Contents

OVERVIEW

- Planning is arguably one of the most demanding and difficult skills to learn. You must first develop **confidence in your practical abilities**.
- It is **not sufficient** that you simply learn to follow instructions; you must **understand the rationale** for using particular *approaches*, pieces of *equipment*, *recording* and *analysing* techniques, rather than simply being trained to perform a given exercise in a particular prescribed way.
- An appreciation of **precision** and **reliability** is essential when choices of measuring equipment are made, and when experimental procedures are worked out.
- An understanding of the **limits of reliability**, frequently described as **errors**, associated with individual pieces of apparatus is fundamental to the successful choice of apparatus for a given task.
- A similar argument applies to the identification of **variables** that need to be controlled, and the proposing of suitable measures to control them.
- The **advantages** and **limitations** of one type of measuring device, control measure or practical approach compared to other possibilities must be understood if the appropriate equipment, approach and quantities are to be used.

TYPE OF PLANNING

- Standalone planning only
- Standalone plan-and-carry-out
- Extension planning only
- Extension plan-and-carry-out

WRITING A PLAN

- The writing of a plan is divided into clearly defined stages, each of which must be addressed when producing an effective plan.
- However, given that practical exercises vary widely in their nature and purpose, it would be unwise to assume that there is a standard 'formula', with predetermined stages, to follow.
- The requirements of a **quantitative** exercise, the purpose of which is to propose and test a hypothesis (**Example 1**), or to measure a trend, will be very different to the requirements of a **qualitative** organic preparation (**Example 2**), where the student is required to devise a plan for the preparation of a given mass of product. The plan for an analytical investigation (**Example 3**) will be different again.
  - ✓ **Example 1** incorporates several different planning tasks. Firstly, you are required to plan how a pH curve for the titration might be obtained, and asked to predict the shape of this curve. Performing your planned titration exercise would then allow this hypothesis to be tested. To be effective, this part of the plan must contain sufficient detail, in terms of quantities, the number and range of measurements to be made and the means by which the results will be used to draw the pH curve, to allow an experienced chemist to perform the task. You must then plan how to deduce the pK_a value for the acid using your pH curve. Finally, the plan must describe how the required buffer solution is to be prepared, and how its effectiveness as a buffer is to be tested.
  - ✓ In **Example 2** you are provided with sufficient background information regarding the chemistry involved in the organic preparation so that no previous experience of this particular preparation is needed. What you do need, however, is experience of the various processes involved in the preparation, together with experience in mole and percentage yield calculations.
  - ✓ The approach to planning required in **Example 3** is very different to the approaches employed above. In this exercise, you must identify the different types of carbonyl compounds given in the question, decide how they differ in their chemical properties, select suitable chemical tests to allow them to be distinguished from each other and then produce a logical sequence for these tests. Finally, you must be able to demonstrate their understanding of the part played in the characterisation of a compound by the preparation of derivatives, and the use of spectroscopic analytical techniques (for H3 students).

Example 1: Measuring the K_a value of a weak acid

You are to plan experiments to find the pK_a value of a weak acid, to prepare a buffer solution using that acid and to test the buffering capacity of your buffer solution.

Background Information

- The weak acid is monobasic and may be represented as HA.
- When a weak acid is titrated with a strong base, then at the half-neutralisation point pK_a = pH (the pH when half the volume of base required to exactly neutralise the acid has been added to the acid).
- You can assume you start with exactly 0.100 mol dm^{-3} aqueous sodium hydroxide and approximately 0.100 mol dm^{-3} aqueous HA.
- A buffer solution resists large changes in pH when small amounts of acid or base are added.

Plan

Your plan should include the following:

1. Full practical detail of the experiments, including the apparatus you would use, and the measurements you would make, from which you could draw a **pH curve** for the reaction.
2. A sketch of the expected pH curve, which clearly shows how the values of the neutralisation volume, V cm^3, and the pK_a values are obtained.
3. A description of how you would prepare a buffer solution by mixing accurately measured volumes of HA and sodium hydroxide. The buffer solution should have a **pH equal to the pK_a value** of HA.

   Explain your choice of volumes by making reference to the expressions: $K_a = \dfrac{[H^+][A^-]}{[HA]}$ and pK_a = pH (at ½ neutralisation point)
4. A description of the experiments you will carry out to check the buffering capacity of the solution you have prepared. You must compare the changes in pH of your buffer with that of a control.

Suggested points for Example 1

1. **Setting up** and buffering pH meter/electrode
2. **Titration:**
   - rinsing pipette and burette;
   - HA in pipette;
   - measures volumes NaOH and pH;
   - records volume – smaller intervals near pH7;
   - continues adding excess NaOH.
3. **pH curve:**
   - axis/scales/shape correct;
   - fits scales;
   - shows working to get pK_a from V/2.
4. **Buffer:**
   - quotes volumes NaOH/HA to use;
   - volume NaOH = V/2;
   - adds small volume of **named** strong acid/base to test buffer;
   - uses water as control;
   - measures pH before/after each addition;
   - compares pH change of buffer/control

Example 2: Planning the preparation and purification of *N*-phenylethanamide

In this experiment you will use your knowledge of previous organic syntheses, and the information given below, to plan the preparation of a sample of *N*-phenylethanamide, $C_6H_5NHCOCH_3$ starting from phenylammonium chloride, $C_6H_5NH_3Cl$, which is a salt of phenylamine.

Intended lesson outcomes

By the end of this exercise you should be able to:

- produce a detailed plan whereby a specified quantity of purified product may be prepared;
- decide how the yield of product will be calculated;
- decide how the purity of the product will be assessed;
- assess the risks involved and suggest appropriate safety precautions.

Background information

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

Phenylamine is most conveniently used in the form of the salt phenyl ammonium chloride.

The reaction is performed in two stages.

1. A solution of sodium ethanoate is treated with phenylammonium chloride, forming phenylamine, ethanoic acid and sodium chloride.
2. Phenylamine then reacts with ethanoic anhydride to form *N*-phenylethanamide as a white solid, together with ethanoic acid.

An aqueous solution of phenylammonium chloride (5.0 g in 150 cm^3) is mixed with ethanoic anhydride (10 cm^3). To this mixture is added a second aqueous solution containing sodium ethanoate (30 g in 125 cm^3). The sodium ethanoate causes the reaction in step 1 to occur. Once phenylamine is released, it reacts readily with ethanoic anhydride to form *N*-phenylethanamide as a white solid. The crude solid product is isolated and recrystallised from water. Typically a yield of around 70% of the theoretical maximum is obtained.

Note

An excess of ethanoic anhydride is used in order to ensure a good yield.

The task

Give **full details** of how a 2.0 g sample of **pure** crystalline *N*-phenylethanamide could be prepared using the above solutions, without preparing an excess of product. When calculating the quantities of materials to be used, you should assume a **maximum overall yield** for the preparation of **70%**.

Give details of a physical test you would perform to confirm the purity of the crystals.

Your plan should include:

1. a list of the essential apparatus you would use;
2. equations for the reactions taking place;
3. the relative formula masses, M_r values, of phenyl ammonium chloride and *N*-phenylethanamide;
4. the mass of phenylammonium chloride needed to make 2.0 g of *N*-phenylethanamide assuming a 100% yield;
5. the quantities of phenylammonium chloride, ethanoic anhydride and sodium ethanoate needed to make 2.0 g of *N*-phenylethanamide assuming a 70% yield;

Note: The workings for all calculations should be shown.

6. full details of procedures by which 2.0 g of **pure**, **dry** *N*-phenylethanamide could be prepared;
7. a physical test that you would do in order to assess the purity of your product;
8. a full description of how you would perform the physical test for purity, and how you would interpret its results;
9. details of any potential risks in the procedure, and appropriate safety precautions to be taken.

Suggested points for Example 2

1 Scale and precision:

1. The correct equation for the reaction between phenyl ammonium chloride and sodium ethanoate.

   $C_6H_5NH_3Cl + CH_3COONa \rightarrow C_6H_5NH_2 + CH_3COOH + NaCl$
2. The correct equation for the reaction between phenylamine and ethanoic anhydride.

   $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3COOH$
3. M_r values: for phenylammonium chloride = 129.5; for *N*-phenylethanamide = 135.
4. Theoretical amount of phenyl ammonium chloride needed for 2.0 g yield = 1.92 g.
5. Actual amount for phenyl ammonium chloride 2.0 g yield = 2.74 g.
6. Sensible quantities of the other reagents.

2 Method, including apparatus:

1. 1 measuring cylinders
2. 2 conical flask or other suitable vessel
3. 3 access to a balance
4. 4 filtering apparatus, e.g. Büchner apparatus
5. 5 mixes solution and stirs
7. removes crude product by filtration
8. washes crude product with cold water

3 Purification of the crude product:

1. dissolves in the minimum quantity of hot water
2. filters while hot
3. cools hot solution, filters crystals, dries crystals
4. weighs dry sample

4 Assessing the purity of the recrystallised product:

1. appropriate method chosen, e.g. melting point (possibly mixed melting point or the use of spectral analysis)

   describes likely outcome – e.g.
2. product melts sharply
3. melting point agrees with data book value

   describes basic technique to be used – e.g.
4. sample placed in melting point tube
5. states type of / describes melting point apparatus
6. heats slowly near melting point

5 Safety:

1. phenyl ammonium chloride and *N*-phenylethanamide are both **toxic**
2. ethanoic anhydride is **corrosive**
3. there are potential **fire hazards** with organics
4. avoid skin contact
5. wash areas affected by spillage with water
6. wear gloves
7. wear eye protection

Example 3: Planning an experiment to identify a carbonyl compound

In this exercise you will use your knowledge of the chemistry of carbonyl compounds to plan a series of experiments to identify a carbonyl compound from a small number of samples. (For H3 students, you may also make use of spectroscopic data to confirm your identification.)

Intended lesson outcomes

By the end of this planning exercise you will be able to:

- identify the relevant structural features of carbonyl compounds;
- select suitable tests to use to identify an unknown carbonyl compound;
- give outline details of each test, including possible observations;
- outline the preparation and purification of a solid derivative;
- discuss the use of spectroscopic data in confirming identity;
- assess the risks involved and suggest appropriate safety precautions.

The exercise

In this exercise you will be assessed on your ability to plan experiments to identify a carbonyl compound and to use spectroscopic data to confirm your identification.

Background Information

The carbonyl compound you have to identify is one of the following.

- propanal
- propanone
- butanal
- butanone
- pentan-2-one
- pentan-3-one

In your plan you must first identify the structural features of these compounds by which you will be able to distinguish between them. You should then propose an appropriate series of tests and spectral analyses to perform.

- Your plan does not need to include quantities but should give reagents and conditions.
- The carbonyl compounds are all colourless, flammable liquids.
- Your plan for the laboratory exercises should allow for the compound being any one of those listed. However, when describing the use of spectroscopic data, you may use one of the compounds as an example.
- You may use the NMR data tables provided to find chemical shift values.

Plan

Your plan should follow the sequence outlined below.

1. Identify the structural features of the carbonyl compounds that you will make use of in your tests and spectral analyses.

Chemical testing

2. Give an outline, including any possible observations, of a test you would perform to confirm that the unknown is a carbonyl compound.
3. Give an outline, including any possible observations, of a test you would perform to distinguish between an aldehyde and a ketone.
4. Give an outline, including any possible observations, of a test you would perform to identify all the compounds with a β-keto group (CH_3CO–).
5. Describe how you would confirm the identity of the compound by preparing a solid derivative. You should include full practical details of how the derivative would be purified and how it would be used to confirm the identity of the carbonyl compound.

Safety considerations

6. Perform a risk assessment of your plan.

Suggested points for Example 3

Structural Features

- Propanal and butanal have –CHO group and so are **aldehyde**.
- Propanone, butanone, pentan-2-one and pentan-3-one have –COC– group and so are **ketones**.
- Propanone, butanone and pentan-2-one have a ®**-keto group** (CH_3CO–) group and so give positive results with the **tri-iodomethane** (**iodoform**) test.

Carbonyl test

- Add compound to 2,4-dinitrophenylhydrazine solution.
- Yellow/orange precipitate with all five compounds.

Aldehyde/ketone test

- Add compound to ammoniacal silver nitrate and warm, or to Fehling's solution and heat.
- If silver mirror/red precipitate formed then compound is an aldehyde.
- If no silver mirror/red precipitate formed then compound is not an aldehyde so, as it is a carbonyl compound, it is a ketone.

Tri-iodomethane (iodoform) test

- To compound add KI(aq) and NaC*l*O(aq) and warm the mixture.
- Cool the mixture; fine yellow crystals form with ®-keto compounds.
- If no yellow precipitate, then compound does not contain a ®-keto group.

Derivative

- Prepares 2,4-dinitrophenylhydrazine derivative (a 2,4-dinitrophenylhydrazone).
- Suggests a suitable quantity to prepare (students could be told to give details of quantities, or a reference to making 'sufficient for a melting point determination' might be acceptable).

Recrystallisation

- Filter off 2,4-DNPH derivative and dissolve in **minimum volume** …
- … of **hot solvent**
- Details of how to filter solution **hot** (e.g. fluted filter paper/pre-heated funnel/Büchner funnel).
- Cool solution and crystals form.
- Filter crystals using Büchner funnel and flask, wash crystals with cold solvent and dry.

Melting point

- Find melting temperature of crystals – brief details of technique to be used.
- Compare melting temperature with those listed in data book or similar.

Safety

- Avoid use of naked flame/use of water bath because liquids flammable.
- Wear eye protection at all times.

1. Defining the Problem

1.1. For a quantitative exercise

- You should be able to use information provided about the **aims** of the investigation, or experiment, to **identify both the independent and the dependent variables**.
  - ✓ Also, the other **key variables** must be identified and effective measures proposed to control them.
- You may be required to use your knowledge and understanding of the topic under consideration to make a **quantitative prediction** of the likely outcome of the experiment.
  - ✓ The purpose of the plan would then be to **test this hypothesis** in a manner which is *reliable*, *unambiguous* and, above all, *reproducible*.
  - ✓ Even if making a formal hypothesis is not a requirement of an exercise, you will still need to have a clear idea of what you **expect the results to show** if you are to analyse and evaluate your results effectively.
- The data obtained in the exercise will then require **processing** in some way in order to allow for **analysis and evaluation**.
  - ✓ The plan must contain details of how these processes are to be carried out.
  - ✓ If the experiment is to generate **quantitative data**, then the *recording*, *graphical* and *numerical* processes involved in the data analysis must be clearly laid out.
  - ✓ The steps by which the analysed data, and the experimental procedure, are to be **evaluated** should also be described.

1.2. For a qualitative exercise

- Examples of this type of planning exercise would be the preparation of a required mass of product in an organic synthesis or the devising of an analysis scheme to identify an unknown compound.
- Clearly, a different approach is required for such examples, compared to that used to plan a quantitative exercise, but you are likely to find them to be just as demanding.
- Whatever the type of planning exercise, the plan should be sufficiently robust that, when performed by competent chemists, the outcomes will not vary beyond anticipated limits. Without first-hand experience of the approach and procedures to be used, it is highly likely that the plan will be flawed.

2. Method

- The proposed **experimental procedure** should be workable. It should, given that the apparatus is assembled appropriately, allow data to be collected without undue difficulty.
- There should be a **description**, including **diagrams**, of how the experiment should be performed and how the key variables are to be controlled.
- **Equipment**, of a level of **precision** appropriate for the measurements to be made, and **quantities** to be used should be specified.
- The use of **control experiments** should be considered.
- Also, details of how the **data** are to be *recorded*, *manipulated*, *analysed* and *evaluated* should be given.

Aspects of the planning process which students frequently find difficult are

- deciding on a **suitable scale** for the experiment, and

  you should frequently question procedures such as 'Why do we use this amount of solid?' or 'Why do we choose this volume of liquid?' when you are following an experiment from a worksheet, rather than blindly follow a recipe.
- choosing **suitable apparatus**.

  the choice of apparatus should be questioned. By doing this, you will gain experience in these areas and so be better prepared when you have to make such decisions.

In some cases, the choice of volume or apparatus will have a significant influence on the **precision** and **reliability** of an experiment. Such knowledge is of great value when choosing suitable volumes in a planning exercise.

3. Planning Analysis, Conclusions and Evaluation

Consideration should be given in the plan of how the data obtained in an experiment are to be **analysed**, **interpreted** and **evaluated**. Valid and reliable conclusions can be drawn only if the strategies devised to address these points are effective.

This may involve the generation of a results table and the use of graphical techniques, the determination of yield and purity in a preparative experiment such as **Example 2**, or the devising of a logical framework for deciding on the identity of an unknown sample such as in **Example 3**. Again, the wide range of possible planning topics requires flexibility, and perhaps even ingenuity, when responding to planning tasks.

3.1. Analysing Data

This skill requires you to apply your understanding of **underlying theory**. Even when that understanding is present, the presentation of a clear, lucid, watertight argument does not come naturally to most people and therefore, much practice in this area is recommended.

Any conclusion made on the basis of data obtained from an experiment must be fully reasoned and justified. This justification may take the form of a

- **written argument**, for example in the interpretation of the results of a series of tests designed to determine the identity of an unknown compound, as in **Example 3**.
- **extended calculation**, as would be required, for example, in the determination of the Avogadro constant.
- **graphical steps**, as would be required, for example in the tracking of changes in concentration with time for a kinetics experiment.

The steps followed as an argument is developed, must be sequential, clear and easy to follow.

3.1.1. Calculations

To confidently analyse numerical data, you must be both proficient in handling the mathematics involved and experienced in the calculation sequence involved.

You should be aware that the **number of significant figures** to which the answer is expressed shows the **precision** of a measured quantity. Therefore, care should be taken with regard to the number of significant figures quoted in answers. The general rule is to use the same number of significant figures as are found in the **least precisely measured quantity**.

3.1.2. Error analysis

Another skill which many find difficult to master is that of error analysis. There are **two** basic **types of error** that affect results; these are:

- **'random' errors**, and

  random errors cause results to fluctuate around a mean value; *can be reduced by **averaging** a set of values, e.g. through graphing.*
- **'systematic errors'**.

  systematic errors affect all measurements in the same way, in that the value of a measured quantity is always higher or always lower than the true value; *systematic errors **cannot** be reduced by averaging.*

You should be familiar with two **sources** of 'error':

- **'apparatus error'**

  inherent in the use of a particular piece of equipment/apparatus. There is a 'range of **uncertainty**' associated with measurements made with that piece of apparatus. This uncertainty will be present no matter how skilled the operator might be, and will generate *random errors*. Also, poor calibration of a piece of apparatus/equipment can generate *systematic errors*; for example, a weighing balance or a voltmeter on which the zero point is incorrectly set.
- **'experimental error'**

  a direct consequence of the level of incompetence of the operator or of flaws in the experimental procedure.

If the **overall error** for an experiment, as measured against a reliable benchmark, is greater than the **combined apparatus errors**, students should look for flaws in technique or experimental procedure.

When more than one piece of apparatus is used to measure quantities in the same experiment, then each piece of apparatus will introduce its own error, or 'uncertainty', and so should be included in the **'overall apparatus error'** for the experiment.

- To do this, it is necessary to separately calculate the error associated with each measurement. The 'overall apparatus error' is the **sum of the errors** associated with each piece of apparatus.
- *E.g.* imagine a 25.0 cm^3 pipette is used once and a burette is read twice in a single titration. The precision of the pipette

may be ±0.060 cm^3, while that for the burette may be ±0.05 cm^3. The error for each reading of the burette is ±0.05 cm^3; however, as the burette is read twice (initial and final readings), the total error in using the burette to obtain a single titre value is $\pm 0.05 \times 2 = \pm 0.10$ cm^3.

- The error in the use of the pipette would be $\frac{0.060}{25.0} \times 100 = \pm 0.24\%$. The error in the use of the burette for a titre of say 23.50 cm^3 would be $\frac{0.10}{23.50} \times 100 = \pm 0.43\%$.

  The 'overall apparatus error' would be $\pm 0.24 \pm 0.43 = \pm 0.67\%$.
- If a weighing balance and a volumetric flask were also used in the experiment, then the 'total apparatus error' would include the errors associated with the use of these pieces of apparatus. These would be calculated in a similar manner to the errors in pipette/burette described above.

3.2. Evaluation

Arguably, this is one of the most important, and probably one of the most difficult, skills to acquire. In order for an evaluation to be effective, you must have a clear understanding of the aims, objectives and predicted outcomes of the exercise. Without such knowledge you will be in no position to judge the effectiveness of the procedures used.

The evaluation procedure may include:

i. the identification of **anomalous values**, deducing possible causes of these anomalies and suggesting appropriate means of avoiding them;

- **Anomalous results** are those which do not fit in with the pattern formed by the other results of an experiment.
- If such results are to be identified, the expected pattern must be known. This pattern could be predicted as part of a hypothesis or deduced from the clear trend shown by the remaining results.
- However, when the anomalous value is identified, the selection of this value must be supported by **evidence**.
- Once an anomalous value has been identified, it is necessary for students to attempt to explain the *origin of the anomaly* and to *propose strategies to deal with it*. These might include repeating the measurement or omitting it.

ii. the **adequacy of the range of data** obtained;

- In some experiments, once a curve has been plotted, it may become clear that the experiment **has not provided sufficient data** in some parts of the curve.
- Thus, the number of measurements taken and/or the range of measurements taken were not adequate.
- When evaluating such an experiment, it would be sensible to propose the inclusion of extra measurements and to specify where these extra measurements should be made.

iii. the **effectiveness** of the measures taken to **control variables**;

- When the results of a quantitative experiment are shown to be **inaccurate**, these results should be evaluated. Students must be able to deduce *whether the errors in the data obtained in an experiment exceed those expected due to the apparatus used*.
- If the errors in the experimental result do **exceed** the total apparatus error, then *flaws in the procedure* that may have generated these excess errors must be identified. Having identified potential flaws, one must have sufficient knowledge of the process involved, that they are able to suggest changes to the procedure that will result in a more accurate or reliable outcome. If the perceived flaw lies, for example, with temperature fluctuation, it would be of little use to simply state that the temperature should be controlled. What is needed is a practical solution to this problem, such as the use of a thermostatically-controlled water bath.
- If the errors in the data **do not exceed** those expected due to the apparatus used, then *improvements to accuracy* could still be achieved by changing the apparatus used. If, for example, the perceived flaw lies with the precision of a mass measurement, rather than making a vague reference to the use of a 'more precise balance', you should specify the precision of the replacement balance to be used, for example, 'instead of using a balance weighing to ±0.1 g, use a balance weighing to ±0.01 g'.

iv. an informed judgement on the **confidence** with which conclusions may be drawn.

- For conclusions to be drawn on the basis of the results of an experiment, it is essential that the results of the experiment inspire confidence.
- If an experiment worked well, it is necessary that this judgement be supported by evidence from the analysis and evaluation of the experimental results.

3.3. Drawing Conclusions

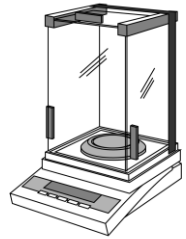
This is also a higher-level skill, which will demand a thorough understanding of the basic theory that underpins the chemistry involved.

The conclusions drawn from a set of data must be judged on the basis of the **strength or weakness** of any **support for or against the original hypothesis**, or on the results of qualitative tests. You should be able to use the detailed scientific knowledge and understanding you have gained in theory classes in order to make judgements about the validity of the conclusions you have drawn.

BASIC LABORATORY PROCEDURES

A. Balances and Weighing


General-purpose Balance


Analytical Balance

There are essentially two types of balance:

1. General-purpose balances which weigh to the nearest 0.01 g with a capacity of about 300 g. Chemicals can be dispensed for weighing, into a suitable weighing container, **directly** onto these balances.
2. **Analytical** (three-figure) **balances** for quantitative work, which weigh to the nearest 0.001 g and have a maximum capacity of about 100 g. Chemical *must not* be transferred onto the balance at any time and analytical balances must be used for **weighing by difference**.

B. Working with Liquids

Table 1 Criteria for choosing a method for measuring out a liquid

Method	Best volume range	Accuracy	Convenience
Pasteur / Dropping pipette	1–5 cm^3	Low	Convenient
Conical flask/beaker	25–1000 cm^3	Very Low	Convenient
Measuring cylinder	**5–1000 cm^3**	**Medium**	**Convenient**
Volumetric flask	**100; 250; 1000 cm^3**	**High**	**Convenient**
Burette	**1–50 cm^3**	**High**	**Convenient**
Pipette	**10; 25 cm^3**	**High**	**Convenient**
Syringe	0.1–100 cm^3	Medium	Convenient
Weighing	Any	Very high	Inconvenient

In general, there are two levels of accuracy required for the preparation of solutions:

1. General-purpose solutions – solutions of chemicals used in qualitative and preparative procedures when the concentration of the chemical need not be known to more than one or two decimal places. *E.g.*
   a. Solutions used in extraction and washing processes
   b. Solutions of chemicals used in **preparative experiments** where the techniques of purification introduce intrinsic losses of substances
   c. **Kinetics** and **thermochemistry** experiments
2. Analytical solutions – solutions used in quantitative analytical procedures where the concentration needs to be known to an accuracy of three to four decimal places. *E.g.*
   a. Volumetric procedures (**titrations**) and gravimetric analysis, where the concentrations of **standard solutions** of reagents and compounds to be analysed need to be accurately known.

b. Spectroscopy

c. Electrochemical measurements: pH titrations, conductivity measurements

d. Chromatographic methods

The procedures for weighing and the glassware used in the preparation of solutions differ according to the level of precision required.

Similar considerations apply to the choice of apparatus used in the measurement of volumes of solutions for different purposes.

C. Preparation of an aqueous solution of known concentration from a solid chemical

Pre-calculation:

1. Decide the concentration of chemical required.
2. Decide on the volume of solution required.
3. Find out the molar mass of the chemical.
4. Work out the mass of chemical that will give you the *concentration* desired in the *volume* required.

$$\text{concentration} = \frac{\text{amount(mol)}}{\text{volume}(\text{dm}^3)} = \frac{\dfrac{\text{mass(g)}}{\text{molar mass}(\text{g mol}^{-1})}}{\text{volume}(\text{dm}^3)}$$

Procedure:

1. Weigh out the required mass of chemical to an appropriate accuracy. *[If the mass is too small to weight with the desired degree of accuracy, consider the following options:*
   - *Make up a greater volume of solution, or*
   - *Make up a more concentrated solution, which can be diluted later on]*
2. Add the chemical to a beaker or conical flask and then add a little less deionised water than the final volume required. *[If some of the chemical sticks to the weighing receptacle, use some of the water to wash it off. For accurate solutions, see D below for accurate weighing and quantitative transfer.]*
3. Stir and, if necessary, heat the solution to ensure all the chemical dissolves.
4. Make up the solution to the desired volume. *[If the concentration needs to be accurate, use a volumetric flask (see D below); if a high degree of accuracy is not required, use a measuring cylinder.]*

D. Preparation of an aqueous solution of known concentration (standard solution) from a solid chemical for use in *quantitative analysis*

1. Weigh out the required mass of chemical into a weighing bottle using an analytical balance.
2. Tip the contents of the weighing bottle into a clean, dry 100 cm^3 beaker.
3. Reweigh the weighing bottle on the analytical balance.
4. Add 50 cm^3 of deionised water to the beaker and stir the mixture gently with a clean glass rod until all the solid has dissolved.
5. Carefully transfer the solution into a clean 250 cm^3 volumetric flask, rinsing the beaker with deionised water.
6. Make the solution up to the mark using deionised water.

In analytical work, you may need to **dilute a standard solution** to give a particular mass concentration or molar concentration:

1. Transfer an appropriate volume of standard solution to a volumetric flask, using appropriate equipment (**Table 1**).
2. Make up to the calibration mark with solvent – add the last few drops from a dropping pipette until the bottom of the meniscus is level with the calibration mark.
3. Mix thoroughly by repeated inversion.

Dilution series are used in a wide range of procedures including the preparation of standard curves for the calibration of analytical instruments and kinetics studies where the rate for a series of different concentrations is determined.

Pre-calculation:

1. Calculate the amount of chemical required for the **standard solution**.
2. Use $[C_1]V_1 = [C_2]V_2$ to calculate the volume of standard solution for each member of the series.

Procedure:

1. Make the standard solution by the quantitative method described in *D* above.
2. Pipette or syringe the calculated volume into an appropriately sized volumetric flask and make up to the mark with deionised water.
3. Repeat the calculation for each of the other diluted solutions as required.

In some procedures, for example, initial rate method in kinetics when the concentration of a dilution series need not be known to a high degree of precision, the dilution can be performed by mixing different volumes of the chemicals in the reaction vessel.

Usually, the *total volume is kept constant*, by topping up with *deionised water*, so that the concentration is *proportional* to the volume of chemical used.

For example, using standard solutions of **A** and **B** of 1.0 mol dm^{-3} and 1.5 mol dm^{-3} respectively,

V_A/cm^3	V_B/cm^3	V_{water}/cm^3	V_{total}/cm^3	[A]/ mol dm^{-3}	[B]/ mol dm^{-3}
5.0	10.0	20.0	35.0	$\frac{5}{35}\times 1 = 0.14$	$\frac{10}{35}\times 1.5 = 0.43$
10.0	10.0	15.0	35.0	$\frac{10}{35}\times 1 = 0.29$	$\frac{10}{35}\times 1.5 = 0.43$
15.0	10.0	10.0	35.0	$\frac{15}{35}\times 1 = 0.43$	$\frac{10}{35}\times 1.5 = 0.43$
20.0	10.0	5.0	35.0	$\frac{20}{35}\times 1 = 0.57$	$\frac{10}{35}\times 1.5 = 0.43$

The volumes of solution **A** and **B** can be measured using a measuring cylinder as a high degree of precision is not required.

E. Temperature Measurement

Any physical property which is dependent on temperature and which is readily reproducible could be considered a potential basis for a 'thermometer' to measure temperature changes.

The absolute thermodynamic scale of temperature, the Kelvin scale devised by Lord Kelvin (1851), is independent of the properties of any particular substance. Only the size of the degree is arbitrarily chosen by making the difference between the ice point and the steam point 100 ºC; the scale is defined by making the temperature of the triple point of water 273.16 K.

The choice of thermometers boils down to the most convenient method of thermometry for the temperature range involved:

Table 2 Method of Thermometry

Method of thermometry	Useful range (ºC)	Advantages	Disadvantages
Platinum resistance thermometer	–260 to +1100	Very high accuracy can be achieved	Construction difficult; costly; size large
Liquid expansion thermometer			
a) Mercury-in-glass	**–38 to +400**	**Simple to use**	**Either range or accuracy limited**
b) Alcohol-in-glass	**–80 to +100**	**Simple to use**	**Accuracy low**
c) Pentane-in-glass	–190 to +20	Convenient for low temperature baths	Accuracy low
Thermocouples			
a) Copper-constantan	–250 to +400		Deteriorates rapidly above 300 ºC
b) Chromel-alumel	–250 to +1100	Usable for short periods up to 1300 ºC	Frequent calibration needed
c) Platinum/ rhodium-platinum	–100 to +1500	Stable and reproducible	High cost

Mercury-in-Glass Thermometers

These thermometers are very convenient provided absolute accuracy of about 0.1 ºC is sufficient. Normally a calibration at the steam point (100 ºC) and the ice point (0 ºC) will show whether a thermometer is sufficiently reliable. The precision of reading using a mercury-in-glass thermometer is taken to be half the smallest division.

Temperature Control – Thermostatically-controlled water bath

As most of the properties studies in physical chemistry are affected by temperature, it is very important to have means whereby experiments can be carried out at constant temperature. Constant temperature baths, or *thermostatically-controlled water baths*, are therefore an essential part of the equipment of a laboratory.

F. Filtration

Filtration is the physical separation of a solid from a liquid and is a process encountered in experimental procedures such as gravimetric analysis and recrystallisation.

The type of filtration equipment depends upon which of the two components, the solid or the liquid, one is trying to isolate. In general,

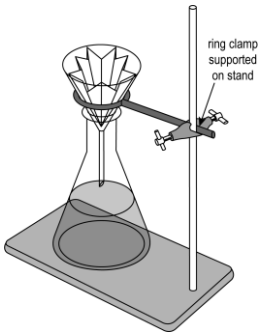
- To isolate the **liquid** – use *gravity filtration*

  A *fluted* filter paper decreases the area of contact between the filter paper and the funnel, thus allowing rapid filtration.

- To isolate the **solid** – use *suction (vacuum) filtration*

  Relies on producing a partial vacuum in the receiving flask. The essential components are:

  ✓ A ceramic funnel containing a flat perforated plate: a Büchner funnel

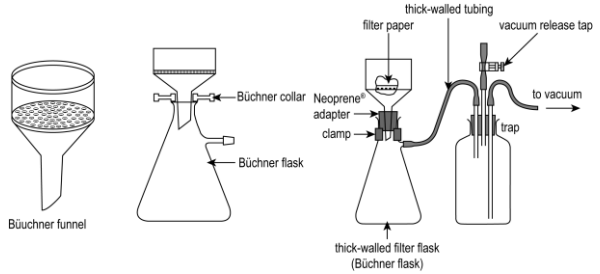


gravity filtration

  ✓ A receiver flask with a side arm for attachment of the vacuum source: a Büchner flask

  ✓ A flexible seal between the ceramic funnel and the receiving vessel: a filter seal

  ✓ A source of vacuum which is connected to the receiving flask by thick walled rubber tubing. Sometimes there will be a trap between the vacuum source and receiving flask



G. Heating

In a laboratory one will be required to heat chemicals in dissolution of a solid, promotion of reaction (reflux), distillation of pure compounds and mixtures, extraction, drying of solid compounds, etc. The choice of heat source depends upon several factors:

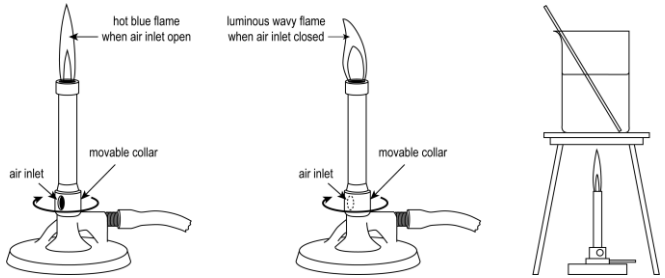
- First and foremost, the *flammability* and *volatility* of the chemical and solvent.
- The operation to be carried out, *e.g.* simple preparation of a solution, reflux or distillation.
- The temperature required for the process.
- The amount of chemical or solvent to be heated.

Bumping

This is when the liquid suddenly boils without any warning and results in hot liquid and vapour shooting uncontrollably out of the container. Add one or two 'boiling stones' or 'anti-bumping granules' to provide a point in the liquid where vaporisation can occur in a controlled manner; these can be filtered off later in the process.

Bunsen burner

Bunsen burner are commonly used for heating aqueous solutions in flat-bottomed vessels supported on a tripod and wire gauze.



Water bath

Maximum temperature of 100 ºC; safe to use even with most flammable chemicals and solvents.

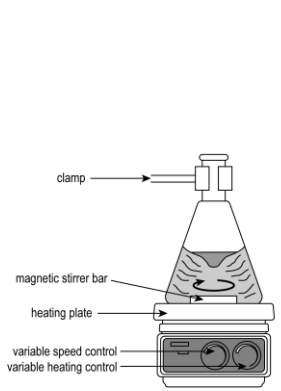
Hot plates and stirrer hot plates

These consists of a flat metal or ceramic plate, which is heated electrically. Normally, have a built-in **magnetic stirrer**, which can be used to stir the liquid with a *magnetic stirrer bar* (this helps to prevent bumping too).

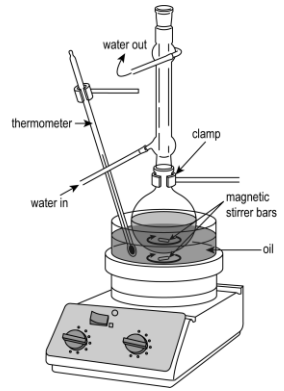
Hot plats should only be used for heating flat-bottom vessels such as beakers or conical flasks and only when the liquid being heated is non-flammable.

Oil baths

These are mostly used to heat round-bottom flask at temperatures above 100 ºC. The oil bath, containing the heating fluid, is usually a glass dish and heated on a stirrer hot plate, and the temperature of the bath is measured with a thermometer.



hot plate stirrer



hot plate stirrer with oil bath

H. Cooling

Ice baths

A slurry of crushed ice and water can be used to give a cooling bath in the range 0 ºC to 5 ºC. Pure crushed ice does not give good contact with the glassware and inefficient cooling results.

If temperatures below 0 ºC are required, mixtures of crushed ice and various inorganic salts can be used as shown in **Table 3**.

Table 3 Ice-salt mixtures

Salt	Ratio (salt : ice)	Temperature
$CaCl_2.6H_2O$	1 : 2.5	–10 ºC
NH_4Cl	1 : 4	–15 ºC
$NaCl$	1 : 3	–20 ºC
$CaCl_2.6H_2O$	1 : 0.8	–40 ºC

I. Drying Glassware

For most general laboratory applications glassware can be dried in an **electric oven** between 80 ºC and 90 ºC or by rinsing the glassware with a small amount of water-miscible solvent, such as propanone or ethanol, and then evaporating the solvent using a compressed-air jet.

If glassware is required for *anhydrous reaction* (e.g. reactions involving $LiAlH_4$), it must be heated in the oven above 100 ºC, assembled while hot and allowed to cool while a stream of inert gas (e.g. N_2) is passed through it.

J. Drying Solids

Here the term 'drying' means removal of a solvent, not specifically water, from a solid by evaporation. The rate of evaporation and thus the rate of drying can be increased by one (or all) of the following:

Heating the chemical

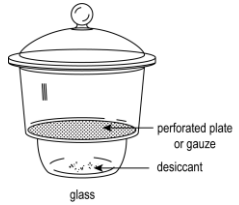
- Only chemicals which are *thermally stable* should be dried by heating.

  ✓ Most *inorganic compounds*, which are salts with relatively high melting points, can be dried in an electric oven to remove water.

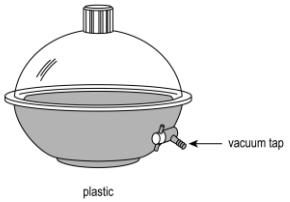
  ✓ On the other hand, *organic compounds*, many of which have relatively low melting points, have to be treated with more care.

Using a drying agent in a closed container to absorb the solvent

- If a compound cannot be dried in the oven, then use a *desiccator*. Desiccators are made from glass or plastic and some, vacuum desiccators, are equipped with a tap to allow evacuation as shown below.



glass



plastic

- The bottom of the desiccator is filled with a drying agent (desiccant) and the chemical, on a watch-glass or clock-glass, is placed on the perforated plate/gauze above and the desiccator closed by sliding the lid onto the desiccator to provide an air-tight seal.
- The desiccant absorbs the solvent from the 'atmosphere' in the desiccator as it evaporates from the solid. The nature of the desiccant depends upon the solvent to be removed.

Table 4 Drying agents for desiccators

Solvent to be removed	Drying agent	Comments
H_2O	**Silica gel**	Most common
	$CaCl_2$	Most common
	Solid KOH	Corrosive
	P_4O_{10}	Corrosive
	Conc. H_2SO_4	Corrosive liquid
ethanol, methanol	$CaCl_2$	
hydrocarbons	Paraffin wax	

Reducing the atmospheric pressure

- The rate of drying can be increased by evacuating the desiccator and vacuum desiccators are specially designed for this purpose.
- If one needs to heat the compound under vacuum, then one will need to use a **vacuum oven**. The principles of operation of these pieces of equipment are similar to those of a vacuum desiccator, except that an electric heater is incorporated.

K. Drying Liquids

This usually means removing water from a liquid chemical or a solution of chemical in a water-immiscible solvent. You will always need to dry solutions after a liquid-liquid extraction (*see* **C: Liquid-liquid extraction** on page 10) and you may need to dry liquids after evaporation or distillation. In both cases the liquid is placed in direct contact with the solid drying agent, *i.e.* the drying agent is added to the liquid or solution.

Table 5 Drying agents for liquids and solutions

Drying agent	Capacity	Speed	Efficiency
$MgSO_4$	High	Fast	Good
Na_2SO_4	High	Slow	Poor
$CaCl_2$	High	Slow	Poor
$CaSO_4$	Low	Fast	Good
K_2CO_3	High	Fast	Good

Capacity: amount of water taken up

Speed: rate of water absorption

Efficiency: extent of drying after treatment

Procedure:

1. Place the solution to be dried in a clean, dry conical flask. *[The flask should not be more than half-full.]*
2. Add small quantities of the dry agent and swirl the conical flask between each addition, until the liquid is no longer cloudy.
3. Allow the mixture to stand for 10 minutes.
4. Gravity filter the dried solvent layer through a fluted filter paper into a clean, dry flask.
5. Rinse the dry agent in the conical flask with a few cm^3 of pure dry solvent and filter it.
6. Remove the solvent *[by rotary evaporation (see **F: Evaporation** on page 12) or distillation (see **D: Distillation** on page 11)]*

L. Pressure of Gas

Pressure measurement is the analysis of an applied force by a fluid (liquid or gas) on a surface. Pressure is typically measured in units of force per unit of surface area. The SI unit for pressure is the Pascal (Pa). Atmospheric pressures are usually stated using kilopascal (kPa), millibar (mbar) or atmospheres (atm).

Many techniques have been developed for the measurement of pressure. Instruments used to measure and display pressure in an integral unit are called pressure meters or pressure gauges. The manometer is a good example.

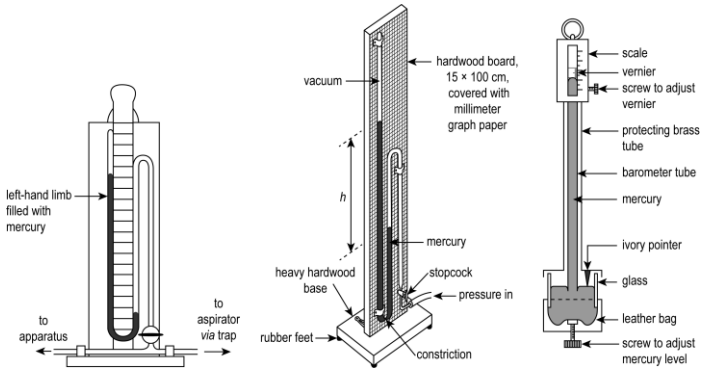
Manometer

A U-tube manometer filled with mercury is simple to construct, requires no calibration, and operates over a wide pressure range. It is now less frequently used due to concerns about safety hazards associated with mercury and its slow visual readout. However, it is a historically important device and it is directly related to barometers.

Most commonly, one arm is *evacuated* and the manometer indicates the total pressure directly. The pressure (in Pa) is proportional to the difference in height between the two mercury levels, *h* (in m):

$$p = h\rho g \text{ Pa}$$

where ρ is the density of mercury = 13593 kg m^{-3}
g is the acceleration due to free all = 9.807 m s^{-2}



Anschutz manometer **manometer** **Fortin barometer**

Barometer

The Fortin **barometer** is simply a single-arm, closed-tube mercury manometer equipped with a precise metal scale (usually brass), used to measure atmospheric pressure.

- The bottom of the measuring arm of the barometer dips into a mercury reservoir that is in contact with the atmosphere.
- The mercury level in this reservoir can be adjusted by means of a knurled screw that presses against a movable plate.
- When the meniscus in the reservoir just touches the tip of a pointed indicator, the zero level is properly established and the pressure can be determined from the position of the meniscus in the measuring arm.
- The height of the arm can be read to the nearest tenth of a millimetre using the Vernier scale.

M. Gas Collection and Volume Measurement

One can investigate a chemical reaction by measuring

- the volume of gas given off (evolved) at certain time intervals (when investigating reaction rates), or
- the total volume of gas produced.

There are different techniques to collect gas during an experiment and your choice of apparatus depends on

1. solubility of the gas in water,
2. the volume of gas produced, and

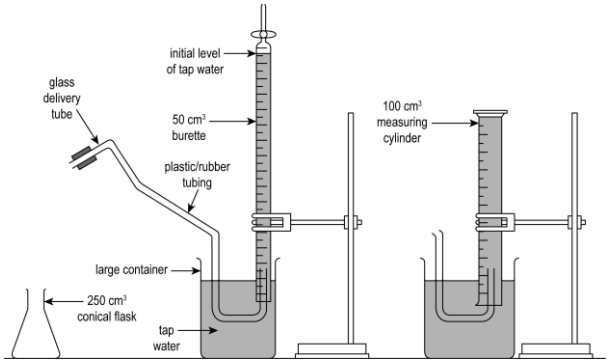
   The volume of measuring cylinder chosen should be about 2–3 times the volume of gas. However, the larger the volume of measuring cylinder used, the greater the error in measurement.
3. the apparatus that is available.

Two common methods for collection gas are shown below. It is important to have some idea of the *volume of gas* that will be generated so that you can choose an appropriate *size* of syringe or measuring cylinder. The volume of measuring cylinder chosen should be about 2–3 times the volume of gas. However, the larger the volume of measuring cylinder used, the greater the error in measurement.

Displacement of water

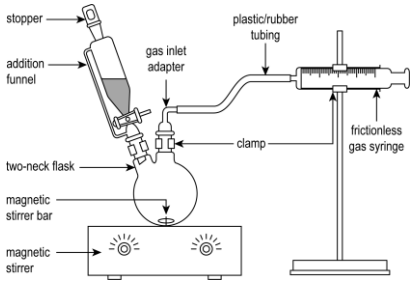
The gas produced must be only slightly soluble or insoluble in water.

Either an inverted burette or measuring cylinder can be used, pending on the total volume of gas to be measured.



Gas syringe

Gas syringe should be clamped *horizontally* to prevent the effect of gravity acting on the piston.



N. Time Measurement

In the Chemistry laboratory, time is taken using a stopwatch like the one shown below:

Press to reset the timing to 0:00:00

Press once to start timing;
Press again to stop/pause;
Press again to resume

For most chemistry experiments, we do not require the high level of precision offered by the digital stopwatch and time is often recorded to the **nearest seconds**. *E.g.*

will be recorded as 13 s, while

will be recorded as 12 s.

In addition, despite the fact that stopwatches readout are as "precise" as $\frac{1}{100}$ second, but it is not possible to measure the time to that level of certainty, because of the *human reaction time* pressing the button at the start and end of the measurement. This can be of the order of about a tenth of a second at each end of the measurement. So if you measure a time with a stopwatch, you could have a typical uncertainty of about ±0.2s.

LABORATORY TECHNIQUES

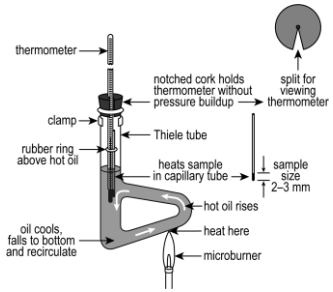
A. Melting points

Melting points are measured (determined) for two reasons:

1. The melting point range and upper limits are an indication of the purity of a sample.
2. Comparison of the melting point with the literature may indicate the identity of a compound or confirm that it is not the compound required.

Criterion of purity

Pure solid covalent organic compounds and many inorganic complexes incorporating organic ligands have **definite melting points**. The pure solid will melt *reproducibly* over a **narrow temperature range**, usually less than 1 ºC, and this melting range is known as the melting point.



The solid is packed into a melting point tube which is a capillary tube.

The melting point is the *temperature range* from where the first drop of liquid appears in the melting point tube, to where the last crystal dissolves into the liquid.

B. Recrystallisation

The products from many synthetic preparations are seldom pure and the technique of *recrystallisation*, which involves dissolving the impure material in a hot solvent and then cooling the solution to produce crystals, is routinely used to purify covalent organic and inorganic solids.

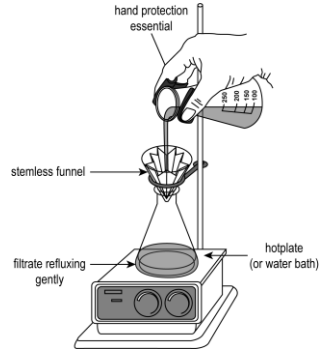
In general there are three types of impurities, which are removed by the recrystallisation process:

1. Insoluble material: anti-bumping granules, pieces of filter paper, traces of drying agents and other materials which may have been present in the starting chemicals.
2. Small quantities of unreacted starting chemicals and/or by-products from side reactions or other isomers.
3. Very small amount of coloured by-products resulting from oxidation or polymerisation of the chemicals used.

Purification by recrystallisation is based on the theory of saturated solutions and a suitable recrystallisation solvent is one in which the chemical to be purified is *insoluble* in the *cold solvent* and *soluble* in the *hot solvent*.

Procedure:

1. Weigh the crude sample.
2. Transfer the solid into a clean, dry conical flask.
3. Add cold solvent and a glass rod as an anti-bumping device to the flask and then heat the mixture on a hot plate. Add more solvent if necessary, until the compound has just dissolved completely.
4. Remove the flask from the heat and allow it to cool for 2 minutes.
5. Add a small amount of decolourising charcoal to the solution, and heat the mixture gently for 5 minutes.
6. Filter the recrystallisation solution through a stemless funnel and fluted filter paper. At the same time, keep the recrystallisation solution hot during the filtration by putting it back onto the hot plate.



7. When filtration is complete, remove collection flask from heat, take out the glass rod and clamp the flask in an ice-water bath.*
8. When the solution is cold (about 5 ºC), collect the solid by suction filtration.
9. Rinse the compound on the filter using a little ice-cold solvent and continue suction, to make the crystals as dry as possible.
10. Transfer the crystals to a clock-glass using a spatula and spread them in a thin layer.
11. Dry the compound by pressing between pieces of filter paper.
12. Air dry the compound.

* If no crystals appear on cooling, a supersaturated solution has been formed. To induce precipitation of the solute, sites for nucleation and crystal growth must be provided:

1. *Seeding* the solution by adding a few crystals ('dust') of the crude compound, or
2. *Scratching* the inside of the flask at the surface of the liquid using a glass rod.

C. Liquid-liquid extraction

This technique separates the components of chemical mixtures by using the dissimilar solubility properties of the components of the mixture in different solvents. Extraction is used mainly to purify a reaction product partially before final purification by recrystallisation (see **B: Recrystallisation** on page 10).

Liquid-liquid extraction uses two immiscible solvents; the desired compound in solution or suspension in one solvent is extracted into the other solvent. For example, covalent organic compounds are extracted from aqueous solution into organic solvent, leaving the ionic by-products or reagents in the aqueous phase.

Several experimental processes in practical chemistry are based on liquid-liquid extraction:

- 'Extraction' : where a solid or liquid suspended or dissolved in one solvent is extracted into another. This technique can be used to separate covalent molecules from ionic compounds in an aqueous solution or suspension.

- 'Washing' : where ionic species are removed from a non-polar solvent by extraction into water.
- 'Acid-base extraction' : where covalent molecules are converted into their salts and thus removed from a non-polar solvent into water, while neutral covalent species will remain in the non-polar solvent. *E.g.*

$$\underset{\substack{\text{acid}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{ArCO_2H} + \underset{\substack{\text{neutral}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{RH} \xrightarrow[CH_2Cl_2]{NaOH} \underset{\substack{\text{salt}\\\text{soluble in } H_2O}}{ArCO_2^-Na^+(aq)} + \underset{\substack{\text{neutral}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{RH}$$

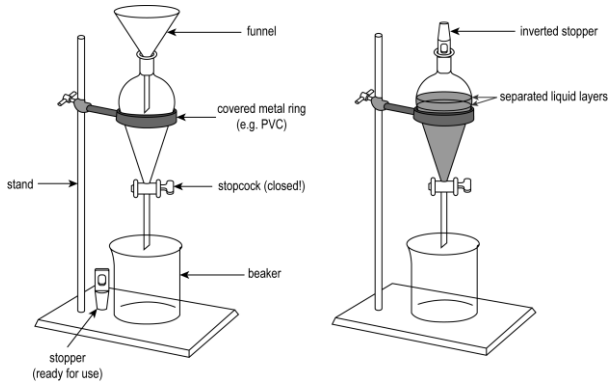
$$\underset{\substack{\text{amine}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{ArNH_2} + \underset{\substack{\text{neutral}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{RH} \xrightarrow[CH_2Cl_2]{HCl} \underset{\substack{\text{salt}\\\text{soluble in } H_2O}}{ArNH_3^+Cl^-(aq)} + \underset{\substack{\text{neutral}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{RH}$$

$$\underset{\substack{\text{acid}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{ArCO_2H} + \underset{\substack{\text{weak acid}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{ArOH} \xrightarrow[CH_2Cl_2]{NaHCO_3} \underset{\substack{\text{salt}\\\text{soluble in } H_2O}}{ArCO_2^-Na^+(aq)} + \underset{\substack{\text{weak acid}\\\text{insoluble in } H_2O\\\text{soluble in } CH_2Cl_2}}{ArOH}$$

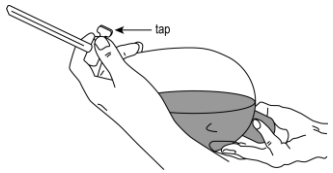
For liquid-liquid extraction, **water** is usually the polar solvent.

Procedure: (*E.g.* $ArCO_2H$ and RH mixture using dichloromethane)

1. Dissolve the mixture in a clean, dry beaker in dichloromethane.
2. Clean and dry the tap of a separatory funnel and set up as shown below.



3. Make sure that the tap is closed and then add the solution containing the mixture, using a stemmed funnel.
4. Add NaOH(aq) to the separatory funnel, place the stopper in the separatory funnel and gently invert it and hold it as shown below.



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

* Always take the stopper from the separatory funnel before attempting to run the liquid from the funnel. Otherwise a vacuum is formed in the funnel after a little of the liquid has run out. Air will be sucked into the funnel through the outlet stem causing bubbles, which will remix your separated layers.

D. Distillation

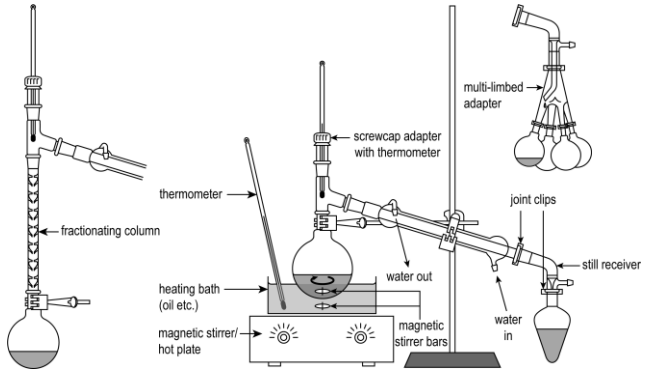
Distillation is used to separate the components of a liquid mixture by vapourising the liquids, condensing the vapours and collecting the liquid condensate. Separation is the result of the *differing boiling points* of the individual constituents of the mixture.

There are several types of distillation process each applicable to different situations depending on the chemicals to be purified or separated:

- *Simple distillation* : used for separating liquids, boiling *below* 200 ºC at atmospheric pressure, from other compounds. For effective separation, there should be a difference in the boiling points of the components of at least 25 ºC.
- *Fractional distillation* : used for separating components of liquid mixtures, which have boiling points differing by less than 25 ºC, at temperatures *below* 200 ºC.
- *Vacuum or reduced-pressure distillation* : used for separating liquids boiling *above* 200 ºC, when decomposition may occur at the high temperature. The effect of distilling at reduced pressure is to lower the boiling point of a liquid.

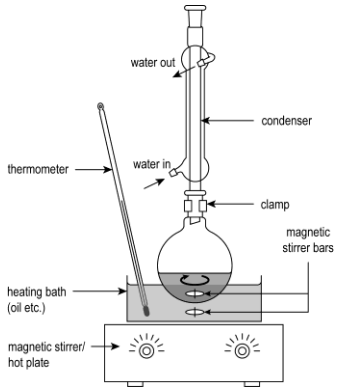
Apparatus used for the various types of distillation has several general features (refer to the diagram on the next page):

- Distillation flask : usually round bottom or pear shaped with one or two necks.
- Still-head : to hold the thermometer and to channel the vapour into the condenser. For fractional distillation, the fractionating column is fitted between the distillation flask and the still-head.
- Condenser : usually with circulating cold water.
- Take-off adapter : to allow the distillate to run into the collecting vessel.
- Receiving (collection) vessel : this can be a test-tube, a measuring cylinder, a conical flask, or a round-bottom flask.



E. Reflux

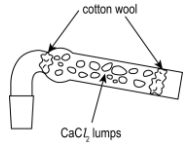
Reflux is one of the most common techniques encountered in chemistry laboratory classes. Since many reactions between covalent compounds are *slow* processes rather than instantaneous reactions, prolonged heating forces the equilibrium to give an acceptable amount of product.



In the reflux process, the reactants are dissolved or suspended in a suitable solvent, the solvent is boiled and then condensed so that it returns on the reaction flask.

Drying tubes

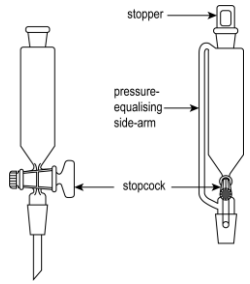
Water can get into the reaction by condensation from the atmosphere or by condensation of the steam produced in a water bath. To exclude water, a guard tube containing a solid drying agent such as anhydrous calcium chloride or calcium sulfate can be fitted to the top of the condenser.



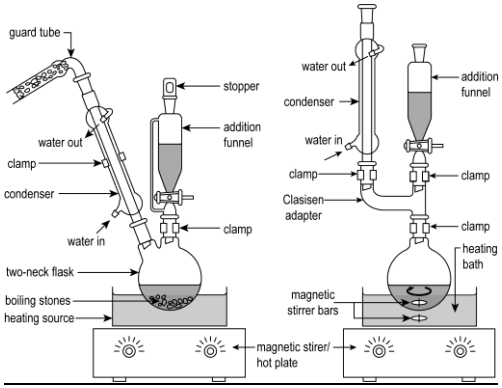
Reflux with addition of chemicals

Instead of stopping the reaction and opening the apparatus, one can put in the new chemicals using an addition or 'dropping' funnel.

Addition funnel: The funnel must *not* be stoppered, otherwise a vacuum is formed and the liquid does not flow out. A guard tube may be used in place of the stopper.

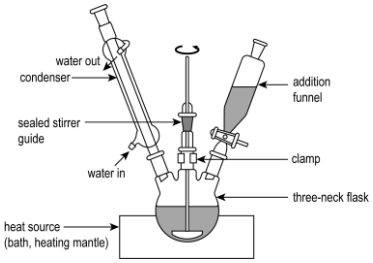


Pressure-equalising dropping funnel: these have a side-arm linking the reservoir of the funnel to the inlet stem below the tap. Liquid will flow even when stoppered.



Reflux with mechanical stirring

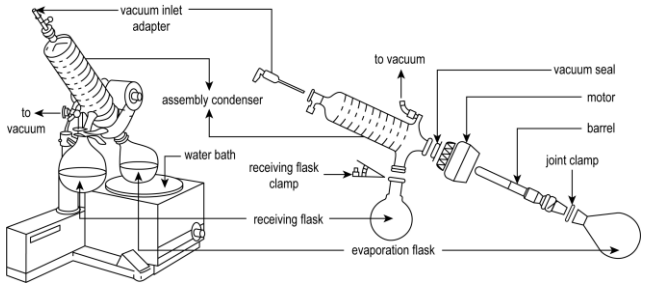
When a magnetic stirrer is unsuitable, *e.g.* in a reaction involving viscous liquids or mixtures of solids and liquids, a mechanical stirrer must be used.



F. Evaporation

Evaporation is the process in which the solvent of a solution is converted into a vapour and leave a solid or liquid solute. One commonly used technique for solvent evaporation is *rotary film evaporator*.

This is the technique of choice for the removal of large volumes of volatile solvents from solutions, *e.g.* from extractions. Rotation of the evaporation flask reduces the risk of 'bumping', inherent in all reduced-pressure distillations, and spreads the solution in a thin film on the walls of the flask. This effectively increases the surface area of the solution and increases the rate of evaporation, which is further enhanced by the use of a vacuum.



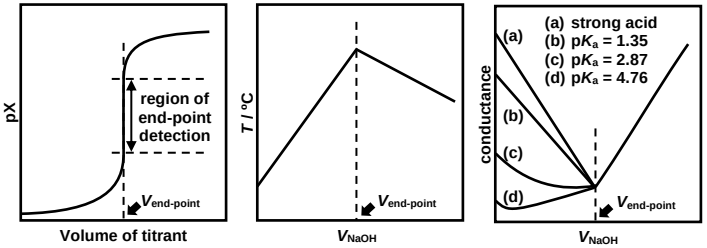
CLASSICAL TECHNIQUES

A. Titrimetric / Volumetric Analysis (VA)

- **Titrand** : a substance whose concentration is *to be determined* by titration. This is usually placed in the *conical flask* using a pipette.
- **Titrant** : The solution containing the *active agent* with which a titration is made. This is usually placed in the *burette*.
- **Titration** : The process of determining a substance A (the *titrand*) by adding increments of substance B (the *titrant*) with provision for some means of recognising the point at which all of A has reacted, thus allowing the amount of A to be found from the known amount of B added up to this point. The reacting ratio of A and B being known from stoichiometry or otherwise.
  - ✓ **Direct** titration : The titrand is titrated with a standard solution of the titrant.
  - ✓ **Back** titration : In certain circumstances, the titrand cannot be titrated directly, *e.g.*
    - o No suitable indicator is available
    - o The titration's reaction is too slow
    - o There is no useful direct titration reaction

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

    E.g. the reaction between HCHO with I_3^- is useful but too slow for titration. If a known excess of I_3^- is added to HCHO and allow to react completely, the unreacted I_3^- can then be titrated with thiosulfate, $S_2O_3^{2-}$.
- **Equivalence-point** : The point in a titration at which the amount of titrant added is *chemically equivalent* to the amount of substance titrated.
- **End-point** : The point in a titration at which some property of the solution (as, for example, the colour imparted by an indicator) shows a pronounced change, corresponding more or less closely to the **equivalence-point**.
  - ✓ The end-point may be represented by the intersection of two lines or curves in the graphical method of end-point determination.
  - ✓ The difference between the amount of titrant added to the sample to achieve the end point of titration and the theoretical amount of titrant necessary to obtain the equivalence point is known as the **titration error**.
- **End-point detection**
  - ✓ *Visual* : The course of the reaction is monitored by visual observation of the colour (or other) change of an added indicator on neutralisation, oxidation-reduction, precipitation or complexation. (In some instances the titrand or the titrant may be sufficiently coloured not to require addition of an indicator.)
  - ✓ *Thermometric* : The course of the reaction is monitored by means of a sensitive temperature measuring device (thermistor, thermocouple or thermometer) immersed in the reaction medium in a thermally isolated vessel. A plot is made of the response of the monitor device against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve.
  - ✓ *Conductimetric* : The course of the reaction is monitored by measuring the conductance (reciprocal of resistance) of the titration medium between two inert electrodes (usually platinised platinum) immersed in the reaction medium. A plot is made of conductance against titrant added. End-points are generally located by extrapolation at changes in slope in the titration curve.



- Preparation of **standard solution** if not provided. (see **D** on page 7).
- Volume required for titration: titre volume between **20.00–40.00 cm³** (2 d.p.)

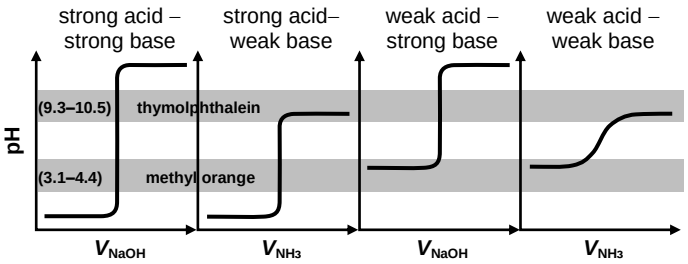
  volume of titrand pipetted can be **10.0 cm³** or **25.0 cm³** (pending volume of pipette provided)

Acid-Base Titrations

- Free bases are reacted with a standard acid (or vice versa). The reactions involve the combination of H^+ and OH^- ions to form water.
  - ✓ Choose suitable **indicators** for acid-base titration.

type of titration	marked pH change	suitable indicator
strong acid – strong base	4 – 10	(screened) methyl orange, thymolphthalein, phenolphthalein
strong acid – weak base	3.5 – 6.5	(screened) methyl orange
weak acid – strong base	7.5 – 10.5	thymolphthalein, phenolphthalein
weak acid – weak base	no marked change	no suitable indicator

  - ✓ Alternatively, a plot of pH against the volume of titrant, known as a titration curve can be obtained by 'potentiometric titration' in which pH is measure after each addition of titrant.
    - o Very sharp and sudden change in pH near to the equivalence point of titration.



- Know the **colour change** at the end-point.

indicator	approximate pH range	colour		
		acid solution	end-point	alkaline solution
methyl orange	3.1 – 4.4	red	orange	yellow
screened methyl orange	3.1 – 4.4	violet	grey	green
thymol-phthalein	9.3 – 10.5	colourless	pale blue (alkali) colourless (acidic)	blue
phenol-phthalein	8.2 – 10.0	colourless	pale pink (alkali) colourless (acidic)	pink/red

Redox Titrations

- Under this heading come all reactions involving change of oxidation number or transfer of electrons among the reacting substances.
  - ✓ Sometimes we need to adjust the oxidation state of analyte before it can be titrated. For example, Mn^{2+} can be pre-oxidised to MnO_4^- and then titrated with standard Fe^{2+}; I^- is first oxidised to I_2 and then titrated with standard $S_2O_3^{2-}$. However, excess preadjustment reagent must be removed so that it will not interfere in the subsequent titration.
  - ✓ **$KMnO_4$** is a strong oxidant with an intense violet colour.

acidic $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^\ominus = +1.52$ V

alkaline $MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O \qquad E^\ominus = +1.67$ V

No indicator is required because the colour change at the endpoint is distinct. Purple $KMnO_4$ turns colourless on one drop of purple $KMnO_4$ in excess produces an easily seen pale pink colour.

- ✓ In acidic solution, **$K_2Cr_2O_7$** is a powerful oxidant, although not as strong an oxidant as $KMnO_4$.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\ominus = +1.33 \text{ V}$$

Dichromate is orange and Cr^{3+} complexes range from green to violet, so indicators with distinctive colour changes are used to find a dichromate end point.

- ✓ Both MnO_4^- and $Cr_2O_7^{2-}$ can be used in the determination of **Fe^{2+}** : $Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\ominus = +0.77$ V

Fe^{3+} is first reduced to Fe^{2+} with Sn^{2+}, then titrated with MnO_4^- or $Cr_2O_7^{2-}$:

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

- ✓ In *iodometry*, an oxidising analyte is added to excess I^- to produce **I_2**, which is then titrated with standard $S_2O_3^{2-}$.

I_2 is only slightly soluble in water (1.3×10^{-3} mol dm^{-3} at 20ºC), but its solubility is enhanced by complexation with I^-:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K = 7.1\times10^2$$

Starch is added *near the endpoint i.e.* when the solution is pale yellow in colour. The presence of starch forms a soluble *bluish black complex* with iodine or the tri-iodide ion (I_3^-). It turns colourless at the end-point.

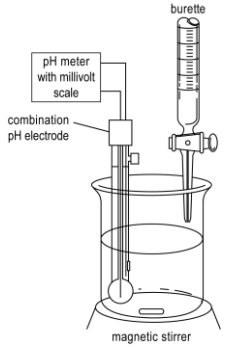
- ✓ **$S_2O_3^{2-}$** is the most universal titrant for I_3^-. In neutral or acidic solution, I_3^- oxidises $S_2O_3^{2-}$ to $S_4O_6^{2-}$:

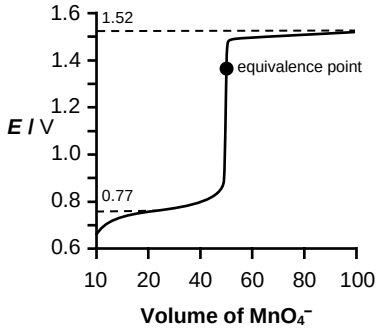
$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$

- ✓ The choice of acid used as a medium must be considered carefully. *E.g.* Hydrochloric acid cannot be used to provide the acidic medium for the titration between $KMnO_4$ and H_2O_2. The Cl^- ion from HCl(aq) would be oxidised by H_2O_2(aq) and $KMnO_4$(aq) to Cl_2(g). (Check $E^\ominus$ values from *Data Booklet*.)
- ✓ Besides visual colour changes, the end-point can also be determined potentiometrically.
  - When the stoichiometry of a redox titration is symmetrical (one mole titrand per mole of titrant), then the equivalence point also is symmetrical.
  - If the stoichiometry is not symmetrical, then the equivalence point will lie closer to the top or bottom of the titration curve's sharp rise. In this case the equivalence point is said to be asymmetrical.

E.g. titration of Fe^{2+} with MnO_4^- in 1 mol dm^{-3} H_2SO_4

$$E_{eqm} = \frac{E^\ominus\left(Fe^{3+}|Fe^{2+}\right) + 5E^\ominus\left(MnO_4^-|Mn^{2+}\right)}{6} - 0.07888\text{pH}$$

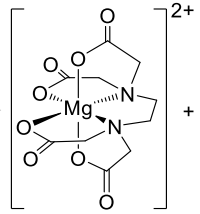




Complexometric Titrations

- Mainly used in determination of the concentration of *cations* in solution. The method is based on the competition between a metal ion (for example) and two ligands, one of which acts as an indicator and the other is a component of a standard solution.
  - ✓ One reagent commonly used as standard is Na_2H_2EDTA.
  - ✓ *E.g.* Mg^{2+} can be titrated directly with Na_2H_2EDTA:

$$Mg^{2+} + H_2EDTA^{2-} \rightleftharpoons$$



$$+ 2H^+$$

The titrand must be buffered at pH 10.5 so that complex formation will be quantitative.

The end-point of the titration is determined by the addition of a blue dye, Eriochrome Black T (ErioT), as the indicator. This blue dye forms a pink complex with Mg^{2+}.

At the end-point, colour changes from (pink to) purple to blue when Mg^{2+} is released to form a complex with $EDTA^{4-}$:

$$\underset{\text{pink}}{MgErioT^+} + EDTA^{4-} \rightarrow MgEDTA^{2-} + \underset{\text{blue}}{ErioT^-}$$

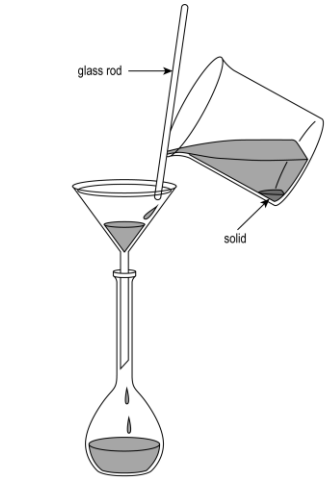
Precipitation Titrations

- These depend upon the formation of a crystalline solid or amorphous solid (the precipitate) when the titrand forms a precipitate with the titrant.
  - ✓ The most common types of precipitation titrations use silver nitrate as the titrant. They are often referred to as argentimetric titrations. *E.g.* the titration of chloride with a solution of silver ions:

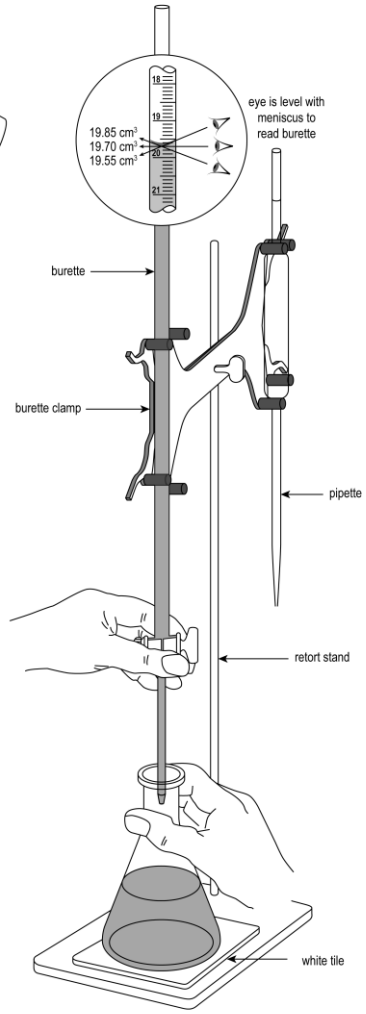
$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

  - ✓ Three techniques are commonly used to determine the end-point in precipitation titrations. They are:
    - *potentiometric* methods
    - *chemical indicator* methods
      - formation of a coloured precipitate by reaction with indicator. *E.g.* in the determination of $[Cl^-]$ with $AgNO_3$ a small amount of K_2CrO_4 is added. This results in the formation of red Ag_2CrO_4 precipitate at the end-point.
      - Formation of a soluble coloured compound. *E.g.* in the back titration of halides with Ag^+, the excess Ag^+ ions are titrated with standard KSCN in the presence of Fe^{3+}. When all the Ag^+ has reacted, the SCN^- reacts with Fe^{3+} to form a red complex, indicating the end-point.
      - adsorption of coloured indicator onto the precipitate at the end-point, resulting in a colour change.
    - *light-scattering methods*, exemplified by turbidimetry

Diagram



Quantitative transfer of a solid to a volumetric flask



Apparatus for a titration

Safety Considerations

- Fill the solution in the burette with the aid of the filter funnel and at eye-level. This is to prevent any accidental spillage of the solution into the eyes.
- Never suck up the solution with your mouth, a pipette filler should be used for pipetting the solution. Prevents accidental contact or ingestion of corrosive and toxic chemicals.

Reliability of results

- Shake the volumetric flask well to ensure a homogeneous solution is obtained.
- Repeat to get at least two **consistent readings** (differ by not more than 0.10 cm^3)

Procedure (acid-base titration)

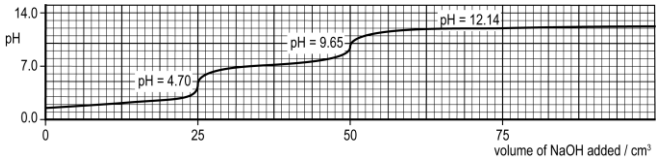
Eg 1 Determination of concentration of H_3PO_4 and NaH_2PO_4 in a mixture *via* double indicator titration with NaOH

H_3PO_4 is a weak triprotic acid. When it is titrated against NaOH, it loses its protons one after another. Equations 1 and 2 show the first and second stages in this neutralisation process.

equation 1 $H_3PO_4(aq) + NaOH(aq) \rightarrow NaH_2PO_4(aq) + H_2O(l)$

equation 2 $NaH_2PO_4(aq) + NaOH(aq) \rightarrow Na_2HPO_4(aq) + H_2O(l)$

The pH curve obtained when 25.0 cm^3 0f 0.100 mol dm^{-3} H_3PO_4 is titrated against 0.100 mol dm^{-3} NaOH is shown below. The pH values shown represent the pH of the solution when each stage of the neutralisation is completed.



(Note: The third end-point, for the complete neutralisation of H_3PO_4, *cannot* be determined by titration as there is no distinction change in pH)

For reaction in equation 1

1. Fill a burette with 0.100 mol dm^{-3} NaOH,
2. Use a pipette to transfer 10.0 cm^3 of the H_3PO_4 solution into a 100 cm^3 conical flask.
3. Add 4 drops of screened methyl orange into the conical flask.
4. Run NaOH from the burette into the conical flask. The end-point is reached when the solution changes from violet to grey. If the solution becomes green, the end-point is exceeded.
5. Record the titration results in the table below, to 2 decimal places.
6. Repeat points 2 to 5 until consistent titre values within 0.10 cm^3 are obtained.

	rough	1	2
Final *burette reading* / cm^3			
Initial *burette reading* / cm^3			
Volume of NaOH used / cm^3		V_1	V_1

For reactions in equation 1 and 2

7. Repeat points 1 to 6 but add thymolphthalein at point 3 in place of screened methyl orange. Using this indicator, the end-point is reached when the solution changes from colourless to a permanent **pale** blue colour. Record the titration results in the table below, to 2 decimal places.

	rough	1	2
Final *burette reading* / cm^3			
Initial *burette reading* / cm^3			
Volume of NaOH used / cm^3		V_2	V_2

Calculation

Using screened methyl orange (pH range 3.1–4.4) as the indicator, the first titre, V_1 cm^3, will give the amount of NaOH required to react with the H_3PO_4 in the sample.

$$n_{NaOH} = \frac{V_1}{1000} \times 0.100 = V_1 \times 10^{-4} \text{ mol}$$

$$n_{H_3PO_4} \text{ in 10.0 cm}^3 \text{ sample} = n_{NaOH} = V_1 \times 10^{-4} \text{ mol}$$

Using thymolphthalein (pH range 9.3–10.5) as the indicator, the second titre, V_2 cm^3, will give the amount of NaOH required to react with **both** H_3PO_4 and NaH_2PO_4 in the sample to give Na_2HPO_4.

$$n_{NaOH} = \frac{V_2}{1000} \times 0.100 = V_2 \times 10^{-4} \text{ mol}$$

$$H_3PO_4(aq) + 2NaOH(aq) \rightarrow Na_2HPO_4(aq) + 2H_2O(l)$$

$$n_{NaOH} \text{ required to react with } H_3PO_4 = 2n_{H_3PO_4} = 2V_1 \times 10^{-4} \text{ mol}$$

$$n_{NaOH} \text{ required to react with } NaH_2PO_4 = V_2 \times 10^{-4} - 2V_1 \times 10^{-4} = (V_2 - 2V_1) \times 10^{-4} \text{ mol}$$

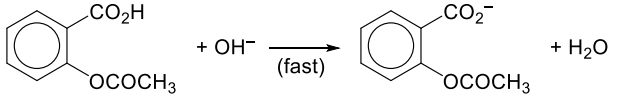
$$n_{NaH_2PO_4} \text{ in 10.0 cm}^3 \text{ sample} = (V_2 - 2V_1) \times 10^{-4} \text{ mol}$$

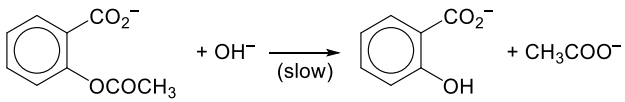
$$[H_3PO_4] = \frac{V_1 \times 10^{-4}}{\frac{10.0}{1000}} = 0.01\, V_1 \text{ mol dm}^{-3}$$

$$[NaH_2PO_4] = \frac{(V_2 - 2V_1) \times 10^{-4}}{\frac{10.0}{1000}} = 0.01(V_2 - 2V_1) \text{ mol dm}^{-3}$$

Eg 2 Determination of percentage by mass of aspirin by **back titration**

Many reactions are slow or present unfavourable equilibria for direct titration. Aspirin is a weak acid that also undergoes slow hydrolysis (*i.e.*, each aspirin molecule reacts with two hydroxide ions):





The first step of the reaction is fast; the second step is very slow. To overcome the slow hydrolysis, a *known excess* amount of 0.1 mol dm^{-3} NaOH is added and allowed to react with the aspirin. The sample is heated to speed the hydrolysis. Then, the excess NaOH is *back-titrated* with 0.1 mol dm^{-3} HC*l*.

1. Use a mortar and pestle to crush an appropriate amount of aspirin tablets to produce a 1.5 g sample.
2. Weigh out accurately about 0.50 g of aspirin into a clean and dry 250 cm^3 conical flask.
3. Using a 25 cm^3 measuring cylinder, add 20 cm^3 of ethanol and three drops of phenolphthalein to the flask. (Ethanol helps to dissolve the sparingly water-soluble aspirin)
4. Fill a burette with 0.10 mol dm^{-3} NaOH.
5. Run NaOH from the burette into the conical flask. The end-point is reached when the solution changes from colourless to a permanent pale pink.
6. Add 10.00 cm^3 + volume of NaOH used in step 4.
7. Add boiling chips and heat the sample for 10 min over a Bunsen burner.
8. Allow the resultant mixture to cool at room temperature for 10 min.
9. Fill another burette with 0.10 mol dm^{-3} HC*l*.
10. Run HC*l* from this second burette into the conical flask. The end-point is reached when the solution changes from pink to colourless.
11. Record the titration results, to 2 decimal places.
12. Repeat step 2 to 11 with two other 0.50 g samples of the powdered aspirin prepared in step 1.

Calculation

For each sample, determine the percentage by mass of aspirin.

Let the mass of powdered aspirin used be m g.

the volume of NaOH required in step 5 be V_1 cm^3 and

the volume of HC*l* required in step 10 be V_2 cm^3.

$$n_{NaOH} \text{ added} = \frac{10.00 + 2V_1}{1000} \times 0.10 = (2V_1 + 10) \times 10^{-4} \text{ mol}$$

$$n_{NaOH} \text{ in excess} = n_{HCl} \text{ reacted with excess NaOH}$$

$$= \frac{V_2}{1000} \times 0.10 = V_2 \times 10^{-4} \text{ mol}$$

$$n_{NaOH} \text{ reacted with aspirin} = (2V_1 + 10) \times 10^{-4} - V_2 \times 10^{-4} \text{ mol}$$

$$= (2V_1 - V_2 + 10) \times 10^{-4} \text{ mol}$$

$$n_{aspirin} \text{ in sample} = \frac{1}{2} n_{NaOH} \text{ reacted with aspirin}$$

$$= \frac{1}{2}(2V_1 - V_2 + 10) \times 10^{-4} \text{ mol}$$

$$m_{aspirin} \text{ in sample} = \frac{1}{2}(2V_1 - V_2 + 10) \times 10^{-4} \times (180.0) \text{ g}$$

$$= 9(2V_1 - V_2 + 10) \times 10^{-3} \text{ g}$$

$$\% \text{ by mass of aspirin} = \frac{9(2V_1 - V_2 + 10) \times 10^{-3}}{m} \times 100\%$$

$$= \frac{0.9(2V_1 - V_2 + 10)}{m}\%$$

Determine the *average* % by mass of aspirin in the three samples.

Procedure (redox titration)

Eg 3 Determination of concentration of $K_2C_2O_4$ by titration with $KMnO_4$.

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

The reaction between the negatively-charged $C_2O_4^{2-}$ and MnO_4^- is slow initially and the colour of MnO_4^- will take some time to disappear. After some MnO_4^- has been added, sufficient Mn^{2+}(aq) ions will be present to catalyse the reaction and allow the reaction to occur faster.

1. Fill the burette with 0.0200 mol dm^{-3} $KMnO_4$.
2. Using a pipette, transfer 25.0 cm^3 of the $K_2C_2O_4$ sample into a 250 cm^3 conical flask.
3. Using a 50 cm^3 measuring cylinder, transfer 50.0 cm^3 of 1.00 mol dm^{-3} H_2SO_4 to the same conical flask.
4. Heat this solution to about 65 ºC by means of a Bunsen burner.
5. Run $KMnO_4$ from the burette into this flask until a **permanent** pale pink colour is obtained.
6. Record the titration results, to 2 decimal places.
7. Repeat points 1 to 6 as necessary until consistent titre values within 0.10 cm^3 are obtained.

Calculation

Let the titre be V cm^3.

$$n_{MnO_4^-} = \frac{V}{1000} \times 0.0200 = 2V \times 10^{-5} \text{ mol}$$

$$n_{C_2O_4^{2-}} = \frac{5}{2} n_{MnO_4^-} = \frac{5}{2} \times 2V \times 10^{-5} = 5V \times 10^{-5} \text{ mol}$$

$$\left[C_2O_4^{2-}\right] = \frac{5V \times 10^{-5}}{\frac{25.0}{1000}}$$

$$= 2V \times 10^{-3} \text{ mol dm}^{-3}$$

Eg 4 Determination of concentration of $CuSO_4$ by **iodometric titration**

The addition of an excess of KI to a solution of Cu^{2+} ions produces I_2, and a stable precipitate of CuI. To determine the concentration of Cu^{2+} *via* iodometric titration, it is necessary that all the Cu^{2+} ions are reduced to Cu^+ ions. A brown suspension will be produced, which is an off-white precipitate of CuI in a yellow-brown solution of I_2.

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

The I_2 formed may be titrated against a standard solution of $Na_2S_2O_3$

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

The solution should be titrated immediately after addition of KI because the I_2 may be adsorbed onto the CuI precipitate, rendering the end-point less sharp.

1. Fill a burette with 0.100 mol dm^{-3} $Na_2S_2O_3$,
2. Use a pipette to transfer 25.0 cm^3 of the aqueous $CuSO_4$ sample into a 250 cm^3 conical flask.
3. Use a 25 cm^3 measuring cylinder to add about 20 cm^3 of 0.5 mol dm^{-3} KI to this flask. A white precipitate forms in a brown solution.
4. Run $Na_2S_2O_3$ from the burette into this flask. Neat the end-point, when the brown solution becomes pale, add about 1 cm^3 of starch indicator.
5. Continue adding $Na_2S_2O_3$ slowly. The end-point is reached when the **solution** first becomes colourless. The white precipitate remains.
6. Record the titration results, to 2 decimal places.
7. Repeat points 1 to 6 as necessary until consistent titre values within 0.10 cm^3 are obtained.

Calculation

Let the titre be V cm^3.

$$n_{S_2O_3^{2-}} = \frac{V}{1000} \times 0.100 = V \times 10^{-4} \text{ mol}$$

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

$$n_{I_2} = \frac{1}{2} n_{S_2O_3^{2-}} = \frac{V}{2} \times 10^{-4} \text{ mol}$$

$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$

$$n_{Cu^{2+}} = 2n_{I_2} = V \times 10^{-4} \text{ mol}$$

$$\left[Cu^{2+}\right] = \frac{V \times 10^{-4}}{\frac{25.0}{1000}} = 4V \times 10^{-3} \text{ mol dm}^{-3}$$

Procedure (complexometric titration)

Eg 5 Determination of Al^{3+} concentration by complexometric back titration with Zn^{2+}

$Al(OH)_3$ precipitates at pH 7 in the absence of EDTA. An acidic solution of can be treated with excess EDTA, adjusted to pH 7–8, and boiled to ensure complete formation of stable, soluble $[Al(EDTA)]^-$. The solution is then cooled, Eriochrome black T indicator is added, and back titration with standard Zn^{2+} is performed.

1. Fill a burette with 0.0100 mol dm^{-3} Na_2H_2EDTA.
2. Use a pipette to transfer 25.0 cm^3 of the Al^{3+}(aq) into a 250 cm^3 conical flask.
3. Run 30.00 cm^3 of Na_2H_2EDTA from the burette to this flask.
4. Use a piece of Universal Indicator paper to check if the solution is acidic. If acidic, use a teat pipette to add aqueous NH_3, slowly, with swirling, until the pH is about 7–8 (check using UI paper).
5. Use a 25 cm^3 measuring cylinder to add 20 cm^3 of ethanoate buffer (pH 7) to the flask.
6. Heat this solution to boil for 3 minutes using a Bunsen burner.

7. Allow the mixture to cool to room temperature.
8. Fill a burette with 0.0100 mol dm^{-3} $ZnSO_4$.
9. Add 5 drops of Eriochrome Black T indicator into the conical flask.
10. Run $ZnSO_4$ from the burette into this flask. The end-point is reached when the solution changes from blue to wine red.
11. Record the titration results, to 2 decimal places.
12. Repeat points 1 to 10 until consistent titre values within 0.10 cm^3 are obtained.

Calculation

Let the titre be V cm^3.

$$n_{Zn^{2+}} = \frac{V}{1000} \times 0.0100 = V \times 10^{-5} \text{ mol}$$

$$Zn^{2+} + H_2EDTA^{2-} \rightarrow [Zn(EDTA)]^{2-} + 2H^+$$

$$n_{\text{excess } H_2EDTA^{2-}} \text{ reacted with } Zn^{2+} = V \times 10^{-5} \text{ mol}$$

$$n_{H_2EDTA^{2-}} \text{ added to sample} = \frac{30.00}{1000} \times 0.0100 = 3.00 \times 10^{-4} \text{ mol}$$

$$n_{H_2EDTA^{2-}} \text{ reacted with } Al^{3+} = 3.00 \times 10^{-4} - V \times 10^{-5}$$

$$= (30 - V) \times 10^{-5} \text{ mol}$$

$$Al^{3+} + H_2EDTA^{2-} \rightarrow [Al(EDTA)]^- + 2H^+$$

$$n_{Al^{3+}} = (30 - V) \times 10^{-5} \text{ mol}$$

$$\left[Al^{3+}\right] = \frac{(30 - V) \times 10^{-5}}{\frac{25.0}{1000}} = 4(30 - V) \times 10^{-4} \text{ mol dm}^{-3}$$

Procedure (precipitation titration)

Eg 6 Determination of silver in an alloy

[Volhard's Method] The silver alloy is first dissolved in 8 mol dm^{-3} HNO_3 to convert all the Ag into Ag^+, which is then titrated with SCN^-:

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$$

giving white AgSCN precipitate. When all the Ag^+ is precipitated, the SCN^- then reacts with Fe^{3+} added as indicator:

$$Fe^{3+}(aq) + SCN^-(aq) \rightarrow Fe(SCN)^{2+}$$

to give red $Fe(SCN)^{2+}$, signalling the end-point.

1. Weigh accurately between 0.3 and 0.4 g of the silver alloy in a 250 cm^3 beaker.
2. Use a 25 cm^3 measuring cylinder to add 20 cm^3 of 8 mol dm^{-3} HNO_3, cover with a watch glass, and warm on a hot plate stirrer in the fumehood until all the alloy has completely dissolved.
3. Remove the watch glass and continue heating the mixture until all brown fumes have disappeared and the solution is colourless.
4. Allow the mixture to cool to room temperature.
5. Transfer the solution quantitatively to a clean 250 cm^3 graduated flask. Rinse the beaker with deionised water several times, adding each rinsing to the graduated flask.
6. Make up the solution to 250 cm^3 with deionised water and mix thoroughly.
7. Fill a burette with 0.100 mol dm^{-3} KSCN.
8. Use a pipette to transfer 25.0 cm^3 of the sample into a 250 cm^3 conical flask.
9. Use a 10 cm^3 measuring cylinder to add 1 cm^3 of saturated $KFe(SO_4)_2 \cdot 12H_2O$ as indicator.
10. Run KSCN from the burette into this flask until a permanent faint reddish-brown colour is obtained.
11. Record the titration results, to 2 decimal places.
12. Repeat points 7 to 11 as necessary until consistent titre values within 0.10 cm^3 are obtained.

Procedure (Determination of K_{sp})

Eg 7 Determination of a value for the solubility product, K_{sp}, of calcium iodate(V), $Ca(IO_3)_2$

The solubility in water of solid calcium iodate(V), $Ca(IO_3)_2$, is low. When a sample of this salt is mixed with water, a small amount dissolves and an equilibrium between the solid salt and its aqueous ions is established.

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

If separate aqueous solutions containing Ca^{2+} ions and IO_3^- ions are mixed, some of the solid salt is formed and, again, an equilibrium is established.

When excess KI is added to an acidified solution containing iodate(V) ions, I_2 is liberated which can be titrated with a standard solution of $Na_2S_2O_3$.

FA 1 is 0.200 mol dm^{-3} potassium iodate(V), KIO_3

FA 2 is 1.00 mol dm^{-3} calcium nitrate, $Ca(NO_3)_2$

FA 3 is 0.0400 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$

FA 4 is an aqueous solution of potassium iodide, KI

FA 5 is dilute hydrochloric acid, HCl

Preparing the reaction mixture

1. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 1** to a beaker labelled **reaction mixture**.
2. Use a 25 cm^3 measuring cylinder to transfer 20.0 cm^3 of **FA 2** to the same beaker.
3. A precipitate will form, stir the mixture thoroughly. Leave this mixture to stand for 5 minutes to allow equilibrium to be reached.

Analysing the filtrate

4. Filter the reaction mixture through a **dry** filter paper into a **dry** conical flask, labelled **FA 6**. This is the filtrate, **FA 6**. Do **not** wash the white precipitate with water.
5. Fill a burette with **FA 3**.
6. Pipette 10.0 cm^3 of **FA 6** into a 250 cm^3 conical flask.
7. Use a measuring cylinder to add about 10 cm^3 of **FA 4** to the flask.
8. Use a measuring cylinder to add about 2 cm^3 of **FA 5** to the flask.
9. Run **FA 3** from the burette into the flask until the brown colour of iodine fades to a pale yellow colour.
10. Add about 5 drops of starch indicator to the flask. Continue adding **FA3** until the blue-black colour <u>just</u> disappears.
11. Repeat points 5 to 10 until consistent titre values within 0.10 cm^3 are obtained. Rinse the conical flask between each titration.

Calculation

Assuming that the titre value is V cm^3.

$$n_{S_2O_3^{2-}} \text{ used} = \frac{V}{1000} \times 0.0400 = 4V \times 10^{-5} \text{ mol}$$

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

$$n_{I_2} \text{ liberated} = \frac{1}{2} n_{S_2O_3^{2-}} = 2V \times 10^{-5} \text{ mol}$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$n_{IO_3^-} \text{ present in 10.0 cm}^3 \text{ of } \textbf{FA 6} = \frac{1}{3} n_{I_2} = \frac{2V}{3} \times 10^{-5} \text{ mol}$$

$$\text{total } n_{IO_3^-} \text{ in } \textbf{FA 6} = \left(\frac{2V}{3} \times 10^{-5}\right) \times \frac{70}{10} \text{ mol}$$

$$= \frac{14V}{3} \times 10^{-5} \text{ mol}$$

$$\text{initial } n_{IO_3^-} = \frac{50.0}{1000} \times 0.200 = 0.0100 \text{ mol}$$

$$n_{IO_3^-} \text{ precipitated as } Ca(IO_3)_2 = 0.0100 - \left(\frac{14V}{3} \times 10^{-5}\right) \text{ mol}$$

$$n_{Ca^{2+}} \text{ precipitated as } Ca(IO_3)_2 = \frac{0.0100 - \left(\frac{14V}{3} \times 10^{-5}\right)}{2} \text{ mol}$$

$$\text{initial } n_{Ca^{2+}} = \frac{20.0}{1000} \times 1.00 = 0.0200 \text{ mol}$$

$$n_{Ca^{2+}} \text{ in } \textbf{FA 6} = 0.0200 - \frac{0.0100 - \left(\frac{14V}{3} \times 10^{-5}\right)}{2} 0 \text{ mol}$$

$$= 0.0150 - \left(\frac{7V}{3} \times 10^{-5}\right) \text{ mol}$$

$$K_{sp} = \left[Ca^{2+}\right]\left[IO_3^-\right]^2$$

$$= \left(\frac{0.0150 - \left(\frac{7V}{3} \times 10^{-5}\right)}{\frac{70.0}{1000}}\right)\left(\frac{\frac{14V}{3} \times 10^{-5}}{\frac{70.0}{1000}}\right)^2$$

B. Gravimetric Analysis

- **Gravimetric analysis** is used for the quantitative determination of an analyte (e.g. the ion being analysed) based on its mass. You need to be able to weigh accurately, by difference, a substance to three decimal places (see **A: Balances and Weighing** on page 6).
  - ✓ In ***precipitation gravimetry***, the analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.
  - ✓ In ***volatilisation gravimetry***, the analyte is separated from other constituents of a sample by converting it to a gas of known chemical composition. The mass of the gas then serves as a measure of the analyte concentration.
  - ✓ In *electrogravimetry*, the analyte is separated by deposition on an electrode by an electrical current. The mass of this product then provides a measure of the analyte concentration.

Precipitation Gravimetry

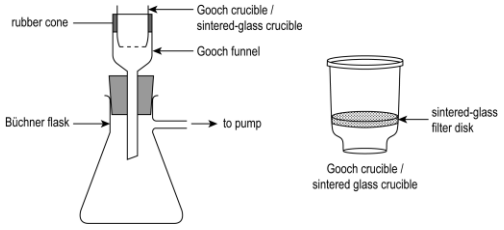
- The analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, and heated until its mass becomes constant (**within 0.010 g**).
- Heating *removes the solvent* and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition.
- For example, the amount of calcium in water can be determined using such a method:
  - ✓ An excess of ethanedioic acid, $H_2C_2O_4$, is added to an aqueous solution of the sample.
  - ✓ Ammonia is then added, which neutralises the acid and causes essentially all of the Ca^{2+} in the sample to precipitate as calcium oxalate. The reactions are

$$2NH_3(aq) + H_2C_2O_4(aq) \rightarrow 2NH_4^+(aq) + C_2O_4^{2-}(aq)$$

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

  - ✓ The CaC_2O_4 precipitate is filtered using a weighed Gooch / sintered-glass crucible, then dried and ignited. This process converts the precipitate entirely to CaO. The reaction is

$$CaC_2O_4(s) \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2(g)$$



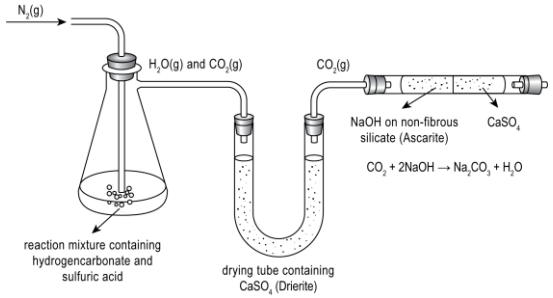
  - ✓ After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible.

Volatilisation Gravimetry

- The two most common gravimetric methods based on volatilisation are those for determining *water* and *carbon dioxide*.
- Water is *quantitatively* distilled from many materials by heating.
  - ✓ In direct determination, water vapour is collected on any of several solid desiccants, and its mass is determined from the mass gain of the desiccant.
  - ✓ The indirect method in which the amount of water is determined by the loss of mass of the sample during heating is less satisfactory because it must be assumed that water is the only component that is volatilised. This assumption can present problems, however, if any component of the precipitate is volatile.
- An example of a gravimetric procedure involving volatilisation of carbon dioxide is the determination of the sodium hydrogen carbonate content of antacid tablets. A weighed sample of the finely ground tablets is treated with dilute sulfuric acid to convert the sodium hydrogen carbonate to carbon dioxide:

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2CO_2(g) + 2H_2O(l) + Na_2SO_4(aq)$$

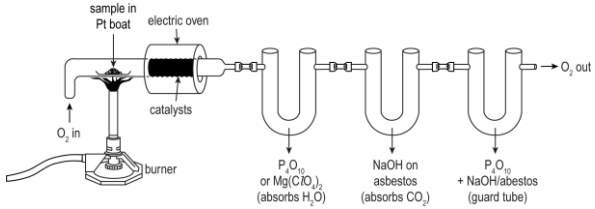
  - ✓ As shown below, this reaction is carried out in a flask connected first to a tube containing $CaSO_4$ that removes water vapour from the initial reaction stream to produce a stream of pure CO_2 in nitrogen.



  - ✓ These gases then pass through a *weighed* absorption tube containing the absorbent *Ascarite II*, which consists of sodium hydroxide absorbed on a non-fibrous silicate. This material retains CO_2 by the reaction

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

  - ✓ The absorption tube must also contain a desiccant such as $CaSO_4$ to prevent loss of the water in this last reaction.
- Finally, the classical method for the determination of carbon and hydrogen in organic compounds is a gravimetric volatilisation procedure in which the combustion products (H_2O and CO_2) are collected selectively on weighed absorbents. The increase in mass serves as the analytical variable:



Procedure (precipitation gravimetry)

E.g. 8 The gravimetric determination of chloride in a soluble sample.

1. Weigh out accurately 2.00 g of sample into a clean and dry empty weighing bottle.
2. In a beaker, dissolve the sample in 100 cm^3 of deionised water to which 2 cm^3 of 6 mol dm^{-3} HNO_3 have been added.
3. Slowly, and with good stirring, add 0.2 mol dm^{-3} $AgNO_3$(aq) to the cold sample solutions until white AgCl is observed to coagulate, and then introduce an addition 5 cm^3 of $AgNO_3$(aq).
4. Heat almost to boiling, and stir for about 10 min.
5. Add a few drops of $AgNO_3$(aq) to confirm that precipitation is complete.
6. If more precipitate forms, add about 3 cm^3 of $AgNO_3$(aq) and repeat step 4 to 5, until no more precipitate forms.
7. Cover the beaker and store in a dark place for 2 hours.
8. Weight and record the mass of a clean and dry sintered-glass crucible.
9. Pour the suspension in the beaker through the pre-weighed sintered-glass crucible.
10. Prepare a wash solution consisting of 5 cm^3 of 6 mol dm^{-3} HNO_3 per dm^3 of deionised water.
11. Transfer the remaining precipitate in the beaker by washing the beaker at least 3 times with wash solution, until the transferred suspension contains little or no solid.
12. Dry the precipitate at 110 ºC for 1 hr in a vacuum oven.
13. Allow the crucible to cool in a desiccator.
14. Weight and record the mass of the crucible and its content.
15. Repeat step 12 to 14 until consecutive weighings agree to within 0.010 g.

Procedure (volatilisation gravimetry)

Eg 9 The gravimetric determination of the percentage by mass of $NaHCO_3$ in **FA 1**, a mixture containing $NaHCO_3$ and NaCl

1. Weigh a crucible with its lid and record the mass.
2. Add between 2.8g and 3.0g of **FA 1** to the crucible. Weigh the crucible and lid with **FA 1** and record the mass.
3. Place the crucible on the pipe-clay triangle. Heat the crucible and contents gently for approximately two minutes, with the lid off.
4. Then heat strongly for approximately three minutes.
5. Replace the lid and leave the crucible and residue to cool for at least five minutes.
6. Reweigh the crucible and contents with the lid on. Record the mass.
7. Heat the crucible and contents strongly for a further two minutes, without the lid.
8. Replace the lid and leave the crucible and residue to cool for at least five minutes.
9. Reweigh the crucible and contents with the lid on. Record the mass.

10. Repeat step 7 to 9 until consecutive weighings agree to within 0.010 g.

Tabulation

mass of empty crucible with lid / g	m_1
mass of crucible + lid + **FA 1** / g	m_2
mass of crucible + lid + residue after 1st heating / g	
⋮	⋮
mass of crucible + lid + residue after $(n-1)^{th}$ heating / g	
mass of crucible + lid + residue after n^{th} heating / g	m_3

Calculation

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

mass of **FA 1** used = $(m_2 - m_1)$ g

mass of CO_2 and H_2O evolved = $(m_3 - m_2)$ g

$$n_{CO_2} = n_{H_2O} = \frac{m_3 - m_2}{M(CO_2) + M(H_2O)} = \frac{m_3 - m_2}{44.0 + 18.0} = \frac{m_3 - m_2}{62.0}$$

$$n_{NaHCO_3} = 2n_{CO_2} = \frac{m_3 - m_2}{31.0}$$

$$m_{NaHCO_3} = n_{NaHCO_3} \times M(NaHCO_3) = \frac{m_3 - m_2}{31.0} \times (84.0)$$

$$\% \text{ by mass of } NaHCO_3 = \frac{m_3 - m_2}{m_2 - m_1} \times \frac{84.0}{31.0} \times 100\%$$

C. Calorimetry

- Calorimetry involves experimentally determining the **enthalpy change**, **Δ*H***, or the internal energy change, Δ*E*, accompanying a given change in state of a system, normally one in which a chemical reaction occurs, at the same temperature.

$$\underset{\text{initial state}}{A(T_0) + B(T_0)} \rightarrow \underset{\text{final state}}{C(T_0) + D(T_0)} \quad \cdots\cdots\cdots\cdots (1)$$

- In practice we do not actually carry out the change in state at the same temperature; this is not necessary because Δ*H* and Δ*E* are state functions, independent of the path. In calorimetry it convenient to use a path composed of two steps:
  - ✓ *Step I.* A change in state is carried out in the **calorimeter** vessel, <u>without the gain or loss of heat</u>, to yield the desired products but in general at another temperature.

$$A(T_0) + B(T_0) + S(T_0) \rightarrow C(T_1) + D(T_1) + S(T_1) \quad \cdots\cdots (2)$$

    where S represents those parts of the system (*e.g.* inside all of the calorimeter vessel, stirrer, thermometer, solvent) that are always at the same temperature as the reactants or products, constitute the system under discussion.
  - ✓ *Step II.* The products of step I are brought to the initial temperature T_0 by adding heat to (or taking it from) the system:

$$C(T_1) + D(T_1) + S(T_1) \rightarrow C(T_0) + D(T_0) + S(T_0) \quad \cdots\cdots (3)$$

    It is often unnecessary to carry out this step in actuality, since the associated change in energy or enthalpy can be calculated from the known temperature difference.

- By adding (2) and (3), we obtain (1) and verify that these two steps describe a complete path connecting the desired initial and final states. Hence

$$\Delta H = \Delta H_{\text{I}} + \Delta H_{\text{II}}, \text{ and } \Delta E = \Delta E_{\text{I}} + \Delta E_{\text{II}}$$

- Since step I takes place without the gain or loss of heat, the heat *q* for step I is zero, while the heat *q* for step II can be calculated from the **temperature change ($T_1 - T_0$)** resulting from step I if the **heat capacity** of the product system is known.
- For step I, $\Delta H_{\text{I}} = q_p = 0$ constant pressure
  $\Delta E_{\text{I}} = q_v = 0$ constant volume

  Thus, if *both* steps are carried out at constant pressure,

$$\Delta H = \Delta H_{\text{II}}$$

  and if *both* are carried out at constant volume,

$$\Delta E = \Delta E_{\text{II}}$$

- Whether the process is carried out at constant pressure or at constant volume is a matter of convenience.
  - ✓ In nearly all cases it is most convenient to carry it out at **constant pressure** (*e.g.* in open vessels onto which the atmosphere exerts a constant pressure)
  - ✓ An exception to the general rule is the determination of a heat of combustion, which is conveniently carried out at constant volume in a *"bomb calorimeter"*.
- However, we can easily calculate Δ*H* from Δ*E* as determined from a constant-volume process (or Δ*E* from Δ*H* as determined from a constant-pressure process) by use of the equation

$$\Delta H = \Delta E + \Delta(pV)$$

  - ✓ When all reactants and products are condensed phases, the Δ(*pV*) term is *negligible* in comparison with Δ*H* or Δ*E*, and the distinction between these two quantities is unimportant.
  - ✓ When gases are involved, as in the case of combustion, the Δ(*pV*) term is likely to be significant in magnitude. Since it is still small in comparison with Δ*H* or Δ*E*, we can employ the ideal gas equation to rewrite the relationship in the form

$$\Delta H = \Delta E + RT\Delta n_{gas}$$

    where Δn_{gas} is the *increase* in amount of gas in the system.
- All calorimetric techniques are based on the measurement of heat that may be generated (**exothermic** process), consumed (**endothermic** process) or simply dissipated by a sample.

heat **LOST** by **SYSTEM** to **SURROUNDINGS**

$$\Delta H = q_{p,\text{II}} < 0$$

physical process or **chemical reaction** at the centre of interest

EXOTHERMIC PROCESS

system *vs* **surrounding**

ENDOTHERMIC PROCESS

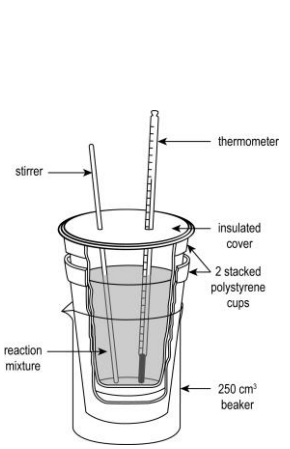
region **outside** system where **measure-ments** are made

$$\Delta H = q_{p,\text{II}} > 0$$

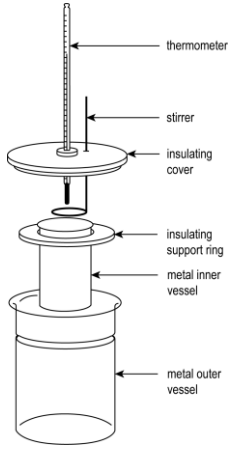
heat **GAINED** by **SYSTEM** from **SURROUNDINGS**

<u>*Calorimeter*</u>

- A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. Scientists use well-insulated calorimeters that all but **prevent the transfer of heat between the calorimeter and its environment**.

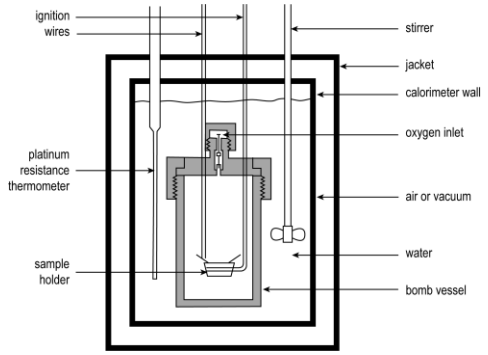


"coffee-cup" calorimeter



metal calorimeter

- Simple calorimeters constructed from polystyrene cups are often used (supported in a beaker). These easy-to-use **"coffee-cup" calorimeters** allow more heat exchange with their surroundings, and therefore produce *less accurate* energy values. Two polystyrene cups are usually stacked for better insulation.
- Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups nested in a way that minimises thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer.
- More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel (operating under *constant-volume environment*), motorised stirring mechanism, and a more accurate temperature sensor, such as the **bomb calorimeter** shown below.
  - ✓ A bomb calorimeter typically is used to carry out the **complete combustion** of a solid or liquid substance in the presence of *excess oxygen*. The combustion reaction is initiated with electrical ignition.



- ✓ From the measured heating curve and known properties of the calorimeter, reactants, and products, it is possible to evaluate the **standard molar enthalpy of combustion**, $\Delta H_c^{\ominus}$, of the substance of interest at a particular temperature called the reference temperature (often chosen to be 298.15 K , which is 25.00 ºC).
- ✓ Bomb calorimetry is the principal means by which standard molar enthalpies of combustion of individual elements and of compounds of these elements are evaluated.

Heat Capacity

- A calorimeter may be operated under constant [atmospheric] pressure ("coffee-cup"), or constant volume (bomb calorimeter). Whichever kind to use, its heat capacity must be known.
- The **heat capacity**, *C*, is the amount of heat required to raise the temperature of the *entire calorimeter* by 1 K. Thus

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

  - ✓ It is usually determined *experimentally* before the actual measurements of heat of reaction.
- The heat capacity of the calorimeter is determined by transferring a *known amount* of heat into it and measuring its temperature increase. Because the temperature differences are very small, sensitive thermometers (calibrated to at least **0.2 ºC precision**) are required for these measurements.

Specific Heat Capacity

- A "coffee-cup" calorimeter is a constant pressure calorimeter. As such, the heat that is measured in such a device is equivalent to the change in enthalpy, ΔH.
- The heat capacity of a coffee cup calorimeter is typically taken to be *that of the water* in the calorimeter, *i.e.*, heat of the reaction is assumed to all go into the temperature change of the water:

$$\boxed{q = mc\Delta T}$$

  where *m* is the mass of water in the calorimeter and *c* is the **specific heat capacity** of water (4.18 J g^{-1} K^{-1}).

Measuring the Temperature Difference

- Consider step I, the step where no gain or loss of heat occurs, and measurement of the temperature difference, $\Delta T\,(=T_1 - T_0)$, which is the fundamental measurement of calorimetry.
- If this step could be carried out in an ideal calorimeter, the temperature variation would be like that shown in Fig. 1.

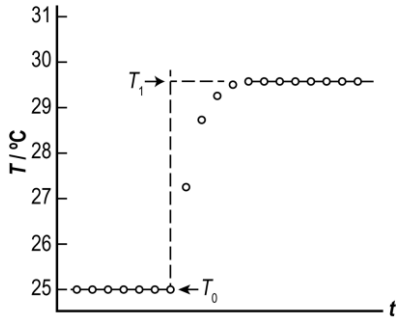


Fig. 1 Ideal temperature–time variation

  - ✓ In this case, it is ease to determine the temperature change, $\Delta T = T_1 - T_0$, since $\frac{dT}{dt} = 0$ before the time of mixing the reactants and after the products achieve thermal equilibrium.
  - ✓ The only cause of temperature change here is the chemical reaction.
- However, it is an unrealistic idealisation to assume that step I takes place *without* any heat exchanges with the surrounding.
  - ✓ No thermal insulation is perfect, *some heat will in general leak into or out of the system* during the time required for the change in state to occur and for the thermometer to come into equilibrium with the product system.
  - ✓ In addition, a stirrer is usually present in the calorimeter to aid in the mixing of reactants or to hasten thermal equilibration. The *mechanical work done on the system by the stirrer* results in the continuous addition of energy to the system. During the time required for the change in state and thermal equilibration to occur, the amount of energy introduced can be significant.
  - ✓ Nevertheless having said these, in the event that the reaction is completed (almost) instantaneously, for example, the ionic reaction between NaOH and HC*l*, heat exchange with the surrounding will be minimal. We can generally read off T_0 and T_1 from the thermometer directly.
- A typical temperature–time variation is shown in Fig. 2, especially for reactions that does not go to completion immediately, for example, the reaction of a piece of Zn with H_2SO_4, or the displacement reaction of Zn with $CuSO_4$. In these cases, the maximum temperature observed in Fig. 2 does not corresponds to the expected maximum temperature achievable if the reaction had been instantaneous. Extrapolation of the observed data points is required to extract the ΔT value.

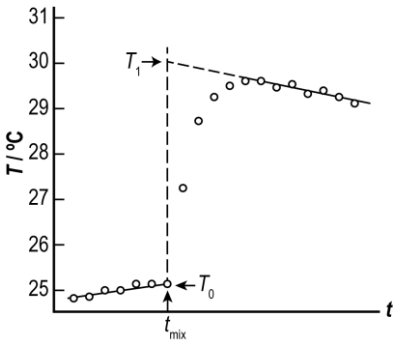


Fig. 2 Actual temperature–time variation

Procedure (instantaneous reaction)

Eg 10 Determination of the enthalpy change of reaction, ΔH_r, of $NaHCO_3$ (**FA 1**) with H_2SO_4 (**FA 2**)

$NaHCO_3(aq) + ½H_2SO_4(aq) \rightarrow ½Na_2SO_4(aq) + CO_2(g) + H_2O(l)$

1. Using a 25 cm^3 measuring cylinder, transfer 25.0 cm^3 of **FA 2** (an excess) into a polystyrene cup. Place the cup inside a second polystyrene cup, which is placed in a 250 cm^3 glass beaker to prevent it tipping over.
2. Stir and measure the temperature of this **FA 2**, $T_{FA\,2}$.
3. Wash and dry the thermometer.
4. Using a 50 cm^3 measuring cylinder, measure 50.0 cm^3 of **FA 1**.
5. Stir and measure the temperature of this **FA 1**, $T_{FA\,1}$.
6. Carefully add **FA 1** from the measuring cylinder to the polystyrene cup containing **FA 2** in **small** portions to avoid too much frothing.
7. Place a lid with a hole in the centre on the cup and insert the thermometer through the lid.
8. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.
9. Wash and carefully dry the polystyrene cup.
10. Repeat steps **1** to **8** to obtain a second value for T_{max}.

Calculation

1. For each experiment, calculate the weighted average initial temperature, T_{ave}, of the two solutions used. T_{ave} is given by

$$T_{ave} = \frac{(\text{vol FA 1} \times T_{FA\,1}) + (\text{vol FA 2} \times T_{FA\,2})}{\text{total volume of reaction mixture}} = \frac{(50.0 \times T_{FA\,1}) + (25.0 \times T_{FA\,2})}{75.0}$$

2. For each experiment, determine the maximum temperature change, $\Delta T_{max} = T_{max} - T_{ave}$. Then determine the average maximum temperature change, ΔT^1_{max} .
3. Calculate the average heat change, *q*, for the reaction between $NaHCO_3$ and excess H_2SO_4.

$$q = mc\Delta T^1_{max}$$
$$= (75.0\ cm^3 \times 1.00\ g\ cm^{-3}) \times (4.18\ J\ g^{-1}\ K^{-1}) \times \Delta T^1_{max}$$
$$= 313.5\Delta T^1_{max}\ J$$

4. Calculate the amount of $NaHCO_3$, $n_{NaHCO_3} = \frac{50.0}{1000} \times [\mathbf{FA\ 1}]$.

5. Calculate the enthalpy change of reaction, ΔH_r, of aqueous $NaHCO_3$ and H_2SO_4.

$$\Delta H_r = -\frac{q}{n_{NaHCO_3}} = \frac{313.5\Delta T^1_{max}}{50.0 \times [\mathbf{FA\ 1}]}$$
$$= \frac{6.27\Delta T^1_{max}}{[\mathbf{FA\ 1}]}\ kJ\ mol^{-1}$$

Eg 11 Determination of concentration of NaOH and enthalpy of reaction, ΔH_r, between $NaHCO_3$ and NaOH [Thermometric Titration]

$NaOH(aq) + NaHCO_3(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$

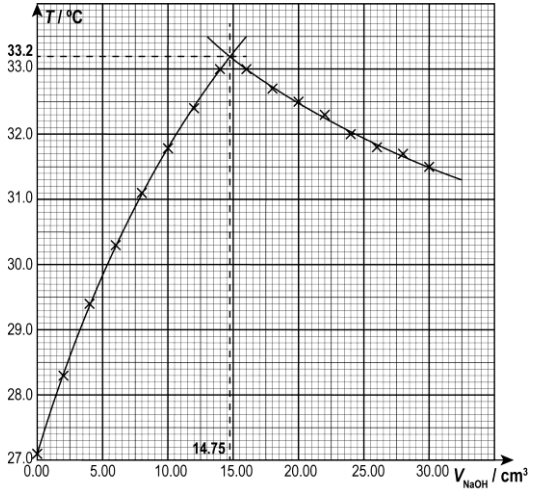
1. Fill a burette with NaOH, of concentration between 1.5 mol dm^{-3} and 2.0 mol dm^{-3}.
2. Place a polystyrene cup inside a second polystyrene cup which is held in a glass beaker to prevent it tipping over.
3. Using a pipette, transfer 25.0 cm^3 of 1.00 mol dm^{-3} $NaHCO_3$ to the first polystyrene cup.
4. Stir the $NaHCO_3$ solution in the cup with the thermometer. Read and record its temperature, to the nearest 0.1ºC.
5. From the burette, add 2.00 cm^3 of NaOH to the cup and stir the mixture thoroughly.
6. Read and record the maximum temperature of the mixture, T, to the nearest 0.1ºC, and the volume of NaOH added.
7. Repeat points 5 and 6 until a total of 30.00 cm^3 of NaOH has been added. After each addition of NaOH, record the maximum temperature of the mixture and the total volume of NaOH added up to that point.

volume of NaOH / cm^3	maximum temperature, T / ºC
0.00	27.1
2.00	28.3
4.00	29.4
⋮	⋮
26.00	31.8
28.00	31.7
30.00	31.5

Processing of data

1. Plot a graph of maximum temperature, T, on the y-axis, against volume of NaOH, V_{NaOH}, on the x-axis.
2. Draw a line-of-best-fit for the points where the temperature is **rising**.
3. Draw a second line-of-best-fit for the points where the temperature is **falling**.
4. Extrapolate both lines until they cross.
5. Read from your graph the maximum temperature, T_{max}, and the volume, V_{equ} cm^3, of NaOH needed to completely react with 25.0 cm^3 of 1.00 mol dm^{-3} $NaHCO_3$.

Sample graph



Calculation

1. To determine the concentration of NaOH:

$$n_{NaHCO_3} = \frac{25.0}{1000} \times 1.00 = 0.0250\ mol$$

$$n_{NaOH}\ \text{required} = n_{NaHCO_3} = 0.0250\ mol$$

$$[NaOH] = \frac{n_{NaOH}}{V_{equ}} = \frac{0.0250}{\frac{14.75}{1000}} = 1.69\ mol\ dm^{-3}$$

2. To determine the enthalpy of reaction, ΔH_r:

$$\Delta T_{max} = T_{max} - T_{initial}$$
$$= 33.2 - 27.1$$
$$= 6.1\ K$$

$$q = mc\Delta T_{max}$$
$$= (25.0 + 14.75\ cm^3)(1.00\ g\ cm^{-3}) \times (4.18\ J\ g^{-1}\ K^{-1}) \times 6.1\ K$$
$$= 1013.5\ J$$

$$n_{NaHCO_3} = n_{NaOH} = 0.0250\ mol$$

$$\Delta H_r = -\frac{q}{n_{NaOH}} = -\frac{1013.5}{0.0250}$$
$$= -40.5\ kJ\ mol^{-1}$$

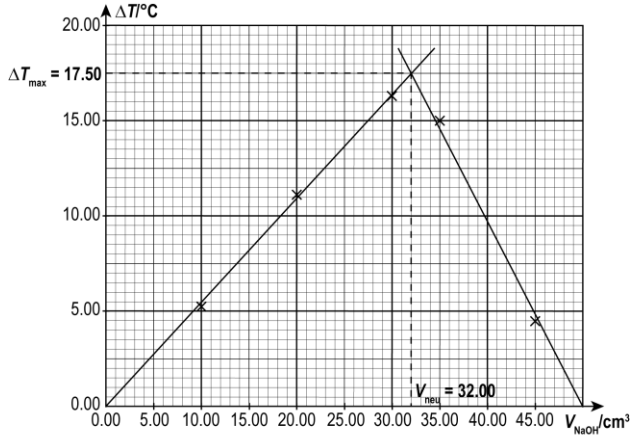
Eg 12 Determination of concentration of H_2SO_4 and enthalpy of neutralisation, ΔH_{neu}, of a strong acid by a strong base

1. Use a burette to transfer 10.00 cm^3 of H_2SO_4 into a polystyrene cup labelled H_2SO_4. Place the cup inside a second polystyrene cup which is placed in a 250 cm^3 glass beaker to prevent it tipping over.
2. Use another burette to transfer 40.00 cm^3 of 2.00 mol dm^{-3} NaOH into the polystyrene cup labelled NaOH.
3. Stir and measure the temperature of the H_2SO_4 solution.
4. Add the contents of the NaOH cup to the H_2SO_4 cup. Use the thermometer to stir the mixture and measure the maximum temperature of the mixture.
5. Wash and carefully dry both the H_2SO_4 and NaOH polystyrene cups.
6. Repeat steps 1 to 5 above using 20.00 cm^3, 30.00 cm^3, 35.00 cm^3, 40.00 cm^3 and 45.00 cm^3 of H_2SO_4, each time using the appropriate volume of NaOH so that the total volume of the reacting mixture is 50.00 cm^3.
7. In an appropriate format, record all measurements of volume, temperature and temperature change, ΔT.

Processing of data

6. Plot a graph of temperature change, ΔT, on the y-axis, against volume of NaOH, V_{NaOH}, on the x-axis.
7. Draw a line-of-best-fit for the points before the maximum temperature change.
8. Draw a second line-of-best-fit for the points after the maximum temperature change.
9. Extrapolate both lines until they meet.
10. Read from your graph the maximum temperature change, ΔT_{max}, and the volume, V_{neu} cm^3, of NaOH needed to obtain this value.

Sample graph



Calculation

1. To determine the concentration of H_2SO_4:

$$n_{NaOH} = \frac{V_{neu}}{1000} \times 2.00 = 2V_{neu} \times 10^{-3} \text{ mol}$$

$$n_{H_2SO_4} = \frac{1}{2} n_{NaOH} = V_{neu} \times 10^{-3} \text{ mol}$$

$$[H_2SO_4] = \frac{n_{H_2SO_4}}{V_{H_2SO_4}} = \frac{V_{neu} \times 10^{-3}}{\frac{50.00 - V_{neu}}{1000}} = \frac{V_{neu}}{50.00 - V_{neu}} \text{ mol dm}^{-3}$$

2. To determine the enthalpy of neutralisation, ΔH_{neu}:

$$q = mc\Delta T_{max}$$
$$= (50.00 \text{ cm}^3)(1.00 \text{ g cm}^{-3}) \times (4.18 \text{ J g}^{-1} \text{ K}^{-1}) \times \Delta T_{max}$$
$$= 209 \Delta T_{max} \text{ J}$$

$$n_{H_2O} = n_{NaOH} = 2V_{neu} \times 10^{-3} \text{ mol}$$

$$\Delta H_{neu} = -\frac{q}{n_{H_2O}} = -\frac{209\Delta T_{max}}{2V_{neu} \times 10^{-3}} = \frac{104.5\Delta T_{max}}{V_{neu}} \text{ kJ mol}^{-1}$$

Procedure (slow reaction)

Eg 13 Determination of the enthalpy change of solution, ΔH_{sol}, of potassium chloride, KC*l* (endothermic)

1. Weigh out accurately *m* g of solid KC*l* into a clean and dry empty weighing bottle. Record the mass of the weighing bottle with KC*l*.
2. Place one polystyrene cup inside a second polystyrene cup. Place these in a glass beaker to prevent them from tipping over.
3. Use a measuring cylinder to transfer 50 cm^3 of deionised water into the first polystyrene cup.
4. Stir the water in the cup with the thermometer. Read and record its temperature, *T* (time, *t* = 0.0 min)
5. Continue to stir the water. Read and record *T* every minute.
6. At **exactly** three minutes, transfer all the **solid KC*l*** to the polystyrene cup. Stir the mixture but do not read *T*.
7. Continue to stir the mixture. Read and record *T* at 3.5 min.
8. Continue to stir the mixture. Read and record *T* at 4.0 min and every minute until the temperature of the mixture starts to rise steadily for **5 consecutive readings**.
9. Reweigh the emptied weighing bottle.

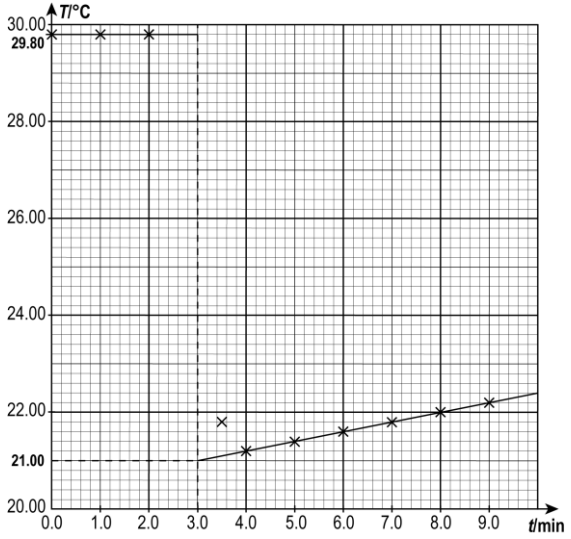
mass of empty weighing bottle / g	
mass of weighing bottle and KC*l* / g	m_1
mass of emptied weighing bottle / g	m_2
mass of KC*l* used / g	$m_1 - m_2$

time / min	temperature, *T* / ºC
0.0	29.8
1.0	29.8
2.0	29.8
3.5	21.8
4.0	21.2
⋮	⋮
9.0	22.2

Processing of data

1. Plot a graph of temperature, *T*, on the *y*-axis, against time, *t*, on the *x*-axis.
2. Draw a best-fit straight line taking into account all of the points before *t* = 3.0 min.
3. Draw another best-fit straight line taking into account all of the points after the temperature of the mixture has started to rise steadily.
4. Extrapolate (extend) both lines to *t* = 3.0 min.
5. From the graph, read the minimum temperature, T_{min}, and the maximum temperature, T_{max}, at *t* = 3.0 min.

Sample graph



Calculation

1. Determine the temperature change, $\Delta T = T_{max} - T_{min}$, at *t* = 3.0 min.
2. Calculate the heat change, *q*, using the formula $q = mc\Delta T$, where *m* is the mass of water (assuming density is 1.00 g cm^{-3}) and *c* is the specific heat capacity of water (4.18 J g^{-1} K^{-1}).
3. Calculate the amount of KC*l* from the mass of KC*l* used.

$$n_{KCl} = \frac{m_1 - m_2}{39.1 + 35.5} = \frac{m_1 - m_2}{74.6} \text{ mol}$$

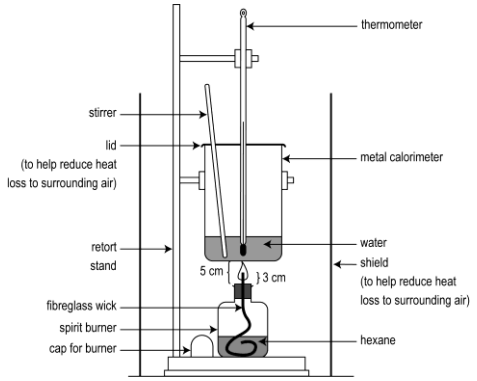
4. Determine the enthalpy change of solution, ΔH_{sol}, of solid KC*l* using $\Delta H_{sol} = +\frac{q}{n_{KCl}} = +\frac{74.6q}{m_1 - m_2}$ J mol^{-1}.

Procedure (metal calorimeter)

Eg 14 Determination of heat capacity of calorimeter

Heat capacity of a calorimeter (metal can and the contents) is the amount of heat required to raise its temperature by 1 K. This can be determined by measuring the temperature rise in a fixed volume of water in the metal can, from the heat evolved in the combustion of a known amount of the hexane (ΔH_c = –4163 kJ mol^{-1}).

1. Set up the apparatus as shown in the diagram below.
2. Fill the metal calorimeter one-fifth with water (sufficient to cover bulb of thermometer).
3. Fill the spirit burner with hexane and cap the burner. Weigh and record the mass of the spirit burner with hexane, m_1.
4. Stir the water in the metal calorimeter and take note of its initial temperature, T_1.
5. Uncap the spirit burner, place it under the metal calorimeter and light the fibreglass wick.
6. Gently stir the water in the calorimeter until there is a rise in temperature of about 5 ºC.
7. Cap the spirit burner to extinguish the flame.
8. Immediately, record the temperature of the water, T_2.
9. Cool the spirit burner and reweigh the cooled burner, m_2.



Tabulation

mass of spirit burner + hexane before combustion / g	m_1
mass of spirit burner + hexane after combustion / g	m_2
temperature of calorimeter before combustion / ºC	T_1
temperature of calorimeter after combustion / ºC	T_2

Calculation

1. Calculate the amount of heat evolved from burning the hexane.

mass of hexane combusted $= (m_1 - m_2)$ g

n_{hexane} combusted $= \dfrac{m_1 - m_2}{M(\text{hexane})} = \dfrac{m_1 - m_2}{86.0}$ mol

using ΔH_c(hexane) = –4163 kJ mol^{-1}

heat evolved from burning hexane $= 4163 \times \dfrac{m_1 - m_2}{86.0}$ kJ

2. Calculate the heat capacity of the calorimeter, C, from the temperature rise, assuming 100% heat transfer from the spirit burner to the calorimeter.

temperature rise, $\Delta T = (T_2 - T_1)$ K

heat gained by calorimeter = heat evolved from hexane

$$C\Delta T = 4163 \times \frac{m_1 - m_2}{86.0}$$

$$C = \frac{4163}{T_2 - T_1} \times \frac{m_1 - m_2}{86.0} \text{ kJ K}^{-1}$$

Eg 15 Determination of the enthalpy change of combustion, ΔH_c, of octan-1-ol (extension from Eg 14)

$CH_3(CH_2)_7OH(l) + 12O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$

1. Use the **same** setup as in **Eg 14** above, but replacing the spirit burner with a *clean identical* one.
2. Repeat steps 3 to 9, replacing the hexane with octan-1-ol.

Tabulation

mass of spirit burner + octan-1-ol before combustion / g	m_3
mass of spirit burner + octan-1-ol after combustion / g	m_4
temperature of calorimeter before combustion / °C	T_3
temperature of calorimeter after combustion / °C	T_4

Calculation

1. Calculate the amount of heat gained by the calorimeter.

temperature rise, $\Delta T = (T_4 - T_3)$ K

heat gained by calorimeter, $q = \dfrac{4163}{T_2 - T_1} \times \dfrac{m_1 - m_2}{86.0} \times (T_4 - T_3)$ kJ

$$= 4163 \times \frac{m_1 - m_2}{86.0} \times \frac{T_4 - T_3}{T_2 - T} \text{ kJ}$$

2. Calculate the amount of octan-1-ol burnt, and hence its enthalpy change of combustion, ΔH_c, assuming 100% heat transfer from the spirit burner to the calorimeter.

mass of octan-1-ol combusted $= (m_3 - m_4)$ g

$n_{\text{octan-1-ol}}$ combusted $= \dfrac{m_3 - m_4}{M(\text{octan-1-ol})} = \dfrac{m_3 - m_4}{130.0}$ mol

$$\Delta H_c = -\frac{q}{n_{\text{octan-1-ol}}} = -4163 \times \frac{m_1 - m_2}{86.0} \times \frac{T_4 - T_3}{T_2 - T_1} \div \frac{m_3 - m_4}{130.0}$$

$$= -4163 \times \frac{m_1 - m_2}{m_3 - m} \times \frac{T_4 - T_3}{T_2 - T_1} \times \frac{130.0}{86.0} \text{ kJ mol}^{-1}$$

D. UV/Visible Spectrophotometry

The absorption and emission of electromagnetic radiation of specific energy (wavelength) is a characteristic feature of many molecules, involving the movement of electrons between different energy states.

UV/visible spectrophotometry is a widely used technique for measuring the absorption of radiation in the visible (390–770 nm) and UV (10–390 nm) regions of the electromagnetic spectrum.

A spectrophotometer is an instrument designed to allow precise measurement at a particular wavelength, while a colorimeter is a simpler instrument, using filters to measure broader waveband (e.g. light in the green, red or blue regions of the visible spectrum).

Principles of Light Absorption

Two fundamental principles govern the absorption of light passing thorough a solution:

- The absorption of light is exponentially related to the number of molecules of the absorbing solute that are encountered, i.e. the solute concentration [C].
- The absorption of light is exponentially related to the length of the light path through the absorbing solution, l.

These two principles are combined in the Beer-Lambert relationship, which is usually expressed in terms of the intensity of the incident light (I_0) and the emergent light (I):

$$A = \lg\left(\frac{I_0}{I}\right) = \varepsilon[C]l$$

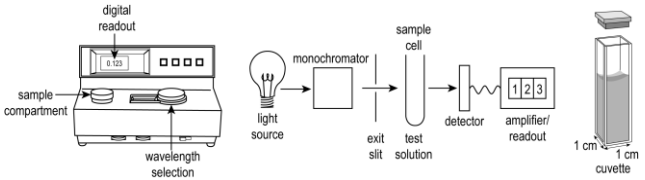
where ε is a constant for the absorbing substance at the wavelength of measurement and is term the *absorptivity*.

[C] is expressed as either mol dm^{-3} or g dm^{-3}

l is given in cm

Most spectrophotometers are constructed to give a direct measurement of $\lg\left(\frac{I_0}{I}\right)$, termed the **absorbance**, ***A***, of a solution.

The instrument is set to zero absorbance using a **blank solution**, which is then replaced by the test solution, to obtain an absorbance reading.



Procedure

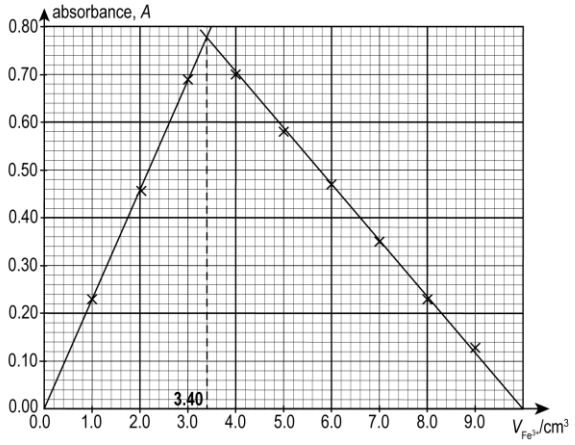
Eg 16 Determination of the formula of complex formed between aqueous iron(III) ions, $Fe^{3+}(aq)$, and aqueous 2-hydroxybenzoate ions, $C_6H_4(OH)CO_2^-$

1. Prepare a 0.0500 mol dm^{-3} standard solution of $Fe^{3+}(aq)$ in a 100 cm^3 volumetric flask, using 2.02 g of $Fe(NO_3)_3.9H_2O$
2. Prepare a 0.0500 mol dm^{-3} standard solution of 2-hydroxybenzoate ions in a 100 cm^3 volumetric flask, using 0.80 g of sodium 2-hydroxybenzoate.
3. Using a 10 cm^3 measuring cylinder, add 1.0 cm^3 of the standard solution of $Fe^{3+}(aq)$ into a clean and dry test-tube.
4. Using another 10 cm^3 measuring cylinder, add 9.0 cm^3 of the standard solution of 2-hydroxybenzoate ions into the same test-tube and swirl to mix well.
5. Transfer the mixture into a cuvette by means of a dropping pipette. Measure and record the absorbance, A, using a UV/visible spectrophotometer at 535 nm.
6. Repeat step 3 to 5 above using 2.0 cm^3, 3.0 cm^3, 4.0 cm^3, 5.0 cm^3, 6.0 cm^3, 7.0 cm^3, 8.0 cm^3 and 9.0 cm^3 of the standard solution of $Fe^{3+}(aq)$, each time using the appropriate volume of the standard solution of 2-hydroxybenzoate ions so that the total volume of the mixture is 10.0 cm^3.
7. In an appropriate format, record all measurements of volume and absorbance, A.

Processing of data

1. Plot a graph of absorbance, A, on the y-axis, against volume of $Fe^{3+}(aq)$, on the x-axis.
2. Draw a line-of-best-fit for the points
   - before the maximum absorbance, and
   - after the maximum absorbance.
3. Extrapolate both lines until they meet.
4. Read from your graph the volume of $Fe^{3+}(aq)$ needed to obtain the maximum absorbance.

Sample graph



Calculation

1. Volume of $Fe^{3+}(aq)$ = 3.40 cm^3
   Volume of 2-hydroxybenzoate = 10.0 – 4.40 = 6.60 cm^3
2. $n_{Fe^{3+}} = \frac{3.40}{1000} \times 0.0500 = 1.70 \times 10^{-4}$ mol

   $n_{\text{2-hydroxybenzoate}} = \frac{6.60}{1000} \times 0.0500 = 3.30 \times 10^{-4}$ mol
3. $n_{Fe^{3+}} : n_{2-\text{hydroxybenzoate}} = 1.70 \times 10^{-4} : 3.30 \times 10^{-4} \approx 1:2$
4. Hence, the complex is $[Fe(H_2O)_2(HO–C_6H_4–CO_2)_2]^+$.

E. Kinetics

Basic Terminology

Rate of Reaction

For the general chemical reaction shown below:

$$aA + bB \rightarrow pP + qQ$$

Assuming that the reaction is *irreversible*, that is, any intermediates formed are reactive and do not accumulate, then the reaction rate is related to the rate of disappearance of reactants or formation of products:

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt}$$

where the symbols within the brackets denote concentrations, (*a*, *b*, *p*, *q*) are the *stoichiometric coefficients*.

In practice, it is usual to define the rate only in terms of the species whose concentration is being monitored.

Rate Equation / Rate Law

The *empirical* differential rate equation (or simply the rate law) is determined *experimentally* and is defined as the expression for the rate of reaction in terms of concentrations of *reactants*:

$$\text{rate} = k[A]^m[B]^n$$

where *k* is the rate constant and the exponents *m* and *n* are determined experimentally and are usually positive whole number.

Note that these exponents are independent of concentration and time; their values are not necessarily the same as the stoichiometric coefficients *a* and *b* above.

Order of Reaction

The order of reaction is the sum of the exponents in the rate equation, that is, the sum of the partial orders with respect to individual reagents, for example, (*m*+*n*) in the case above.

Molecularity

Molecularity is the number of colliding molecular entities that are involved in a *single* reaction step. While the order of a reaction is derived experimentally, the molecularity is a *theoretical concept* and can only be applied to *elementary* (*i.e.* single step) reactions.

In elementary reactions, the reaction order, the molecularity, and the stoichiometric coefficient are numerically the same but represent different concepts.

Rate Constant

The rate constant, *k*, is the proportionality constant that relates the reaction rate to the concentration of the reacting substances. The value of *k* for two reactions of different orders (*e.g.* first, second) cannot be compared directly because their units are different.

Rate-Determining Step

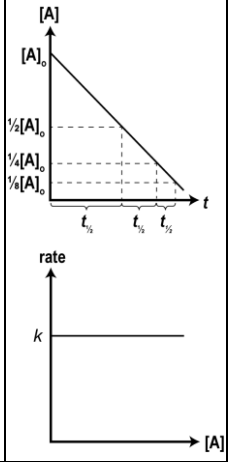
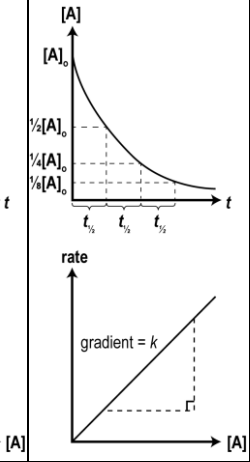
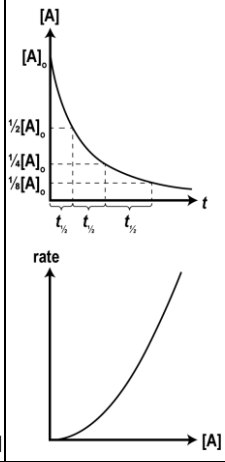
A rate-determining step is the slowest step of a chemical reaction that determines the rate of the overall reaction. In a simplified model, it can be compared to the neck of a funnel. The rate at which water flows through a funnel is limited roughly by the width of the neck of the funnel and not by the rate at which the water is poured into the funnel.

Reaction Half-Life ($t_{½}$)

The half-life, $t_{½}$, of a reaction is the time required for the concentration of a given reactant to reach a value that is the arithmetic mean of its initial and final, or equilibrium, values.

For a reactant that is entirely consumed, it is the time required for the reactant concentration to fall to one-half of its initial value.

Empirical Rate Equations and Approximations

order	zero	first	second
rate eqn	$\text{rate} = k[A]^0 = k$	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$
graphs			
$t_{½}$	decreases with *t*	**constant** $\left(t_{½} = \frac{\ln 2}{k}\right)$	increases with *t*

Pseudo Order Reaction Conditions

- A practical simplification for reactions that are second- or higher order is to convert their kinetics into *pseudo order*. If the overall rate of reaction is, for example, given by $\text{rate} = k[A]^m[B]^n$.
- If $[B]_o \gg [A]_o$, the amount of *B* consumed is negligible, that is, $[B]_t \approx [B]_o$. Then the order of the reaction will be *m* because $[B]$ remains constant, and the rate of disappearance of *A* can be expressed as $\text{rate} = k_{obs}[A]^m$.
- The proportionality factor k_{obs} deduced from such an experiment is called the *observed rate constant* and it is related to *k* by the relation $k_{obs} = k[B]^n$.

Conventional Monitoring Methods

- For slow reactions, the composition of the reaction mixture may be analysed *while the reaction is in progress* either by withdrawing a small sample or by monitoring the bulk. This is known as a **real time analysis**.
- Another option is to use the *quenching method*, in which reaction is stopped a certain time after initiation so that the composition can be analysed at leisure. Quenching may be achieved in a number of ways. For example:
  - ✓ Sudden cooling
  - ✓ Adding a large amount of solvent
  - ✓ Rapid neutralisation of an acid reagent
  - ✓ Removal of a catalyst
  - ✓ Addition of a quencher

  The key requirement is that the reaction must be slow enough (or the quenching method fast enough) for little reaction to occur during the quenching process itself.
- Often, the real time and quenching techniques are *combined* by withdrawing and quenching small samples of the reaction mixture at a series of times during the reaction.
- The composition of the reaction mixture may be followed in any one of a variety of different ways by tracking any *chemical* or *physical changes* as the reaction proceeds, e.g.
  - ✓ For reactions in which at least one reactant or product is a gas, the reaction's progress may be followed by monitoring the **pressure**, or the **volume**. (see **L: Pressure of Gas** and **M: Gas Collection and Volume Measurement** on page 9)
  - ✓ For reactions involving ions, **conductivity** or **pH measurements** may often be employed.
  - ✓ If the reaction is slow enough, the reaction mixture may be **titrated**. (see **A: Titrimetric / Volumetric Analysis (VA)** *on* page 12)
  - ✓ If one of the components is coloured or absorbs uv radiation, then **colourimetry** or **spectrophotometry** may be appropriate. (see **D: UV/Visible Spectrophotometry** on page 22)

- ✓ For reactions involving chiral compounds, **polarimetry** (see Error! Reference source not found.**:** Error! Reference so urce not found. on page **Error! Bookmark not defined.**) may be useful.

Temperature Control and Measurement

- For any reaction with a non-zero activation energy, the rate constant is dependent on temperature. The temperature dependence is often modelled by the *Arrhenius equation*:

$$k = Ae^{-\frac{E_a}{RT}}$$

where E_a is the activation energy for the reaction, and A is a constant known as the pre-exponential factor.

- This temperature dependence means that in order to measure an accurate value for k, the temperature of the reaction mixture must be maintained at a constant, known value. If activation energies are to be measured as part of the kinetic study, rate constants must be measured at a series of temperatures.
- The temperature is most commonly monitored using a thermocouple, due to its wide range of operation and potential for automation; however, standard thermometers are also commonly used. (see **E: Temperature Measurement** on page 7)
- There are numerous ways in which the temperature of a reaction mixture may be controlled. For example, reactions in the liquid phase may be carried out in a *thermostatically-controlled water bath*, while reactions in the gas phase are usually carried out inside a stainless steel vacuum chamber.

Experimental Determination of Rate Equation

A kinetics experiment consists of measuring the concentrations of one or more reactants or products at *a number of different times* during the reaction. (see **N: Time Measurement** on page 10) We will look at the methods that allow us to use the experimental data to determine the reaction orders with respect to each reactant, and therefore the rate equation.

Isolation Method

- The isolation method is a technique for simplifying the rate equation in order to determine its dependence on the concentration of a *single* reactant. (see "Pseudo Order Reaction Conditions" on page 23)
  - ✓ The dependence of the reaction rate on the chosen reactant concentration is isolated by having all other reactants present in a **large excess**, so that their concentration remains essentially constant throughout the reaction.
- Once the rate equation has been simplified, the *initial rates* or *continuous/graphical methods* below may be used to determine the reaction orders.
  - ✓ When the rate law contains contributions from a number of reactants, a series of experiments may be carried out in which each reactant is isolated in turn.

Initial Rates Methods

- When a rate equation only depends on the concentration of one species, either because there is only a single species reacting, or because the isolation method was used to simplify the rate equation, then the rate equation may be written $\text{rate} = k[A]^n$.
- We can make a series of measurements of the initial rate of the reaction *with different initial concentrations* $[A]_o$. These may then be compared to determine the order, n.

Graphical Methods

- If we have measured concentrations as a function of time, we may *plot the graph* and compare their time dependence with the appropriate shapes of the concentration-time graphs for zero, first and second order kinetics. (see "Empirical Rate Equations and Approximations", page 23)
  - ✓ Again, this is most straightforward if we have simplified the rate equation so that it depends on only one reactant concentration.
- Only zero order kinetics will give a straight time graph. All high order kinetics will give a curve.
- To differentiate between first and second order kinetics, we can measure a series of successive half-lives.
  - ✓ $t = 0$ is used as the start time from which to measure the first half-life, $t_{½(1)}$.
  - ✓ Then $t_{½(1)}$ is used as the start time from which to measure the second half-life, $t_{½(2)}$, and so on.
  - ✓ Only the half-lives for a first order kinetics will be constant.

Procedure (Initial Rates Methods)

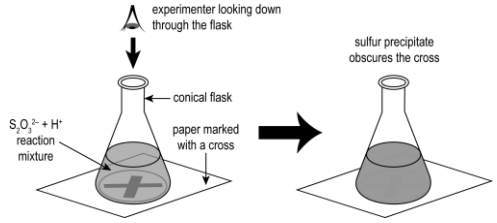
Eg 17 Determination of the kinetics of the decomposition of thiosulfate ions

Solid sulfur if one of the products formed in the reaction between sodium thiosulfate and hydrochloric acid:

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

The presence of sulfur cases the solution to become opaque.

In this experiment, the rate of this reaction is studied by measuring the time taken for the reaction mixture to become opaque, covering a cross marked on a piece of paper placed beneath the mixture.



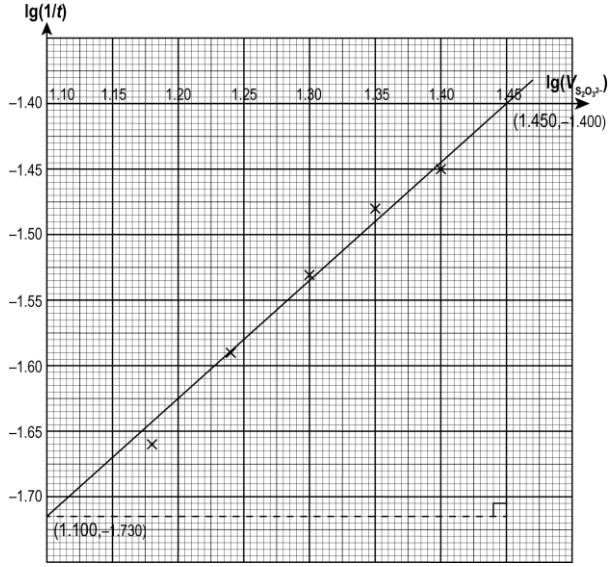
1. Fill the burette with 0.100 mol dm^{-3} $Na_2S_2O_3$.
2. Transfer 25.00 cm^3 of $Na_2S_2O_3$ into a 100 cm^3 conical flask.
3. Fill a second burette with 2.0 mol dm^{-3} HCl.
4. Rinse out a test-tube with HCl and discard this solution.
5. Transfer 5.00 cm^3 of hydrochloric acid to this test-tube.
6. Pour the hydrochloric acid rapidly into the conical flask. Start the stopwatch during this addition.
7. Mix the contents thoroughly by swirling the flask 5 times. Then place the flask on the piece of paper marked with a cross.
8. Stop the stopwatch then the solution **first** becomes opaque, obscuring the cross.
9. Record the time taken, t, to 0.1 s.
10. Wash out the conical flask and stand it upside down on a paper towel to drain.
11. Repeat step 1 to 10, adding 22.50, 20.00, 17.50 and 15.00 cm^3 respectively, of $Na_2S_2O_3$ at point 2. In each case, adding the appropriate volume of deionised water using a third burette, so that the total volume of reaction mixture is 30.00 cm^3.
12. Record all required volumes, time taken and the calculated values in the table below.

expt	$V_{S_2O_3^{2-}}$ /cm^3	V_{water}/cm^3	t/s	$\frac{1}{t}$ /s^{-1}	$\lg\left(\frac{1}{t}\right)$	$\lg\left(V_{S_2O_3^{2-}}\right)$
1	25.00	0.00				
2	22.50	2.50				
3	20.00	5.00				
4	17.50	7.50				
5	15.00	10.00				

Processing of data

1. Plot a graph of $\lg\left(\frac{1}{t}\right)$ on the y-axis against $\lg\left(V_{S_2O_3^{2-}}\right)$ on the x-axis.
2. Draw the best-fit straight line taking into account all of the plotted points.

Sample graph



Calculation

Since amount of sulfur taken to obscure the cross is constant,

$$\text{rate} \propto \frac{1}{t}$$

Since the total volume of the five experiments are kept constant,

$$\left[S_2O_3^{2-}\right] \propto V_{S_2O_3^{2-}}$$

Let the rate equation be

$$\text{rate} = k\left[S_2O_3^{2-}\right]^n$$

$$\frac{1}{t} \propto \left(V_{S_2O_3^{2-}}\right)^n$$

$$\frac{1}{t} = k'\left(V_{S_2O_3^{2-}}\right)^n$$

$$\lg\left(\frac{1}{t}\right) = \lg k' + n\lg\left(V_{S_2O_3^{2-}}\right)$$

Hence, the gradient of the graph of $\lg\left(\frac{1}{t}\right)$ against $\lg\left(V_{S_2O_3^{2-}}\right)$ will give n, the order of reaction w.r.t. $S_2O_3^{2-}$.

$$\text{Gradient} = \frac{-1.400-(-1.730)}{1.450-1.100} = \frac{0.330}{0.350} = 0.943$$

Hence, order of reaction with respect to $S_2O_3^{2-}$ is **one**.

Eg 18 Determination of the rate equation for an iodine clock reaction

A solution containing H_2O_2 and CH_3COOH is mixed with one containing KI, $Na_2S_2O_3$, CH_3CO_2Na and starch. After a few seconds a dark blue colour suddenly appears. This is one of a number of reactions referred to as iodine clock reactions.

$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$ **reaction 1**

$2S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$ **reaction 2**

When the above solutions are mixed, I_3^- are generated in reaction **1**. Reaction **2** causes I_3^- to be consumed as they are generated. Therefore, only a small amount of I_3^- is present in the mixture.

Reaction **2** stops once all the $S_2O_3^{2-}$ have reacted. The concentration of I_3^- now increases and the dark blue colour of the I_3^-–starch complex appears.

Reaction **1** is the rate determining step and it is first order with respect to the H^+ ion. So a CH_3CO_2H/CH_3CO_2Na buffer is used to maintain the pH of the reaction mixture.

FA 1 is 1.67 mol dm^{-3} hydrogen peroxide, H_2O_2

FA 2 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 3 is 0.600 mol dm^{-3} potassium iodide, KI

FA 4 is 0.121 mol dm^{-3} sodium ethanoate, CH_3CO_2Na

FA 5 is 2.50 mol dm^{-3} ethanoic acid, CH_3CO_2H

1. Fill a burette with **FA 1**.
2. Fill a second burette with **FA 3**.

Solution A

3. Transfer 25.00 cm^3 of **FA 1** to a clean 100 cm^3 conical flask labelled **Solution A**.
4. Using a 10 cm^3 measuring cylinder, add 10.0 cm^3 of **FA 5** to the same conical flask.
5. Mix the contents thoroughly by swirling the flask.

Solution B

6. Transfer 15.00 cm^3 of **FA 3** to a clean 250 cm^3 conical flask labelled **Solution B**.
7. Using a 25 cm^3 measuring cylinder, add 20.0 cm^3 of **FA 2** to the same conical flask.
8. Using another 25 cm^3 measuring cylinder, add 20.0 cm^3 of **FA 4** to the same conical flask.
9. Using another 10 cm^3 measuring cylinder, add 10.0 cm^3 of starch indicator to the same conical flask.
10. Mix the contents thoroughly by swirling the flask.
11. Pour **Solution A** rapidly into the conical flask containing **Solution B**. Start the stopwatch when you have added about half of **Solution A**.
12. Mix the contents thoroughly by swirling the flask.
13. Stop the stopwatch when the dark blue colour first appears.
14. Note the time elapsed, *t*, to the nearest 0.1 s.
15. Wash both conical flasks thoroughly with water and allow to drain.
16. Repeat points 1 to 15, with the volume of **FA 1** and **FA 3** in the table below in point 3 and 6, respectively. In each case, adding the appropriate volume of deionised water so that the total volumes of **Solution A** and **Solution B** is 100 cm^3, while using the same volume of **FA 2**, **FA 4**, **FA 5** and starch indicator.

expt	$V_{FA\,1}$ /cm^3	$V_{FA\,3}$ /cm^3	V_{water} /cm^3	$[H_2O_2]_o$ /mol dm^{-3}	$[I^-]_o$ /mol dm^{-3}	t /s	initial rate /mol dm^{-3} s^{-1}
1	25.00	15.00	0.0	0.418	0.0900	21.2	9.43×10^{-4}
2	20.00	15.00	5.0	0.334	0.0900	26.4	7.58×10^{-4}
3	15.00	15.00	10.0	0.251	0.0900	35.5	5.63×10^{-4}
4	25.00	10.00	5.0	0.251	0.0600	31.6	6.33×10^{-4}
5	25.00	5.00	10.0	0.251	0.0300	63.1	3.17×10^{-4}

Processing of data

1. Calculate an estimate for the experimental initial rate of reaction for each experiment, using the following equation:

$$\text{experimental initial rate} \approx \frac{\text{change in } \left[S_2O_3^{2-}\right]}{\text{time taken, } t} = \frac{\frac{20}{100}\times 0.100}{t} = \frac{0.0200}{t} \text{ mol dm}^{-3}$$

2. Calculate the initial concentrations of hydrogen peroxide, $[H_2O_2]_o$, and iodide ions, $[I^-]_o$, for each experiment.

Conclusion

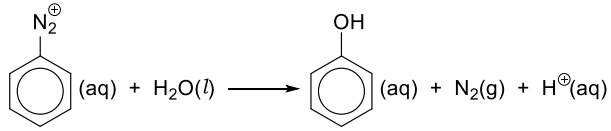
1. Using Expt 1 and 2, and Expt 1 and 3, when $[H_2O_2]_o$ increases by $\frac{5}{4}$ and $\frac{5}{3}$ times, the initial rate also increases by $\frac{5}{4}$ and $\frac{5}{3}$ times, hence **first order** w.r.t. H_2O_2.
2. Using Expt 1 and 4, and Expt 1 and 5, when $[I^-]$ increases by $\frac{3}{2}$ and 3 times, the initial rate also increases by $\frac{3}{2}$ and 3 times, hence **first order** w.r.t I^-.
3. Hence rate equation is

$$\text{rate} = k\left[H_2O_2\right]\left[I^-\right]\left[H^+\right]$$

Procedure (Graphical Methods)

Eg 19 Determination of the order of reaction for decomposition of benzenediazonium ion in water

Benzenediazonium tetrafluoroborate, $C_6H_5N_2^+BF_4^-$, (M_r = 191.9) is a reasonably stable salt containing the otherwise reactive benzenediazonium ion, $C_6H_5N_2^+$, which reacts with water at elevated temperature as shown:



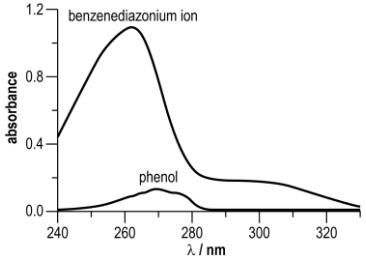
An aqueous solution is stable when cold (*e.g.* 0–5ºC), but decomposes rapidly when the temperature is increased.

This reaction can be followed by tracking with time,

- the **absorbance** of $C_6H_5N_2^+(aq)$
- the **volume** of N_2 produced
- the **pH** of the solution

Absorbance

The absorbance should be measured between 295 and 325 nm, as below 295 nm, the phenol product produce interfering absorption, while above 325 nm, the absorptivity is too small to permit effective measurement of changes in concentration of $C_6H_5N_2^+$.

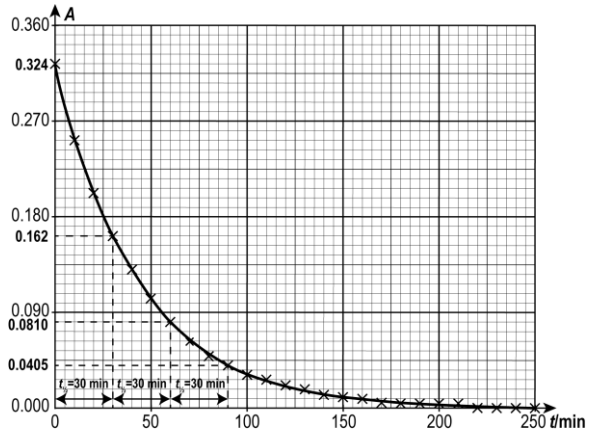


1. Weigh accurately between 0.015 g and 0.020 g of benzenediazonium tetrafluoroborate in a clean and dry weighing bottle.
2. Tip the contents of the weighing bottle into a clean, dry 100 cm^3 beaker. Wash out the weighing bottle with 0.20 mol dm^{-3} HC*l* and add the washing to the beaker.
3. Add 50 cm^3 of 0.20 mol dm^{-3} HC*l* to the beaker and stir the mixture gently with a clean glass rod until all the solid has dissolved.
4. Carefully transfer the solution into a clean 100 cm^3 volumetric flask, rinsing the beaker with 0.20 mol dm^{-3} HC*l*.
5. Make the solution up to the mark using 0.20 mol dm^{-3} HC*l*.
6. Using a 5 cm^3 syringe, withdraw a 5.00 cm^3 sample and place it in a labelled test-tube set in a crushed ice bath for chilling.
7. Suspend the volumetric flask in a thermostatically-controlled water bath set at 40ºC. Start the stopwatch.
8. After the sample in point 6 is chilled for 5 min, use about 1 cm^3 of it to rinse out the spectrophotometer cuvette. Fill the cuvette with the remaining sample and measure its absorbance, *A*, using a spectrophotometer at 305 nm.
9. Repeat point 6 **and** point 8 to obtain the absorbance after every 10 min, until the absorbance reaches **zero**. Record the time of discharge into the test-tube, *t* min, to 1 decimal place, for each of the sample.

Processing of data

1. Plot a graph of absorbance, *A*, on the *y*-axis against time, *t*, on the *x*-axis.
2. Draw the most appropriate best-fit line taking into account all of the plotted points.
3. Determine three half-lives from the graph.

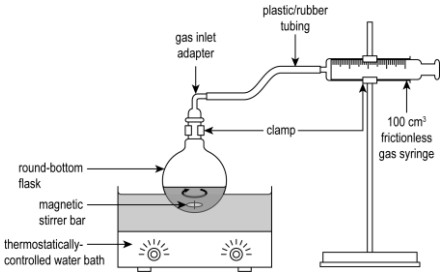
Sample graph



Conclusion

Since the half-life is constant at 30 min, the reaction is **first order** w.r.t. $C_6H_5N_2^+$.

Volume



1. Set up the apparatus as shown above, with the thermostatically-controlled water bath set at 40ºC and the piston of the frictionless gas syringe at 0.0 cm^3.
2. Using a 100 cm^3 measuring cylinder, add 100.0 cm^3 of 0.2 mol dm^{-3} HC*l* into the round-bottom flask. Set the magnetic stirrer to slow constant stirring and allow thermal equilibration.
3. Weigh accurately about 0.40 g of benzenediazonium tetrafluoroborate in a clean and dry weighing bottle.
4. Tip the contents of the weighing bottle into the round-bottom flask and attach the gas inlet adapter. Start the stopwatch.
5. Read and record the volume of N_2 gas evolved, to 1 decimal place, every 10 min, until three constant readings are obtained.
6. Reweigh and record the mass of the emptied weighing bottle.

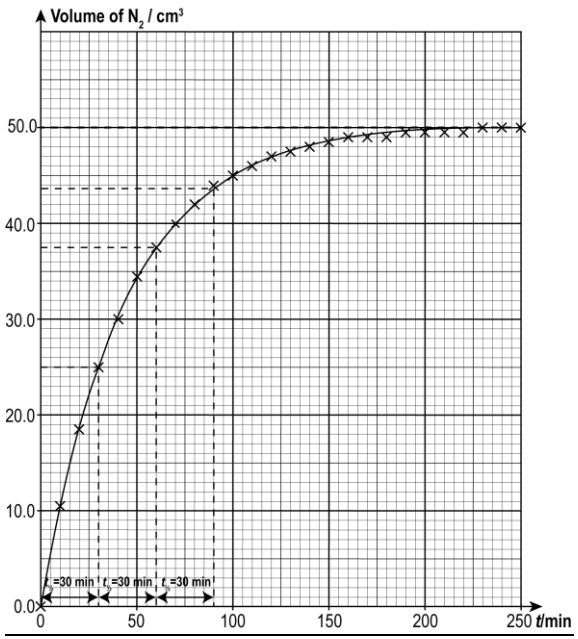
mass of empty weighing bottle / g	
mass of weighing bottle and $C_6H_5N_2^+BF_4^-$ / g	
mass of emptied weighing bottle / g	
mass of $C_6H_5N_2^+BF_4^-$ used / g	

time / min	volume of N_2 / cm^3
0.0	0.0
10.0	10.3
20.0	18.5
⋮	⋮
230.0	49.8
240.0	49.8
250.0	49.8

Processing of data

1. Plot a graph of volume of N_2 on the *y*-axis against time, *t*, on the *x*-axis.
2. Draw the most appropriate best-fit line taking into account all of the plotted points.
3. Determine three half-lives from the graph.

Sample graph



Conclusion

Since the half-life is constant at 30 min, the reaction is **first order** w.r.t. $C_6H_5N_2^+$.

pH

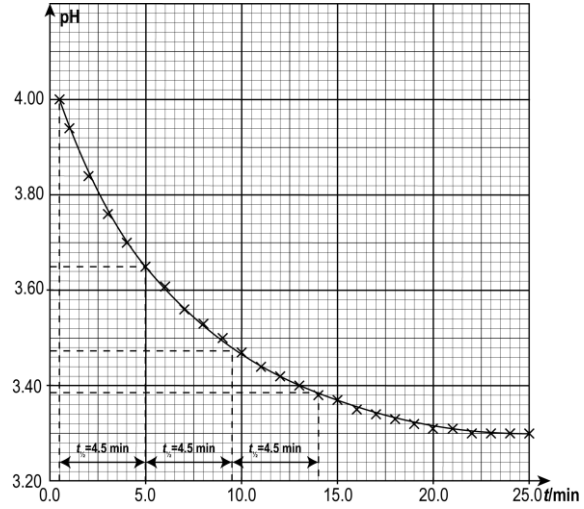
Since H^+ ion and phenol are products of the reaction, the pH will decrease during the course of the reaction. Phenol does not significantly affect the pH since it is a very weak acid.

1. Using a 100 cm^3 measuring cylinder, add 100.0 cm^3 of 0.0200 mol dm^{-3} KC*l* into a 250 cm^3 beaker, equipped with a magnetic stirrer bar and a pH probe.
2. Suspend the beaker in a thermostatically-controlled water bath set at 40ºC. Set the magnetic stirrer to slow constant stirring and allow thermal equilibration.
3. Weigh accurately about 0.25 g of benzenediazonium tetra-fluoroborate in a clean and dry weighing bottle.
4. Tip the contents of the weighing bottle into the beaker. Start the stopwatch.
5. Read and record the pH, to 2 decimal places, every min, until three constant readings are obtained.
6. Reweigh and record the mass of the emptied weighing bottle.

Processing of data

4. Plot a graph of volume of N_2 on the *y*-axis against time, *t*, on the *x*-axis.
5. Draw the most appropriate best-fit line taking into account all of the plotted points.
6. Determine three half-lives from the graph.

Sample graph



Conclusion

Since the half-life is constant at 4.5 min, the reaction is **first order** w.r.t. $C_6H_5N_2^+$.

Eg 20 Determination of the order of reaction with respect to iodine in the iodination of propanone reaction

The iodination of propanone, to form iodopropanone, proceeds as shown in the equation below:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I(aq) + HI(aq)$$

The reaction is first order with respect to both CH_3COCH_3 and H^+.

FA 1 is 1.00 mol dm^{-3} propanone, CH_3COCH_3

FA 2 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4

FA 3 is 0.0200 mol dm^{-3} aqueous iodine, I_2

FA 4 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 5 is 0.50 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$

*Titration of **FA 3***

1. Fill a burette with **FA 4**.
2. Fill a second burette with **FA 3**.
3. Transfer 5.00 cm^3 of **FA 3** into a clean 250 cm^3 conical flask.
4. Using a 25 cm^3 measuring cylinder, add about 15 cm^3 of deionised water into the conical flask.
5. Titrate the iodine in this solution with **FA 4**. When the colour of the solution turns pale yellow, add about 1 cm^3 of starch indicator. The solution will turn dark blue/black. The end-point is reached when the dark blue/black colour just disappears. Record your result.

Preparing the test-tubes

6. Label the large test-tubes, 4 minutes, 9 minutes, 14 minutes, 19 minutes and 24 minutes.
7. Add approximately 10 cm^3 of **FA 5** to each of these test-tubes using a 10 cm^3 measuring cylinder.

Preparing the reaction mixture

8. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the 100 cm^3 beaker.
9. Using a different pipette, transfer 25.0 cm^3 of **FA 2** into the same 100 cm^3 beaker.
10. Using the burette, transfer 50.00 cm^3 of **FA 3** into the 250 cm^3 conical flask, labelled **reaction mixture**.
11. Pour the contents of the 100 cm^3 beaker into this 250 cm^3 conical flask. Start the stopwatch, **insert the stopper** and swirl the mixture thoroughly.

Removing aliquots of reaction mixture

12. At approximately 4 minutes, use a 10 cm^3 pipette to remove a 10.0 cm^3 aliquot of the reaction mixture. **Immediately** transfer this aliquot into a test-tube labelled **4 minutes** and swirl the mixture. Note the *actual time*, ***t***, in minutes, recorded to 1 decimal place, when half of the reaction mixture has emptied from the pipette. Replace the stopper in the flask.
13. At 9 minutes, 14 minutes, 19 minutes and 24 minutes, repeat point 7 but transfer each aliquot to its appropriately labelled large test-tube.

Titrations

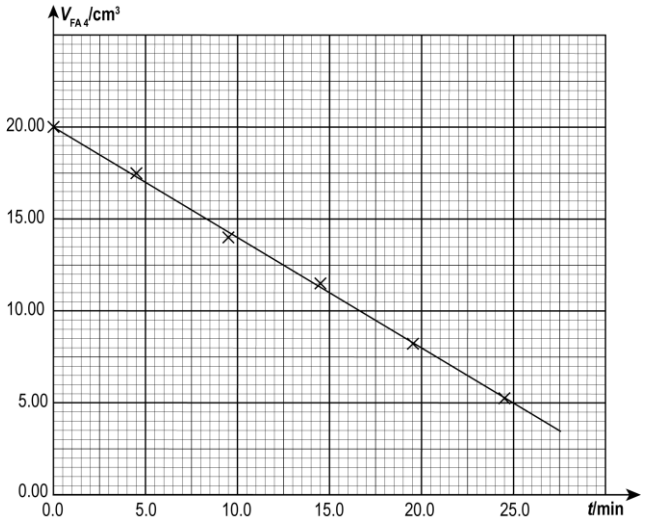
14. Pour the whole of the contents of a test-tube into a clean 250 cm^3 conical flask. Wash out the test-tube with deionised water and add the washings to the conical flask.
15. Titrate the iodine in this solution with **FA 4** as in point 5. Record your results.
16. Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
17. Repeat points 14 to 16 for each of the test-tubes.

expt	***t***/min	final burette reading/cm^3	initial burette reading/cm^3	volume of **FA 4**/cm^3
1	0.0			
2	4.5			
3	9.5			
4	14.5			
5	19.5			
6	24.5			

Processing of data

1. The titre value in point 5 corresponds to the volume of **FA 4** required at *t* = 0 min.
2. Plot a graph of volume of $Na_2S_2O_3$, **FA 4**, on the *y*-axis against time, *t*, on the *x*-axis, including the value at *t* = 0 min.
3. Draw the most appropriate best-fit line taking into account all of the plotted points.

Sample graph



Conclusion

The volume of **FA 4** used is proportional to the $[I_2]$ in the reaction mixture at time, *t*.

Thus gradient of graph of volume of **FA 4** against *t* is proportional to rate of reaction, which is a constant since the graph is a straight line.

Since the rate of reaction is independent of the $[I_2]$, the reaction is **zero order** w.r.t. I_2.

Procedure (Determination of E_a)

Eg 21 Determination of the activation energy for the iodination of propanone (extension from Eg 20)

From Eg 20, the rate equation for the iodination of propanone is

$$\text{rate} = k\left[CH_3COCH_3\right]\left[H^+\right]$$

If we determine the **initial rate** of the reaction, together with the **initial concentration** of CH_3COCH_3 and H^+, we can then obtain a value for the *rate constant*, *k* :

$$k = \frac{\text{initial rate}}{\left[CH_3COCH_3\right]_o\left[H^+\right]_o}$$

In this case, as $\left[CH_3COCH_3\right]_o \gg \left[I_2\right]_o$ and $\left[H^+\right]_o \gg \left[I_2\right]_o$, and the reaction is zero order w.r.t. I_2, the initial rate will also be the rate of the reaction at any time.

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

$$n_{I_2} = \frac{1}{2}n_{S_2O_3^{2-}} = \frac{1}{2}\left(V_{\mathbf{FA\,4}} \times 0.0100\right)$$

Since 10.0 cm^3 aliquot of the reaction mixture is pipetted out for each titration,

$$\text{initial rate} = -\frac{\Delta\left[I_2\right]}{\Delta t}$$

$$= -\frac{\frac{1}{2}\left(\frac{5.00}{1000}\times 0.0100\right) - \frac{1}{2}\left(\frac{20.00}{1000}\times 0.0100\right)}{\frac{10.0}{1000}} \text{ mol dm}^{-3}$$

$$= -\frac{\frac{10.0}{1000}}{(25.0 - 0.0)\text{ min}}$$

$$= 3.00\times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

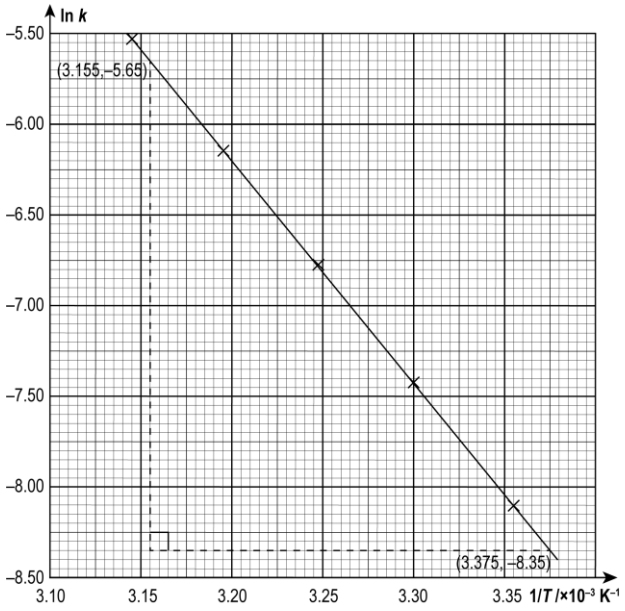
Hence, $$k = \frac{\text{initial rate}}{\left[CH_3COCH_3\right]_o\left[H^+\right]_o} = \frac{3.00\times 10^{-4}}{1.00\times(2\times 1.00)}$$

$$= 1.50\times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$$

If the procedure in Eg 20 is repeated at **four other temperatures**, *T* K, and the corresponding rate constants, *k*, are determined from each of the graphs, we can then use Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}} \Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

to determine the activation energy, E_a, by plotting a graph of ln *k* against $\frac{1}{T}$. The gradient of the straight line will be $-\frac{E_a}{R}$. *E.g.*



$$\text{gradient} = \frac{-8.35 - (-5.65)}{(3.375 - 3.155)\times 10^{-3}}$$

$$-\frac{E_a}{R} = -12273$$

$$E_a = +102 \text{ kJ mol}^{-1}$$

Eg 22 Determination of the activation energy for the iodination of propanone

Under acidic conditions, iodine reacts with propanone to form 1-iodo-propanone as shown below:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I(aq) + HI(aq)$$

The rate-determining step for this reaction involves the protonation of propanone.

The reaction is first order with respect to both CH_3COCH_3 and H^+ ions but zero order with respect to iodine:

$$\text{rate} = k\left[CH_3COCH_3\right]\left[H^+\right]$$

The activation energy, E_a, can be determined from the Arrhenius equation, where *T* is the reaction temperature in Kelvin and *k* is the rate constant at temperature, *T*. The pre-exponential factor, *A*, can be regarded as a constant under the conditions of this experiment.

$$k = Ae^{-\frac{E_a}{RT}}$$

FA 1 is 4.00 mol dm^{-3} propanone, CH_3COCH_3

FA 2 is 1.00 mol dm^{-3} hydrochloric acid, HC*l*

FA 3 is 5.00×10^{-3} mol dm^{-3} aqueous iodine, I_2

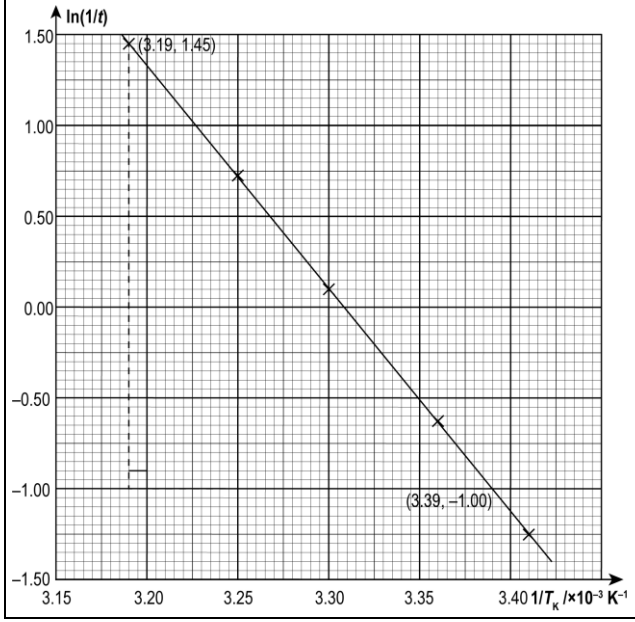
1. Use a 10 cm^3 measuring cylinder to add 10.0 cm^3 of **FA 1** to a clean dry boiling tube.
2. Use another 10 cm^3 measuring cylinder to add 10.0 cm^3 of **FA 2** to the same boiling tube.
3. Place the boiling tube into a thermostatically-controlled water bath at 20ºC, and clamp the boiling tube to the retort stand. Place a white tile behind the boiling tube. Stand a thermometer (range of 0 to 50ºC, calibrated to 0.2ºC) in the boiling tube.
4. Use another 10 cm^3 measuring cylinder to add 10.0 cm^3 of **FA 3** to a test-tube labelled **FA 3**.
5. Place the test-tube contained **FA 3** in the same water bath.
6. Stir the solution in the boiling tube with the thermometer. When its temperature is within about 1ºC of that of the water bath, pour the **FA 3** solution **rapidly** from the test-tube, in a steady stream, into the boiling tube. Start the stopwatch when about half of the **FA 3** solution has been added.
7. Stir the mixture using the thermometer. Measure and record the initial temperature, $T_{initial}$, of the reaction mixture
8. Continue to stir the mixture. Stop the stopwatch when the reaction mixture becomes colourless.
9. Measure and record the final temperature, T_{final}, of the reaction mixture.
10. Record the time elapsed on the stopwatch, t_m, in minutes and seconds, to the nearest second.
11. Wash thermometer with water and dry it on a paper towel.
12. Repeat points 1 to 10, with the thermostatically-controlled water bath set to 25ºC, 30ºC, 35ºC and 40ºC at point 3.

expt	$T_{initial}$ /ºC	T_{final} /ºC	T_{avg} /ºC	T_K /K	t_d /min s	t /min	$\frac{1}{t}$ /min^{-1}	$\frac{1}{T_K}$ /K^{-1}	$\ln\left(\frac{1}{t}\right)$
1	20.0								
2	25.0								
3	30.0								
4	35.0								
5	40.0								

Processing of data

1. Convert the reaction times, t_m, to decimal minutes, t, recorded to three significant figures.
2. Calculate the average temperature, T_{avg}, of the $T_{initial}$ and T_{final} values, recorded to 0.1ºC.
3. Convert each T_{avg} into Kelvin, T_K (0.0ºC = 273.0 K), recorded to 0.1 K.
4. Calculate $\frac{1}{T_K}$, recorded to three significant figures.
5. Calculate $\frac{1}{t}$ and $\ln\left(\frac{1}{t}\right)$, recorded to three significant figures.
6. Plot a graph of $\ln\left(\frac{1}{t}\right)$ on the *y*-axis against $\frac{1}{T_K}$ on the *x*-axis.
7. Draw a straight line-of-best-fit, taking into account all the plotted points.

Sample graph



Calculation

In this case, the reaction is zero order w.r.t. I_2, thus

$$\text{rate} = -\frac{\Delta[I_2]}{t} = -\frac{0-[I_2]_o}{t} = \frac{[I_2]_o}{t}$$

Combining this with the rate equation and Arrhenius equation,

$$\frac{[I_2]_o}{t} = Ae^{-\frac{E_a}{RT}}[CH_3COCH_3][H^+]$$

Since $[CH_3COCH_3]_o \gg [I_2]_o$ and $[H^+]_o \gg [I_2]_o$, the $[CH_3COCH_3]$ and $[H^+]$ essentially do not change as the reaction progresses. Also, $[I_2]_o$ is the same for all five experiments. Thus,

$$\frac{1}{t} = k'e^{-\frac{E_a}{RT}} \Rightarrow \ln\left(\frac{1}{t}\right) = \ln k' - \frac{E_a}{RT}$$

The gradient of the straight line graph of $\ln\left(\frac{1}{t}\right)$ against $\frac{1}{T_K}$ is $-\frac{E_a}{R}$, where R is the molar gas constant (= 8.31 J K^{-1} mol^{-1}).

$$\text{gradient} = \frac{-1.00-1.45}{(3.39-3.19)\times10^{-3}} = \frac{-2.45}{0.20\times10^{-3}}$$

$$-\frac{E_a}{R} = -12250$$

$$E_a = +12250\times8.31$$

$$= +102 \text{ kJ mol}^{-1}$$

- In this case, because the reaction is zero order w.r.t. I_2, and the rest of the reactants are in excess, the rate of reaction is **constant** and is inversely related to the time taken, *t*, for the *reaction to complete*. However, this is a special case!
- If the order of reaction w.r.t. to a reactant is **not zero**, and concentrations of the reactants changes during the course of a reaction, which is usually what we encounter in other reaction, the *rate of reaction will also change with time*.
- In such cases, we can still plot the graph of $\ln\left(\frac{1}{t}\right)$ against $\frac{1}{T_K}$, and use the gradient to find the E_a, provided
  - ✓ The initial concentrations of all reactants are kept the same for all experiments at different T_k.
  - ✓ The time taken, *t*, is that for a **small fixed amount** of reactants to react or a **small fixed amount** of products to form. In other words, we are estimating the **initial rate** $\propto \frac{1}{t}$.
  - ✓ For example, this method can be applied to the systems in Eg 17 (page 24, small fixed amount of sulfur to form) and Eg 18 (page 25, small fixed amount of I_3^- to form), by *repeating* any one of the experiments and obtain the time taken, *t*, at 5 different temperatures (minimum number of data points to draw a straight line).

F. Polarimetry

- A sample of material able to rotate the plane of polarisation of a beam of transmitted plane-polarised light is said to possess **optical activity** (or to be **optically active**).
- Only **chiral** compounds, which have non-superimposable mirror images, can exhibit optical activity.
- The **specific rotation**, $[\alpha]_\lambda^T$, of a chiral compound is characteristic of the compound, just like its melting/boiling point.

$$[\alpha]_\lambda^T = \frac{\alpha_\lambda^T}{l\times c}$$

where T is the measurement temperature, in ºC,

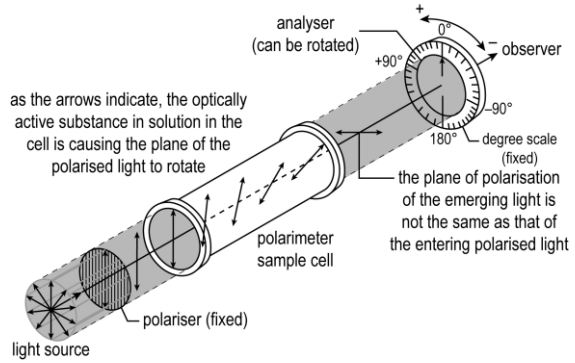
λ is the wavelength of light employed (normally the sodium D-line, or 589 nm),

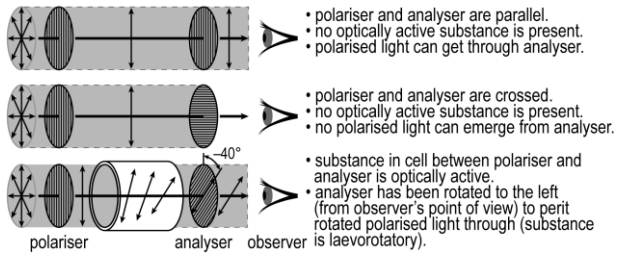
α is the observed optical rotation, in º,

l is the path length of the cell, in dm, and

c is the concentration, in g cm^{-3} (for pure substances, it is the density).

- ✓ Solvent must be identical.
- ✓ Measured using a **polarimeter**.





- In fact, optical rotation can be used to distinguish two **enantiomers** which differs only in the **direction of rotation** of plane-polarised light.
  - ✓ Clockwise (+) : dextrorotatory
  - ✓ Anti-clockwise (–) : laevorotatory
- A **racemic mixture** consisting of 50% each of the two enantiomers, will be optically inactive.

- The **optical purity** of a *mixture of enantiomers* is given by:

$$\%\ \textbf{optical purity of sample} = \frac{[\alpha]^T_\lambda \text{ of sample}}{[\alpha]^T_\lambda \text{ of a pure enantiomer}} \times 100$$

  - ✓ Hence a racemic mixture has 0% optical purity.
  - ✓ Optical rotation can in fact be used to track the kinetics of reaction involving optically active chiral compounds.

Eg 23 Determination of specific rotation of sucrose; order of reaction and rate constant for its hydrolysis.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Sucrose, $C_{12}H_{22}O_{11}$, is a naturally occurring sugar found in sugarcane and many fruits. It can be hydrolysed in acidic solution to give glucose and fructose. All three molecules are chiral and will rotate the plane of polarised light.

In the presence of excess water, the reaction will be pseudo-zero order w.r.t. H_2O.

The progress of the reaction can be monitored using a polarimeter, which measures the optical rotation, α, of the solution. The more concentrated the solution, the greater the optical rotation of the solution.

The concentration of sucrose at any time, *t*, can be represented as $(\alpha - \alpha_{final})$, where α_{final} is the optical rotation of the solution after 6 hours, assuming complete hydrolysis had taken place.

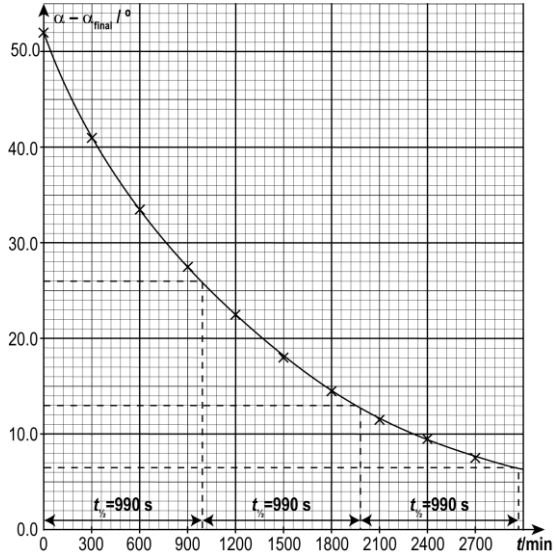
1. Weigh accurately about 120.0 g of sucrose in a clean and dry 100 cm^3 beaker.
2. Add 50 cm^3 of deionised water to the beaker and stir the mixture with a clean glass rod until all the solid has dissolved.
3. Carefully transfer the solution into a clean 100 cm^3 volumetric flask, rinsing the beaker with deionised water.
4. Make the solution up to the mark using deionised water.
5. Using a 5 cm^3 syringe, place 5.00 cm^3 of the sucrose solution into a 10 cm^3 polarimeter sample cell of path length 10 cm.
6. Using a 5.0 cm^3 syringe, add 5.00 cm^3 of deionised water into the sample cell and mix well. Read and record the optical rotation, α, at the wavelength of sodium D-line (589 nm). This is the optical rotation at time, t = 0 s.
7. Wash and dry the sample cell.
8. Using a 5 cm^3 syringe, place 5.00 cm^3 of the sucrose solution into the sample cell.
9. Using another 5 cm^3 syringe, place 5.00 cm^3 of 0.50 mol dm^{-3} HC*l* into the sample cell, mix well and start the stopwatch.
10. Read and record the optical rotation, α, at time, t = 300 s.
11. Read and record the optical rotation, α, every 300 s until time, t = 2700 s.
12. Wait for 6 hours. Read and record the optical rotation. This is α_{final}.

time, *t* / s	optical rotation, α / º	$\alpha - \alpha_{final}$ / º
0	+39.9	51.9
300	+29.1	41.1
⋮	⋮	⋮
2400	–2.5	9.5
2700	–4.5	7.5
α_{final}	–12.0	–

Processing of data

1. Calculate the value of $\alpha - \alpha_{final}$ for all the readings.
2. Plot a graph of $\alpha - \alpha_{final}$, on the *y*-axis against time, *t*, on the *x*-axis, including the value at t = 0 min.
3. Draw the most appropriate best-fit line taking into account all of the plotted points.
4. Determine the values of 3 half-lives.

Sample graph



Conclusion

1. $c = \frac{5\ cm^3}{10\ cm^3} \times \frac{120.0\ g}{100\ cm^3} = 0.60\ g\ cm^{-3}$

$$[\alpha]_D = \frac{39.9°}{1 \times 0.60} = 66.5°$$

2. Since the half-life is constant at 990 s, the hydrolysis is **first order** w.r.t. sucrose.
3. The rate constant, *k*, is given by

$$k = \frac{\ln 2}{t_{½}} = \frac{\ln 2}{990} = 7.00 \times 10^{-4}\ s^{-1}$$

G. Qualitative Analysis (QA)

Qualitative analysis may be carried out on various scales. At the A-level, **semi-micro analysis** is carried out, where the quantity of the substance employed is **0.05 g** and the volume of solution taken for the analysis is about **1 cm^3**.

Qualitative analysis utilises two kinds of tests, *dry reactions* and *wet reactions*. The former are applicable to solid substances and the latter to substances in solution.

Dry Reactions

Heating

- Wear goggles when performing experiments.
- Whenever heating is done in a test-tube, use a **test-tube holder** and never point the mouth of the test-tube at other people.
- If a poisonous gas is liberated during an experiment, the rest of the experiment should be carried out in a **fume cupboard**.
- Normal heating is usually done with a Bunsen flame in which the air hole of the burner is *half opened*.

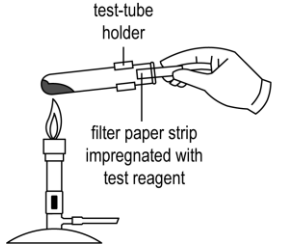
Heating Solid Sample

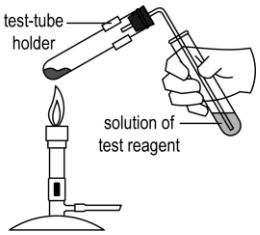
- Use dry test-tube.
- For heating solid salt, use about '**1 cm depth**' of solid sample. Tube should be held in an *almost horizontal* position
- Heat should be applied **gently initially** to the whole length of tube and both sides (to prevent condensation of water vapour on cold parts of the test-tube and hence cracking of test-tube).
- Then, heat the sample **strongly**, continue heating even if the sample appears to have melted (especially hydrated salt).
- *Sublimation* may take place, or the solid may *melt* or *decompose* with an attendant *change in colour*, or a *gas* may be evolved.

Testing of Gas During Heating

- For testing of gas during heating using litmus paper or filter paper impregnated with the test solution, do not let the litmus paper or filter paper strip touch the test-tube.
- For testing of gas using delivery tube:
  1. Fix delivery tube to the test-tube
  2. Heat the test-tube.
  3. Submerge delivery tube into test solution while still heating.

  To stop
  1. Remove test solution (otherwise, suck-back may occur which could cause the test-tube to crack)
  2. Remove test-tube from flame.





Confirmatory Test for Gases

Gas	Test	Observation
H_2 (neutral)	lighted splint or burning splint	Gas evolved extinguishes lighted/ burning splint with a 'pop' sound.
O_2 (neutral) (usually accompanied by other gas, *e.g.* *Solid* NO_3^- salt gives NO_2 and O_2 gas *Solid* XO_3^- salt gives X_2 and O_2 gas (X is C*l*, Br, I)	glowing splint	Gas evolved rekindles the glowing splint.
CO_2 (acidic)	aqueous $Ca(OH)_2$ (**do not use too much**, add just enough $Ca(OH)_2$ to cover the tip of the delivery tube)	Gas evolved forms a white ppt with $Ca(OH)_2$. (White ppt dissolves with excess CO_2.)
NH_3 (alkaline)	moist red litmus paper	Gas evolved turns moist red litmus paper blue.
SO_2 (acidic)	acidified potassium manganate(VII) (add dil. H_2SO_4 to acidify $KMnO_4$, then use filter paper strip dipped into acidified $KMnO_4$.)	Gas evolved decolourises purple $KMnO_4$.
NO_2 (brown gas; acidic)	$FeSO_4$ solution	Gas evolved turns green $FeSO_4$ black.
C*l*$_2$ (pale greenish yellow; pungent)	moist blue litmus paper	Pale greenish yellow gas evolved turns moist blue litmus paper red and then bleached it.
Br_2 (reddish brown vapour)	moist blue litmus paper	Reddish brown gas evolved turns moist blue litmus paper red and then bleached it.
I_2 (violet vapour, condenses to a black crystals)	starch iodide paper	Violet gas evolved turns starch iodide paper blue-black.

Wet Reactions

These tests are made with substances in solution. A reaction is known to take place

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

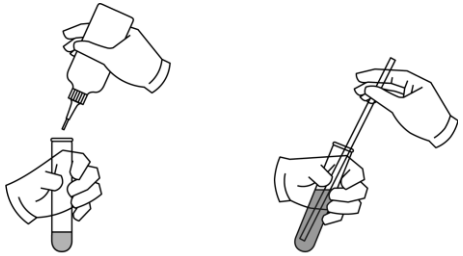
The majority of the reactions of qualitative analysis are carried out in the wet way.

Preparation of Solution

- Unless specified, it is recommended to place enough solid sample to **cover the hemisphere** of the test-tube followed by solvent to make up **2/3 test-tube full** of solution.

Handling of Reagents

- The use of large quantities of a chemical often leads to a waste of time as it takes longer time to dissolve. Besides this may lead to wrong results.
- In transferring a liquid reagent from a drop bottle into the test-tube containing the solution of the unknown, hold the tip of the drop bottle <u>just above</u> the mouth of the test-tube and allow the reagent to drop into the test-tube.

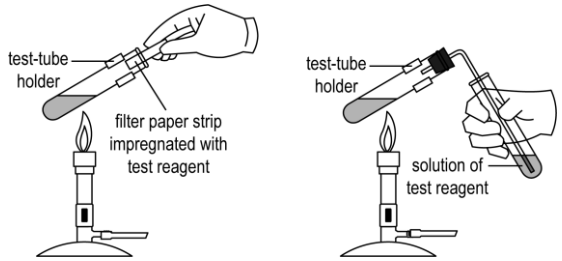


Mixing of Solution

- Well mixing of solution can be ensured by stirring with a clean glass/plastic rod.
- For small volume of solution (~5 cm^3), gentle shaking of the test-tube usually suffices.

Warming

- For heating liquid sample, use about '**1 cm depth**' of liquid.
- The flame should be placed around **meniscus** of the solution.
- Testing for gas :



Addition of Reagent

- Reagent should always be added **dropwise**, shaking after the addition of each drop and noting down any changes, unless otherwise stated.
- Once it is observed that *no further changes* happen when the reagent is added dropwise, an excess of the reagent (in the case of NaOH (aq) or NH_3 (aq)) can then be added (usually about half the test-tube) and the solution mixed. Note down any changes.

Recording

- If ppt is expected to be formed, record as:
  - ✓ '(colour) ppt formed' or
  - ✓ 'no ppt formed'
- If ppt formed can be <u>soluble</u> in excess reagent added, (*e.g.* in aqueous NaOH, NH_3, H_2SO_4) record as:
  - ✓ '(colour) ppt formed soluble in excess of (name of reagent added) to give (colour of solution)'
  - ✓ '(colour) ppt formed insoluble in excess of (name of reagent added)'
- If gas is expected to be evolved from a **solution**, record as '**effervescence** evolved which (test for gas, if any)'.

  If gas is evolved from <u>heating of solid</u>, the term '**fume**' or '**<u>gas</u>**' should be used instead of 'effervescence'.)
- ***Do not*** use term such as milky, chalky for limewater.

Data Booklet

9 Qualitative Analysis Notes
[ppt. = precipitate]

9(a) 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

9(b) Reactions of 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 with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

9(c) Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

9(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Inorganic QA

SODIUM HYDROXIDE

PRECIPITATES

Colour ⇒ test for cations

COLOUR OF PRECIPITATES

- White ppt.
  Soluble in excess ⇒ Al^{3+} (→ $[Al(OH)_4]^-$)
  Zn^{2+} (→ $[Zn(OH)_4]^{2-}$)
- White ppt.
  Insoluble in excess ⇒ Mg^{2+}, Ca^{2+} (high conc)
- Off-white ppt.
  Insoluble in excess ⇒ Mn^{2+}
  (turns brown on standing) → $Mn^{IV}O(OH)_2$

SODIUM HYDROXIDE

PRECIPITATES

- Blue ppt.
  Insoluble in excess ⇒ Cu^{2+}
  (turns black on warming) → CuO
- Grey-green ppt.
  Soluble in excess ⇒ Cr^{3+}
  giving dark green solution → $[Cr(OH)_6]^{3-}$
- Green ppt.
  Insoluble in excess ⇒ Fe^{2+}
  (turns brown on standing) → $Fe(OH)_3$
- Reddish-brown ppt.
  Insoluble in excess ⇒ Fe^{3+}
- No ppt. ⇒ Ba^{2+}, Na^+, K^+ or NH_4^+

WARM

GASES

Colour, alkalinity ⇒ test for NH_4^+

ALKALINE

- Colourless NH_3 ⇒ NH_4^+
  (Red litmus turns blue)

WARM WITH *Al* FOIL

GASES

Colour, alkalinity ⇒ test for NO_2^-, NO_3^-

ALKALINE

- Colourless NH_3 ⇒ NO_2^-, NO_3^-
  (Red litmus turns blue)

COLOUR CHANGES

Colour ⇒ test for transition metal ions

- Orange to yellow ⇒ $Cr_2O_7^{2-}$ $\left(\rightarrow CrO_4^{2-}\right)$

AQUEOUS AMMONIA

PRECIPITATES

Colour ⇒ test for cations

COLOUR OF PRECIPITATES

- White ppt.
  Soluble in excess ⇒ Zn^{2+} (→ $[Zn(NH_3)_4]^{2+}$)
- White ppt.
  Insoluble in excess ⇒ Al^{3+}, Mg^{2+}

AQUEOUS AMMONIA

PRECIPITATES

- Off-white ppt.
  Insoluble in excess ⇒ Mn^{2+}
  (turns brown on standing) → $Mn^{IV}O(OH)_2$
- Blue ppt.
  Soluble in excess ⇒ Cu^{2+}
  giving dark blue solution → $[Cu(NH_3)_4(H_2O)_2]^{2+}$
- Grey-green ppt.
  Insoluble in excess ⇒ Cr^{3+}
- Green ppt.
  Insoluble in excess ⇒ Fe^{2+}
  (turns brown on standing) → $Fe(OH)_3$
- Reddish-brown ppt.
  Insoluble in excess ⇒ Fe^{3+}
- No ppt. ⇒ Ca^{2+}, Ba^{2+}, Na^+, K^+ or NH_4^+

@ NH_4Cl FOLLOWED BY NH_3

- Presence of ppt. ⇒ Al^{3+}, Cu^{2+}, Cr^{3+}, Fe^{3+}
  These cations form hydroxides of low K_{sp} values.

@ SODIUM CARBONATE

@ PRECIPITATES

Colour ⇒ test for cations

COLOUR OF PRECIPITATES

- White ppt. ⇒ Al^{3+} (→ $Al(OH)_3$)
  Zn^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+} $\left(CO_3^{2-}\right)$
- Off-white ppt. ⇒ Mn^{2+}
  (turns brown on standing) → $Mn^{IV}O(OH)_2$
- Blue ppt. ⇒ Cu^{2+}
  (turns black on heating) → CuO
- Green ppt. ⇒ Cr^{3+} (→ $Cr(OH)_3$)
  Fe^{2+} (→ $FeCO_3$)
- Reddish-brown ppt. ⇒ Fe^{3+} (→ $Fe(OH)_3$)

GASES

Acidity/Alkalinity ⇒ test for H^+, NH_4^+

ALKALINE

- Colourless NH_3 ⇒ NH_4^+
  (Red litmus turns blue)

ACIDIC

- Colourless CO_2 ⇒ H^+ or Al^{3+}, Cr^{3+}, Fe^{3+}
  (White ppt. with $Ca(OH)_2$)

ACIDS (DILUTE, CONCENTRATED HC*l*, H_2SO_4, HNO_3)

GASES

Colour ⇒ test for anions

DILUTE ACIDS

ACIDIC (turns moist blue litmus red)

- Brown NO_2 (turns $FeSO_4$ black) ⇒ NO_2^-
- Colourless SO_2 ($KMnO_4/H^+$ turned colourless, bleached litmus) ⇒ SO_3^{2-}
- Colourless CO_2 (White ppt. with $Ca(OH)_2$) ⇒ CO_3^{2-}

NEUTRAL

- @ Colourless H_2 (Slight explosion in air) ⇒ metals

CONCENTRATED ACIDS

ACIDIC

- @ Brown NO_2 ⇒ NO_2^-

BLEACHING ***(conc. H_2SO_4 only)***

- Colourless HC*l* (White fumes with NH_3) ⇒ C*l*$^-$
- @ Reddish-brown Br_2 (Bleaches litmus)
  Colourless HBr (White fumes with NH_3) ⇒ Br^-
- @ Violet I_2 (Bleaches litmus)
  Colourless HI (White fumes with NH_3) ⇒ I^-

PRECIPITATES

Colour ⇒ test for cations

H_2SO_4

- White ppt. ⇒ Ba^{2+} ($\rightarrow BaSO_4$)

HNO_3

- No ppt.

COLOUR CHANGES

Colour ⇒ test for transition metal ions

- Yellow to orange/red ⇒ CrO_4^{2-} $\left(\rightarrow Cr_2O_7^{2-}\right)$

(Conc. HC*l* only)

- @ Blue to green, then yellow ⇒ Cu^{2+} ($\rightarrow [CuCl_4]^{2-}$)

@ HEAT

GASES

Colour ⇒ test for anions

ACIDIC

- Brown NO_2 (turns $FeSO_4$ black) ⇒ NO_2^-, NO_3^-
- Colourless SO_2 ($KMnO_4/H^+$ turned colourless, bleached litmus) ⇒ SO_3^{2-}, SO_4^{2-}
- Colourless CO_2 (White ppt. with $Ca(OH)_2$) ⇒ CO_3^{2-}

NEUTRAL

- @ Colourless O_2 (Relights glowing splint) ⇒ O^{2-}, oxy salts

ALKALINE

- Colourless NH_3 (Red litmus turns blue) ⇒ NH_4^+

BLEACHING

- Greenish-yellow C*l*$_2$ (Bleaches litmus) ⇒ C*l*$^-$, C*l*O_3^-
- Reddish-brown Br_2 (Bleaches litmus) ⇒ Br^-, BrO_3^-
- Violet I_2 (Bleaches litmus) ⇒ I^-, IO_3^-
- Colourless SO_2 (Bleaches litmus; turns $KMnO_4/H^+$ colourless) ⇒ SO_3^{2-}, SO_4^{2-}

RESIDUE

Colour ⇒ test for cations

COLOUR OF RESIDUE

- Yellow when hot, white when cooled ⇒ Zn^{2+}
- Green ⇒ Cr^{3+}
- Brown ⇒ Fe^{2+}, Fe^{3+}
- Black ⇒ Cu^{2+}, Mn^{2+}
- White ⇒ All above absent

ANION REAGENTS

$AgNO_3$(aq)

PRECIPITATES

Colour ⇒ test for anions

- White ppt.
  @ Soluble in NH_3
  Soluble in HNO_3 ⇒ SO_3^{2-}, NO_2^-
- @ White ppt.
  Insoluble in NH_3
  Soluble in HNO_3 ⇒ CO_3^{2-}
- White ppt
  Soluble in NH_3
  @ Insoluble in HNO_3 ⇒ C*l*$^-$
- Cream ppt
  Partially soluble in NH_3
  @ Insoluble in HNO_3 ⇒ Br^-
- Yellow ppt
  Insoluble in NH_3
  @ Insoluble in HNO_3 ⇒ I^-

BaC*l*$_2$(aq), $Ba(NO_3)_2$(aq)

PRECIPITATES

Colour ⇒ test for anions

- White ppt.
  Soluble in acid ⇒ SO_3^{2-}, @ CO_3^{2-}
- White ppt
  Insoluble in acid ⇒ SO_4^{2-}

REMARKS:

If acid is added before the reagents, the presence of a ppt. ⇒ presence of the anion which gives a ppt. with the reagent and is insoluble in the acid.

@ denotes reactions not found in the *Data Booklet*.

REDOX REAGENTS

OXIDISING AGENTS

⇒ test for reducing agents

COLOUR CHANGES

- Br_2(aq) Turns colourless ($Br_2 \rightarrow Br^-$)
- Fe^{3+}(aq) Turns pale green ($Fe^{3+} \rightarrow Fe^{2+}$)
- I_2(aq) Turns colourless ($I_2 \rightarrow I^-$)
- MnO_4^- (aq) / H^+ Turns colourless ($MnO_4^- \rightarrow Mn^{2+}$)
- MnO_4^- (aq) Brown/black solid ($MnO_4^- \rightarrow MnO_2$)
- H_2O_2 Turns brown with black solid ($I^- \rightarrow I_2$)
  Turns orange/ reddish-brown ($Br^- \rightarrow Br_2$)

PRECIPITATES

- Ag^+(aq) Black ppt. ($Ag^+ \rightarrow Ag$)
- Cu^{2+}(aq) Solution decolourised
  White ppt in brown solution of I_2 ($Cu^{2+} + I^- \rightarrow CuI$)
  (brown soln decolourised on adding $S_2O_3^{2-}$)
  Pink/Brown solids ($Cu^{2+} \rightarrow Cu$)

REDUCING AGENTS

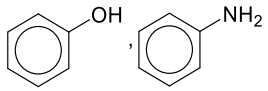
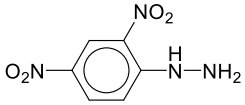
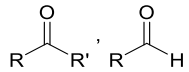
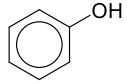
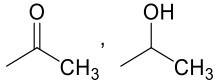
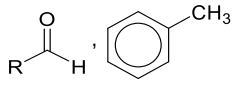
⇒ test for oxidising agents

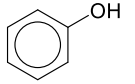
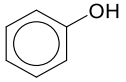
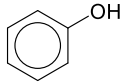
COLOUR CHANGES

- Br^- Organic layer turns orange-red
  Aq. layer turns orange ($Br^- \rightarrow Br_2$)
- I^- Organic layer turns purple
  Aq. layer turns brown ($I^- \rightarrow I_2$)
  Brown aq. solution decolourised in $Na_2S_2O_3$
- Fe^{2+}(aq) Turns yellow ($Fe^{2+} \rightarrow Fe^{3+}$)
- Fe(*s*) Turns pale-green ($Fe \rightarrow Fe^{2+}$)
- Mn^{2+}(aq) Turns brown ($Mn^{2+} \rightarrow MnO_2$)
  Turns purple ($Mn^{2+} \rightarrow MnO_4^-$)
- H_2O_2 / H^+ O_2 produced ($H_2O_2 \rightarrow O_2$)
- SO_3^{2-} Colourless solution; ($SO_3^{2-} \rightarrow SO_4^{2-}$)
  forms white ppt. with Ba^{2+}(aq)
- Mg (or other reactive metals) Colourless H_2 (Slight explosion in air) ($H^+ \rightarrow H_2$)

Organic QA

- *Never* use a **naked flame** for heating organic compounds. Always use a **hot water bath**.

Reagent / Test	Observation	Functional Group
Br_2(aq), r.t.	Orange Br_2(aq) decolourised	C=C
	Orange Br_2(aq) decolourised; white ppt	
Brady's reagent, r.t.; **2,4-DNPH**; 2,4-dinitrophenylhydrazine; 	Orange ppt	
Neutral FeC*l*$_3$	Purple colouration	
Fehling's reagent; $Cu(C_4H_4O_6)_2^{2-}$(aq), OH^-(aq); Cu^{2+}(aq), OH^-(aq); Warm the mixture in a beaker of hot water.	Brick-red ppt (of Cu_2O)	aliphatic  only
HC*l*, HNO_3, H_2SO_4 (aq)	Dissolves	amines
Iodoform test; **I_2(aq), NaOH(aq)** Place 5 drops of the compound in a test-tube. Add about 1 cm depth of aqueous I_2. Add NaOH(aq) a drop at a time, with shaking, until the brown colour *just disappears*. Warm the mixture in a beaker of hot water.	Yellow ppt (of CHI_3)	
$KMnO_4$(aq), H_2SO_4(aq), warm the mixture in a beaker of hot water.	Purple $KMnO_4$ decolourised	C=C, 1º, 2º alcohol, 
$KMnO_4$(aq), NaOH(aq), warm the mixture in a beaker of hot water.	Purple $KMnO_4$ decolourised; Brown MnO_2 ppt	

Reagent / Test	Observation	Functional Group
$K_2Cr_2O_7$(aq), H_2SO_4(aq)	Orange $K_2Cr_2O_7$ turns green	1º, 2º alcohol, 
Na metal, r.t.	Effervescence of H_2 which gives a 'pop' sound with a lighted splint	RCO_2H, 
$NaHCO_3$(aq)/(s), r.t.	Effervescence of CO_2 which gives a white ppt with $Ca(OH)_2$	RCO_2H
Na_2CO_3(aq)/(s), r.t.	Effervescence of CO_2 which gives a white ppt with $Ca(OH)_2$	RCO_2H
	Dissolves without CO_2 gas	
NaOH(aq), r.t.	Dissolves	RCO_2H, 
PC*l*$_5$, r.t.	White fumes of acidic HC*l*	ROH, RCO_2H
Tollen's reagent; $[Ag(NH_3)_2]^+$, OH^-(aq); Add 30 drops of $AgNO_3$(aq) into a test-tube followed by 5 drops of NaOH(aq). Then add dilute NH_3(aq) drop-by-drop until the brown Ag_2O(s) is *just dissolved*. Warm the mixture in a beaker of hot water.	Silver mirror	aliphatic and aromatic 
RCO_2H, conc. H_2SO_4, warm	Sweet smell (ester)	ROH
ROH, conc H_2SO_4, warm		RCO_2H

- Propanone (acetone) is a good solvent to remove organic compounds from test-tubes after use. However, the test-tubes should be washed with ample amount of water after rinsing with propanone as otherwise, false observations may result (*e.g.* with Brady's and iodoform test) due to residual propanone.

H. Organic Synthesis

- Organic synthesis is a special branch of chemical synthesis and is concerned with the construction of **organic compounds** *via* **organic reactions**.
- Each step of a synthesis involves a *chemical reaction*, and **reagents** and **conditions** for each of these reactions need to be designed to give a *good yield* and a *pure product*.

Eg 24 Synthesis of 1-bromobutane from butan-1-ol

[Nov 2010/2/Q2]

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

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

compound	boiling point / °C	density / g cm^{-3}	M_r	solubility in water
1-bromobutane	102	1.35	137	Insoluble
butan-1-ol	118	0.81	74	Moderate
sodium bromide	1390	3.20	103	soluble
concentrated sulfuric acid	330	1.84	98	soluble
water	100	1.00	18	–

Preparation of impure 1-bromobutane

1. Place 35 g of powdered sodium bromide, 30 cm^3 of water and 25 cm^3 of butan-1-ol in a 250 cm^3 two-necked flask. In one neck is placed a tap funnel and in the other neck is placed a reflux condenser.
2. Place 25 cm^3 of concentrated sulfuric acid in the tap funnel and then add the acid drop by drop to the reagents in the flask. Keep the contents well shaken and cool occasionally in an ice-water bath.
3. When all the acid has been added, gently boil the mixture for about 45 minutes, shaking the flask gently from time to time.
4. Rearrange the apparatus for distillation. Distil off the impure 1-bromobutane (about 30 cm^3).

(a) The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.

Write an equation for **each** of these stages.

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

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

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

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

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

$$n_{\text{NaBr}} = \frac{35}{103} = 0.340 \text{ mol}$$

Since they react in a 1:1 ratio, hence **NaBr** is in excess.

(c) When the concentrated sulfuric acid is added to the reaction mixture (step 2), cooling is necessary. Two by-products, one inorganic and one organic, may be produced if the temperature is not controlled carefully.

(i) Suggest the main cause of heat being produced at this stage.

The dilution of concentrated sulfuric acid is highly exothermic. ~~lower~~

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

inorganic by-product Br_2

equation $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

organic by-product $CH_3CH_2CH{=}CH_2$

equation $CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH{=}CH_2 + H_2O$

(d) The reaction mixture is heated for 45 minutes (step 3).

Why is this process necessary for the preparation of many covalent organic compounds?

Explain your answer.

Even if the reaction is exothermic, due to the need to break and form covalent bonds, organic reactions are usually associated with **high activation energy**, hence the need to heat.

(e) When the mixture is distilled (step 4), the main product is 1-bromobutane. Two other compounds are also present as impurities **in the distillate**.

Use the data in the table to suggest the identities of these two compounds and a reason for their presence.

compounds are butan-1-ol and water

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

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

The purification of crude 1-bromobutane is described below.

Purification of impure 1-bromobutane

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

(f) After distillation from the reaction mixture, the impure 1-bromobutane is shaken with water (step 9) and the two layers are allowed to separate.

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

Explain your answer.

The density of 1-bromobutane (1.35 g cm^{-3}) is higher than that of water (1.00 g cm^{-3})

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

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

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

Butan-1-ol

(ii) By using structural formulae, construct an equation for this reaction.

$CH_3CH_2CH_2CH_2OH + HCl \rightarrow CH_3CH_2CH_2CH_2OH_2^+Cl^-$

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

Due to the stronger ion-dipole interaction of the charged product compared to hydrogen bonding in butan-1-ol itself

(h) What impurity will be removed when the 1-bromobutane is then treated with dilute aqueous sodium carbonate (step 7)?

Write an equation for this reaction.

impurity HCl

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

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

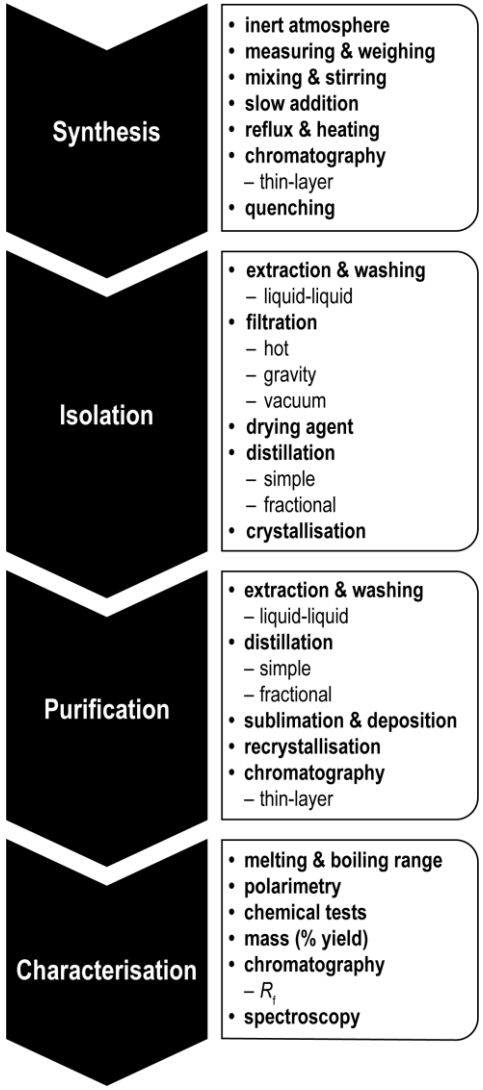
water

(j) The final step in the process of purification is distillation of the pure product (step 9).

Suggest a suitable range of temperature for the collection of the required fraction.

from 101 °C to 103 °C

4 Critical Stages in an Organic Synthesis

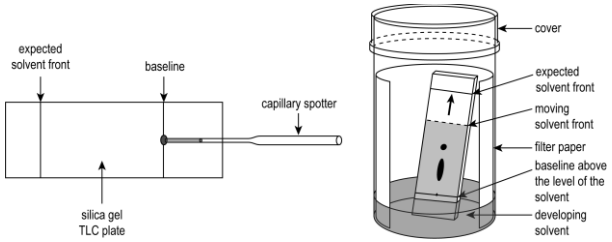


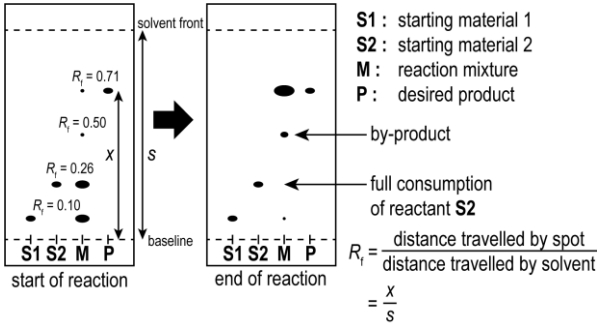
Synthesis

1. **Decide on a reaction** to accomplish the synthesis.
2. **Calculate the reactant and reagent quantities**.
3. **Calculate the total volume of solution**, and use a flask with at least twice that capacity.
4. If the reaction is moisture or air sensitive (*e.g.* $LiAlH_4$ reduction), oven-dry the flask and prepare to run the experiment under an inert atmosphere.
5. **Weigh your reactants**, into your reaction flask, onto weighing paper, or into a separate flask. Do not mix anything yet, and do not weigh sensitive reagents (*e.g.* $NaBH_4$) until just before use.
6. Save a small sample of each reactant in a vial, for TLC comparison.
7. Take a TLC of the reaction as soon as addition is complete. **Co-spot with the reactant sample(s)**.
8. **TLC the reaction at regular intervals**. The appropriate interval to employ will depend on the reaction rate – (*e.g.* every 10 minutes, or 30 minutes, or every hour). When one of the reactants has been consumed, **quench** the reaction immediately.

- Inert atmosphere
  - ✓ It is sometimes necessary (*e.g.* in reactions involving $LiAlH_4$ or in certain Grignard preparations) to carry out a reaction in *an atmosphere of an inert gas*, such as N_2. A suitable set-up is shown in **Eg 25** on page 37.
    - Dry N_2 is introduced at the top of the condenser and initially can be allowed to sweep through the apparatus and escape at the mouth of the dropping funnel with a pressure-equalising side tube.
    - After a few minutes the flow of inert gas may be reduced.
    - The level of mineral oil in the bubbler (or the escape valve) should be such that a slight pressure of gas within the apparatus is maintained when the funnel is closed.
    - Alternatively, a continuous stream of N_2 can be maintained throughout the reaction, bubbling through the mineral oil bubbler.
- Measuring & weighing (see **A: Balances and Weighing** on page 6 and **B: Working with Liquids** on page 6)
  - ✓ Large excess of reagents is avoided to prevent wastage and possible undesirable further side reactions.
    - Usually at most **1.1 equivalent** of the reagent is used, with respect to the substrate.
  - ✓ Catalysts are usually employed in small amounts, at most **10 mol%** (*i.e.* 0.1 equivalent) with respect to the substrate.
- Mixing & stirring
  - ✓ Even and consistent stirring is achieved by means of a magnetic stirrer with magnetic stirring bar (see "Hot plates and stirrer hot plates" in **G: Heating** on page 8).
  - ✓ In the event of highly viscous liquid mixture or reaction mixture involving large amount of solid, mechanical stirring may be required (see "Reflux with mechanical stirring" in **E: Reflux** on page 12).
- Slow addition
  - ✓ In the addition of a solid reactant to a liquid reactant, take special caution in the order of mixing to avoid **overheating** as most reactions are exothermic.
  - ✓ In the addition of a liquid reactant to another liquid, ensure that the liquid is introduced *via* a graduated **syringe** or **dropping funnel** (see "Reflux with addition of chemicals" in **E: Reflux** on page 11) to ensure **smooth flow** and **no spillage**.
- Reflux & heating
  - ✓ Although many reactions are exothermic. However, organic reactions are usually associated with significant **activation energies** due to the breaking and forming of covalent bonds. Hence, heating if often necessary for the reaction to complete in a reasonable period of time.
  - ✓ Direct heating using a Bunsen burner should be *avoided* as most organic compounds are highly flammable.
  - ✓ Heating (see **G: Heating** on page 8) is commonly done using a sand bath, **water bath** or **oil bath** in conjunction with a hot plate.
    - Sand bath: >250°C, Oil bath: <250°C, Water bath: <100°C
    - If without magnetic stirring, **boiling / anti-bumping chips** are usually added to ensure smooth boiling (see "Bumping" in **G: Heating** on page 8).
  - ✓ **Refluxing** (see **E: Reflux** on page 11) is carried out when prolonged heating of a reaction mixture is required. No loss of reaction mixture as vapour is immediately condensed in the condenser during the process.
- **Thin-Layer Chromatography** (TLC)
  - ✓ Thin-layer chromatography (TLC) is used for identifying compounds and determining their purity.
    - The most common adsorbent used is silica gel (SiO_2), although alumina (Al_2O_3) is gaining popularity, on a glass slide.
    - A fluorescent powder is put into the adsorbent to help with visualisation, which glows a bright green when exposed to 254-nm wavelength ultraviolet light.
  - ✓ The steps in performing a TLC involve
    - **Spotting** the compounds on the TLC plate, and
      - By means of a thin capillary spotter as shown below
    - **Developing** the plate by running an *eluent* through the adsorbent, and finally
      - Choose a suitable solvent to develop the plate.
      - Put no more than 0.6 cm depth of the eluent in the developing chamber.
      - Place the slide into the developing chamber as shown below (ensure that solvent in the chamber does not touch the spots on the plate).

- Cover the chamber and allow the eluent to travel up the plate. The filter paper keeps the air in the chamber saturated with solvent so that it doesn't evaporate from the plate.
- Then the solvent reaches the line, *immediately* remove the plate. Drain the solvent from it, and blow gently on the plate until *all* the solvent is gone.





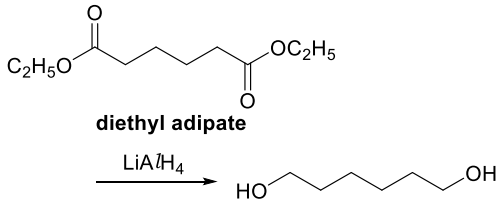
- **Visualising** the spots by examining the plate.
  - **Destructive visualisation**. Spray the plate with concentrated sulfuric acid, then bake in an oven at 110ºC for 15–20 min. Any spots of compound will be charred blots, utterly destroyed. *All* spots of compound will be shown.
  - **Semi-destructive visualisation**. Set up a developing chamber, but just add a few crystals of **iodine**. Iodine vapours will be absorbed onto most spots of compound, colouring them. Not all spots may be visible.
  - **Non-destructive visualisation**. Most TLC adsorbents contain a fluorescent powder that glows bright green when under long-wave UV light. The background glows green and the spots are either dark or glow some other colour.

✓ Interpretation of a TLC plate involves
- Measuring the distance from the solvent front to the baseline.
- Measuring the distance from where the spot stopped to the baseline. Measure to the *centre of the spot*, rather than to one edge. If there are more than one spot, get a distance for each.
- Divide the distance the solvent moved into the distance the spot(s) moved. The resulting ratio is called the ***R*f value**.
- In identical circumstances, this value would always be the *same* for a single compound, all the time.

- Once TLC indicates that the reaction is complete, **quench** the reaction mixture.
  - ✓ Commonly involves adding **water** (or aqueous solution such as brine, saturated NH_4Cl, etc.) to the reaction mixture.
  - ✓ If quenching the reaction is exothermic, cool the flask with an ice bath.
  - ✓ Otherwise, if a gas is evolved during the quench, watch the reaction carefully to be sure it is under control.
- If possible, **workup** the reaction immediately after quenching it, to isolate the crude product.

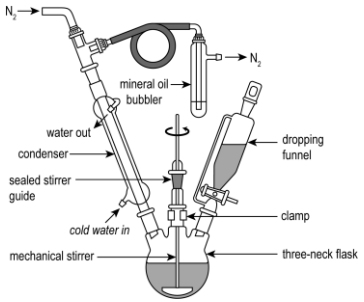
Procedure (Synthesis under inert atmosphere)

Eg 25 Synthesis of hexane-1,6-diol from diethyl adipate



Synthesis

1. Setup the apparatus as shown below, purging the set-up with dry N_2 before the reaction.



2. Remove the dropping funnel from the flask neck and replace it by a funnel with a very short wide stem and introduce 10.5 g (0.263 mol) of powdered $LiAlH_4$ into the flask through this funnel, and use about 300 cm^3 of anhydrous ether to transfer the last traces into the flask.
3. Replace the dropping funnel and ensure a slight pressure of gas within the apparatus.
4. Set the stirrer in motion and place a solution of 50.5 g (0.25 mol) of diethyl adipate, in 150 cm^3 of anhydrous ether in the dropping funnel.
5. After stirring for 10 min (some of the $LiAlH_4$ may remain undissolved), add the diethyl adipate solution so that the ether refluxes gently (b.p. of ether : 34.6ºC; from heat generated by the reaction).
6. The reaction mixture rapidly becomes viscous and four 50 cm^3 portions of anhydrous ether is added during the reduction to facilitate stirring.
7. Continue the stirring for 10 min after the diethyl adipate has been added.

Isolation and *Purification*

1. Decompose the excess $LiAlH_4$ by the dropwise addition, with stirring, either of 75 cm^3 water, or preferably, by the more rapid addition of 22 g (24.5 cm^3) of ethyl ethanoate.
2. Filter the reaction product from the sludge through a sintered glass funnel (see "sintered-glass crucible" in **B: Gravimetric Analysis** on page 17).
3. Dry the ethereal solution with anhydrous $MgSO_4$ and distil off the ether with a rotary evaporator (see **F: Evaporation** on page 12).
4. The colourless viscous residue (18.5 g) solidifies completely on cooling and has a melting point of 41–42ºC, *i.e.* is pure hexane-1,6-diol.
5. Dissolve the sludge remaining in the filter funnel in 20% H_2SO_4, extract the resulting solution with 6 times 100 cm^3 portions of ether.
6. Remove the ether by means of a rotary evaporator.
7. The residue (6 g) crystallises completely on cooling, melting point 41–42ºC.
8. The total yield of hexane-1,6-diol is 24.5 g (91%).

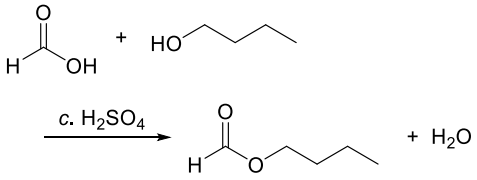
<u>Isolation</u>

- For an **aqueous workup** of most organic reactions this involve:
  1. **Diluting** the reaction mixture **with a solvent** for workup (this is the organic layer).
  2. **Washing** the organic layer with various aqueous solutions. Some of the by-products generated during the reaction will be neutralised or removed by dissolving in the aqueous layer. Ideally, the two layers will be clearly visible.
  3. **Drying** the organic layer with one of the drying agents (see **K: Drying Liquids** on page 9).
  4. **Filtering** off the drying agent (see **F: Filtration** on page 8).
  5. **Rotoevaporation** (see **F: Evaporation** on page 12) to remove the solvent.
- Extraction & washing
  - ✓ After quenching with water, the organic compounds are extracted into a suitable organic solvent and the organic layer washed with various aqueous solutions.

- ✓ Washing is performed *via* liquid-liquid extraction of the organic layer (see **C: Liquid-liquid extraction** on page 10). The function of different aqueous wash solution is as follows:
  - Saturated NH_4Cl (pH 5–6) : to neutralise bases
  - 1 mol dm^{-3} HCl (pH 1) : to neutralise bases; to acidify mixture
  - Saturated $NaHCO_3$ (pH 9) : to neutralise acids
  - 1 mol dm^{-3} NaOH (pH 14) : to neutralise acids; to basify mixture
  - 1 mol dm^{-3} NH_3 (pH 11) : to neutralise acids; to basify mixture
  - Brine (saturated NaCl) : to remove residual water from organic layer
  - 10% $Na_2S_2O_3$: to remove Br_2 or I_2
  - 10% $KNaC_4H_4O_6{\cdot}4H_2O$ (Rochelle's salt) : to remove aluminium salts
  - Saturated $CuSO_4$: to remove amines
  - NH_3(aq)/NH_4Cl(aq) (pH 8) : to remove Cu(I) salts

Procedure (Isolation with washing)

Eg 26 Synthesis of butyl methanoate (ester)



Synthesis

1. Into a 250 cm^3 round-bottomed flask provided with a reflux condenser (see **E: Reflux** on page 11)), place 46 g (38 cm^3, 1 mol) of methanoic acid and 37 g (46 cm^3, 0.5 mol) of butan-1-ol.
2. Reflux the mixture for 24 hours.

Isolation

1. Allow the reaction mixture to cool to room temperature and transfer the mixture into a separatory funnel.
2. Wash the cold mixture with 3 times 10 cm^3 portions of saturated NaCl solution.
3. Then wash with 10 cm^3 portions of saturated $NaHCO_3$ solution in the presence of a little solid $NaHCO_3$ until effervescence ceases.
4. Finally, wash with 10 cm^3 of saturated NaCl solution.
5. Dry the organic layer with anhydrous Na_2SO_4.

Purification

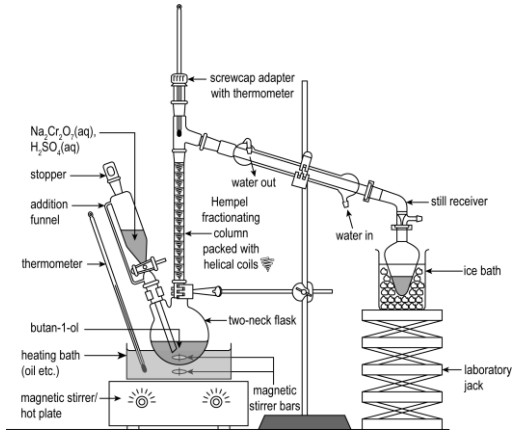
1. Distil the dried organic layer through a short fractionating column (see **D: Distillation** on page 11)).
2. Collect the fraction that distil over at 106–107ºC.
3. Yield: 38 g (74%).

- Filtration (see **F: Filtration** on page 8)
  - ✓ There are two scenarios where filtration may be required:
    - The product is insoluble and crashes out from the reaction mixture either directly or upon quenching. The crude product can then be isolated by *gravity* or *vacuum* filtration, pending on the particle size.
    - There are insoluble by-products which must first be removed before liquid-liquid extraction can be performed.
  - ✓ In either case, should either the desired product or the by-product(s) have higher solubility at elevated temperature, *hot filtration* (using a stemless filter funnel) may also be required to maximise the differences in solubilities of the different components to increase the effectiveness of separation.
- Drying agent (see **K: Drying Liquids** on page 9)
  - ✓ Even after extraction with brine, there will still be substantial amount of water left in the organic layer. The residual water in the liquid can be removed by treating it with a suitable drying agent, before removal of the solvent and purification.
- Distillation
  - ✓ In some cases, the reaction need not be quenched and the (crude) product may be isolated by either simple or fractional distillation (see **D: Distillation** on page 11).
  - ✓ An example is the synthesis of aldehyde *via* the dichromate oxidation of a primary alcohol.

Procedure (Isolation *via* distillation)

Eg 27 Synthesis of butanal *via* oxidation of butan-1-ol

Synthesis



1. Setup the apparatus as shown above.
2. Dissolve 56 g (0.188 mol) of $Na_2Cr_2O_7{\cdot}2H_2O$ in 300 cm^3 of water in a 500 cm^3 beaker and add cautiously, with stirring, 40 cm^3 of concentrated H_2SO_4.
3. Fill up the addition funnel with the $Na_2Cr_2O_7/H_2SO_4$ mixture.
4. Using a 100 cm^3 measuring cylinder, place 51 cm^3 (41 g, 0.55 mol) of butan-1-ol together with a magnetic stirrer bar in the two-neck flask.
5. Heat the butan-1-ol to boiling using the hot plate stirrer, with constant gentle stirring.
6. Run in the $Na_2Cr_2O_7/H_2SO_4$ mixture *via* the addition funnel during about 20 min.

* The oxidation to butanal proceeds with the evolution of heat, but it is necessary to continue to heat the flask so that the mixture boils vigorously to maintain steady distillation. The temperature at the top of the column, however, should **not** exceed 80–85ºC.

7. When all the $Na_2Cr_2O_7/H_2SO_4$ mixture has been added, continue heating the mixture for 15 min and collect all that passes over below 90ºC.

Isolation

1. Separate the water from the distillate using a separatory funnel.
2. Dry the residue for 60 min with 4 g of anhydrous Na_2SO_4.

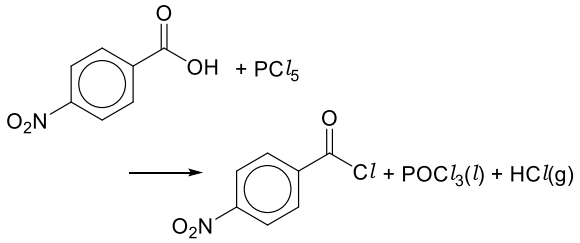
Purification

1. Filter the dried distillate into a 100 cm^3 conical flask and arrange for distillation as for the synthesis, using a clean and dry set of apparatus.
2. Distil the dried distillate slowly (1–2 drops per second) through the column and collect as fairly pure butanal all that distils below 76ºC.
3. The yield is 13 g (32%).

* Pure butanal boils at 74.5ºC.

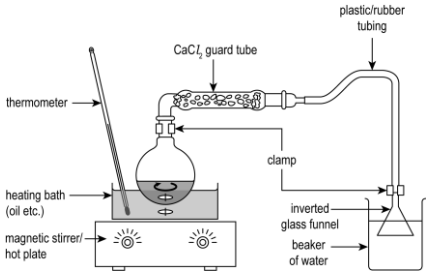
- The more volatile butanal (boiling point of butan-1-ol is 118ºC) is distilled immediately to prevent further oxidation to the carboxylic acid.
- The fractionating column prevents the boiling butanol from distilling over, and subsequently when butanal is formed, the lower boiling butanal will distil over.
- Water will distil over with the butanal as it forms a lower boiling *azeotrope*.
- The acidified $Na_2Cr_2O_7$(aq) oxidant is added dropwise to the primary alcohol with immediate distillation as the aldehyde first-formed may be further oxidised by acidified $Na_2Cr_2O_7$(aq) to the corresponding carboxylic acid.

Eg 28 Synthesis of 4-nitrobenzoyl chloride from 4-nitrobenzoic acid



Synthesis

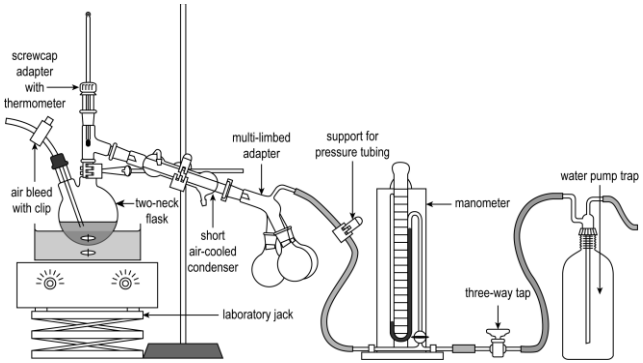
1. Set up the apparatus shown below.



2. In a 3 dm^3 round-bottomed flask are mixed 501 g (3 mol) of pure 4-nitrobenzoic acid and 626 g (3 mol) of pure phosphorus pentachloride.
3. The flask is connected to a calcium chloride guard tube from which emerges a tube attached to an inverted glass funnel, leading to the surface of a beaker of water, in order to absorb the hydrogen chloride formed during the reaction.
4. The reaction mixture heated with gentle magnetic stirring until the reaction starts, signalled by vigorous evolution of hydrogen chloride gas.
5. Heating is continued until the reaction is complete, where a light yellow, homogeneous liquid is obtained.

Isolation

1. The reaction mixture is transferred to a two-neck flask connected with a water-cooled condenser, and the phosphorus oxychloride is distilled off at ordinary pressure by raising the temperature of the oil bath gradually to 200–220ºC.



2. The water condenser is then replaced by a short air-cooled condenser, and the residual liquid is distilled under reduced pressure (see "Vacuum or reduced-pressure distillation" in **D: Distillation** on page 11) using the setup above.
3. A small quantity of phosphorus oxychloride first distils over, after which the temperature rises rapidly to the boiling point of 4-nitrobenzoyl chloride, 155 ºC @ 20 mmHg. During this distillation the oil bath is kept at a temperature of about 210–215ºC.
4. The yield is 500–534 g (90–96 per cent of the theoretical amount). The distillate solidifies to a yellow crystalline mass melting at 71ºC.

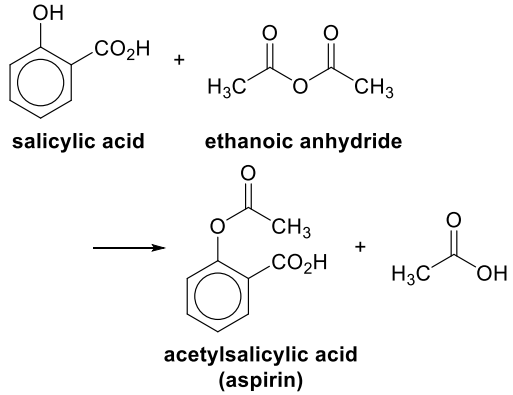
Purification

1. The product may be recrystallised from carbon tetrachloride, from which it separates in fine yellow needles melting at 73ºC.

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

Procedure (Isolation *via* crystallisation)

Eg 29 Synthesis of acetylsalicylic acid (aspirin) from salicylic acid



Synthesis

1. Weigh 2.0 g (0.015 mol) of salicylic acid into a 100 cm^3 conical flask.
2. Add 5 cm^3 (0.05 mole) of ethanoic anhydride using a 10 cm^3 measuring cylinder, followed by 5 drops of concentrated sulfuric acid by means of a dropper and swirl the flask gently until the salicylic acid dissolves.
3. Heat the flask gently in a hot water bath for 10 min.

Isolation

1. Allow the flask to cool to room temperature. If acetylsalicylic acid does not begin to crystallise out, scratch the walls of the flask with a glass rod.
2. Cool the mixture slightly in an ice bath until crystallisation is completed. The product will appear as a solid mass when crystallisation is completed.
3. When crystal formation is complete, add 50 cm^3 of water and cool the mixture in an ice bath.
4. Vacuum filter the product using a Buchner funnel (see "suction (vacuum) filtration" in **F: Filtration** on page 8). Rinse the conical flask with some of the filtrate, if necessary.
5. Rinse the crystals 3 times with 5 cm^3 of cold water and air dry the crystals on a Buchner funnel by suction until the crystals appear to be free of solvent.

* Test this crude product for the presence of unreacted salicylic acid using neutral $FeCl_3$.

Purification

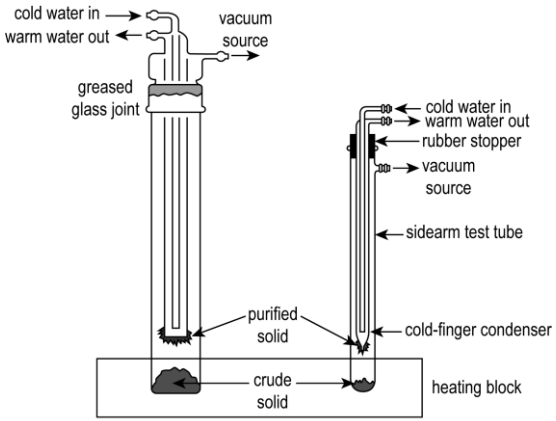
1. Stir the crude solid with 25 cm^3 of a saturated aqueous sodium bicarbonate solution in a 150 cm^3 beaker until all signs of reaction have ceased (evolution of CO_2 ceases).
2. Filter the solution through a Buchner funnel to remove any insoluble impurities or polymers that may have been formed. Wash the beaker and the funnel with 10 cm^3 of water.
3. Carefully pour the filtrate with stirring, a small amount at a time, into an ice cold HCl solution (prepared from 3.5 cm^3 of concentrated HCl in 10 cm^3 of water) in a 150 cm^3 beaker and cool the mixture in an ice bath. Ensure that the resulting solution is acidic (blue litmus paper) and that the aspirin has completely precipitated out.
4. Filter the solid by suction and wash the crystals 3 times with 5 cm^3 of cold water each.
5. Dissolve the crude crystals in a minimum amount (no more than 2–3 cm^3) of hot ethyl acetate in a 25 cm^3 conical flask. Ensure that the product is completely dissolved while gently and continuously heating on a hot plate.
6. Cool the solution to room temperature and then in an ice-bath.
7. Collect the crystals by vacuum filtration and rinse out of the flask with 5 cm^3 of cold petroleum ether.
8. When the product is completely dry, weigh the crystals and determine its melting point (lit. mp 135ºC).

<u>Purification</u>

- If the crude product isolated upon aqueous workup is not sufficiently pure for whatever purpose of the synthesis, further purification can be performed.
- Extraction & washing
  - ✓ If the crude product proved to be still contaminated with impurities that can be removed by washing with suitable aqueous solution (see "Extraction & washing" in **Isolation** on page 37), the procedure can be repeated to better the purity of the product.
- Distillation (see **D: Distillation** on page 11)
  - ✓ A crude *liquid* product obtained after rotoevaporation (see **F: Evaporation** on page 12) of the organic solvent from an organic extract, can be further purified by either simple or fractional distillation, pending on the boiling point differences.

- ✓ If the relative molecular mass of the product is above 350, usually the boiling point is too high for distillation at normal pressure and the compound could decompose before boiling occurs. Distillation under *reduced pressure* (see "Vacuum or reduced-pressure distillation" in **D: Distillation** on page 11) may be considered for such cases.

- Sublimation & deposition
  - ✓ Only for compounds which sublimes (*i.e.* from solid to gaseous phase, without going through a liquid phase) instead of melting when heated.
    - Application of a vacuum is often key to the process of sublimation. For a substance to change phase into a gas, its molecules must reach a vapour pressure equal to that of its external air pressure.
    - Because a vacuum lowers the air pressure, the compound can reach this vapour pressure at a *lower temperature* and bypass the liquid phase.
  - ✓ *E.g.* Purification of crude caffeine is possible through sublimation if impurities are *non-volatile*.
    - Crude material is placed on the bottom of a sublimation chamber below a cold-finger condenser.
    - A vacuum is applied to the airtight environment by sucking all of the air out of the chamber through the vacuum/gas line as shown below.



    - When heated, sublimed caffeine gas rises from the base of the apparatus, forming solid crystals when it makes contact with the surface of the cold-finger condenser.
    - Solid non-volatile impurities are left at the base of the apparatus after sublimation.

- Recrystallisation
  - ✓ *Solid* crude product isolated after aqueous workup can be purified by recrystallisation (see **B: Recrystallisation** on page 10).

- Chromatography (Prep TLC)
  - ✓ When an analytical technique (like TLC) is used to *isolate compounds*, it is often called a **preparative (prep) technique**. So TLC becomes "prep TLC".
  - ✓ The same method is used, only on a larger scale.
    - Instead of a microscope slide, prep TLC uses a 30 × 30 cm glass plate coated with a thick layer of the adsorbent (0.5–2.0 mm).
    - A solution of the mixture to be separated is **streaked** (rather than spotted) across the plate near the bottom.
    - The plate is then placed in a large developing tank to develop and visualise as usual.
    - The thin line separates and spreads into bands of compounds, much like a tiny spot separates and spreads on the analytical TLC plates.
    - Rather than just looking at the bands, the adsorbent holding the different bands is scraped into different flasks.
    - The adsorbents are then treated with appropriate solvents to **leach out** the compounds.
    - The adsorbent is filtered off and the solvent evaporated to recover the separate compounds.

<u>Characterisation</u>

- Melting & boiling range (see **A: Melting points** on page 10)
  - ✓ A melting point is the temperature at which the first crystal **just starts to melt** until the temperature at which the **last crystal just disappears**. Thus the melting point is actually a melting **range**.
  - ✓ The melting point of a solid can be determined using the Thiele tube.
  - ✓ Boiling point can be approximated by the temperature range where a liquid is collected during distillation (see **D: Distillation** on page 11).
  - ✓ Generally, a melting or boiling range **greater than 2ºC** usually indicates an *impure* compound.
- Polarimetry (see **F: Polarimetry** on page 29)
  - ✓ Similar to melting and boiling point, the **specific rotation**, $[\alpha]_{\lambda}^{T}$, of a **chiral** compound is characteristic of the compound, at temperature T ºC, in a specific solvent.
  - ✓ If a synthesis is stereoselective, then one of the enantiomers will be produced in greater amount over the other (*i.e.* not racemic). The **optical purity** of the product should also be determined.
- Chemical tests (see "Organic QA" in **G: Qualitative Analysis (QA)** on page 34)
  - ✓ Chemical test can be performed to show the presence or absence of certain **functional group(s)**.
  - ✓ An example is seen in **Eg 29**: Synthesis of acetylsalicylic acid (aspirin) from salicylic acid on page 39, where neutral $FeCl_3$ can be used to ascertain if the crude aspirin contains unreacted salicylic acid *via* the phenolic group.
- Mass (% yield)
  - ✓ The **percentage yield** of an organic synthesis should always be reported as this will allow determination of the amount of starting material to use.
- Chromatography (see "Thin-Layer Chromatography (TLC)" under *Synthesis* on page 36)
  - ✓ The R_f **value** for the product should always be reported, together with the solvent system used to develop the TLC.
  - ✓ There are other more sophisticated chromatography methods, *e.g.* gas chromatography (GC), high-performance liquid chromatography (HPLC), *etc.* which allows for the analysis of the components of a mixture.
    - In these cases, the time taken for a particular component to elute from the analytical column, known as the **retention time**, is reported.
- Spectroscopy
  - ✓ Powerful spectroscopy methods are available which allows for the confirmation of the identity of the desired product in a synthesis. These data should also be reported.
  - ✓ *E.g.* infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry