Some Possible Practical/Planning Exercises Involving Titration

Types of Expts	Some Examples	To ensure reliability	Remarks

(a) Acid-Base
 	
(b) Redox: MnO_4^- + reducing agents like H_2O_2, Fe^{2+}, NO_2^- and $C_2O_4^{2-}$.
 	
(c) Iodometric titrations: I_2 (formed by analyte) + reducing agent $S_2O_3^{2-}$
 	
(d) Back Titration: HC*l* is added in excess to react with and dissolve the insoluble carbonate compound. The excess HC*l* is then titrated against a standard solution of sodium hydroxide
	• To determine the formula of a compound
	• To determine the unknown concentration / % by mass of a reactant in a given mixture
	• To determine the solubility product of sparingly soluble salts.
		• Dropwise addition of titrant (solution in burette) when approaching the end-point.
		
		• Repeat titration until results are consistent
		• (**two titres within ± 0.10 cm^3**)
			For (a) – (c): **ALL titrations**
			• For a given solid sample or aqueous sample of high concentration, preparation of its bulk / diluted solution in a graduated flask is required so that titration can be repeated to obtain consistent results.
			
			For (a): **Acid-Base Titrations**
			• only 2–3 drops of indicator (eg. phenolphthalein, thymol blue or methyl orange) are required.
			
			For (b): **Redox Titrations**
			• Add excess dilute H_2SO_4 (**not** HNO_3 or HC*l*) to provide the acidic medium required for MnO_4^- titration.
			• No indicator is required as MnO_4^- is self-indicating.
			
			For (c): **Iodometric titrations** normally involve two steps:
			
			(i) An oxidising agent + KI to produce iodine, I_2.
			
			(ii) The I_2 produced is then titrated against sodium thiosulfate(VI), $Na_2S_2O_3$.
			
			1 cm^3 of starch solution serves as the indicator and is only added near the end-point when most of the I_2 has been reacted away by $Na_2S_2O_3$.
			
			For (d): **Back Titrations**
			• For substances that are insoluble in water. A bulk solution of the sample is prepared through the use of a reaction (usually acid-base reaction). The unreacted excess reagent that is used to dissolve the sample is then titrated against a standard solution.

TITRATION

1 Standard Solution

- **Standard solution:** A solution of accurately known concentration.
- **Primary standard solution:** A solution of known concentration prepared by dissolving an accurately known mass of solute in a known volume of solution. Such a solution can only be prepared using a solute which has the following properties:
  (a) is available in high purity
  (b) forms a stable solution which is unaffected by air or light
  (c) does not have the following properties: volatile[2], deliquescent[3], hygroscopic[4]
- **Secondary standard solution (bulk solution):** A solution whose concentration is determined by titration with another standard solution (usually a primary standard solution).

2 Preparation of a Standard / Bulk Solution

Depending on the reagent given, a standard solution can either be prepared by dissolving an accurately measured amount of solid or concentrated aqueous sample and making up the solution with deionised water in a standard graduated / volumetric flask.

(A) Preparation of a Standard / Bulk Solution from a Solid sample

*To memorise standard phrasing shown below:

1. Weigh accurately about _____ g of the solid in a clean and dry weighing bottle.
2. Transfer solid to a small clean beaker. Reweigh the weighing bottle and the residual solid and calculate the actual mass of solid transferred.
3. Record the readings in the table below:

Mass of solid used to prepare standard solution

Mass of weighing bottle	/ g	s
Mass of weighing bottle with solid	/ g	t
Mass of weighing bottle and **residual** solid	/ g	u
Mass of solid transferred to small beaker	/ g	**(t – u) = m**

4. Dissolve the solid with some deionised water in a small beaker.
5. Transfer the solution and ALL of the washings into a 100 cm^3 (or 250 cm^3) graduated / volumetric flask.
6. Make up to the mark with deionised water, stopper and shake well to ensure a homogeneous solution.

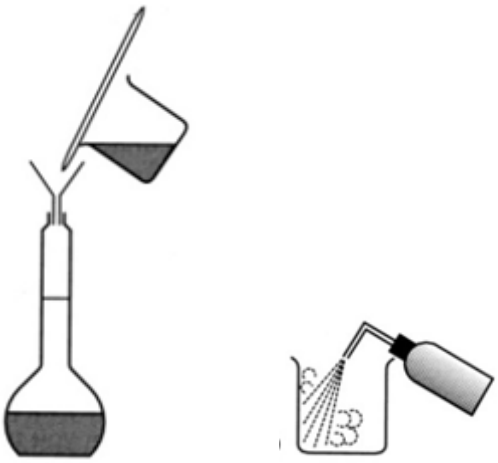
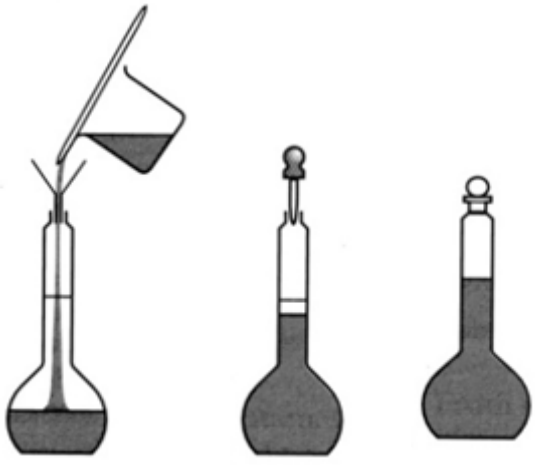
[2] Liquid substance easily evaporates into gaseous state at a low temperature due to its low boiling point.
[3] the process by which a substance absorbs moisture from the atmosphere until it dissolves in the absorbed water and forms a solution.
[4] A substance that readily attracts water from its surroundings, through either absorption or adsorption.

(B) Preparation of a Standard / Bulk Solution from a concentrated aqueous solution

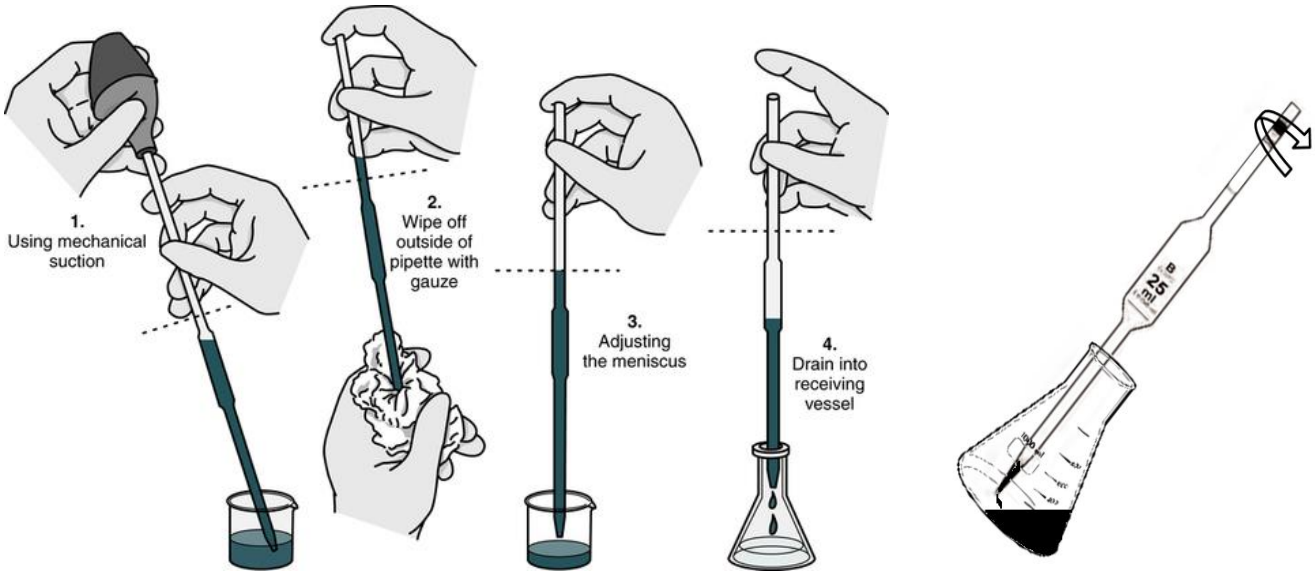
*To memorise standard phrasing shown below:

1. Measure _____ cm^3 of solution using a burette (or pipette) into a 100 cm^3 (or 250 cm^3) graduated / volumetric flask.
2. Make up to the mark with deionised water, stopper and shake well to ensure a homogeneous solution.

Preparing a Standard / Bulk Solution for Use in Titration

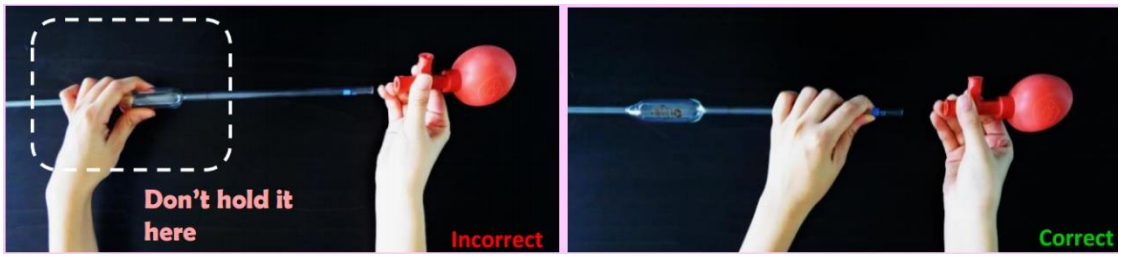
Procedure	Step	Remarks
 (a) (b) (c)	(a)	Accurate mass of the solid measured by electronic balance. Weighing bottle must be **clean and dry**. The beaker and glass rod are to be **washed with tap water and rinsed with deionised water before use. Wipe dry with tissue.**
	(b)	Solid is transferred to a small, clean beaker. The mass of the weighing bottle and residual solid is measured again to calculate the actual mass transferred.
	(c)	Stir with glass rod to ensure <u>all solid is dissolved</u> in a <u>minimal volume of water.</u>
 (d) (e)	(d)	To avoid spillage, the concentrated solution is transferred from the beaker to the volumetric flask via a filter funnel, using the glass rod to direct the flow of the solution. **Do not rinse the volumetric flask with solution before transfer.**
	(e)	Wash <u>the glass rod and inner walls of the beaker</u> with minimal volume of deionised water.
 (f) (g) (h)	(f)	Transfer washings to volumetric flask. Repeat steps (e) and (f) 2 times.
	(g)	Top up with deionised water till it is 0.5 cm below the calibration mark and use a dropper to adjust to meet the mark.
	(h)	Stopper, invert and shake the flask to attain a homogeneous solution.

3 Use of Pipette



1. Wash the pipette by rinsing its interior with tap water followed by deionised water.
2. Dry the exterior of the pipette. (to prevent introduction of water into solution when step 3 is done)
3. Rinse the pipette with the solution to be used to ensure solution is not diluted by water in pipette.
4. Hold the upper end of the pipette to insert the pipette filler to avoid breakage.
5. Draw the solution into the pipette using the pipette filler and adjust until the bottom of the meniscus level touches the calibration mark.
6. Ensure that there are no air bubbles trapped in the solution.
7. Wipe off the outside of the pipette with a clean tissue paper.
8. Transfer the solution into a conical flask by using the pipette filler to eject the solution or gently removing the pipette filler to drain the solution.
9. Tilt the conical flask slightly and rotate the pipette tip against the bottom of the conical flask. Do not blow out or force the last drop at the tip as it is already calibrated for.

When fitting a pipette into a pipette filler, position the hand at the top of the pipette, instead of below the pipette bulb. Do not push the pipette too deeply into the pipette filler. When removing the pipette from the pipette filler, twist the pipette out gently instead of pulling it out forcefully and laterally. This will minimise the chance of breakage and cutting injuries.



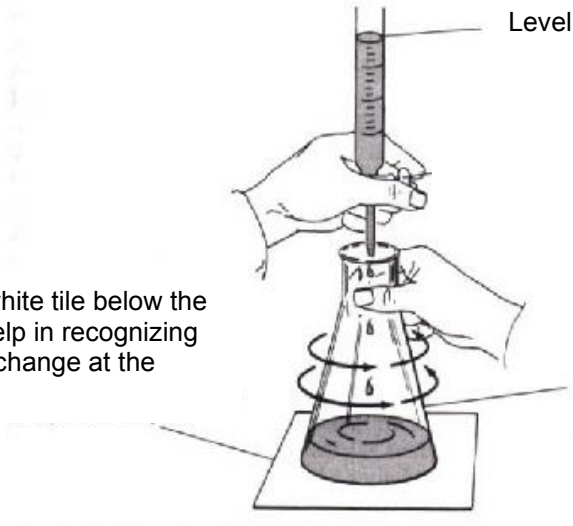
4 Use of Burette

1. Wash the burette by rinsing the interior with tap water followed by deionised water.
2. Rinse burette with solution to be used (titrant).
3. Clamp the burette vertically upright with a retort stand.
4. Fill the burette with solution using a filter funnel.
5. Remove the filter funnel.
6. Run some solution out to ensure:
   - burette tip is filled with solution.
   - any air bubbles trapped is flushed out.
7. Take the readings of burette at eye level.
   - For clear solutions, take readings at the bottom of meniscus.
   - For dark coloured solutions, e.g. KMnO4, take readings at top of meniscus.

5 Titration Procedure

1. Get the burette ready. Record the initial burette reading.
2. Place a white tile on the base of the retort stand.
3. Pipette the analyte into the conical flask.
4. For titrations involving the use of an indicator, add two drops of indicator into the conical flask. Avoid adding too much indicator as it will cause inaccuracy in the titration result.
5. Run solution from the burette into the conical flask, swirling the conical flask continuously with every addition.
6. Rinse the inner walls of the conical flask with deionised water when approaching the end-point to wash down any solution. You are able to tell that the end-point is near when it takes a longer time for the colour to disappear.
7. Add the solution from the burette drop-wise till the end-point is reached. End-point is indicated by a distinct colour change attained when one drop of titrant is added.
8. Read the final burette reading at eye level and **record to 2 decimal places**, eg. 23.30 cm^3, 23.35 cm^3.
9. **Repeat titration to get two consistent results** which are **within ± 0.10 cm^3** and put a "√" under the chosen values for further calculations later.

Note: You may choose to do a fast 1st titration to determine roughly where the end-point is so that the subsequent ones can be carried out more meticulously. If such, you may skip step 6 and label the titration as 'Rough' in your table.



Considerations for Titration Experiments

(i) Preliminary Calculation to show justification for using certain amounts, volumes and concentrations of the chemicals provided.

Based on:

- **mole ratio** of reactants involved; and
- volume of titrant to be between **20.00 to 40.00 cm^3**

Prepare a standard or bulk solution by stating:

- capacity of standard flask to be used (100 cm^3 or 250 cm^3).
- mass of solid sample to be weighed; or
- volume of concentrated aqueous sample (measured with a pipette or burette) to be introduced into the standard flask.

(ii) Procedure

- Detailed write-up of preparation of standard solution if required.
- Indicate the capacity of pipette used (10.0 cm^3 or 25.0 cm^3)
- State the chemical in the burette.
- Name a suitable indicator with description of the colour change expected at the end-point.
- Repeat titration until results are consistent (**two titres within ± 0.10 cm^3**).

Indicator	pH working range	colour change when **base (or alkali)** is in the conical flask	colour change of indicator when **acid** is in the conical flask
Phenolphthalein [colour in base – pink colour in acid – colourless]	8.3 to 10	pink to colourless	colourless to pink
Thymolphthalein [colour in base – blue colour in acid – colourless]	9.3 to 10.5	blue to colourless	colourless to blue
Methyl orange (MO) [colour in base – yellow colour in acid – red]	3.2 to 4.4	yellow to orange	red to orange
Bromothymol blue [colour in base – blue colour in acid – yellow]	6.0 to 7.6	blue to green	yellow to green
Screened methyl orange (SMO) [colour in base – green colour in acid – purple]	3.2 to 4.2	green to grey	purple to grey
Note: SMO , MO, phenolphthalein and thymolphthalein are suitable indicators for strong acid with strong base titrations			

Indicator	Type of Titration	Iodine produced by adding excess aqueous iodide solution to a certain volume of oxidizing agent of unknown concentration in the conical flask
1 cm^3 of starch solution when most I_2 is removed (pale yellow)	Iodine/thiosulfate titration	Blue black colour is discharged

Note: No indicator is required for titrations involving MnO_4^- as MnO_4^- is self-indicating.
Titrate till a first permanent pale pink is observed if MnO_4^- is placed in the burette.
Titrate till pink colour turns colourless if MnO_4^- is placed in the conical flask.

(iii) Result Analysis and Conclusion

You may need to **generate a table of results** and show how the ***results*** obtained in the experiment can be used to calculate or determine the ***information required*** in the question. State any ***formula*** needed and ***describe clearly the steps*** needed to arrive at the final answer.

Example of a Titration Table used for Recording the Results:

Titration of solution **X** (analyte) with **Y** (titrant) using **Z** as indicator

		1	2	3
Final burette reading	/ cm^3	a_1	a_2	
Initial burette reading	/ cm^3	b_1	b_2	
Volume of titrant **Y** added	/ cm^3	$a_1 - b_1 = c_1$	$a_2 - b_2 = c_2$	

Average volume of titre **Y** used = $\frac{C_1+C_2}{2} = C_{ave}$ cm^3 (to 2 d.p.)

In conclusion, _____ cm^3 of **X** requires _____ cm^3 of **Y** for complete reaction.

Example 1

Titration of aqueous sodium hydroxide with aqueous hydrochloric acid using methyl orange as indicator

		1	2	3
Final burette reading	/ cm^3	25.30	28.10	30.75
Initial burette reading	/ cm^3	0.00	2.50	5.40
Volume of aqueous sodium hydroxide added	/ cm^3	25.30	25.60	25.35

Average volume of aqueous sodium hydroxide used = $\frac{25.30 + 25.35}{2}$ = 25.325 cm^3
= 25.33 cm^3 (to 2 d.p.)

In conclusion, 25.0 cm^3 of aqueous hydrochloric acid requires 25.33 cm^3 of aqueous sodium hydroxide for complete reaction.

Example 2

Titration of aqueous sodium hydroxide with aqueous hydrochloric acid using methyl orange as indicator

		1	2	3
Final burette reading	/ cm^3	25.30	28.00	30.80
Initial burette reading	/ cm^3	0.00	2.50	5.40
Volume of aqueous sodium hydroxide added	/ cm^3	25.30	25.50	25.40

When you obtain results similar to the above, you should choose consistent results from either experiment 1 & 3 or experiment 2 & 3.

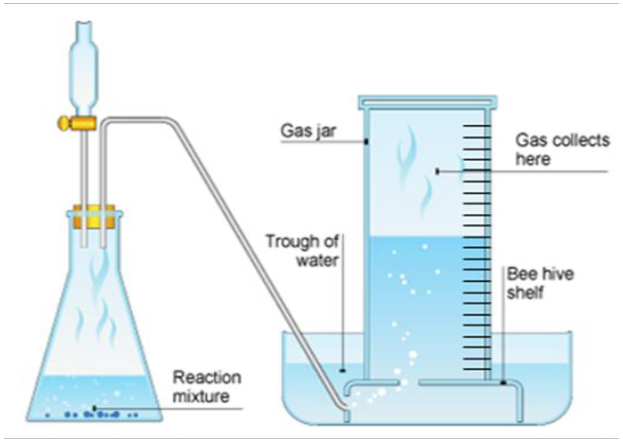
Either: Average volume of aqueous sodium hydroxide used = $\frac{25.30 + 25.40}{2}$ = 25.35 cm^3

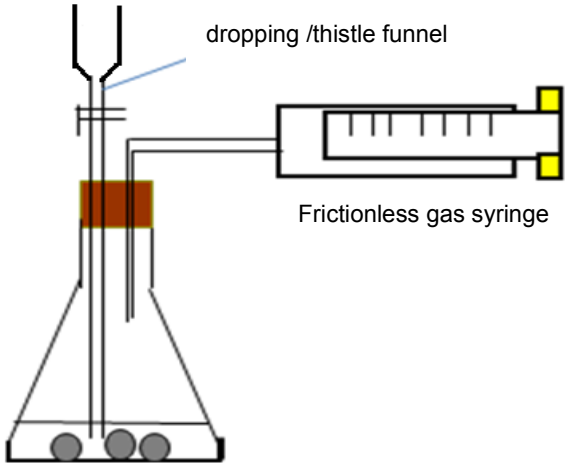
Or: Average volume of aqueous sodium hydroxide used = $\frac{25.50 + 25.40}{2}$ = 25.45 cm^3

Some Possible Practicals/Planning Exercises Involving Gas Collection

Examples	To ensure reliability	Remarks
(i) Determination of the stoichiometry of reactants and/or the products of a chemical reaction. • To verify the stoichiometric equation for the reaction between Mg and aqueous H_2SO_4. **(ii)** Determination of parameters in the ideal gas equation. • To determine the M_r of a gas or volatile liquid. • To determine the molar gas constant, R **(iii)** Determination of the composition of a solid sample. • To determine the % purity or % composition of solid MCO_3.	Volume of gas is recorded: When reaction is complete. • fizzing stops • plunger of the frictionless syringe stops moving At appropriate temperature. • reaction system is given time to return to room temperature especially for exothermic or endothermic reaction • temperature is kept constant by using a water bath of suitable temperature	• Use a dropping funnel (thistle funnel) to introduce liquid reagent to minimise loss of gas at start of experiment. • Use a frictionless gas syringe to collect the gas so that gas exerts a pressure equal to room pressure. • Depending on the nature of the gas collected, specific set-ups involving various methods of gas collection have to be considered. (refer to pg 4) - solubility in aqueous medium - density • To check for consistency between experiments carried out on a measured mass of sample: $\frac{Vol_{gas}/m1 - vol_{gas}/m2}{(Vol_{gas}/m)_{\text{smaller}}} \times 100 < 5\%$ **For set-ups where gas is collected over water:** • When gas is collected via downward displacement of water, volume of gas is only measured after equalizing the water levels inside and outside of gas measuring tube. By doing so, it ensures that pressure in the gas column is equal to atmospheric pressure. • The gas collected over water also contains water vapour which contributes to the pressure, therefore the pressure of the gas in the column is determined via the following equation: . $P_{total} = P_{gas} + P_{water\ vapour} = P_{atm}$

Methods of Gas Collection for Measurement in the Laboratory

<table>
<tr><th>Method</th><th>Collection over water</th><th>Collection in gas syringe</th></tr>
<tr><td>When to use?</td><td>Gas to be collected is insoluble / has low solubility in water</td><td rowspan="2">Any gas, especially when an accurate volume of the gas is required</td></tr>
<tr><td>Examples of gases</td><td>CO_2, H_2, O_2
NOTE: Gases such as SO_2, NH_3, HCl, NO_2 are highly soluble in water and should NOT be collected over water.</td></tr>
<tr><td></td><td colspan="2">A dropping funnel is used to introduce the last reactant. This is to ensure that all gases produced are collected and measured.</td></tr>
<tr><td>Apparatus & Methodology</td><td> 

The gas produced in the reaction is bubbled through a trough of water and into a gas measuring tube / burette filled with water. The gas collects at the top of the gas measuring tube / burette and pushes the water down.</td><td> 

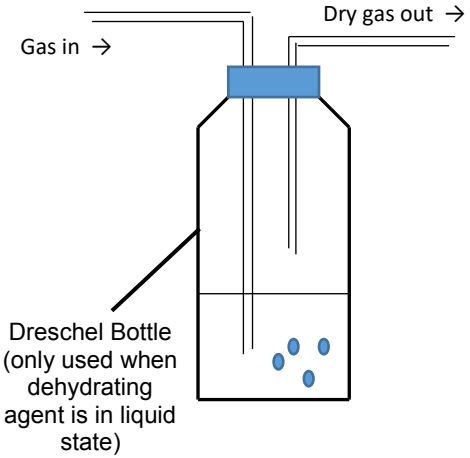
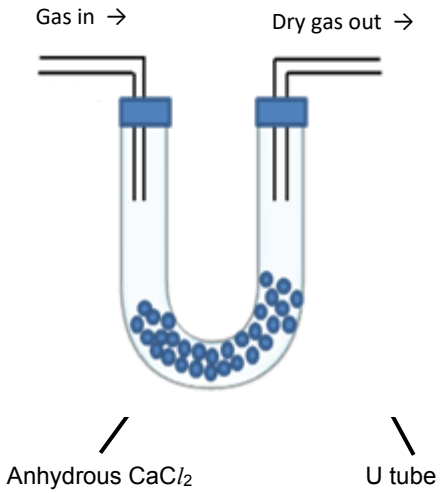
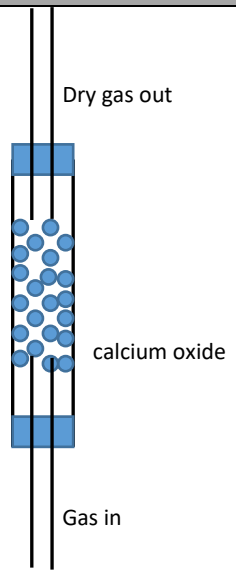
The gas produced in the reaction collects in the syringe, pushing out against the plunger. The reaction is completed when the fizzing stops/ plunger of the frictionless syringe stops moving.</td></tr>
</table>

	When the reaction is complete, the water level in the gas measuring tube / burette is adjusted to ensure the pressure inside and outside the gas measuring tube / burette are the same (i.e. at atmospheric pressure). The pressure inside the gas measuring tube / burette is partially from the gas being collected and partially from the water vapour that has escaped from the surface of the water in the gas measuring tube / burette. Hence, $\mathbf{P_T = P_{gas} + P_{H2O}}$ (where $\mathbf{P_T}$ = atmospheric pressure) $\mathbf{P_{H2O}}$ is called the **vapour pressure of water** and is temperature dependent. Once $\mathbf{P_{gas}}$ is known, the number of moles of gas can be calculated using the ideal gas equation: **PV= nRT**	The temperature of the reaction system is then given time to return to room temperature before reading off the volume of gas collected from the markings on the gas syringe.
Considerations	• The gas produced displaces the water column in the delivery tube first before displacing the water column in the gas measuring tube / burette. The volume of gas that displaces the water column in the delivery tube cannot be measured. Therefore **the volume measured is less than actual.** • Gas bubbles may adhere to the wall of the gas measuring tube / burette, therefore the **volume measured is less than actual**. To eliminate this, tap the gas measuring tube / burette to allow the gas bubbles to travel up. • Temperature of the reaction system should be allowed to return to room temperature as volume of gas is affected by temperature.	• Maximum amount of gas that can be collected depends on the capacity of the gas syringe. (Typical capacities include 100 cm^3 & 250 cm^3) - 80% of maximum capacity • If too small a volume of gas is collected, it will give rise to a large % error due to measurement.

Methods of Drying Gases collected in the Laboratory

If a dry gas is needed, drying agents have to be introduced to absorb moisture from the gas collected. This is especially necessary for gases collected over water.

The selected apparatus containing various types of drying agents are then inserted into the experimental set up between the reaction container and the gas collection system.

Drying agent	Concentrated Sulfuric Acid	Anhydrous Calcium Chloride	Calcium Oxide
Apparatus			
Considerations	Dry all gases except for alkaline gases like NH_3. NH_3 and concentrated sulfuric acid undergo acid-base reaction, which causes the amount of alkaline gas collected to be less than actual.	Dry all gases except NH_3 which forms a complex with calcium chloride.	Dry alkaline NH_3 and neutral gases. (CaO is a basic oxide, it is not suitable for drying acidic gases)

Some Possible Practical/Planning Exercises Involving Gravimetric Analysis

Types of Expts	Some Examples	To ensure reliability	Remarks
(a) Types: (i) Heating a given mass of solid to remove volatile components like H_2O, CO_2, NO_2 etc. Note: Weighing of the given sample may be carried out using a clean and dry weighing bottle before transferring to boiling tube or crucible for heating. (ii) To add a reagent to a solid mixture such that the components in the solid mixture can be separated. (iii) Precipitation where two solutions are mixed to form a precipitate. Filtration is then carried out, using a pre-weighed filter paper, to obtain the solid residue.	**(i)** Heating to remove volatile component so as to determine ● no. of water of crystallisation ● formula of an unknown compound ● % by mass of species in a mixture **(ii)** Acid added to react away metal carbonate present in a solid mixture. Filtration is then carried out to determine the mass of the residue. Mass loss = mass of metal carbonate. (Assuming that carbonate is the only species in the solid mixture that reacts and dissolves in the aqueous acid.) **(iii)** Precipitation to determine ● % by mass of Cu^{2+} in a mixture of Cu^{2+} and Zn^{2+} ● the stoichiometry of a reaction between reactants in solutions where one of the products formed is insoluble in water.	● Heat solid and tap intermittently against heat-proof mat to ensure even heating. ● Repeat heat, cool and reweigh process till a ***consistent mass of ±0.01 g*** is obtained. For type **(c)** experiment that requires filtration, (refer to **Appendix** on pg 15) ● Need to test filtrate for the absence of a particular ion to ensure complete precipitation of that ion has taken place. ● After filtration, need to wash precipitate (with cold water) to free it from soluble impurities. Dry it in oven and allow to cool in desiccator. Repeat until *consistent mass of ±0.01 g* is achieved.	For (a): ● Mass used must not be too small (results in large % error in measurement) or too large (results in incomplete decomposition due to uneven exposure to heat). ● More gentle heating (to slow down reaction so that changes are more observable) or use of lid during heating to reduce loss of solid may be considered as a modification to an experimental procedure in order to improve the accuracy of the experiment. In general: Repeating the whole experiment can be considered as means of: ● identifying consistent results, $\frac{\Delta m1/m1 - \Delta m2/m2}{\Delta m/m\ smaller} \times 100 < 5\%$ ● displaying reproducibility of results; or ● eliminating anomalous results.

APPENDIX

Technique for Gravimetric Analysis involving Aqueous Solutions (containing a mixture of ions)

Carry out selective precipitation of certain ions in the mixture, then isolate the precipitate via filtration.

Procedure:

(i) A suitable reagent is added to precipitate one of the ions in the mixture.

(ii) Fold a piece of filter paper in half as shown in Fig 1(i),

Fig 1(i) Fig 1(ii) Fig 1(iii) Fig 1(iv)

Alternatively, use a fluted filter paper (refer to pg 10) which provides a larger surface area through which the solvent can seep.

Tear off about 0.5 cm piece from one corner of the paper to imp and then fold it into quarters.

Open up the "pocket" of the filter paper that does not have the corner torn off so that the filter paper is in the form of a cone and place it in the funnel. [Fig 1(iii) - (iv)]

(iii) Using a wash bottle, wet the paper.

(iv) Use the set-up for filtration as shown in Fig 2

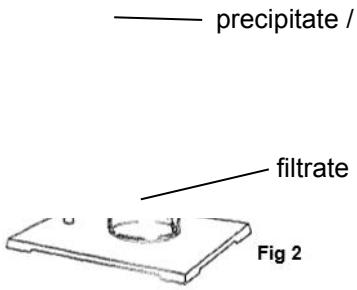


Fig 2

(v) Transfer mixture to the filter paper with the aid of a glass rod and make sure not to overload the filter paper. (the liquid should not rise to less than 0.5 cm from the top of the paper.

(vi) Add small portions of the liquid each time and after all the liquid has been transferred to the funnel, use a wash bottle to direct spurts of water at the remaining solid in the beaker and transfer this mixture to the funnel. Continue this procedure until virtually all the solid (precipitate) has been transferred.

(vii) When the liquid has drained from the filter paper, "wash" the precipitate by directing a stream of water from a wash bottle into it. This is to remove soluble impurities adsorbed on the residue.

(viii) The stream should be forceful enough to agitate the precipitate but not so forceful that spatters it.

(ix) When the wash water has drained, wash the precipitate once more with water and allow it to filter through until dripping ceases.

(x) The residue is then dried and the mass was measured to determine the composition of ions in the original mixture.

Thermochemistry (Calorimetry)

Introduction:

Most chemical reactions are accompanied by the absorption or release of heat**.** The study of these energy changes that accompany chemical reactions is called thermochemistry.

Basic Principles:

1. Change in the energy of a reacting system
    - is a summation of energy required to break ALL bonds and energy released due to formation of ALL bonds
    - can only be deduced by **measuring temperature** of the surrounding before and after mixing the reagents

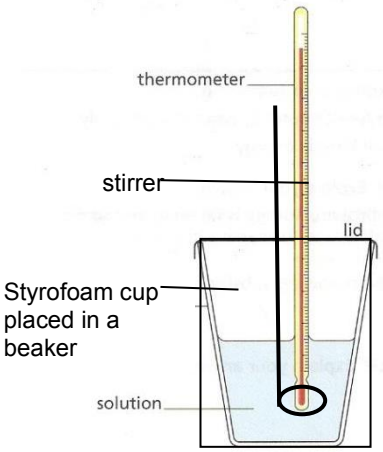
    Note: surrounding refers to aqueous medium and reaction vessel and air
2. Exothermic reaction
    - releases thermal energy (heat) into the surrounding
    - causes an increase in the temperature of the surrounding. Reaction mixture thus feels hot
3. Endothermic reaction
    - absorbs thermal energy from the surrounding
    - causes a decrease in the temperature of the surrounding. Reaction mixture thus feels cold

Experimental Set-up:

The **vessel containing water** (part of the surrounding) which absorbs heat or loses heat to the reaction is known as the **calorimeter**. The temperature of the calorimeter is measured before and after a reaction to determine the enthalpy change of the reaction. The **heat exchange with air (other part of surrounding) is assumed to be negligible** if there are measures taken to minimize heat exchange between the reaction mixture and the surrounding air.

The following are two commonly used experimental set-up in a chemistry laboratory:

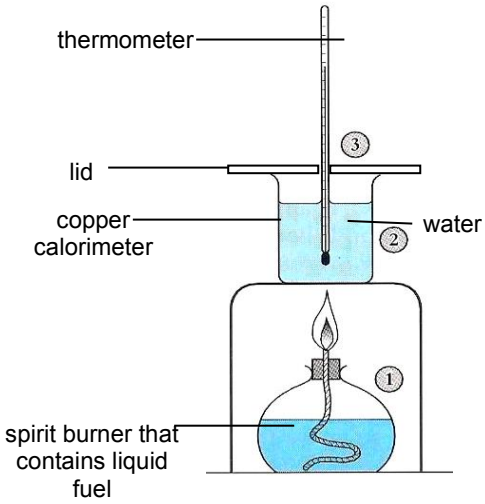
Set-up A:
To determine enthalpy change of a reaction taking place in aqueous medium



Note:
There are 2 types of thermometers:
Smallest interval: 1 °C
Smallest interval: 0.2 °C (higher precision)

Lagging of the calorimeter is enhanced when it is placed in another styrofoam cup in a beaker where the trapped (stagnant) air between the beaker and the styrofoam cup provides additional insulation.

Set-up B:
To determine enthalpy change of combustion



Considerations for Thermochemical Experiments

Dependent variable for this experiment is the magnitude of temperature rise/fall (i.e ΔT).

- ΔT should be between **a certain range stated in the question** because:

If T is too small: % error due to measurement will be very high, especially when the thermometer used is of low precision. If T is too big: heat exchange with air (other part of surrounding) becomes significant.

- **Assuming negligible heat exchange with air**,

$$\Delta H \times \eta_{\text{limiting reagent}} = mc_{water}\Delta T \text{ where } \Delta T = T_{final} - T_{initial}$$

After rearranging the equation: $\Delta T = -\frac{\Delta H \times \eta_{limiting\ reagent}}{mc_{water}}$

Therefore independent variables affecting the magnitude of ΔT are
  - ΔH, the independent variable to be determined by carrying out the experiment
  - $\eta_{\text{limiting reagent}}$
  - mass of water

For reactions involving dilute solutions,
  - specific heat capacity of the reaction mixture is taken to be that of water (c_{water})
  - mass of water = total volume of reaction mixture (density of water = 1 g cm^{-3})

- The assumption that there is negligible heat exchange with air in the experimental **set-up B** is not valid.
  - This is because the thermal energy has to be conducted through air to reach the calorimeter to be absorbed by the calorimeter.
  - Calibration of the calorimeter enables us to determine the actual ΔT.

- The assumption that there is negligible heat exchange with air also fails when reaction taking place in aqueous medium is not instantaneous.
  - Usually this type of reaction involves a solid reactant and an aqueous reactant or a redox reaction involving ions of the same electrical charge eg. both are negatively charged.
  - Calibration of the calorimeter or monitoring the change in temperature with time can enable us to determine the actual ΔT.

To Process Results Obtained from Calorimetry Experiments

Step 1: Define the reaction system by

(i) **Writing the thermochemical equation.**
State symbols must be included in **all thermochemical equations**. This is because the physical state of reactants and their products affects the energy changes in the reaction.

(ii) Calculate the number of moles of reactants used and **check for the limiting reagent**.

Step 2: To calculate heat change:

- Calculate heat transfer using:

$$\mathbf{q = mc_{water}\Delta T}$$

where m = mass of SOLUTION in which heat transfer has occurred, and does **not** include any mass of solid reacted. (1 cm^3 of solution is assumed to have a mass of 1 g)

c = specific heat capacity of water, 4.18 J g^{-1} K^{-1}

$\Delta T = T_{final} - T_{initial}$ (temperature change measured during experiment)

If **calibration** of a calorimeter is done, then apply:

$$\mathbf{q = C\Delta T}$$

C = energy needed to raise temperature of a fixed mass of water and container by 1°C.

$\Delta T = T_{final} - T_{initial}$

The calibration of the calorimeter using a reaction of known ΔH would have taken the heat exchanged with the reaction vessel and surrounding air into account.

Step 3: Then **calculate** ΔH of reaction where:

$$q = mc_{water}\Delta T$$

$$\therefore \Delta H = -\frac{q}{n} \quad \text{or } \Delta H = -\frac{mc\Delta T}{n}$$

Therefore an exothermic reaction has $\Delta H < 0$ while an endothermic reaction has $\Delta H > 0$

**n = no. of moles of limiting reagent (for calculating ΔH_r) or no. of moles of chemical species according to the definition of enthalpy change (i.e. n = no. of moles of water when finding the enthalpy change of neutralisation or n = no. of mole of fuel when finding the enthalpy change of combustion)

Methods of Determining Enthalpy Changes of Reactions Using Calorimetry

(A) FOR REACTIONS IN SOLUTIONS

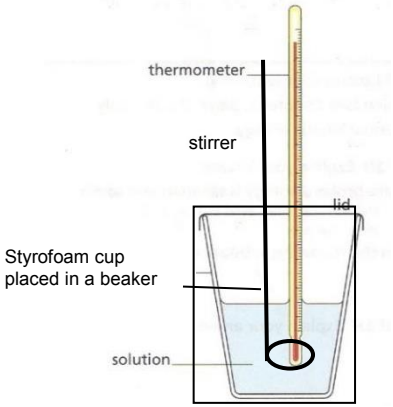
To find the enthalpy change of:

- neutralisation
- reaction involving
  - displacement
  - precipitation
  - dissolution of a solid

Apparatus

- styrofoam cup (capacity of 100 cm^3 or 250 cm^3)
- 0.2 ^oC thermometer
- beaker (250 cm^3)

Experimental Set-Up



For <u>Instantaneous Reactions</u> (e.g. neutralisation, precipitation)

Refer to the Practicals in this Booklet for detailed procedure.

<u>To Ensure Reliability</u>

- Ensure that there is minimal heat exchange with the surrounding air by:
  - Ensuring that the calorimeter is <u>well-lagged.</u>
  - Conducting the experiment in a draft-free environment (turn off fan, close window, use of lid /draught shield).

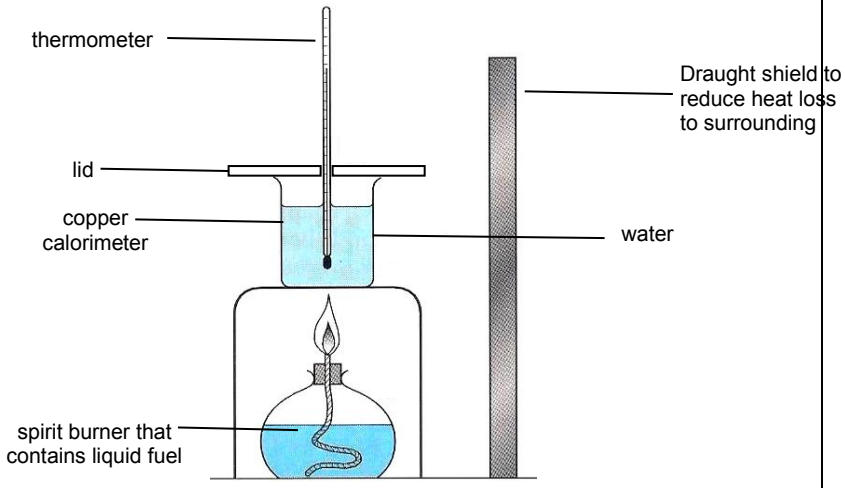
(B) FOR COMBUSTION REACTIONS

To find the enthalpy change of combustion of liquids such as methanol, ethanol, propanone and hexane which burn <u>cleanly</u> and <u>completely</u> without producing soot.

Apparatus

- copper calorimeter
- 1 ^oC thermometer
- spirit burner

Experimental Set-Up



Procedure for conducting experiment

- Measure and record a fixed volume of water to be placed into calorimeter using measuring cylinder.
- Weigh and record mass of spirit burner with lid containing the liquid fuel.
- Place spirit burner under calorimeter and light the wick (wet with liquid fuel).
- Stir the water until it reaches a ΔT **within the temperature range stated in question**, then put out the flame by replacing the lid.
- Immediately reweigh and record the mass of the spirit burner with the fuel.

(A) REACTIONS IN SOLUTIONS

Sample Results or Data to Collect

(I) For reaction involving two SOLUTIONS
(e.g. neutralisation and precipitation)

Expt. No.		1	2
Initial Temperature of soln A	/^{o}C	26.8	
Initial Temperature of soln B	/^{o}C	26.7	
Average initial Temperature	/^{o}C	$\frac{26.8+26.7}{2} = 26.8$	
Final Temperature of mixture	/^{o}C	33.8	
Temperature Rise, ΔT	/^{o}C	+7.0	

Note: To <u>check for consistency to ensure reliability</u>:
- You may choose to ***repeat*** the experiment until the ΔT measured is within 0.2 ^{o}C in two attempts on mixing the two solutions.
- Different measuring cylinders should be used to measure solutions **A** and **B**.

Calculation of Average initial temperature

- If the volume of the two solutions are similar,

$$T_{av} = \frac{initial\ temp\ \boldsymbol{FA\ 1} + initial\ temp\ \boldsymbol{FA\ 2}}{2}$$

- If the volume of the two solutions are different, the question may suggest a more accurate method to determine the <u>weighted average</u>:

$$T_{av} = \frac{(volume\ \boldsymbol{FA\ 1} \times initial\ temp\ \boldsymbol{FA\ 1}) + (volume\ \boldsymbol{FA\ 2} \times initial\ temp\ \boldsymbol{FA\ 2})}{total\ volume\ of\ reaction\ mixture}$$

(B) COMBUSTION REACTIONS

Sample Results or Data to Collect

Volume of water	/cm^3	**m**
Initial temperature of water	/^{o}C	**e**
Final temperature of water	/^{o}C	**f**
Initial mass of burner + liquid fuel	/g	**a**
Final mass of burner + liquid fuel	/g	**b**

(II) For reaction involving one SOLID and one SOLUTION
(e.g. displacement and dissolution of solid)

Expt. No.		1	2
Mass of weighing bottle	/g	**a**	
Mass of weighing bottle and solid	/g	**b**	
Mass of weighing bottle and residual solid	/g	**c**	
Mass of solid used	/g	**(b – c)**	
Initial Temperature of Solution A	/^{o}C	**T_1**	
Highest/lowest temperature reached	/^{o}C	**T_2**	
Temperature Rise/Fall, ΔT	/^{o}C	**($T_2 - T_1$)**	

Note: To check for consistency to ensure reliability:

- You may choose to ***repeat*** the experiment until the ratio, $\frac{\Delta T}{measured\ mass\ of\ limiting\ reagent\ used}$ is within 5% in two attempts on mixing a solid and a solution.
- If solution is limiting, then ***repeat*** until the ΔT measured is within 0.2^{o}C.

(A) REACTIONS IN SOLUTIONS

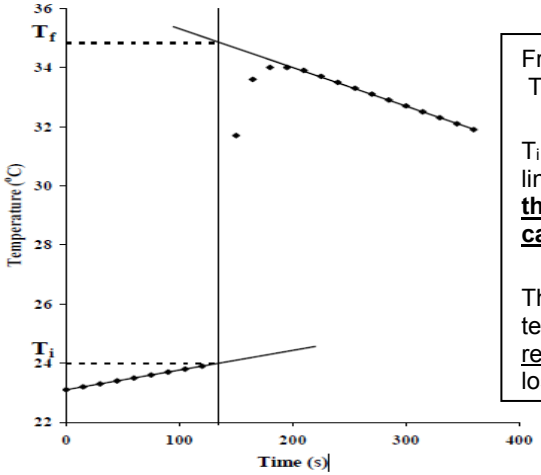
For <u>Non-Instantaneous Reactions</u> (e.g. displacement, dissolution)

In many experiments, after mixing the reactants, temperature does not immediately reach a maximum/minimum. As such, the ΔT obtained may not be accurate as there is a significant heat exchange with the environment.

In such cases, to <u>account for the heat exchanged with the environment</u> (i.e. to get more accurate ΔT), find the highest/lowest temperature upon mixing the reactants from **<u>a plot of temperature versus time</u>**. (refer to the detailed procedure below)

Procedure for conducting experiments involving <u>non-instantaneous reactions</u>

- Before mixing, record temperature of solution for a stated period of time until the temperature has stabilised.
- Mix reactants together, stirring continuously and note the temperature at a time interval stated in the question after mixing.
- Continue to record the temperature at stated time interval for a duration stated in the question.
- Plot a **<u>temperature versus time graph</u>**.(e.g. dissolution of $CaCl_2$)



From extrapolation:
T_i = 24.0 °C and T_f = 34.8 °C.

T_i and T_f are determined by extrapolating the linear portion of each curve forward or back to **<u>the time of mixing of the reactants in the calorimeter</u>**.

The value of T_f obtained in this manner is the temperature of the final mixture, <u>had the reaction occurred instantaneously</u> with no heat loss to the surroundings.

(B) COMBUSTION REACTIONS

<u>Calibration of the SAME set-up is necessary</u>

This is because there is significant heat lost during combustion taking place at the spirit burner as well as during heat absorption by calorimeter. To account for this, a <u>calibration</u> as described below must be performed to obtain a more accurate ⊗H.

Procedure Involving Calibration of Combustion Experiments

- The above experiment is <u>done twice</u>:
  - Once with a liquid of known enthalpy change of combustion, ΔH_c, (for calibration);
  - and another for the liquid fuel for which its ΔH_c is to be determined.

<u>To Ensure Reliability</u>

- In both cases, the following variables MUST be kept <u>the same</u>:
  - Volume of water in the calorimeter
  - Distance between the base of the calorimeter and the spirit burner containing the fuel
  - The temperature rise should be kept similar so that similar heat losses are involved. The heat capacity determined from calibration can then be used to determine the unknown enthalpy change.

Note: Plotting a temperature versus time graph (cooling curve) will **not** work. Cooling curve only accounts for the heat lost by the calorimeter during heat absorption but not heat lost during combustion at the spirit burner.

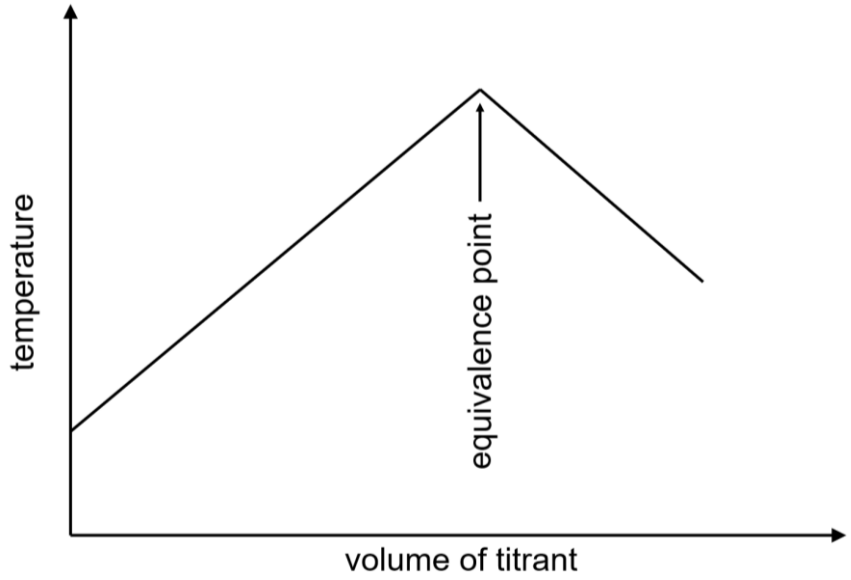
Energetics Practical 6 : Thermometric Titration & Direct Mixing

Determine the enthalpy change of reaction using two different methods: Thermometric titration & Direct mixing

Theory:
Thermometric titration is an analytic technique which makes use of the thermometric property of a reaction to accurately determine the end-point of the reaction. Thermometric titration is usually adopted when determining the unknown concentration of a reagent or to determine the stoichiometric ratio between two reagents.

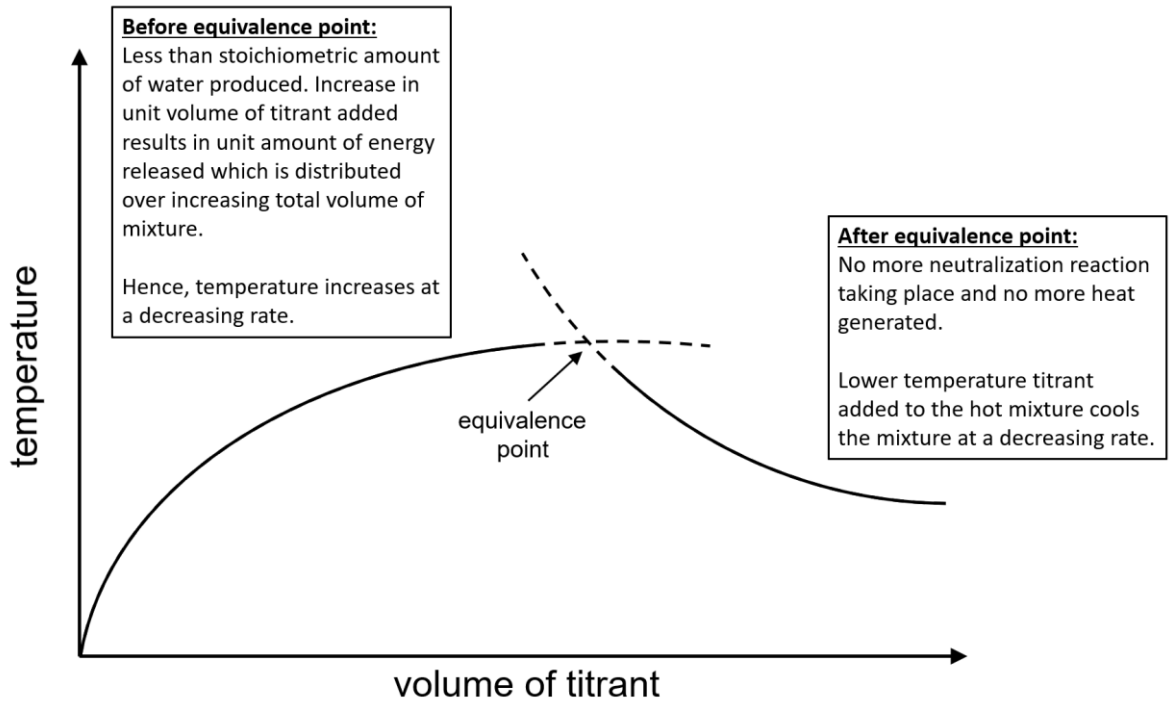
Ideally, a small and fixed amount of titrant is continuously added to the solution and the highest/lowest temperature is recorded for each addition. By making suitable inferences from the data points, the volume of titrant required to reach the end-point can be determined.

Ideal graph of thermometric titration:



However, it is difficult to read off the temperature with every small addition of titrant, making data collection very tedious. In addition, the same amount of heat released with every addition of titrant is shared by an increasingly larger mass of solution. Hence linear increase/ decrease in temperature towards the end-point is not observed. Addition of titrant of a different temperature from the reaction mixture after end-point causes further dispersion of the thermal energy. Therefore extrapolation of the graph obtained from experimental data is required to determine the end-point.

Typical graph of a thermometric titration (eg. Neutralization reaction) is as follows:



REACTION KINETICS

Reaction kinetics is the study of the rate of chemical reactions.
The rate equation (rate law) can be obtained by investigating how the rate of a reaction depends on

- concentrations of the reactants
- temperature
- presence of catalysts

rate equation: rate = $k[A]^n[B]^m$ where A & B are reactants

Rate constant, k, is affected by temperature and catalyst.

Comparing 'n' and 'm' in the rate equation and the coefficients in the overall balanced equation enable us to propose a reaction mechanism.

Reaction Rate = change in concentration per unit time. (always > 0)

For aqueous reactions:

$$rate = -\frac{d[reactant]}{dt} \text{ or } rate = \frac{d[product]}{dt}$$

For gaseous reactions, rate can be monitored by the change in pressure per unit time.

$$rate = -\frac{dP_{reactant(g)}}{dt} \text{ or } rate = \frac{dP_{product(g)}}{dt}$$

Basic Principles

The kinetics of a reaction can be studied mainly *via* two methods:

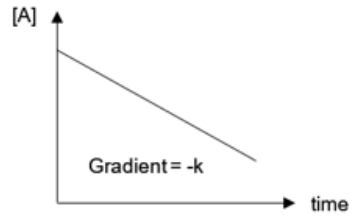
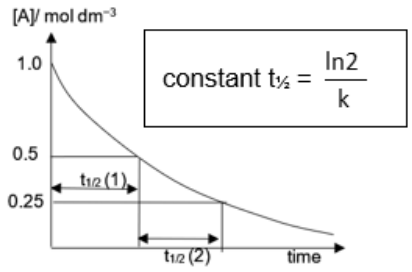
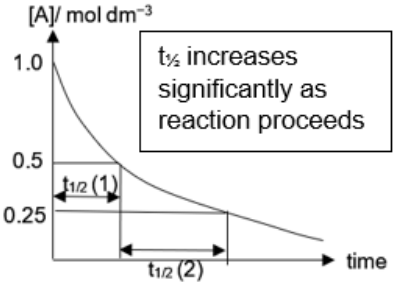
- Continuous method
- Initial Rate method

Continuous Method

- A ***single*** experiment is carried out to determine the dependence of rate on the changing concentration of reactant **A**. (order of reaction with respect to a reactant **A**).
- dependent variable– a **measurement** α $[reactant]_{remaining}$ or $[product]_{formed}$.
- independent variable – **time** at which the [reactant] or [product] of the reaction mixture is being **analysed**.

Manipulation of Data

To **determine** the **order** of reaction with respect to a reactant **A,** a graph of **dependent variable** (y-axis) **against time** (x-axis) is plotted and **analysed for its shape or half-life pattern**.

Zero order	First order	Second order
		

Initial Rate Method

- The same experiment is carried out ***multiple times***, each time with a different initial concentration of one reactant, while keeping the initial concentration of all other reactants constant.

- dependent variable – initial rate of reaction

  - Initial rate can be obtained from

    (i) the gradient of concentration-time graph at time zero
    (ii) the time taken for a reaction to reach a pre-fixed point

- independent variable – the initial concentration (volume) of a reactant in the reaction mixture

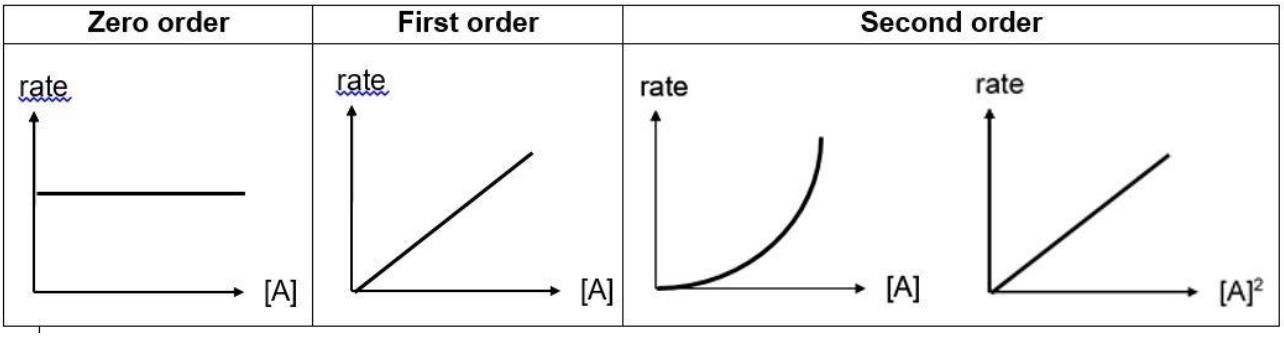
  - the **initial concentration** of **any reactant** may be varied by **changing the volume** of that reactant in different reaction mixture systematically, with **total volume** of each reaction mixture kept **constant** by adding an appropriate volume of water.

Manipulation of Data

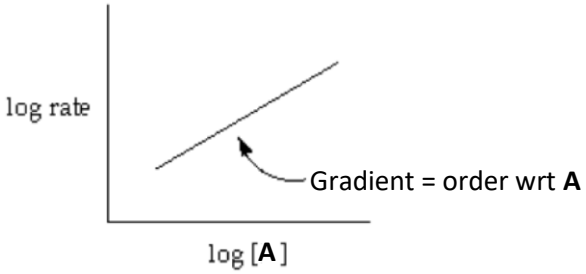
The order of reaction with respect to a reactant **A** can be deduced by either graphical method or non-graphical methods:

Graphical methods:

- Plotting a graph of **rate vs [A]** to investigate the relationship between rate and [**A**]**.**



- Plotting a graph of **log rate against log [A]** and calculate the gradient. The gradient is the order with respect to reactant **A.**



Non-graphical methods:

By comparing a pair of experiments that involve a different concentration of reactant **A** only:

- **Mathematical method**

  Let the rate equation be: rate = $k[A]^x[B]^y[C]^z$

  $\frac{\text{rate}_1}{\text{rate}_2} = \left(\frac{[A]_1}{[A]_2}\right)^x \times \left(\frac{[B]_1}{[B]_2}\right)^y \times \left(\frac{[C]_1}{[C]_2}\right)^z$, since $[B]_1 = [B]_2$ and $[C]_1 = [C]_2$,

  $\frac{\text{rate}_1}{\text{rate}_2} = \left(\frac{[A]_1}{[A]_2}\right)^x$

- **Inspection method**

Order of reaction	Discussion of results relating time ratio to rate ratio	Deduction
0	if time taken for experiment 1 and 2 are the same, rate for both reactions are the same	⇒ halving the concentration (or volume) of **A** does not affect the rate of reaction, ∴ zero order
1	if time taken for experiment 2 is double that of experiment 1, rate for experiment 2 is half that of experiment 1	⇒ halving the concentration (or volume) of **A** caused the rate to be halved, ∴ 1st order
2	if time taken for experiment 2 is quadruple that of experiment 1, rate for experiment 2 is one-quarter that of experiment 1	⇒ halving the concentration (or volume) of **A** caused the rate to be ¼ of original, ∴ 2nd order

- **V × t method (for clock reaction)**

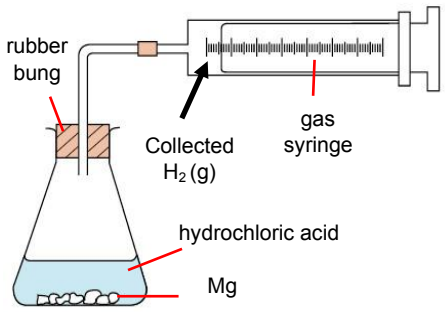
  where **t is time taken to reach a pre-determined point** of reaction, **V is volume of reactant** used in a reaction where total volume of reaction mixture is kept constant across experiments.

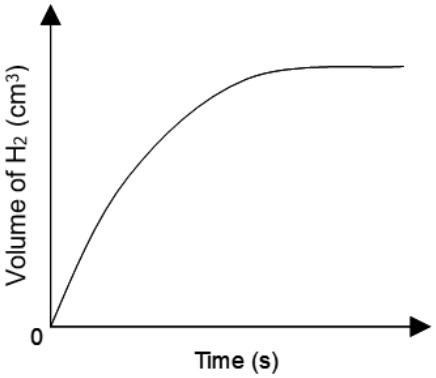
  Rate $\propto \frac{\mathbf{1}}{\textbf{time taken}}$ and $\mathbf{V_A} \propto$ **[A]** in the reaction mixture.

Order of reaction	Determining factor
0	t is constant, rate is independent of [A], ∴ zero order
1	$V_A \times t$ = constant Hence $V_A \propto \frac{1}{t}$ Rate increases linearly with [A], ∴ 1st order wrt A
2	$(V_A)^2 \times t$ = constant Hence $V_A^2 \propto \frac{1}{t}$ Rate increases linearly with $[A]^2$, ∴ 2nd order wrt A

1 Gas Collection Method

- for reactions which form gaseous products
- gas is collected in a **frictionless gas syringe** to prevent build-up of pressure
- For continuous method: measure the increase in volume of gas at regular time intervals under constant pressure and temperature.
- For initial rate method: measure the time taken to obtain a certain volume of gas. (or measure the volume of gas collected at a fixed time)





Example: Mg (s) + 2HC*l* (aq) → MgC*l*$_2$ (aq) + **H_2 (g)**

*(the volume of gas increases with time as gaseous **H_2** is being produced)*

2 Data Logger/ pH Meter

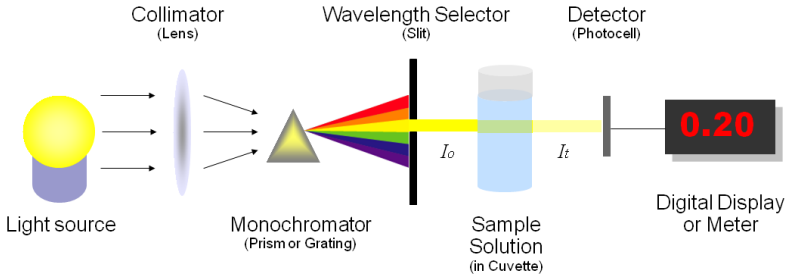
- for reactions involving a change in pH
- a pH probe is used to measure the change in pH over time.
- for continuous method: measure the change in pH at regular time intervals.
- for initial rate method: measure the time taken to attain a certain pH value.

Example: $CH_3Br + NaOH \rightarrow CH_3OH + NaBr$

(the pH of the solution decreases with time as NaOH is being consumed

3 Colorimetry Method

- applicable for reactions involving a coloured substance
- intensity of colour is proportional to the concentration of the coloured substance
- For continuous method: measure the change in colour intensity per unit time
- For initial rate method: measure the time taken to reach a certain colour intensity

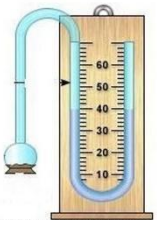


Example: $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_2ICOCH_3(aq) + HI(aq)$

(the colour intensity decreases with time as brown $I_2(aq)$ is being consumed)

4 Changes in pressure

- applicable for gaseous reactions where the number of moles of gaseous reactants is different from the number of moles of gaseous products
- for continuous method: measure change in pressure at regular time intervals under constant volume and temperature.
- For initial rate method: measure time taken to reach a certain pressure value.

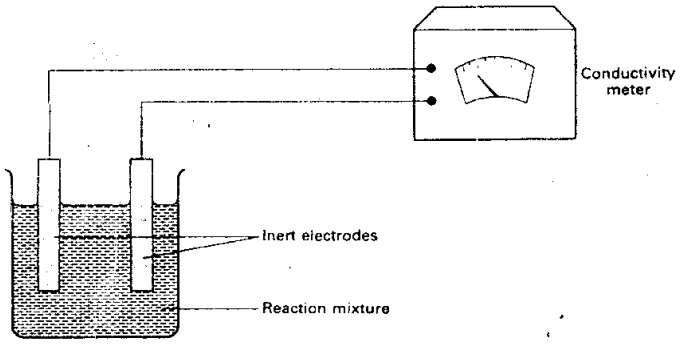


Example: $N_2O_4(g) \rightarrow 2NO_2(g)$

(Reaction is accompanied by a increase in number of moles of gas, and hence pressure increases with time at constant volume)

5 Change in electrical conductivity

- applicable for reactions involving a change in the number of ions in the solution and thus affecting the electrical conductivity of the solution.
- The change in electrical conductivity of the solution over time is measured.

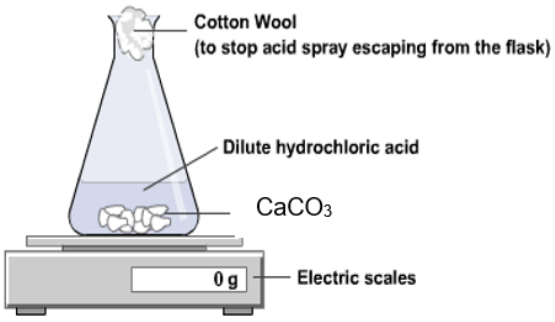


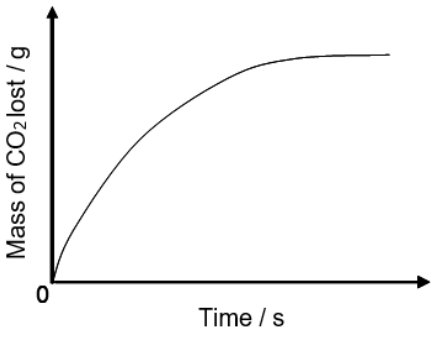
Example: BrO_3^- (aq) + $5Br^-$ (aq) + $6H^+$ (aq) → $3Br_2$ (aq) $3H_2O$ (*l*)

(decrease in number of ions present and thus the conductivity of the solution falls as reaction proceeds, and hence electrical conductivity decreases with time.)

6 Gravimetric Method

- measuring loss of mass and hence applicable for reactions involving gaseous product.
- An open reaction vessel is placed on an electronic balance to measure change in mass with time.
- Insignificant change in mass may be observed if the gas has a low density (e.g. hydrogen).
- for continuous method: measure the decrease in mass per unit time.
- for initial rate method: measure the time taken to attain certain magnitude of mass loss.





Example: $CaCO_3$(s) + 2HC*l* (aq) → $CaCl_2$ (aq) + **CO_2 (g)** + H_2O(*l*)

7 Titrimetric Method (a continuous method)

Procedure

- A reaction mixture made up of known amounts of the reactants is prepared. Fixed portions of the reaction mixture (samples) are then withdrawn regularly, using a pipette, put into conical flasks.

- The withdrawn portions are then "quenched" i.e. slowing it abruptly, **at a measured time from the start of the reaction**. This minimises further changes in concentration **at that point of time**.

  Quenching can usually be achieved by

  (i) removing the catalyst, **(ii)** addition of excess of another reagent which can use up the limiting reactant rapidly or **(iii)** by adding a large volume of cold water, causing both temperature and concentration of reactants to be lowered.

- The **concentration** of the remaining reactant or product formed as reaction progresses can be determined via **titration**.

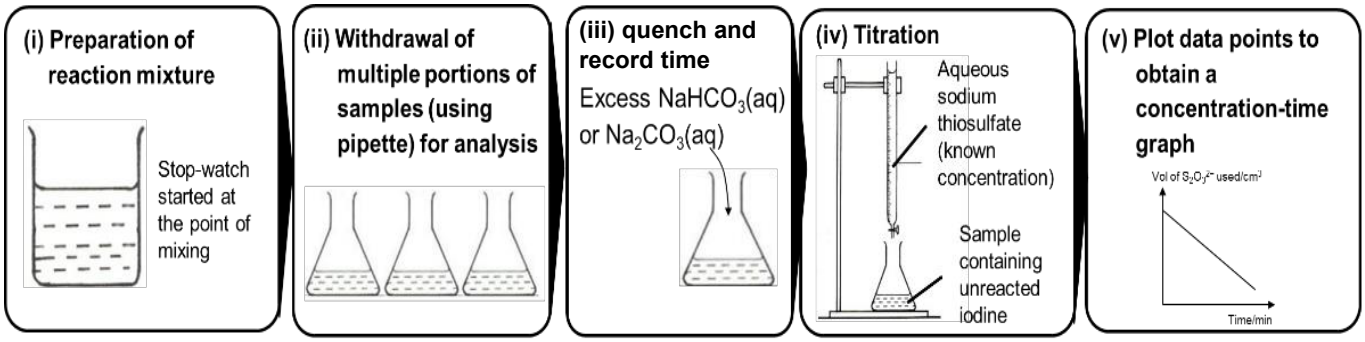
Processing of data:

- **Titration result** (proportional to the concentration of a reactant or product) are plotted **against time**. (need 5 data points)

- **Analysis of this titration result-time graph** (shape and half- life pattern) will enable us to **determine the overall order of reaction**.

- **Order with respect to reactant A** can be **investigated if all other reactants are present in large excess.**

Example: $CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_2COCH_2I\ (aq) + HI\ (aq)$

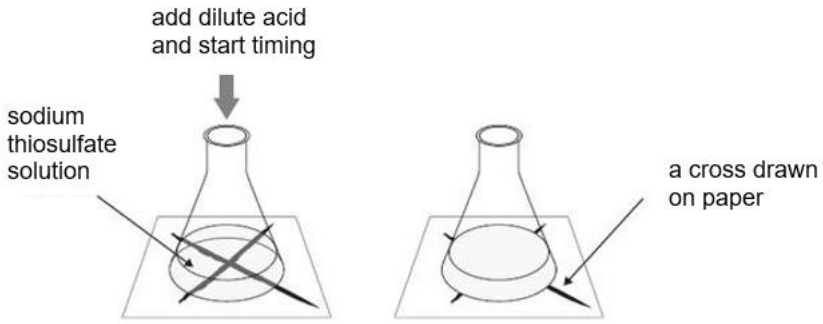


8 Clock Method (initial rate method)

- a reaction set up to measure time taken to produce a *sudden change* (usually visual).
- It involves setting up a number of reaction mixtures in which the **initial concentration of one of the reactant is varied**, while keeping the concentrations of other reactants and temperature constant.

$$\text{Initial rate of reaction} = \frac{\text{small change in concentration of reactants/products}}{\text{time taken for sudden observable change}}$$

Example 1: $S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow \mathbf{S\ (s)} + SO_2(g) + H_2O(l)$



The average rate of reaction for the reaction mixture can be measured by noting the time taken for a **small, fixed amount of product, sulfur** to be formed such that the "X" on the white paper is no longer visible.

$$\text{rate} = \frac{\textbf{small, fixed concentration of sulfur formed}}{\text{time taken for "X" to be masked}}$$

Example 2: $I_2 + CH_3COCH_3 \rightarrow HI + CH_3COCH_2I$

For reactions involving a **small concentration of coloured reactant used up.**

The rate of reaction may be studied by measuring the time taken for the coloured iodine to disappear.

$$\text{Rate of reaction} = -\frac{\text{concentration of iodine used up}}{\text{time taken for coloured iodine to disappear}}$$

Summary for clock reactions

1) Appearance of colour (**Example 1**)

We measure the time taken for a **small, fixed amount** of coloured/ insoluble product to be formed.

$$\text{rate} = \frac{\textbf{fixed concentration of products formed}}{\text{time taken for sudden observable change}}$$

It can be simplified as rate $\propto \frac{1}{\text{time taken for sudden observable change}}$

2) Disappearance of colour (**Example 2**)

As the **initial concentration of coloured reactant must vary** between a pair of experiments in order **to investigate its effect on rate**,

$$\text{Rate of reaction} = \frac{\text{concentration of coloured reactant used up}}{\text{time taken for coloured reactant to disappear}}$$

It **CANNOT** be simplified as rate $\propto \frac{1}{\text{time taken}}$

KINETICS

Rates of reaction vary with concentration of reactants, particle size of any solid reactant, temperature and the presence of catalyst. With so many variables, it important to have a plan that **varies one factor at a time** while keeping the other variables constant.

There are basically two methods of data collection and analysis involving the concepts of kinetics: (Refer to practical handouts for details on the experiment procedure)

- Initial rate method
- Continuous method

Initial rate method

Concentration of all reagents **EXCEPT A** must be kept constant between a pair of experiments, so that rate dependence on **A** can be found.

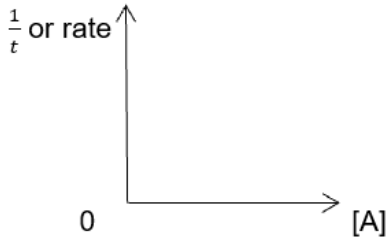
This usually done by performing a **series of experiments**, varying the volume of water to keep the **total volume of all reaction mixtures constant** so that:

$V_A \propto$ [A] in reaction mixture

The **time taken, t**, for (i) a **small fixed amount of coloured reactant to disappear or** (ii) **A small fixed amt of** coloured/ insoluble **product** can be used as an identifiable point in determining the initial rate of reaction using this expression: rate $\propto \frac{1}{t}$

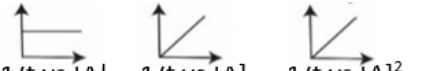
$$A + B \rightarrow C + D$$

e. g. of axes used to determine order of reaction writ A.



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

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



Continuous method

- Concentration of a particular reactant or product is being monitored throughout the whole course of reaction.
- Dependence of rate on concentration of a particular reactant is investigated by keeping the **other reactants in large excess** so that the concentrations of other reactants are effectively constant during the course of reaction. (pseudo reaction)
- Volume of a suitable reagent used α [reactant] or [product] in reaction mixture of interest.

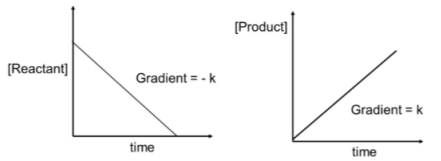
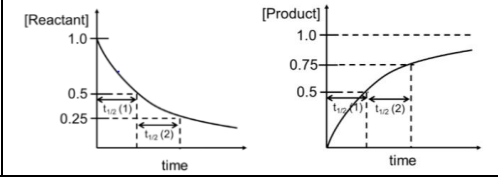
∴ can just plot volume vs time graph to determine the order of a particular reactant.

$$A + B \rightarrow C + D$$

If dependence of rate on A is monitored, [B] must be in large excess.

Order of reaction is deduced from the graph.

Rate = $-\frac{d[reactant]}{dt}$ or $\frac{d[product]}{dt}$

(i) Straight line: **zero order**	(ii) Curve with constant $t_{½}$: **1st order**
	

Qualitative Analysis

1. Introduction

While quantitative analysis requires you to make measurements to determine unknown quantities, ***Qualitative Analysis*** requires you to make observations to determine the unknown identity or nature of chemical substances.

In general, chemical substances fall into two classes:

(a) **electrolytes** (inorganic acids, bases and salts)
(b) **non-electrolytes** (most organic compounds)

Most electrolytes dissociate into cations and anions in water. In solution, each of these ions undergoes chemical reactions independently and hence can be detected by performing simple reactions with suitable reagents.

Organic compounds contain functional groups which can be identified only by specific reactions.

1.1 General Working Guidelines and Safety

- Students are **not to** put on contact lenses, as they are difficult to be removed during an emergency, may trap fumes and fuse with the eye when reacted with some reagents.
- Wear safety goggles when performing experiments.
- Whenever heating is done in a test-tube, use a test tube holder and a heat proof-mat. Never point the mouth of the test tube at your classmate, and **do not** look from the mouth of the test-tube.
- When gases are evolved, **do not** breathe too deeply when noting the odour of the gas evolved.
- **Keep** your bench and apparatus **clean**, **as contamination often gives wrong observations and conclusions**.
- Dispose chemical waste carefully.
    - **Concentrated acids and alkalis are to be diluted before pouring them away and the sink is to be flushed with plenty of water.**
    - **Dispose solids into the waste bins provided, NOT into the sink.**
    - **Organic waste is to be disposed of in the 'Organic Waste' bin.**

1.2 Bench and Side-Bench Reagents

- Be familiar with these reagents and their locations.
    - Student's bench: common acids, alkalis and reagents

      Top row: strong acids
      2nd row: bases
      3rd row: all other relevant reagents e.g. $AgNO_3$, $KMnO_4$

    - Side-bench: Reagents are arranged in alphabetical order. Litmus paper, filter paper and wooden splint are also placed here.
    - Fume cupboard: concentrated acids
- DO NOT REMOVE reagent bottles from the rack.
  To AVOID CONTAMINATION:
    - All reagent bottles come with their own dropper. Return dropper immediately after use.
    - DO NOT leave the dropper on the bench.
    - The tip of the dropper must not touch the inner-side of test-tube.
    - Inform Teacher if any reagents becomes chalky or contain solid deposits.
- Use clean, dry spatula provided to take solids. Clean up any spillage.

1.3 Good Practical Techniques

(i) Heating of a Solid

- When heating solids, a boiling tube should be used.
- Unless specified, use just enough of the solid to **fill the hemisphere** at the bottom of the boiling tube.
- The tube should **be held in an almost horizontal position** and heat should be applied gently initially (luminous flame) and then strongly (non-luminous flame) later to ensure that all solid has decomposed.
- For a crystalline solid sample, it may appear to melt after heating for some time, but it is actually dissolved in its own water of crystallisation. Therefore, continue to heat to drive off all water of crystallisation so that the dried solid sample can undergo thermal decomposition.

(ii) Heating or Boiling of Solutions or Suspensions

When a solution or a suspension is heated, care should be taken to prevent spurting.

- Fill a small test tube with about 1 cm depth of sample solution.
- For **inorganic** sample solutions, apply a small flame (turn down gas supply). The test-tube should not be held in a fixed position all the time but should be removed from the flame every now and then and shaken gently.
- **Move the test tube back and forth through the flame at an angle**. Do not heat above the liquid level. The test-tube may shatter if the liquid splashes over the hot glass.
- For **organic liquid samples, place test-tube in a water bath to** avoid direct exposure to flame as organic liquid is highly flammable.

➢ **Watch and Learn (Practical Skills)**

Heating of a Solid: https://tinyurl.com/zz6s36x	**Heating of Solutions:** https://tinyurl.com/jbattqj

(iii) Mixing of Reagents

(a) Adding aqueous reagent to solid reactant

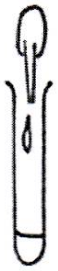
Use ≈ 0.5 cm depth of solid (sufficient **to cover bottom hemisphere only**) unless otherwise stated.

Add reagent **dropwise with shaking, until no further change.**

Dropper should not touch test-tube

(b) Adding aqueous reagent to aqueous reactant

Use ≈ **1 cm depth** of the given solution unless otherwise stated.



Add reagent **dropwise with shaking, until no further change.**

Dropper should not touch test-tube

Note:

- Ensure good mixing by holding the test-tube near its mouth with one hand and tapping the bottom of the test-tube against the palm of other hand
- It is a good practice to keep the tip of the dropper in a beaker of deionised water ready for use. After use, rinse dropper with deionised water and replace it in the beaker. You then know it is clean and ready for further use.
- DO NOT leave the dropper on the bench as this may contaminate the stock sample solution.

(iv) Test for Gases

(a) Litmus paper moistened with deionised water or other papers moistened with reagent

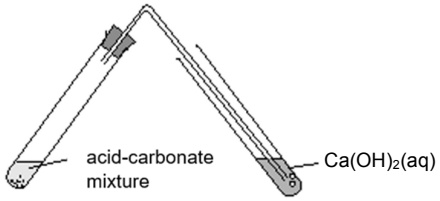
(e.g. $KMnO_4/H^+$) should be **held at mouth of test-tube** without touching the inner walls.

(b) Collection and test for CO_2(g)

A dropper is used in place of a delivery tube. The air is squeezed out of the teat by pressing the rubber teat. The dropper void of any gas will gently draw up the gas from just above the surface of the reaction mixture in the test tube by releasing the teat.

Dropper full of CO_2 is then transferred into a small test tube containing calcium hydroxide solution. The teat is squeezed to release the CO_2 gas in the dropper into calcium hydroxide solution in the small test-tube.

Alternatively, a delivery tube can be used to direct the CO_2 produced into the small test-tube containing calcium hydroxide solution.



➢ **Watch and Learn**

Testing for NH_3 gas:
https://tinyurl.com/jnzpy3m

Testing for CO_2 gas using dropper:
https://tinyurl.com/zvwddkg

Testing for CO_2 gas using delivery tube:
https://tinyurl.com/jv5obgt

(v) Filtration

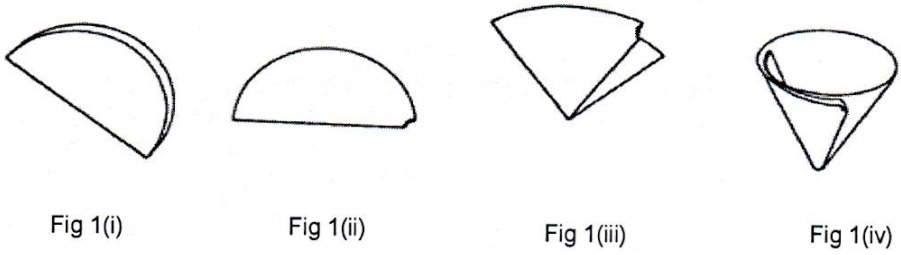


Fig 1(i) Fig 1(ii) Fig 1(iii) Fig 1(iv)

- Fold a piece of filter paper in half as shown in Fig 1(i)
- Tear off about 0.5 cm from one corner of the paper to improve filtering [Fig 1(ii)] and then fold it into quarters
- Open the pocket of the filter paper that does not have the corner torn off so that the filter paper is in the form of a cone and place it into the funnel [Fig 1(iii) – (iv)]
- Wet the filter paper with deionised water. This is so that
    - Filter paper adheres tightly to the sides of the funnel to increase efficiency of filtration.
    - Most of the solution in reaction mixture can be collected as filtrate for further analysis instead of being absorbed by the filter paper.
- Sit the funnel in a clean test tube and transfer the mixture to the filter funnel in small portions so that the liquid does not overflow. Do not fill the filter paper beyond ¾ full, as the precipitate may flow over the edge. You might be required to work on the filtrate collected in the test tube or the residue on the filter paper.
- If the residue is required, it should be washed by directing a stream of deionised water from a wash bottle onto it.
- When the water has drained, wash the precipitate once more with deionised water and allow it to filter through until the dripping ceases. Do not collect the washings of the residue together with the filtrate.

➢ **Watch and Learn (Practical Skills)**

Filtration:
https://tinyurl.com/zk4385l

1.4 Recording of Observations

- All recordings, to be ***recorded in ink***, should be ***clear*** *and* ***concise*** and must be done immediately after each test.
- **Record the observations and deductions alongside each step of a test.**

  Include details such as:

  - **colour changes** (place against white tile)**;** initial and final colour of both the solution and precipitate.
  - **precipitates formed** and **its solubility in excess reagent.** See the QA notes on pg 75-76 for reactions of cation and anions respectively.
  - **gas** (**colour**, **smell and colour change of a moist litmus paper** are preliminary tests of gases), **identity of each gas** must be verified by **a chemical test**. See page 24-25 for notes on tests for gases.
  - Colour of the universal indicator paper gives the value of pH, indicating the acid base property of the unknown.

Note:

Although chemical equations are **not** required and will **not** be given any marks if written in the table of observation and deduction, **equations may be required to support your answer under evaluation.** Do note that theory can also be tested in the practical assessment.

You will be assessed on manipulative skills, ability to make accurate observations and record them systematically with good details in a table form and make appropriate inferences and explanations for the observations.

Example of Recording:

Test	Observations	Deductions
a) Heat **FA6** strongly in a boiling tube. Test the gas with a glowing splint. Allow to cool.	• ***On gentle heating, colourless liquid condenses on the cooler parts of the test tube.*** • *On stronger heating: brown pungent gas observed..* • *Gas rekindled a glowing splint* • *Residue was yellow when hot, white when cool.*	• *H_2O from hydrated FA6* • *NO_2 evolved* • *NO_3^- of heavy metal present* • *O_2 evolved* • *ZnO formed* • *Zn^{2+} salt present*
b) Make a solution of FA6 in distilled water and use separate portions of it for each of the tests (i) to (iv).	• ***White solid dissolves to form colourless solution.***	*Coloured ions absent:* ***Cr^{3+}, Fe^{3+}, Fe^{2+}, Cu^{2+}***
(i) Add aqueous silver nitrate.	• *No ppt*	• *Cl^-, Br^-, I^- absent*
(ii) Add aqueous sodium hydroxide Filter the mixture and add dilute sulfuric acid to the filtrate.	• *White ppt* • *Insoluble in excess* • *White ppt formed which dissolves on shaking in excess acid to give a colourless solution*	• *$Ca(OH)_2$ or $Mg(OH)_2$ formed.* • *Ca^{2+} or Mg^{2+} is present* • *$Zn(OH)_2$ or $Al(OH)_3$ formed* • *Zn^{2+} or Al^{3+} present*
(iii) Add aqueous ammonia. Filter the mixture and add dilute sulfuric acid to the filtrate.	• *White ppt formed insoluble in excess* • *White ppt formed soluble on shaking in excess acid to give a colourless solution*	• *$Al(OH)_3$ or $Mg(OH)_2$* • *$Zn(OH)_2$* • *Zn^{2+} present*
(iv) Add dilute nitric acid.	• ***Moist blue litmus remains blue.***	***No acidic gas evolved.*** ***Absence of CO_3^{2-}, SO_3^{2-}, NO_2^-***

***Note:**

- **Do not use the word 'clear' when you mean 'colourless'. All solutions are clear/ transparent, but not necessarily colourless.**

- **Precipitation takes place when the reaction mixture in the test tube changes from 'clear' to 'opaque',**
  transparent formation of ppt.

- Generally, **acidic gases** (e.g. CO_2) can be produced when **acid is added** to unknown anion while **alkaline gas** could be produced when **NaOH(aq) is added** to unknown ion.

- Addition of **acid to grey solid powder or shiny strips** (suspected metals) gives H_2 gas which gives a pop sound with lighted splint.

Cations and anions may be identified by the colour of the precipitates formed and their solubilities in excess of certain reagents added.

Reactions of aqueous Cations

cation	*reaction with*	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

Reactions of aqueous anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and *Al* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and *Al* foil; NO liberated by dilute acids (colourless NO –→ (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite,SO_3^{2-}(aq)	SO_2 liberated by dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

➢ Watch and Learn

Flowchart for the identification of CATIONS in QA experiment:
http://tinyurl.com/solvecation

2.1 Commonly Used Reagents for Identifying Ions

(A) NaOH(aq)

- **Precipitation of metal cations (except Group 1)**

  For sparingly soluble metal hydroxide, mixing of alkali (OH^- ions) and the aqueous metal cations (M^{2+}/ M^{3+}) causes the ionic product > K_{sp} value.

  This causes **precipitation**:

  General equation: $M^{n+}(aq) + nOH^-(aq) \rightarrow M(OH)_n(s)$

  Coloured precipitate => presence of transition metal cation

  White precipitate => presence of main group metal cation

  When the precipitate is an amphoteric hydroxide, it will be **soluble in excess NaOH(aq)** due to **formation of a soluble complex ion.**

  In general, the following occurs when $OH^-(aq)$ is added to a solution of these cations:

Solution	**Ppt formed** with first few drops of NaOH(aq)	**Formulae of the soluble complex ion** with excess of NaOH(aq) added
Al^{3+} (colourless solution)	$Al(OH)_3$ (white ppt)	$[Al(OH)_4]^-$ (colourless solution)
Zn^{2+} (colourless solution)	$Zn(OH)_2$ (white ppt)	$[Zn(OH)_4]^{2-}$ (colourless solution)
Cr^{3+} (green solution)	$Cr(OH)_3$ (grey-green ppt)	$[Cr(OH)_6]^{3-}$ (dark green solution)

  Using Al^{3+}as an example.
  As NaOH(aq) is added dropwise to Al^{3+} (aq), ionic product of $Al(OH)_3(s)$ > K_{sp} value, precipitation occurs.

  $$Al^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Al(OH)_3(s) \text{ ----------(1)}$$

  With excess alkali, a soluble complex is formed.

  $$Al^{3+}(aq) + 4OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq) \text{ ---------- } \textbf{equilibrium 2}$$

  This decreases the **ionic product to be lower than K_{sp}** value. Solution is **no longer saturated** with $Al^{3+}(aq)$ and $OH^-(aq)$, thus **all $Al(OH)_3(s)$ can dissolve when sufficient amount of $[Al(OH)_4]^-$** is formed.

This process of **selective precipitation of the metal hydroxide** allows a solution of **two different cations to be separated physically via filtration.** Separation is required to give **more reliable observations** to identify the different ions**.**

For example: For a mixture of $Al^{3+}(aq)$ and Fe^{2+} (aq), $Fe(OH)_2$ which **does not form a soluble complex with excess NaOH(aq)**, remains **insoluble** and isolated as **residue** in filtration. The filtrate will contain the soluble complex, $[Al(OH)_4]^-$ (aq).

To **verify the presence of the colourless cation** in the filtrate, acid is added dropwise, slowly.
H^+ will neutralise the $OH^-(aq)$, hence **equilibrium 2** shifts left to partially offset decreases in concentration of $OH^-(aq)$.
This causes the ionic product of $Al(OH)_3(s)$ > K_{sp}, causing the reappearance of the white precipitate. When all $OH^-(aq)$ is removed with excess H^+, all precipitate of $Al(OH)_3(s)$ is reacted away, giving a colourless solution.

- **Absence of precipitate indicates the presence of either Group 1 metal cation or NH_4^+ ion.**

NH_4^+ cation can be distinguished from group 1 metal cations by a positive test for alkaline gas (NH_3, damp red litmus turns blue) upon warming the alkaline mixture.

Demo video:
https://tinyurl.com/marlyo6
shows the formation of ppt with NaOH(aq), ppt dissolves in excess of NaOH(aq) to form colourless solution. Addition of HNO_3(aq) dropwise causes the white ppt of $M(OH)_n$ to appear.

(B) NH_3(aq)

NH_3(aq) is a weak base. In water, **some** of the NH_3 molecules accepts a proton from H_2O to form NH_4^+ and OH^- ions as shown:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Even though NH_3(aq) is a weaker source of OH^-, it is sufficient to cause the ionic product ($M(OH)_n > K_{sp}$ value.

This causes **precipitation**:

$$\text{General equation:} \quad M^{n+}(aq) + nOH^-(aq) \longrightarrow M(OH)_n(s)$$

$Zn(OH)_2$ and $Cu(OH)_2$ ppt are **soluble in excess NH_3(aq)** due to the formation of **soluble complex ions**.

In general, the following occurs when NH_3(aq) is added to the solutions containing Zn^{2+} and Cu^{2+} ions.

Solution	**Ppt** with first few drops of NH_3(aq)	**Formulae of soluble complex ion** with excess of NaOH(aq) added
Zn^{2+} (colourless solution)	$Zn(OH)_2$ (white ppt)	$[Zn(NH_3)_4]^{2+}$ (colourless solution)
Cu^{2+} (blue solution)	$Cu(OH)_2$ (blue ppt)	$[Cu(NH_3)_4]^{2+}$ (dark blue solution)

Using Cu^{2+}as an example.
As NH_3(aq) is added dropwise to Cu^{2+} (aq), ionic product of $Cu(OH)_2$(s) > K_{sp} value, precipitation occurs.

$$Cu^{2+}(aq) + 2\ OH^-(aq) \rightleftharpoons Cu(OH)_2(s) \text{ ---------- equilibrium (1)}$$

With excess NH_3(aq), a soluble complex is formed.

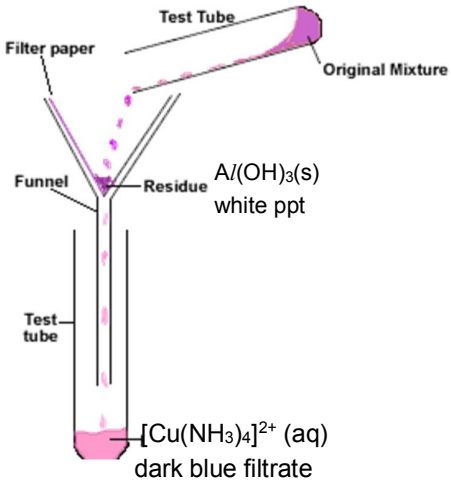
$$Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \text{ ---------- equilibrium (2)}$$

This decreases the **ionic product to be lower than K_{sp}** value. Solution is **no longer saturated** with Cu^{2+} (aq) and OH^-(aq), thus **all $Cu(OH)_2$(s) can dissolve when sufficient amount of** $[Cu(NH_3)_4]^{2+}$ is formed.

This process of **selective precipitation of the metal hydroxide** allows a solution of two different cations to be **separated physically via filtration**.

For example: For a mixture of $Al^{3+}(aq)$ and Cu^{2+} (aq), $Al(OH)_3(s)$ which **does not form a soluble complex with excess $NH_3(aq)$**, remains **insoluble** and isolated as **residue** in filtration. The filtrate will contain the soluble complex, $[Cu(NH_3)_4]^{2+}$ (aq), dark blue in colour.

To **verify the presence of the Cu^{2+} cation** in the filtrate, acid is added dropwise, slowly.
H^+ will neutralise the $NH_3(aq)$, hence **equilibrium 2** shifts left to partially offset decreases in concentration of $NH_3(aq)$. This causes the ionic product of $Cu(OH)_2(s) > K_{sp}$, causing the reappearance of the blue precipitate. When all $NH_3(aq)/OH^-(aq)$ are removed with excess H^+, all precipitate of $Cu(OH)_2(s)$ is reacted away, giving a blue solution.



(C) $H_2SO_4(aq)$

- Provides SO_4^{2-} ion to distinguish between **Ba^{2+} and Ca^{2+}**.

  White ppt is formed due to **precipitation** of the cation with SO_4^{2-}.

  For example, $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

- Provides H^+ ion to test for **CO_3^{2-}, NO_2^- or SO_3^{2-}** through the evolution of gases, CO_2, NO_2 and SO_2 respectively.

  (Refer to pg. 34, 35)

- Provides H^+ ion to test for **metals**

  H_2 evolved (colourless, odourless gas which extinguishes a lighted splint with a "pop" sound.)

  For example, $2H^+(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + H_2(g)$

(D) Dilute HC*l*(aq)

- Provides Cl^- ion to test for **Ag^+**

  White ppt is formed due to **precipitation** of the cation with Cl^-.

  For example, $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

- Provides H^+ ion to test for **CO_3^{2-}, NO_2^- or SO_3^{2-}**

  Same observations as for $H_2SO_4(aq)$ above.

- Provides H^+ ion test for **metals**

  Same observations as for $H_2SO_4(aq)$ above.

- Provides Cl^- ion to test for presence of strong oxidising agents such as $KMnO_4$ or MnO_2.

  (Refer to pg. 35)

(E) $AgNO_3$(aq)

- Test for **halides (Cl^-, Br^-, I^-)**

  Precipitation occurs between Ag^+ and each anion to give a different colour ppt.

  The solubility of the ppt in NH_3 (aq) can help in the identification of the anions.

  For example, $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

- Test for reducing agents

  A grey ppt. of Ag is formed.

  For example, $Fe^{2+}(aq) + Ag^+(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

(F) $Ba(NO_3)_2$(aq) / $BaCl_2$ (aq)

- Provides Ba^{2+} ion to test for polyatomic anions such as **SO_3^{2-}, SO_4^{2-}, CO_3^{2-}**

  For example, $Ba^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow BaCO_3(s)$

  White ppt is formed due to **precipitation** of Ba^{2+} with the polyatomic anions.

  The solubility of the ppt in acid, with the evolution of gases, can help in the identification of the anions.

(G) KI (aq)

- Test for **Ag^+**

  For example, $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$

  Precipitation occurs between I^- and Ag^+ to give a yellow ppt of AgI.

- Test for oxidising agents to liberate I_2 ***(Refer to pg. 47)***

  $2I^-(aq) \longrightarrow I_2(aq) + 2e^-$
  (brown solution)

(H) Na_2CO_3 (aq)

- Except for group 1 metal cations and NH_4^+ ion,

  all other **metal cations** is precipitated with CO_3^{2-}.

  For example, $Ba^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow BaCO_3(s)$

- Test for **acidic property** in organic RCO_2H and highly charged $Fe^{3+}(aq)$ / $Al^{3+}(aq)$ through the evolution of CO_2 ***(Refer to pg. 34)***

  For example, $2H^+(aq) + CO_3^{2-}(aq) \longrightarrow H_2O(l) + CO_2(g)$

2.3 Precipitation of Anions

Unlike anions from weak acids, anions from strong acids cannot be displaced from their salts to give gases (***refer to Section 1***); hence to identify anions from strong acids, it must be through precipitation reactions.

Reactions of Anions

anions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO $\longrightarrow$ (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated by dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

3. Identification of Gases

Gas	Observations, Test and Test Result	Theoretical Background (Common reactions which liberate this gas)
hydrogen, H_2	• colourless and odourless gas • insert a **lighted splint** into test-tube, H_2 gas extinguishes the **lighted splint** with a "pop" sound.	• Use of dil. HC*l* or H_2SO_4 to **identify reactive metals** (shiny strips or greyish solid sample). $M + 2H^+ \rightarrow M^{2+} + H_2(g)$
oxygen, O_2	• colourless and odourless gas • insert a **glowing splint** into test-tube, O_2 gas relights the **glowing splint**	• Use of thermal decomposition to **identify solid nitrates** $2M(NO_3)_2(s) \xrightarrow{\text{heat}} 2MO + O_2(g) + 4NO_2(g)$ (brown gas (when brown gas is observed, check for O_2 gas too)) • Use of heat to **identify compounds containing peroxide** (O with −1 oxidation state) via disproportionation $2H_2O_2\ (aq) \xrightarrow{\text{heat}} 2H_2O + O_2(g)$ $H_2O_2(aq) + 2Fe^{3+}(aq) \rightarrow O_2(g) + 2H^+ + 2Fe^{2+}$
carbon dioxide, CO_2	• colourless and odourless gas • pass gas (using either a dropper or delivery tube) into separate test-tube containing **$Ca(OH)_2$** (limewater). CO_2 gas forms white ppt. with **$Ca(OH)_2$** (ppt. dissolves with excess CO_2)	• Use of thermal decomposition to **identify solid carbonates** (except those of Group 1, which do not thermally decompose). $MCO_3\ (s) \xrightarrow{\text{heat}} MO + CO_2(g)$ • Use of dilute acids to **identify carbonates** $CO_3^{2-} + 2H^+ \xrightarrow{\text{heat}} CO_2(g) + H_2O$ • Use of carbonates to identify $\mathbf{M}^{3+}$ (aq) where **M** = A*l*, Fe, Cr Aqueous **cations with high charge density** have acidic properties. They hydrolyse in aqueous solutions to form H_3O^+ which reacts with the CO_3^{2-}. ***(covered in Periodic Table chapter)*** $2[\mathbf{M}(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[\mathbf{M}(OH)_3(H_2O)_3](s) + 3CO_2(g) + 3H_2O$

Gas	Observations, Test and Test Result	Theoretical Background Common reactions which liberate this gas
ammonia, NH_3	• colourless, pungent gas • place **damp red litmus paper** at mouth of test-tube, NH_3 gas turns **damp red litmus paper** blue	• Use of base (CaO, NaOH or aq Na_2CO_3) to **identify ammonium salts**. $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ • Devarda's alloy test $2Al + NO_2^- + 5H_2O + OH^- \rightarrow 2Al(OH)_4^- + NH_3$ $8Al + 3NO_3^- + 18H_2O + 5OH^- \rightarrow 8Al(OH)_4^- + 3NH_3$
sulfur dioxide, SO_2	• colourless gas with burning sulfur smell • insert filter paper strip dipped in **acidified aqueous potassium manganate(VII).** SO_2 gas reduces **acidified aqueous potassium manganate(VII)** from purple to colourless (or use delivery tube method)	• Use of dilute acid to **identify sulfites**. $SO_3^{2-} + 2H^+ \rightarrow SO_2(g) + H_2O$
chlorine, Cl_2	• pale greenish-yellow, pungent gas • place **damp red / blue litmus paper** at mouth of test-tube. Cl_2 gas bleaches **damp litmus paper**	• Use of conc. HCl or conc. chloride salt to **identify MnO_4^- or MnO_2** or to **test for strong oxidising agent** $2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$ $4HCl + MnO_2 \xrightarrow{\text{heat}} MnCl_2 + Cl_2 + 2H_2O$
nitrogen dioxide, NO_2	• brown, pungent fumes	• Use of thermal decomposition to **identify metal nitrates**. $2\mathbf{M}(NO_3)_2\ (s) \xrightarrow{\text{heat}} 2\mathbf{M}O + O_2 + 4NO_2(g)$ • Use of dilute acid to **identify nitrites**. $2H^+ + NO_2^- \rightarrow H_2O + NO$ colourless gas $NO + \frac{1}{2}O_2 \rightarrow 2NO_2(g)$ brown gas

4. Identification of Ions with Redox Properties

Other than precipitation, certain ions undergo redox reactions which result in characteristic observations. Hence, the identities of such ions can be deduced by the selective use of oxidising and reducing agents.

	Reagent	Observations	Examples of Chemical Species that can be Identified and Equations for the reactions
OXIDISING AGENT	acidified manganate(VII) solution $MnO_4^-(aq)/H^+(aq)$	• **Purple** solution (MnO_4^-) turns **colourless** (Mn^{2+}) • Describe the colour change of sample solution if applicable.	**Fe^{2+}:** $5Fe^{2+} + 8H^+ + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ e.g. sample solution turns from pale green to yellow
	acidified dichromate(VI) solution $Cr_2O_7^{2-}(aq)/H^+(aq)$ ***Remark:*** ***Not in use due to toxicity but tested in theory***	• **Orange** solution ($Cr_2O_7^{2-}$) turns **green** (Cr^{3+})	**Fe^{2+}:** $6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
			I^-: $6I^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$
	aqueous hydrogen peroxide H_2O_2	Respective colour changes when: • transition metal cations undergo oxidation. e.g. pale green solution (Fe^{2+}) turns yellow (Fe^{3+})	**transition metal cations** (e.g. Fe^{2+}) $2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O$
		• halide ions undergo oxidation. e.g. colourless solution (I^-) turns brown (I_2)	**halide ions** (e.g. I^-) $2I^- + H_2O_2 + 2H^+ \longrightarrow 2H_2O + I_2$
	Chlorine water (obtained by acidifying NaOC*l*), Cl_2 (aq) ≡ (NaOC*l* + HC*l*)	When an organic solvent (e.g. hexane) is added to the reaction mixture and shaken, the organic layer becomes coloured due to the halogen, X_2, dissolved in it. $2X^- + Cl_2 \longrightarrow X_2 + 2Cl^-$ (X = Br, I)	
		• orange aqueous layer; and • orange-red organic layer	**Br^-:** $2Br^- + Cl_2 \longrightarrow Br_2 + 2Cl^-$
		• brown aqueous layer; and • purple/violet organic layer.	**I^-:** $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

https://tinyurl.com/5ybrhfv4

Importance of adding dropwise to observe color change of both the unknown and the reagent added.

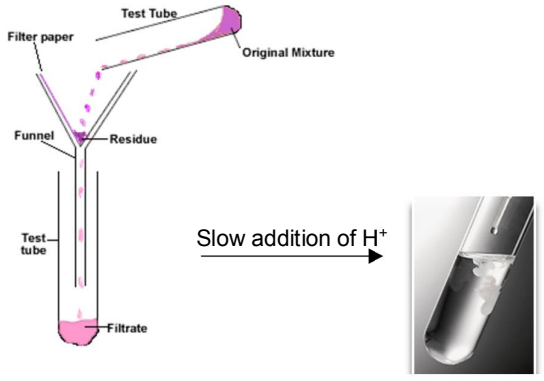
	Reagent	Observations	Examples of Chemical Species that can be Identified and Equations for the reactions
REDUCING AGENT	Aluminium / zinc / Devarda's Alloy A*l*(s)/ Zn(s) + NaOH(aq), heat	• NH_3 evolved that turns damp red litmus blue	**NO_3^-:** $8Al + 5OH^- + 18H_2O + 3NO_3^- \longrightarrow 8Al(OH)_4^- + 3NH_3$
			NO_2^-: $2Al + OH^- + 5H_2O + NO_2^- \longrightarrow 2Al(OH)_4^- + NH_3$
	aqueous potassium iodide KI(aq)	• Colourless solution (KI) turns brown (I_2).	**Sample contains unknown with oxidising property or it contains** oxidising agents such as:
		• Blue solution gives white ppt (Cu_2I_2) in a brown solution (I_2). (leave mixture to stand to see a separation of ppt and solution) **Note:** sometimes the test requires further adding of thiosulfate to reduce brown iodine to colourless iodide to reveal the colour of the ppt	**Cu^{2+}:** $4I^- + 2Cu^{2+} \longrightarrow 2CuI(s) + I_2$ $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ *ppt will dissolve in excess $S_2O_3^{2-}$ to give a colourless solution due to the formation of complex ion as shown below $Cu^+ + 2S_2O_3^{2-} \rightleftharpoons [Cu(S_2O_3^{2-})_2]^{3-}$
		• Pale yellow solution (Fe^{3+}) turns brown (I_2). (green Fe^{2+} is masked by the brown colouration of I_2)	**Fe^{3+}:** $2I^- + 2Fe^{3+} \longrightarrow 2Fe^{2+} + I_2$
	aqueous iron(II) sulfate $FeSO_4(aq)$	• green solution (Fe^{2+}) turns yellow (Fe^{3+}).	**Sample contains unknown with oxidising property or it contains oxidising agents such as:** **MnO_4^-; $Cr_2O_7^{2-}$ and H_2O_2**
	aqueous hydrogen peroxide H_2O_2	• Effervescence; colourless, odourless gas which relights a glowing splint.	Oxidising agent such as **MnO_4^-**: $5H_2O_2 + 6H^+ + 2MnO_4^- \longrightarrow 5O_2 + 2Mn^{2+} + 8H_2O$

General skills in Inorganic Compounds QA

Experimental recording of observation	
When <u>adding reagents</u> and <u>ppt. forms</u>: ▪ Record the colour of any ppt. formed. ▪ For NaOH(aq)/NH_3(aq)/H^+(aq), record the solubility of the ppt. in excess. ▪ If ppt. is soluble in excess, record the colour of the solution formed.	When <u>filtering</u>: ▪ Record the colour of the filtrate. ▪ Record the initial colour of the residue and after exposure to air (upon standing).
When <u>adding reagents</u> and the <u>colour of the solution changes</u>: ▪ Record all colour changes, initial and final colour. ▪ If a coloured reagent is used, important to add dropwise to record colour change of the reagent as well as the colour of the unknown.	When <u>heating</u> a <u>solid sample</u>: ▪ Record all the colour changes of the solid, including the initial colour. ▪ Gas is produced If moist litmus paper at the mouth of test tube changes colour ▪ Describe the chemical test to confirm the gas identity and the unknown ion.
When <u>adding reagents</u> and <u>gas liberated</u>: ▪ Gas is liberated o If bubbles are observed without heating. o If moist litmus paper at the mouth of test tube changes colour ▪ Describe the chemical test to confirm the gas identity and the unknown ion.	When <u>heating</u> a <u>solution sample</u>: ▪ Record all the colour changes of the solution, including the initial colour. ▪ Gas is produced If moist litmus paper at the mouth of test tube changes colour ▪ Describe the chemical test to confirm the gas identity and the unknown ion.

Separation of mixture of ions in solution:

- Concept of ***selective precipitation*. See section 2.1 pg 12 -14.**
- **Separation is required to give more reliable observations to identify the different ions.**
- **General procedure (**With reference to QA table on pg 76 – 77)**:**
  1. A reagent until in excess to precipitate only one ion, leaving the others in solution.
  2. Filtration is used to collect ions in residue (ppt) and filtrate (soluble complex solution).
  3. **'locate the ions'** in the filtrate or in the residue based on
     - the colours.
     - Whether reprecipitation takes place with careful addition of to the basic filtrate.



Summary Table 1: Summary of reactions of Cations with common Reagents

Reagents Cations	NaOH (aq)	NH_3 (aq)	Na_2CO_3 (aq)	KI (aq)	Other Reagents
Ag^+	Brown ppt	Brown ppt soluble in excess, produces Tollen's reagent	–	Yellow ppt (insoluble in aqueous NH_3)	• HCl (aq): White ppt
Cu^{2+}	Blue ppt	Blue ppt, soluble in excess to form a dark blue solution, $[Cu(NH_3)_4]^{2+}$	Blue ppt, $CuCO_3$	White ppt, CuI in brown solution	• Conc. HCl: blue to green to yellow solution $[CuCl_4]^{2-}$
Fe^{2+}	Green ppt, turns brown on standing	Green ppt, turns brown on standing	Green ppt, $FeCO_3$, turns brown on standing	–	• H_2O_2(aq): pale green solution turns yellow • $AgNO_3$(aq): grey ppt (Ag)
Fe^{3+}	Red-brown ppt	Red-brown ppt	* Red-brown ppt of $Fe(OH)_3$, with CO_2 evolved	Yellow solution turns brown (I_2 formed)	• NH_4SCN (aq): blood red colouration
Al^{3+}	White ppt, soluble in excess to form a colourless solution, $[Al(OH)_4]^-$	White ppt	* White ppt of $Al(OH)_3$ formed, with CO_2 evolved	–	–
Cr^{3+}	Grey-green ppt, soluble in excess to form a dark green solution, $[Cr(OH)_6]^{3-}$	Grey-green ppt	* Grey-green ppt of $Cr(OH)_3$, with CO_2 evolved	–	–
Zn^{2+}	White ppt, soluble in excess to form a colourless solution, $[Zn(OH)_4]^{2-}$	White ppt, soluble in excess to form a colourless solution, $[Zn(NH_3)_4]^{2+}$	White ppt, $ZnCO_3$	–	–
Mn^{2+}	Off-white ppt, turns brown on standing	Off-white ppt, turns brown on standing	White ppt, $MnCO_3$	–	–
Mg^{2+}	White ppt	White ppt	White ppt, $MgCO_3$	–	–
Ba^{2+}	–	–	White ppt, $BaCO_3$	–	• H_2SO_4(aq): white ppt $BaSO_4$
Ca^{2+}	White ppt with high $[Ca^{2+}(aq)]$	–	White ppt, $CaCO_3$	–	–
NH_4^+	NH_3 gas liberated on warming	–	–	–	–
H^+	Heat evolved from neutralisation	Heat evolved from neutralisation	Effervescence, CO_2 evolved	–	• Mg: H_2 evolved

** Cationic hydrolysis of M^{3+} (aq) as covered in the Periodic Table chapter*

Table 2: Summary of reactions of Anions with common Reagents

Reagents Anions	Heat	Dil HCl / H_2SO_4	$AgNO_3$ (aq)	$Ba(NO_3)_2$ / $BaCl_2$ (aq)	Acidified $KMnO_4$	KI(aq)	Other Reagents
CO_3^{2-}	Effervescence, CO_2 evolved	Effervescence, CO_2 evolved	White ppt, soluble in acid with effervescence	White ppt, soluble in acid with effervescence	–	–	–
SO_3^{2-}	SO_2 evolved	SO_2 evolved	–	White ppt, soluble in HCl / HNO_3	Purple $KMnO_4$ decolourised	–	–
SO_4^{2-}	–	–	–	White ppt, insoluble in HCl / HNO_3	–	–	–
NO_2^-	–	NO_2 evolved	–	–	Purple $KMnO_4$ decolourised	I_2 liberated	• Al/Zn + NaOH + heat: NH_3 evolved
NO_3^-	NO_2 evolved	–	–	–	–	–	• Al/Zn + NaOH +heat: NH_3 evolved
Cl^-	–	–	White ppt soluble in NH_3(aq)	–	Cl_2 evolved	–	
Br^-	–	–	Cream ppt sparingly soluble in NH_3(aq)	–	Br_2 evolved	–	• Cl_2(aq)+hexane: orange solution formed, orange-red solution formed in organic layer
I^-	–	–	Yellow ppt insoluble in NH_3(aq)	–	I_2 liberated	–	• Cl_2(aq)+ hexane: brown solution formed, violet solution formed in organic layer • $CuSO_4$ (aq): white ppt in brown solution • H_2O_2(aq): brown solution formed

1 Introduction to Organic Chemistry Qualitative Analysis (QA)

Qualitative analysis can be used to distinguish / identify organic compounds of different functional groups. If you are given a few unknown organic compounds, each possessing a specific functional group, you can systematically determine each of their identities by:

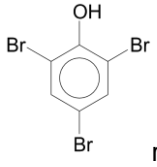
1. knowing the **characteristic tests** for each of the **functional group**
2. using **simple chemical tests** that would lead to **visible changes**

1.1 Safety precautions

- Short chain organic compounds which are liquid at room temperature are usually volatile. They should be capped in bottles when not in use. Any spillage should also be cleaned up immediately to prevent the spread of the volatile vapour.
- Test–tube holders are used to handle the test-tubes and hand gloves are worn to avoid direct contact with the chemicals, especially compounds which contain **benzene** and **halogen** as they are toxic and corrosive. Safety goggles should be put on.
- If warming is necessary, the test-tubes are put in a warm water bath (usually boiling temperature is not required). Since organic compounds are highly flammable, **direct heating using naked flame should be avoided**.
- Carry out the reaction in fume cupboard if
    - reaction produces toxic gas (and goggles should be worn to protect eyes from the fumes)
    - reaction requires the use of acids or alkalis of high concentration or use of flammable chemicals or chemicals that are sensitive to moisture

1.2 Quantities used

- In all chemical tests, unless otherwise stated, the unknown liquid is of 1 cm depth while the quantity of unknown solid should cover the bottom hemisphere of test-tube.
- If colour change is used to identify certain functional groups, only 2−3 drops of coloured reagent should be added to avoid excessive addition which may lead to inaccurate conclusion.
- If precipitation is used to identify certain functional groups, add only 2−3 drops of the unknown liquid. This is because excessive amount of the **unknown organic liquid** may cause **organic precipitates** like tri-iodomethane and hydrazone (product formed from condensation reaction between carbonyl compound and 2,4−dinitrophenylhydrazine) to become soluble. When that happens, the precipitate can no longer be observed, leading to inaccurate conclusion.
- If hydrolysis is being carried out, 1 cm^3 of acid or alkali is used, and the reaction mixture has to be placed in warm water bath for at least 5 minutes before the addition of other reagents.
- When I_2(aq) and Br_2(aq) are added to form yellow precipitate, CHI_3 and white precipitate,



respectively, they should be added dropwise until no further change is observed. This is because I_2(aq) and Br_2(aq) have to be added in excess before the precipitate can be observed.

- The unknown organic liquid and the aqueous reagent may form 2 immiscible layers, ensure proper mixing to observe accurate results.

1.3 Reactions to identify different functional groups

<table>
<tr><th>Functional group</th><th>Reagent / conditions</th><th>Procedure</th><th>Observations</th></tr>
<tr><td rowspan="2"><u>Alkenes</u>

e.g.
  </td><td>Br_2 (aq)

(Electrophilic addition)

Note:
When colour change of coloured reagent is expected, <u>SMALL</u> quantity is to be used (should be limiting in order to observe the colour change)

Excess Br_2 (aq) used will not be decolourised and may result in inaccurate conclusion.</td><td>To 1 cm depth of unknown liquid, add 1-2 drops of bromine water.

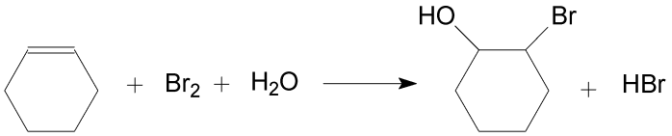
<u>Demo video:</u>

https://tinyurl.com/y7zeoqmz</td><td>Orange Br_2 solution is decolourised.

Theoretical background / chemical equations:

C=C is electron-rich and will attack the bromine molecule.

<u>Electrophilic addition</u>

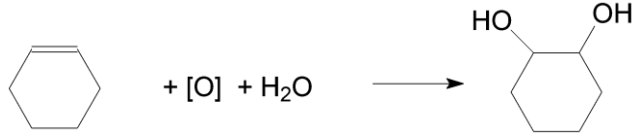
 

Orange</td></tr>
<tr><td>$KMnO_4$(aq), NaOH(aq), cold

(Mild oxidation)</td><td>To 1 cm depth of unknown liquid, add 1 cm^3 of aq NaOH, followed by 1-2 drops of aq $KMnO_4$.</td><td>Purple $KMnO_4$ decolourised, brown ppt of MnO_2 formed upon leaving to stand.

Theoretical background / chemical equations:

<u>Mild oxidation</u> of C=C to give a diol.

MnO_4^- ⟶ MnO_2
Purple Brown ppt</td></tr>
</table>

<table>
<tr><th>Functional group</th><th>Reagent / conditions</th><th>Procedure</th><th>Observations</th></tr>
<tr>
<td><u>Alkenes</u>

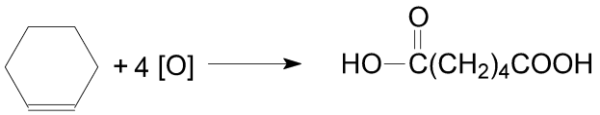
e.g.
  </td>
<td>$KMnO_4$(aq), H_2SO_4(aq), warm

(Vigorous oxidation)</td>
<td>To 1 cm depth of unknown liquid, add 1 cm^3 aq H_2SO_4, followed by 1-2 drops of aq $KMnO_4$.

Warm in hot water bath.</td>
<td>Purple $KMnO_4$ decolourised.

Theoretical background / chemical equations:

C=C undergoes <u>oxidative cleavage</u> with $KMnO_4$.

  </td>
</tr>
<tr>
<td><u>Halogenoalkanes</u>

e.g.
$CH_3CH_2CH_2C\mathit{l}$</td>
<td>i) NaOH(aq), heat
ii) Cool, acidify with HNO_3(aq)
iii) Add $AgNO_3$(aq)

(Nucleophilic substitution, followed by precipitation)</td>
<td>To 1 cm depth of unknown liquid, add 1 cm^3 of aq NaOH. Warm in water bath for 5 mins.

Cool the mixture and add an excess of aq HNO_3 (check if resulting solution is acidic using moist blue litmus paper).

Add aq $AgNO_3$ dropwise.

<u>Demo video:</u>

https://tinyurl.com/hfwak6b</td>
<td>
<table>
<tr><th>C–X</th><th>Precipitate</th><th>Colour of ppt</th><th>Rate for formation of ppt</th></tr>
<tr><td>C–Cl</td><td>AgCl</td><td>white</td><td>Slowest</td></tr>
<tr><td>C–Br</td><td>AgBr</td><td>cream</td><td></td></tr>
<tr><td>C–I</td><td>AgI</td><td>yellow</td><td>Fastest</td></tr>
</table>
Theoretical background / chemical equations:

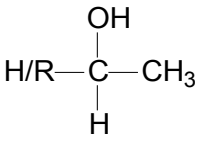
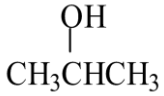
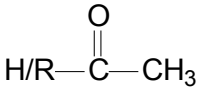
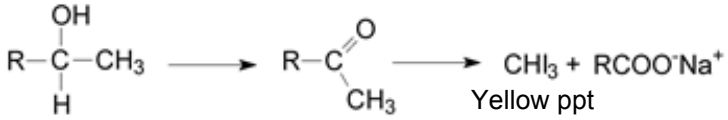
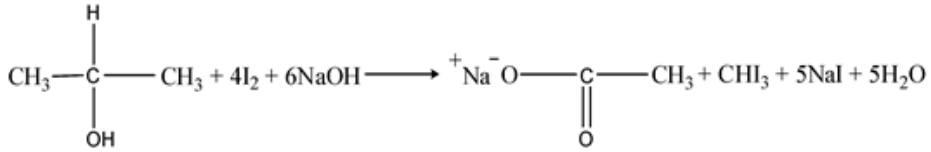
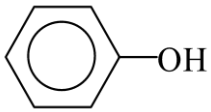
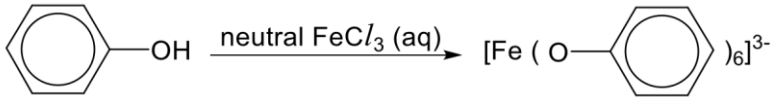
<u>Nucleophilic substitution, followed by precipitation</u>

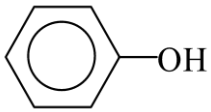
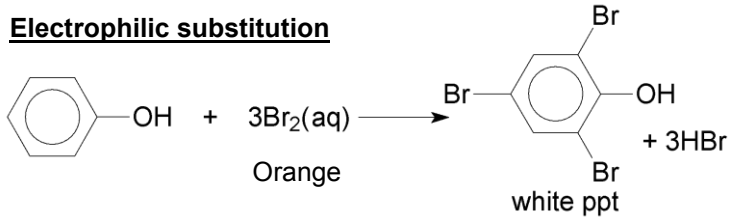
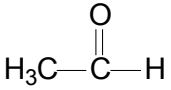
OH^- attacks the $C^{\delta+}$ of C–X bond and displaces free X^- ion, which is subsequently precipitated out as AgX(s).

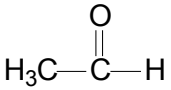
(i) $OH^- + R{-}X \longrightarrow R{-}OH + X^-$ Hydrolysis (nucleophilic substitution)
(ii) $H^+ + OH^- \longrightarrow H_2O$ Neutralisation (remove excess OH^-)
(iii) $Ag^+(aq) + X^-(aq) \longrightarrow AgX\ (s)$ precipitation of AgX(s)

Note:
Aromatic halogen compounds where the X is directly attached to the benzene ring, do NOT hydrolyse in this way and no AgX ppt will be seen. Aromatic C–X is a stronger bond than aliphatic C–X due to partial double bond character.
</td>
</tr>
</table>

Functional group	Reagent / conditions	Procedure	Observations
<u>Alcohols</u> ROH	Na metal Anhydrous condition **(Redox)** **Note:** Need to know reaction with Na metal in theory, but will not carry this out in practical.	Add a small piece of Na metal to 1 cm depth of unknown liquid. **<u>Demo video:</u>** https://tinyurl.com/h3sntoj	**Effervescence and Na metal dissolves.** **Gas evolved extinguishes a lighted splint with a pop sound.** **Theoretical background / chemical equations:** Even though alcohols are weaker acids than water, they can still undergo **<u>redox reaction</u>** with reactive metal Na(s) to give H_2 gas. $ROH + Na \longrightarrow RO^-Na^+ + \frac{1}{2}H_2(g)$
<u>1° alcohol</u> CH_3CH_2OH **<u>and 2° alcohol</u>** $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$	$KMnO_4(aq)$, $H_2SO_4(aq)$, warm $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, warm **Note:** Need to know reaction with $K_2Cr_2O_7$ in theory, but will not carry out in practical. **(Oxidation of alcohol)**	To 1 cm depth of unknown liquid, add 1 cm^3 aq H_2SO_4, followed by 1-2 drops of aq $KMnO_4$ / $K_2Cr_2O_7$ Warm reaction mixture in hot water bath. Note: Excess aq $KMnO_4$ / $K_2Cr_2O_7$ used will not give any colour change and may result in inaccurate conclusion.	**Purple MnO_4^- decolourises to colourless Mn^{2+}.** **Orange $Cr_2O_7^{2-}$ reduces to green Cr^{3+}.** **Theoretical background / chemical equations:** **<u>Oxidation of 1° alcohol to RCOOH</u>** $CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$ **<u>Oxidation of 2° alcohol to ketone</u>** $CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$

Functional group	Reagent / conditions	Procedure	Observations
Alcohol with  Methyl carbinol structure e.g. 	I_2(aq), NaOH(aq), warm **(oxidation of methyl carbinol)** **Tri-iodomethane Test / Iodoform Test**	To 1 cm^3 of NaOH(aq), add I_2(aq) dropwise until no further change. Add 2−3 drops of unknown liquid. Warm if necessary. **Demo video:** https://tinyurl.com/y83rkzn4	**Yellow ppt of CHI_3 formed, brown I_2 decolourises.** **Theoretical background / chemical equations:** The alcohol is **oxidised** to  (carbonyl compound) first before it reacts with iodine to form yellow ppt CHI_3.  Yellow ppt 
Phenol 	Neutral $FeCl_3$(aq)	Add a drop of freshly prepared neutral iron(III) chloride solution to a small quantity of phenol in water.	**Yellow Fe(III) solution gives violet colouration with phenol.** **Theoretical background / chemical equations:** **Complex formation** with Fe^{3+} (aq), Need not know the structure of complex  violet complex

Functional group	Reagent / conditions	Procedure	Observations
Phenol 	$Br_2(aq)$ **(Electrophilic substitution)**	To a small quantity of phenol, add $Br_2(aq)$ dropwise, until in excess.	**Orange $Br_2(aq)$ decolorised, white ppt formed.** **Theoretical background / chemical equations:** −OH group of phenol is strongly activating. Hence, multiple substitutions at benzene can take place without the need of a halogen carrier (e.g. FeX_3). **Electrophilic substitution** 
Aldehyde RCHO e.g. 	Tollens' reagent: $[Ag(NH_3)_2]^+$, Warm **(Oxidation of aldehyde)**	**Preparation of Tollens' reagent:** To 1 cm depth of aq $AgNO_3$, add 1 cm depth of aq NaOH, followed by aq ammonia dropwise until the precipitate formed dissolves. Add 2−3 drops of unknown liquid and warm if necessary.	**Silver mirror formed / grey ppt formed.** **Theoretical background / chemical equations:** **ALL aldehydes** are **oxidised** to carboxylic acid which is neutralised by the alkaline medium to form the carboxylate salt. Ag^+ reduced to Ag. $RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O$ Silver/grey solid

<table>
<tr><th>Functional group</th><th>Reagent / conditions</th><th>Procedure</th><th>Observations</th></tr>
<tr><td rowspan="2"><u>Aldehyde</u>
RCHO
e.g.
  </td><td>Fehling's solution:
Alkaline Cu^{2+} complex, Warm

(Oxidation of aliphatic aldehyde)</td><td>Preparation of Fehling's solution:

Mix 1 cm^3 of $CuSO_4(aq)$ with 1 cm^3 of sodium tartrate dissolved in NaOH(aq).

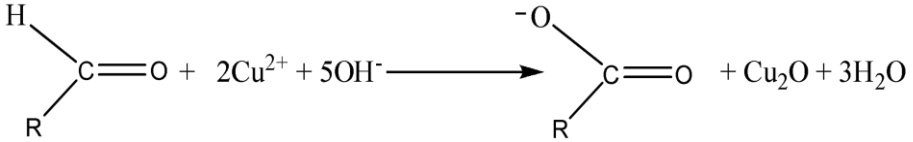
Add 2−3 drops of unknown liquid and warm if necessary.

Note:
Long duration of heating is required for brick-red ppt to be observed.</td><td>A brick-red ppt of Cu_2O is formed.

Theoretical background / chemical equations:

<u>Only aliphatic aldehyde</u> is <u>oxidised</u> to carboxylic acid which is neutralised by the alkaline medium to form the carboxylate salt. Benzaldehyde (aromatic aldehyde) will not produce brick-red ppt.

Blue Cu^{2+} reduced to brick-red Cu_2O ppt.

 
Brick-red ppt</td></tr>
<tr><td>$KMnO_4(aq)$, $H_2SO_4(aq)$, warm

(Oxidation of aldehyde)

$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, warm

Note:
Need to know reaction with $K_2Cr_2O_7$ in theory, but will not carry out in practical.</td><td>To 1 cm depth of unknown liquid, add 1 cm^3 aq H_2SO_4, followed by 1−2 drops of aq $KMnO_4$ / $K_2Cr_2O_7$

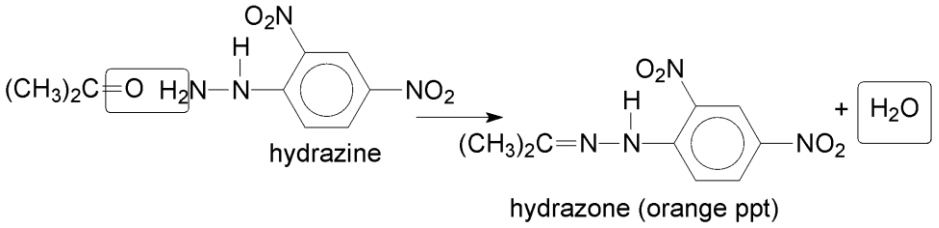
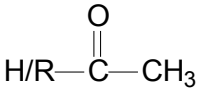
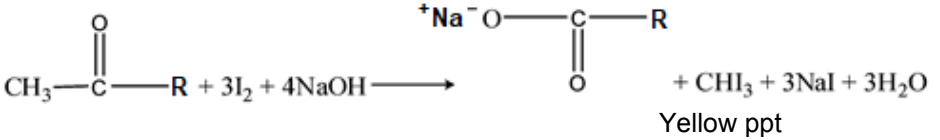
Warm reaction mixture in hot water bath.</td><td>Purple MnO_4^- decolourises. It reduces to colourless Mn^{2+}.

Orange $Cr_2O_7^{2-}$ reduces to green Cr^{3+}

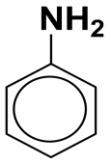
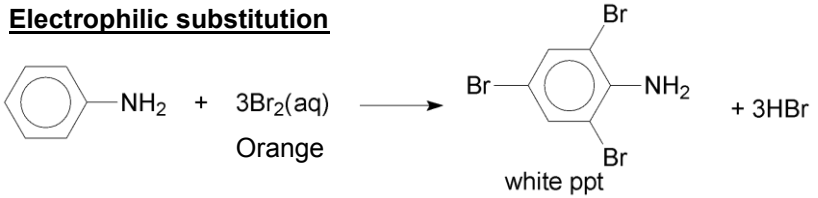
Theoretical background / chemical equations:

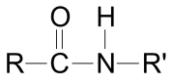
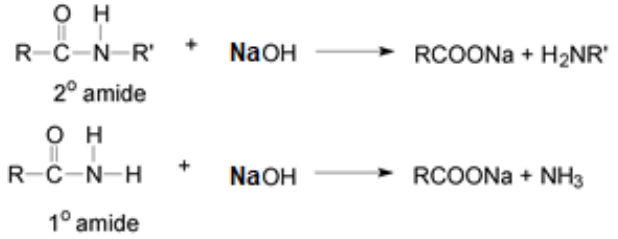
Aldehyde <u>oxidised</u> to carboxylic acid

$CH_3CHO + [O] \longrightarrow CH_3COOH$</td></tr>
</table>

Functional group	Reagent / conditions	Procedure	Observations
Carbonyl compounds (Ketone/Aldehyde)	2,4-dinitrophenylhydrazine (2,4−DNPH). **(Condensation)**	Add 2−3 drops of 2,4−DNPH (Brady's reagent) to 2−3 drops of unknown liquid. Note: Since an organic ppt is formed, hence a small quantity of organic reagent and organic compound is used to avoid ppt dissolving in the solvent.	**An orange ppt is formed.** **Theoretical background / chemical equations:** Hydrazone formation. **Condensation** reaction between $-NH_2$ of 2,4−DNPH and C=O of carbonyl compound. e.g. 
Carbonyl compounds with structure:  Methyl carbonyl structure	I_2(aq), NaOH(aq), warm **(Oxidation of methyl carbonyl)** **Tri-iodomethane Test / Iodoform Test**	To 1 cm^3 of NaOH(aq), add I_2(aq) dropwise until no further change. Add 2-3 drops of unknown liquid. Warm if necessary.	**Yellow ppt. of CHI_3 formed and brown I_2 solution decolourised.** **Theoretical background / chemical equations:** 

Functional group	Reagent / conditions	Procedure	Observations
Carboxylic acid e.g. CH_3COOH	Na_2CO_3(aq)	Add aq Na_2CO_3 to 1 cm depth of unknown liquid. Note: Prepare $Ca(OH)_2$(aq) for testing of CO_2 gas before adding in aq Na_2CO_3.	**Effervescence of colourless, odourless CO_2 gas.** **Gas evolved forms white ppt with $Ca(OH)_2$ solution (lime water).** **Theoretical background / chemical equations:** **Acid-Base reaction** $2RCOOH + Na_2CO_3 \longrightarrow 2RCOO^-Na^+ + H_2O + CO_2$ Effervescence $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$ White ppt
Acid chloride R—C(=O)—C*l*	$AgNO_3$(aq) **(Precipitation)** **Note:** Need to know reaction of acyl chloride in theory, but will not carry out in practical.	Add aq $AgNO_3$ to 1 cm depth of unknown liquid. **Demo video of RCOC*l* with different nucleophiles:** https://tinyurl.com/jtmb6l3	**White ppt of AgC*l* formed.** **Theoretical background / chemical equations:** **Hydrolysis, followed by precipitation of chloride ion.** Acid chlorides are readily hydrolysed, even by water, to liberate free chloride ions. $RCOCl + H_2O \longrightarrow RCOOH + HCl$(aq) HCl (aq) $\longrightarrow H^+$ (aq) + Cl^- (aq) Ag^+(aq) + Cl^-(aq) $\longrightarrow AgCl$ (s) (white ppt)

Functional group	Reagent / conditions	Procedure	Observations
Amine	Moist red litmus paper **(Litmus test used as there is no other alternative test)**	Amines are basic.	**Moist red litmus turned blue.**
Phenylamine  	Br_2 (aq) (**Electrophilic substitution**)	To 2−3 drops of unknown liquid, add Br_2(aq) dropwise until in excess.	**Orange Br_2 (aq) decolourised, white ppt formed.** **Theoretical background / chemical equations:** $-NH_2$ group of phenol is strongly activating. Hence, multiple substitutions at benzene can take place without the need of a halogen carrier (e.g. FeX_3). **Electrophilic substitution** 
Amine salts e.g. $CH_3CH_2NH_3^+Cl^-$	NaOH(aq), warm (**Neutralisation**)	Add NaOH(aq) to a solution of unknown and warm. Hold moist red litmus paper at the mouth of the test tube.	**Pungent gas evolved, which turns moist red litmus blue.** **Theoretical background / chemical equations:** **Acid-Base reaction.** Amine salts are conjugate acids, they are acidic and can react with a strong base e.g. NaOH(aq) to regenerate amines. Amine will evaporate upon warming. $CH_3CH_2NH_3^+Cl^- + NaOH \longrightarrow CH_3CH_2NH_2 + NaCl + H_2O$

Functional group	Reagent / conditions	Procedure	Observations
Amide 	NaOH(aq), prolonged heating in hot water bath. **(Alkaline hydrolysis)**	To 1 cm depth of unknown liquid, add 1 cm^3 of NaOH(aq). Warm in hot water bath for 5 minutes. Hold moist red litmus paper at the mouth of the test tube. Note: Check for the evolution of gas within 5 minutes.	**Pungent gas evolved, which turns moist red litmus blue.** **Theoretical background / chemical equations:** **Hydrolysis** will yield **ammonia** for 1° amide or **volatile amine** for 2° amide which turns moist red litmus blue.  Suggest a reason why volatile amines are those with shorter hydrocarbon chain. **Answer:**

Planning Experiments

Organic Synthesis

A chemical reaction seldom yields only the desired product. Side-products, unreacted or excess starting materials and solvents are found together with the desired product. Thus, after an organic synthesis, we need to separate the product from the impurities and then purify it.

There are **5 stages** in the planning of organic syntheses.

1 Quantities to be used

1.1 Calculate the reagents and their volumes of solutions/ mass of solid required to synthesise a certain mass of product at a given percentage yield.

1.2 You are required to suggest a suitable apparatus with appropriate precision to measure the quantities calculated.

2 Experimental set-up (see **Figure 1** on pg 38)

1. If heat is required, **heat** is most often provided **over a period of time.** To avoid heating the reaction mixture to dryness, carry out **heating under reflux** (reaction mixture boils at the boiling pt of the solvent as its' vapour is returned to the reaction mixture with the help of a condenser.)

2. If a particular step in a multiple step synthesis is highly exothermic (suggested by the question), **slow addition of the chemical reagent** via a dropping funnel, coupled with **cooling** of the reaction vessel in an ice bath may be required before the reaction mixture undergoes reflux.

3 Isolation & Purification

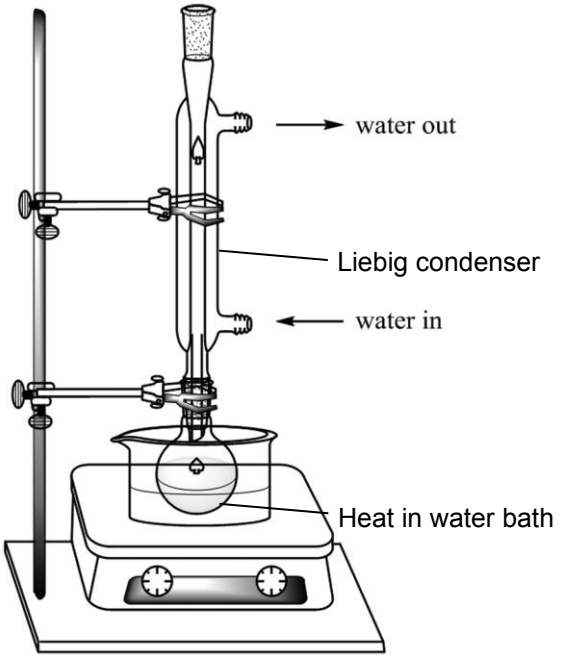
1. **Separation / isolation** of the desired product from the unreacted reactants, as not all reactants are converted to products.

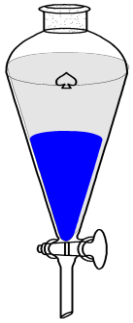
2. **Purify the product followed by drying the product** obtained using a suitable drying agent /method.

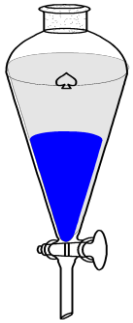
4 **Determine the purity** of the product by checking its melting or boiling point or by running a chromatogram.

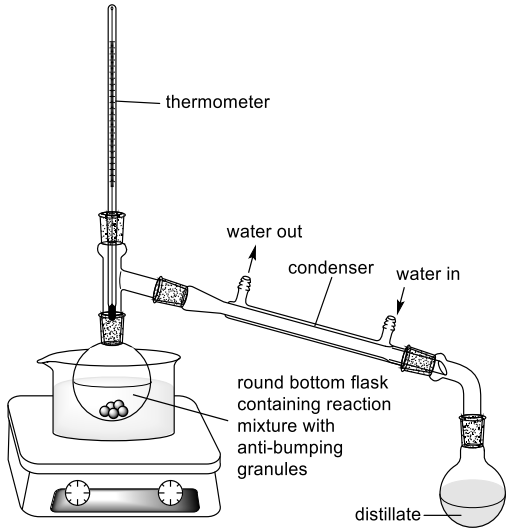
5 **Percentage yield calculation** can be used to compare the efficiency of different methods used to synthesise a particular product.

Techniques encountered in Organic Syntheses

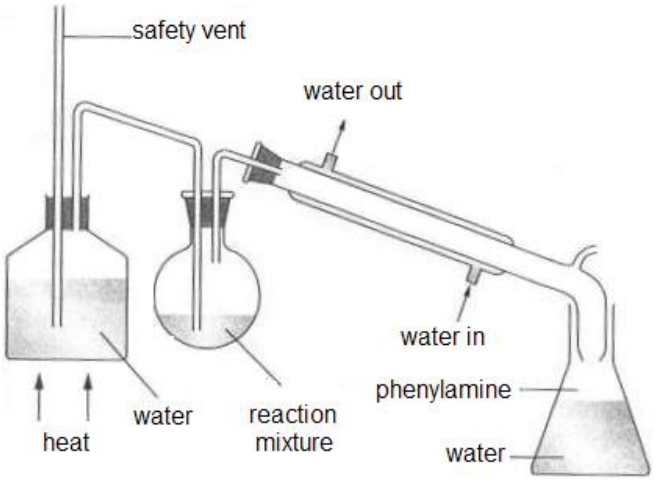
Purpose	Techniques	Remarks
Synthesis	▪ **Setting up a hot water bath and heating under reflux**  **Figure 1**	● Heating the reaction mixture under reflux involves heating a solution with an attached condenser to prevent organic reagents/products from escaping. Any vapour will condense on the cool surface of the attached condenser into liquid and flow back into the flask. Hence, heating a reaction mixture under reflux ensures: – **a higher yield (more complete reaction)** – **an increase in reaction rate** – **no loss of reactants and products due to vapourisation** – **prevents heating to dryness which may cause decomposition** ● Common apparatus: round bottom flask (ensures uniform heating of the mixture), Liebig condenser, electric heating mantle / water bath. ● Boiling chips / anti-bumping granules / magnetic stirrers are often added in the round bottom flask to ensure smooth boiling. ● No naked flame should be used for heating. Instead, an electric heating mantle / water bath should be used. (Note: a water bath limits the reaction temperature to 100 °C.) ● Water enters the Liebig condenser from the bottom to ensure that the temperature at the bottom of the condenser is the lowest so that all vapours will be condensed; none will escape. ● The opening at the top of the Liebig condenser is not stoppered to prevent build-up of pressure inside, resulting in explosion.

purification of product	**A** **Separatory funnel** – to separate liquid organic products that are immiscible(insoluble in) with water **Note**: Refer to the "density" data given by the question to tell if the organic layer is at the bottom or top layer. 	Separatory funnel can be used to: • Separate liquid organic product from water−soluble reactants / by−products so that the organic layer can be isolated. • By controlling the tap of the separatory funnel, the aqueous layer is discarded and the organic layer is washed with water to remove any residual water−soluble reactants / by−products or solvents, such as ethanol. • If acidic impurities are present, aq Na_2CO_3 can be added to wash the liquid organic product. Aq Na_2CO_3 reacts with the acidic impurities to form water-soluble salts. The aq layer is then discarded and the organic layer is washed with water again. • The liquid product is then dried with a suitable drying agent to remove any trace of water. • Fractional distillation is typically carried out to isolate the desired organic product. The different fractions are identified by their different boiling points. (Boiling point of a pure liquid should be ±2 °C of its actual boiling point) Note: A pure liquid should have a sharp boiling point. With impurities, the boiling point of the liquid is affected in two ways: 1.) The boiling point is increased. The more impurities the liquid contains, the higher its boiling point. 2.) The liquid would boil over a range of temperatures. **Example 1** (in general) Separation of organic product (small quantity) from inorganic impurities (large quantities): • Shake the aqueous solution with ether (solvent A) in a separatory funnel. • The organic compound will dissolve in the ether layer, leaving the inorganic impurities in the aqueous layer (solvent B). • Collect the ether organic layer and add a drying agent to remove any trace of water (when the organic layer is no longer cloudy). • Then carry out distillation to obtain the desired organic product.

purification of product	**A** **Separatory funnel** – to separate liquid organic products that are immiscible(insoluble in) with water 	**Example 2:** Preparation of 1-chloropentane by adding excess PCl_5 to pentan-1-ol. $CH_3(CH_2)_4OH(l) + PCl_5(s) \rightarrow CH_3(CH_2)_3CH_2Cl(l) + HCl(g) + POCl_3(l)$ ● $POCl_3$ has a b.p. of 105 °C, very close to that of 1-chloropentane (108 °C). ● Not possible to separate the two liquid products via fractional distillation, thus they are dissolved into two immiscible solvents, which can then be separated with the help of a separatory funnel. ● 1-chloropentane is soluble in ether (non-polar) while $POCl_3(l)$ which exhibits acidic property in aq medium dissolves readily in aq Na_2CO_3. ● After the removal of the aq layer, the organic layer is washed with water to remove traces of acidic impurities. ● It is then dried with anhydrous $CaCl_2$ and the organic product is obtained via distillation. **Example 3:** To separate miscible organic products with different acidic / basic properties. ● If there are 2 non-polar organic compounds miscible with each other and only one is acidic, treat the mixture with an alkaline solution so that the acidic compound is converted into a soluble salt and remains in aq layer which is immiscible with the non-polar organic compound. ● Similarly, if one of the organic compounds is basic, the mixture can be treated with aq acid to convert it into soluble salt in aq layer. $RNH_2 \rightleftharpoons RNH_4$ ● The soluble organic salt in the aq layer can then be recovered through addition of acid or alkali.

purification of product	**B** **Simple Distillation** – to separate liquid product with **b.p. different from other liquid reagents**. It does not decompose at the boiling temperature of the mixture.  	Simple distillation can be used to: • remove a volatile liquid from non-volatile ionic salts, which remain behind in the distillation flask. • separate 2 volatile liquids with significantly different boiling points from a homogeneous mixture. e.g. Separation of water from ethanol (b.p. of ethanol is 78 °C, b.p of water is 100 °C) • The thermometer bulb is placed near the opening of the Liebig condenser to measure the temperature of the gas entering the condenser. This is the boiling point of the distillate collected in the receiving flask. • A few boiling chips / anti-bumping granules are added to the reaction vessel to ensure smooth boiling. • Distillate collected should boil over ±2 °C of actual b.p of product. Sometimes, the receiving flask is placed in a beaker of ice to minimise the evaporation of the volatile distillate.

C **Steam distillation** followed by the use of a separatory funnel – for **unstable liquids** (decompose at the boiling point) **and immiscible with (insoluble in) water**



- Steam is passed into the reaction mixture, causing the pressure inside the flask to increase. This will enable the liquid organic product to boil off at a temperature lower than its normal b.p., preventing thermal decomposition.
- The distillate contains a mixture of water and the liquid product.
- The mixture is poured into a separatory funnel and the aqueous layer is removed. The liquid product is then dried with a suitable drying agent before distillation is used to determine its b.p. to check its identity and purity.

Example

When nitrobenzene is warmed with tin and conc HC*l*, tin is oxidised to $SnCl_4$ and nitrobenzene is reduced to phenylamine. Phenylamine reacts with conc HC*l* to from the salt, $C_6H_5NH_3Cl$.

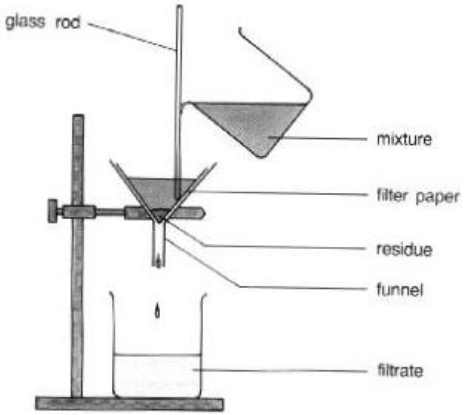
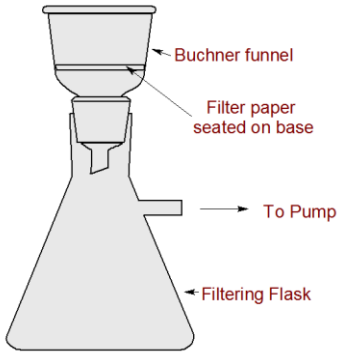
$$C_6H_5NO_2 + 6[H] + HCl \rightarrow C_6H_5NH_3Cl + 2\ H_2O$$

When an alkali is added, phenylamine and solid tin hydroxide are produced.

$$C_6H_5NH_3Cl\ (aq) + NaOH \rightarrow C_6H_5NH_2(l) + H_2O(l) + NaCl(aq)$$

$$SnCl_4(aq) + NaOH(aq) \rightarrow Sn(OH)_4(s) + 4\ NaCl(aq)$$

The volatile phenylamine is removed from the suspension of $Sn(OH)_4$ by steam distillation. The organic layer is separated from the aqueous layer using a separatory funnel and then dried with anhydrous $MgSO_4$.

purification of product	**C Simple filtration – separate solid from liquid**  **D Vacuum filtration – separate solid from liquid**  	• A simple filtration using a filter funnel to separate a solid from a liquid, but the process is slow as we need the help of gravity to "pull' the liquid through the filter funnel. To accelerate the filtrating process, vacuum filtration can be performed. • The filter flask is connected to a vacuum pump which creates a partial vacuum environment within the flask. The high atmospheric pressure above the surface of the liquid mixture pushes the liquid through the filter paper and filtrate is sucked into the flask. Proceeds **much faster** than normal filtration. **Demo Video of Vacuum Filtration** https://tinyurl.com/y866jg4c

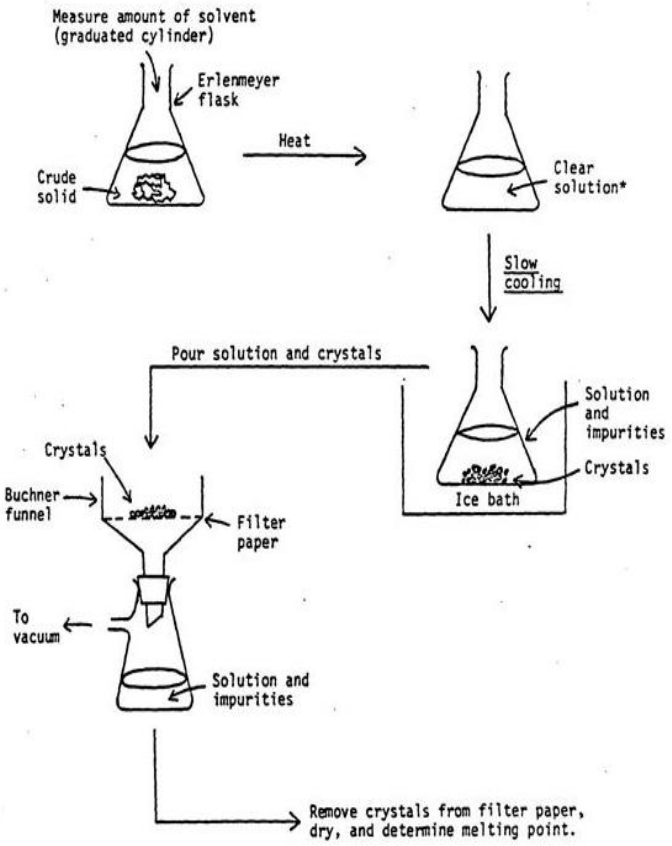
Purification of product

Demo Video of Recrystallization

https://tinyurl.com/yay3q24p

Recrystallization for solid product

The purpose of recrystallization is to obtain a pure solid product.



- Dissolve the impure substance in a **minimum amount of a hot solvent** to obtain a **saturated solution**.
- Filter the hot solution, using *fluted paper* and ***pre-heated*** *funnel* to remove insoluble impurities. Funnel has to be pre-heated so as *to prevent the desired solid product to precipitate out of solution.*
- Cool the filtered hot solution to allow the crystals of the pure substance to crystallize out.
- Filter the mixture to obtain pure crystals using a Buchner funnel.
- Collect the pure crystals on the filter paper and discard the filtrate that contains the soluble impurities.
- Wash the crystals with a little ice-cold solvent to remove any impurities which might have deposited on the surface.
- Leave the crystals on a watch glass to dry overnight or dry in a desiccator or an oven if solid is thermally stable.

To **determine the melting point in order to check purity** and confirm its identity:

- Put a small amount of solid in a capillary tube, placed in a heating bath
- Raise the temperature of the heating bath gradually (b.p. of heating bath must be higher than m.p. of the solid.)
- Observe the temperature at which melting begins and completes. Pure solid should have m.p. $\pm$ 2 °C of actual compound.

Note: A pure solid should have a sharp melting point. With impurities, the melting point of the solid is affected in two ways: 1.) The melting point is decreased. The more impurities the solid contains, the lower its melting point. 2.) The solid would melt over a range of temperatures.

Worked Example 1

Below is an account of the laboratory preparation of ethyl ethanoate (b.p = 77 ^{o}C). Addition of concentrate H_2SO_4 to the reaction mixture will evolve a lot of heat, therefore the addition had to be carried out with caution.

(a) Given that the densities of ethanol and ethanoic acid are 0.789 g cm^{-3} and 1.049 g cm^{-3} respectively, calculate the volumes of ethanol and ethanoic acid required to obtain 3 g of ethyl ethanoate where % yield of this reaction is 65%.

(b) Study the account of a procedure given below. Give an explanation for the purpose of each step /chemical underlined.

Measure ____ cm^3 ethanol and _____cm^3 ethanoic acid using measuring cylinder and transfer to a round bottom flask. Add slowly, with *swirling and cooling*, 1 cm^3 of *concentrated sulfuric acid*. Fit a *reflux condenser* and boil gently *for at least 30 minutes*.

Rearrange the apparatus for distillation and distil off everything with boiling point up to 82 ^{o}C. Transfer the distillate to a separatory funnel and shake with sodium carbonate solution. Run off the aqueous layer and discard it. Add a few pieces of anhydrous calcium chloride to the remaining organic product. When liquid is no longer cloudy, decant it into a small distillation flask. Distil and collect the fraction boiling between 75 to 79 ^{o}C. Expect a yield of about 3 g.

swirling and cooling	Addition of conc H_2SO_4 to reaction mixture is highly exothermic. Large amount of heat released may cause vaporisation of ethanol (loss of reactants). Thus slow addition accompanied with cooling is necessary.
concentrated sulfuric acid	It catalyses the condensation reaction between ethanol and ethanoic acid.
reflux condenser	To prevent loss of volatile reactants / products by condensing the vapour back to the reaction flask.
at least 30 minutes.	Prolong heating is necessary to ensure more complete reaction as reactions involving organic compounds are generally slow (have high E_a).
distil off	This is to separate organic compounds from non-volatile reactants. In this reaction, temperature has to be raised to 82 ^{o}C (b.p of ester is 79 ^{o}C). The inorganic reactants of higher b.p will remain in the flask.
sodium carbonate solution	As the organic layer may contain unreacted ethanoic acid / conc H_2SO_4, aq Na_2CO_3 is added to react with the acids to form water-soluble ionic salts, which can then be removed using a separatory funnel as the aq layer is immiscible with the organic layer.
Run off the aqueous layer and discard it	It contains water soluble impurities, does not contain the desired product.
few pieces of anhydrous calcium chloride(s)	It is to remove any trace of water from the organic product.
Distil and collect the fraction boiling between 75 to 79°C.	To isolate pure ester (organic product). Distillate collected at temperature (±2 °C of its boiling point) confirms its identity and purity.