm³ of **FB 1**, **FB 2** and **FB 3**.
2. Mix separately, 5.0 cm³ of **FB 1** to 5.0 cm³ of **FB 2** and 5.0 cm³ of **FB 1** to 5 cm³ of **FB 3**, into 2 **test-tubes**
3. Measure for the rise in temperature using a **0.2 °C division thermometer**

Deduction:

- If both reaction mixture gives a temperature rise, **FB 1** is **HCl**.
- If one of the 2 reaction mixture does not give a temperature rise, then this pair of solutions must be NH₃(aq) and KOH(aq). **HCl** can be identified.

Upon identifying **HCl**,

4. Using a 10.0 cm³ measuring cylinder, add 10.0 cm³ of **HCl** to a **Styrofoam cup** and measure the initial temperature, T₁, using a **0.2 °C division thermometer**.
5. Using another 10.0 cm³ measuring cylinder, transfer 10 cm³ of **one of the bases** into another Styrofoam cup.
6. Wash and dry the thermometer
7. Measure the initial temperature, T₂, of the **base** solution.
8. Add **HCl** to **base** and stir with the thermometer and note the highest temperature reached, T_f and determine ΔT.
9. Wash and dry the Styrofoam cup.
10. Repeat steps 4 – 9 but replace base with the other base solution.

Assuming if **FB 1** is **HC/**

	FB 2	FB 3
$T_i / ^\circ\text{C}$		
$T_f / ^\circ\text{C}$		
$\Delta T / ^\circ\text{C}$		

Deduction of results:

Since **HC/** is 2 mol dm^{-3} , the limiting reagent is the base and the same amount of base is used / same amount of H_2O is produced in each reaction.

When total volume of reaction mixture is kept constant and the no of moles of water formed in the reaction is the same, ΔT depends only on the strength of the base used.

As weak acid dissociates partially, a portion of the energy released from neutralisation is used to complete the dissociation of the weak acid. Therefore less energy is released compared to a neutralisation between a strong acid and a strong base.

The reaction mixture that gives a lower ΔT must contain 1 mol dm^{-3} aqueous ammonia.

Alternative solution

Procedure:

1. To 1 **test-tube**, add 5.0 cm^3 of **FB 1** using a **10.0 cm^3 measuring cylinder** and measure the initial temperature, T_1 , using a **$0.2 ^\circ\text{C}$ division thermometer**.
2. Using another 10.0 cm^3 measuring cylinder, measure 5.0 cm^3 of **FB 2**.
3. Wash and dry the thermometer.
4. Measure the initial temperature, T_2 , of **FB 2**.
5. Transfer **FB 2** into the test-tube. Stir with the thermometer and note the highest temperature reached, T_f and determine ΔT .
6. Wash and dry the test-tube.
7. Repeat steps 1 – 6 but by mixing 5.0 cm^3 of **FB 1** to 5 cm^3 of **FB 3** and 5.0 cm^3 of **FB 2** to 5 cm^3 of **FB 3** respectively.

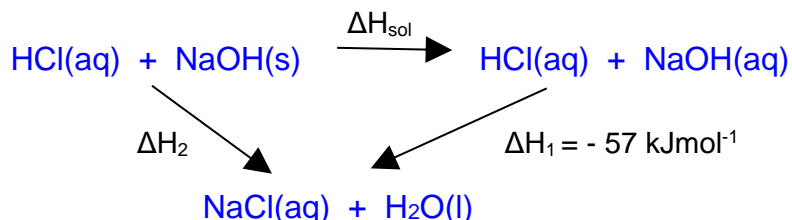
	FB 1	FB 2	FB 3
FB 1		$T_1 =$ $T_2 =$ $T_f =$ $\Delta T =$	$T_1 =$ $T_2 =$ $T_f =$ $\Delta T =$
FB 2			$T_1 =$ $T_2 =$ $T_f =$ $\Delta T =$

Results analysis: similar to first solution of using ΔT to identify the 3 solutions.

Q22 Calculation of enthalpy change [Assignment]**[TJC Prelim 2017]****Task: To calculate the enthalpy change of solution of NaOH(s)**

The enthalpy change of solution of solid NaOH can be calculated using the enthalpy change of neutralisation of aqueous NaOH with aqueous HCl, ΔH_1 and the enthalpy change of reaction of solid NaOH with aqueous HCl, ΔH_2 .

- (i) Given that the enthalpy change of neutralisation of aqueous NaOH with aqueous HCl is $-57.0 \text{ kJ mol}^{-1}$, construct an energy cycle and show how it can be used to determine the enthalpy change of solution of NaOH.



Using Hess' Law,
 $\Delta H_{\text{sol}} = \Delta H_2 - \Delta H_1$

[1]

- (ii) You are to plan an experiment to determine the enthalpy change of reaction of solid NaOH with aqueous HCl, ΔH_2 . You are provided with the following reagents and the usual laboratory apparatus.

Reagents: 50 cm³ of 1 mol dm⁻³ HCl solution
sodium hydroxide solid

Your plan should include

- calculation to show the appropriate mass of solid sodium hydroxide to be used.
- a sequence of numbered steps, the details of the experimental procedure including the measurements to be taken and tabulation of measurements and results.
- calculation of the enthalpy change of reaction of solid NaOH with HCl (aq)

(Assume that **4.2 J** of heat energy changes the temperature of 1.0 cm³ of solution by 1 °C.) [A_r Na: 23.0, H:1.0; O:16.0] [5]

Pre-calculation

Using 30 cm³ of 1 mol dm⁻³ HCl solution to react completely with solid NaOH.

Amt of HCl used = $30/1000 \times 1 \text{ mol} = 3.00 \times 10^{-2} \text{ mol}$

NaOH is the limiting reagent.

Let amount of NaOH used be $1.00 \times 10^{-2} \text{ mol}$

Mass of solid NaOH = $1.00 \times 10^{-2} \times 40 \text{ g}$
= 0.400 g

1. Using a measuring cylinder, place 30 cm³ of 1 mol dm⁻³ HCl into the styrofoam cup.
2. Measure and record the initial temperature of the HCl solution.
3. Using the electronic weighing balance, weigh accurately about 0.4 g solid NaOH in a clean and dry weighing bottle.
4. Add the solid NaOH into the cup. Stir and record the highest temperature reached.
5. Reweigh the weighing bottle.

Mass of empty dry weighing bottle/g	M
Mass of weighing bottle and solid NaOH/g	M ₁
Mass of weighing bottle and residual NaOH/g	M ₂
Mass of NaOH added/g	M ₁ – M ₂

Calculation

$$\text{Amt of NaOH used} = (M_1 - M_2) / 40 \text{ mol}$$

$$\Delta H_2 = - (40)(30 \times 4.2 \times T_2 - T_1) / 1000(M_1 - M_2) \text{ kJ mol}^{-1}$$

.....[5]