Edexcel International A Level (IAL) Chemistry

Your notes

Advanced Inorganic & Organic Chemistry Core Practicals

Contents

Your notes

Core Practical 13a: Iron(II) & Manganate(VII) Titration

Redox Titrations

- In a **titration**, the concentration of a solution is determined by titrating with a solution of known concentration.
- In redox titrations, an **oxidising agent** is titrated against a **reducing agent**
- Electrons are transferred from one species to the other
- **Indicators** are sometimes used to show the endpoint of the **titration**
- However, most **transition metal ions** naturally change colour when changing **oxidation state**
- There are two common **redox titrations** you should know about **manganate(VII) titrations** and **iodine-thiosulfate titrations**

Potassium manganate(VII) titrations

- In these redox titrations the manganate(VII) is the oxidising agent and is reduced to Mn^{2+}(aq)
- The iron is the reducing agent and is oxidised to Fe^{3+}(aq) and the reaction mixture must be acidified
  - So, excess acid is added to the iron(II) ions before the reaction begins
- The choice of acid is important, as it must not react with the manganate(VII) ions, so the acid normally used is dilute sulfuric acid
  - As it does not oxidise under these conditions and does not react with the manganate(VII) ions
- You could be asked why other acids are not suitable for this redox titration in the exam so make sure you understand the suitability of dilute sulfuric acid

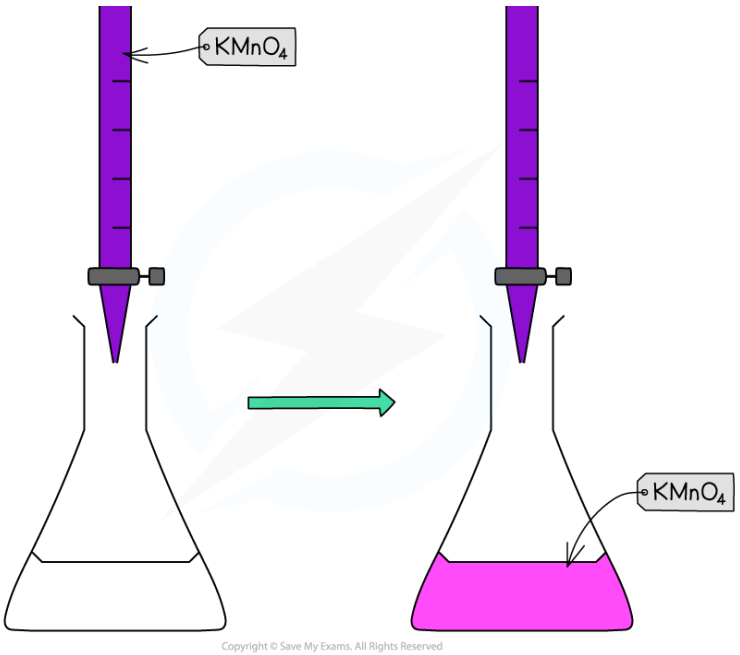
Table Explaining why Other Acids are not Suitable for the Redox Titration

Acid	Reason for not choosing it in the redox titration
Hydrochloric acid	Can be oxidised to chlorine by the manganate(VII) ions
Nitric acid	Is an oxidising agent and may oxidise the substance being analysed
Ethanoic acid	Weak acid and the concentration of hydrogen ions will be insufficient
Concentrated sulfuric acid	May oxidise the substance being analysed

Your notes

Indicator and end point

- Potassium permanganate acts as its own indicator, as the purple potassium permanganate solution is added to the titration flask from the burette and reacts rapidly with the $Fe^{2+}(aq)$
  - The burette used in this practical should be one with white numbering not black, as you would struggle to read the values for your titres against the purple colour of the potassium permanganate if black numbering was used
- The manganese(II) ions, $Mn^{2+}(aq)$, have a very pale pink colour but they are present in such a low concentration that the solution looks colourless
- As soon as all of the iron(II), $Fe^{2+}(aq)$, ions have reacted with the added manganate(VII) ions, $Mn^{7+}(aq)$, a pale pink tinge appears in the flask due to an excess of manganate(VII) ions, $Mn^{7+}(aq)$



Redox titration colour change for potassium permanganate and iron(II) ions

Your notes

Worked Example

Equations

Find the stoichiometry for the reaction and complete the two half equations:

$$MnO_4^-(aq) + 5e^- + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

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

Answers:

Balance the electrons:

$$MnO_4^-(aq) + 5e^- + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$

Add the two half equations:

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

- Manganate(VII) titrations can be used to determine:
  - The percentage purity of iron supplements
- Percentage purity = $\frac{\text{mass of sample}}{\text{mass of impure sample}} \times 100$
  - The formula of a sample of hydrated ethanedioic acid

Worked Example

Analysis of iron tablets

An iron tablet, weighing 0.960 g was dissolved in dilute sulfuric acid. An average titre of 28.50 cm^3 of 0.0180 mol dm^{-3} potassium manganate(VII) solution was needed to reach the endpoint.

What is the percentage by mass of iron in the tablet?

Answer:

- $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
  - 1 : 5 ratio of MnO_4^- : Fe^{2+}
  - Number of moles of $MnO_4^-(aq) = \frac{0.0180 \times 25.0}{1000} = 5.13 \times 10^{-4}$ moles
  - Moles of iron(II) = $5 \times 5.13 \times 10^{-4} = 2.565 \times 10^{-3}$ moles
  - Mass of iron(II) = $56.0 \times 2.565 \times 10^{-3} = 0.14364$ g

- Percentage by mass = $= \frac{0.14364}{0.960} \times 100 =$ 15.0%

Your notes

Your notes

Core Practical 13b: Thiosulfate & Iodine Titration

Iodine-Thiosulfate Titrations

- A redox reaction occurs between iodine and thiosulfate ions:

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

- The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions
- When the solution is a straw colour, **starch** is added to clarify the end point
- The solution turns blue/black until all the iodine reacts, at which point the colour disappears.
- This titration can be used to determine the concentration of an **oxidising agent**, which **oxidises** iodide ions to iodine molecules
- The amount of iodine is determined from **titration** against a known quantity of sodium thiosulfate solution

Worked Example

Analysis of household bleach

Chlorate(I) ions, ClO^-, are the active ingredient in many household bleaches.

10.0 cm^3 of bleach was made up to 250.0 cm^3. 25.0 cm^3 of this solution had 10.0 cm^3 of 1.0 mol dm^{-3} potassium iodide and then acidified with 1.0 mol dm^{-3} hydrochloric acid.

$$ClO^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$$

This was titrated with 0.05 mol dm^{-3} sodium thiosulfate solution giving an average titre of 25.20 cm^3.

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

What is the concentration of chlorate(I) ions in the bleach?

Answer:

- One mole of $ClO^-(aq)$ produces one mole of $I_2(aq)$ which reacts with two moles of $2S_2O_3^{2-}(aq)$
  - Therefore, 1 : 2 ratio of $ClO^-(aq) : S_2O_3^{2-}(aq)$

- Number of moles of $S_2O_3^{2-}$ (aq) = $\frac{0.05 \times 25.20}{1000}$ = 1.26 x 10^{-3} moles
- Number of moles of I_2 (aq) and ClO^- (aq) in 25.0 cm^3 = $\frac{1.26 \times 10^{-3}}{2}$ = 6.30 x 10^{-4} moles
- Number of moles of ClO^- (aq) in 250.0 cm^3 = 6.30 x 10^{-4} x 10 = 6.30 x 10^{-3} moles
- The 250.0 cm^3 was prepared from 10.0 cm^3 bleach
  - 10 cm^3 bleach = 6.30 x 10^{-3} moles of ClO^- ions
  - 1.0 dm^3 bleach = 0.630 moles of ClO^- ions
  - Therefore, the concentration of ClO^- ions in the bleach is **0.630 mol dm^{-3}**

Your notes

Examiner Tips and Tricks

General sequence for redox titration calculations

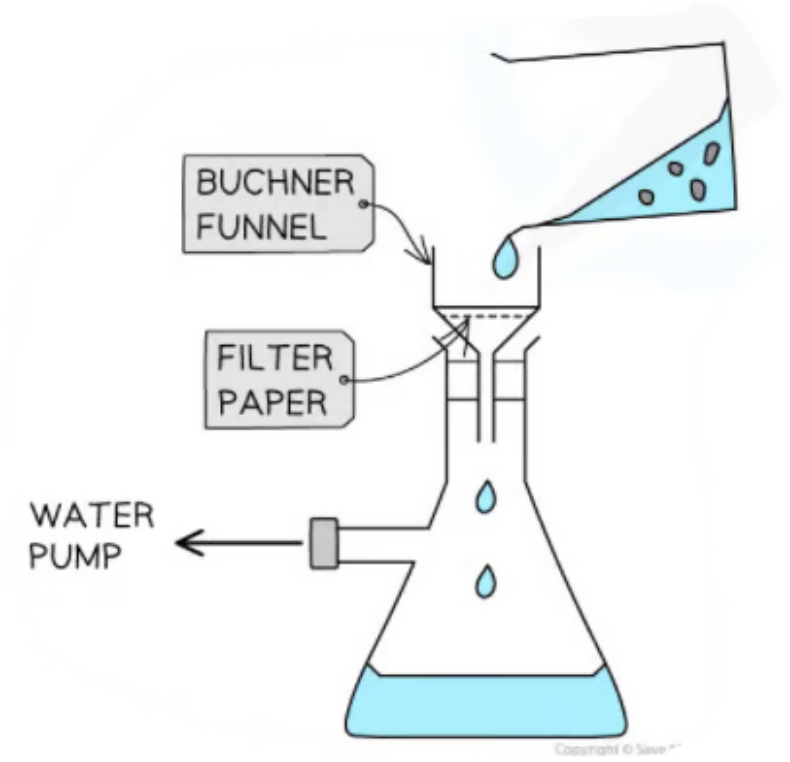
1. Write down the half equations for the oxidant and reductant
2. Deduce the overall equation
3. Calculate the number of moles of manganate(VII) or dichromate(VI) used
4. Calculate the ratio of moles of oxidant to moles of reductant from the overall redox equation
5. Calculate the number of moles in the sample solution of the reductant
6. Calculate the number of moles in the original solution of reductant
7. Determine either the concentration of the original solution or the percentage of reductant in a known quantity of sample

Your notes

Core Practical 12: Preparing a Transition Metal Complex

Method

1. Weigh between 1.4 g and 1.6 g of copper(II) sulfate.
    - To do this you should weigh a test tube and record its mass.
    - Then add the copper(II) sulfate to the test tube, reweigh and record the mass.
    - The mass of the copper(II) sulfate is the difference between the two masses.
2. Add 4 cm^3 of water to the test tube using a graduated pipette.
3. Prepare a water bath using hot water from a kettle in a 100 cm^3 beaker and stand the test tube in the water bath.
4. Stir gently to dissolve the copper(II) sulfate.
5. Remove the test tube containing copper(II) sulfate solution from the water bath.
6. *Perform this step in the fume cupboard wearing gloves*. Add, while stirring, 2 cm^3 of concentrated ammonia solution to the copper(II) sulfate solution.
7. Pour the contents of the test tube into 6 cm^3 of ethanol that has been pipetted into a beaker – mix well and then cool the mixture in an ice bath.
8. Using a Büchner funnel and flask, filter the crystals. Wash your test tube with cold ethanol and add the washings to the Büchner funnel. Finally, rinse the crystals with cold ethanol.
9. Carefully scrape the crystals off the filter paper onto a fresh piece of filter paper. Cover the crystals with a second piece of filter paper, Carefully pat the paper to dry the crystals. Note that to get the crystals completely dry, you may need to repeatedly move the crystals to dry parts of the filter paper.
10. Once dry, measure and record the mass of crystals



Buchner filtration set-up to filter crystals

Your notes

Examiner Tips and Tricks

You may be asked about some of the steps in more detail.

The solution produced in step 6 is a dark blue solution due to the formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion.

Adding ethanol in step 7 causes the precipitation of dark blue $Cu(NH_3)_4SO_4 \bullet H_2O$ crystals. This is because ethanol is less polar than water and any ionic compounds will be less soluble in it than they are in water. As ethanol is added, the solubility of $Cu(NH_3)_4SO_4 \bullet H_2O$, decreases and crystals are formed.

In step 8, ethanol is added to remove any impurities. Cold ethanol is used as $Cu(NH_3)_4SO_4 \bullet H_2O$ is less soluble in cold ethanol - if hot ethanol were used, $Cu(NH_3)_4SO_4 \bullet H_2O$ would dissolve.

Worked Example

A student carried out the method mentioned above and measured the final mass of $Cu(NH_3)SO_4 \cdot H_2O$ after drying the crystals of 1.2 g.

1. Write an equation for this reaction

2. Calculate the relative formula masses of $CuSO_4 \cdot 5H_2O$ and $Cu(NH_3)SO_4 \cdot H_2O$
3. Calculate the number of moles of copper(II) sulfate used in the reaction (assume 1.5 g was used)
4. Use your answer to calculate the theoretical yield of tetraaminecopper(II) sulfate-1-water your reaction should have produced
5. Calculate the percentage yield obtained in this reaction

Answers

1. $CuSO_4 \bullet 5H_2O + 4NH_3 \rightarrow Cu(NH_3)_4SO_4 \bullet H_2O + 4H_2O$

2. M_r of $CuSO_4 \bullet 5H_2O$: = 63.5 + 32.1 + (4 x 16.0) + 5 x ((2 x 1.0) + 16.0) = **249.6** M_r of $Cu(NH_3)_4SO_4 \bullet H_2O$ = 63.5 + (4 x (14.0 + 3 x 1.0) + 32.1 + (4 x 16.0) + (2 x 1.0) + 16.0 = **245.6**

3. Moles of copper(II) sulfate used (based on 1.5 g of $CuSO_4 \bullet 5H_2O$):

$$\text{moles} = \frac{1.5}{249.6} = \mathbf{0.00601}$$

4. Theoretical yield of $Cu(NH_3)_4SO_4 \bullet H_2O$:

As there is a molar ratio of 1:1 we know we will have 0.00601 moles of $Cu(NH_3)_4SO_4 \bullet H_2O$

The theoretical mass that we would expect to produce can then be calculated

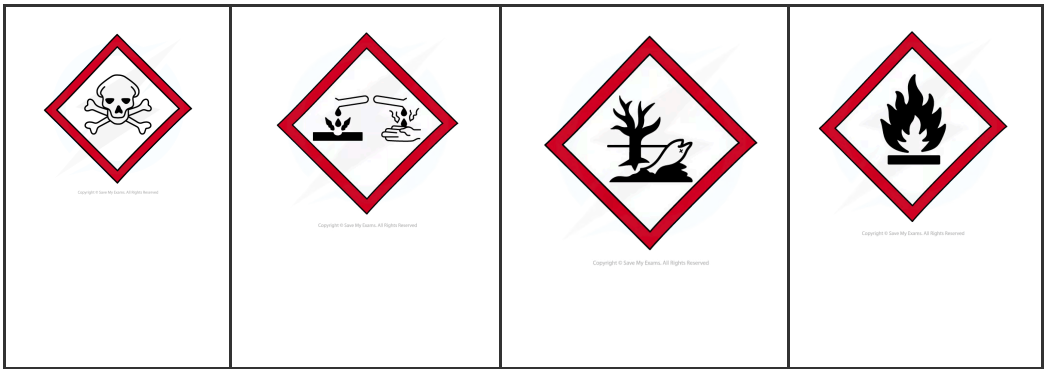
$$\text{mass} = 0.00601 \times 245.6 = 1.48 \text{ g}$$

5. Percentage yield = $\frac{1.2}{1.48}$ x 100 = 81%

Examiner Tips and Tricks

The percentage yield in this preparation is often calculated to be greater than 100%. This is usually because the crystals have not been completely dried. This causes the final mass to be greater than the actual value as it also includes the mass of the water remaining.

Safety



Your notes

TOXIC	CORROSIVE	ENVIRONMENTAL HAZARD	FLAMMABLE

The hazard symbols associated with this experiment

- Wear a lab coat and use eye protection.
- Tie long hair back.
- Concentrated ammonia solution is corrosive and dangerous to the environment. It must be kept in the fume cupboard and handled wearing gloves. Ammonia gas can also be evolved from the solution, which is toxic.
- Copper salts are harmful and dangerous to the environment.
- Ethanol is flammable and must be kept away from flames.

Errors

- Losses could be from the reaction not going to completion and product staying in solution (i.e. not crystallising out)
- Gains could be from impure or wet crystals.

Your notes

Your notes

Core Practical 15: Analysis of Inorganic and Organic Unknowns

Testing for positive ions

Simple test tube reactions can be done to identify the following positive ions: Group 2 ions (M^{2+}) Ammonium ions (NH_4^+)

- If the sample to be tested is a solid, then it must be dissolved in deionised water and made into an aqueous solution

Testing for Group 2 Metal ions Four test tubes should be placed in a test tube rack Around 10 drops of 0.1 mol dm^{-3} barium chloride solution should be added to the first test tube Around 10 drops of dilute sodium hydroxide solution (NaOH) should be added to the same test tube Swirl the test tube carefully to mix well Continue to add sodium hydroxide dropwise to the test tube, until it is in excess This should then be repeated in the other test tubes, for calcium chloride solution, magnesium chloride solution and strontium chloride solution Any observations should be noted down in a suitable results table The same test as above can also be done using ammonia solution and sulfuric acid solution

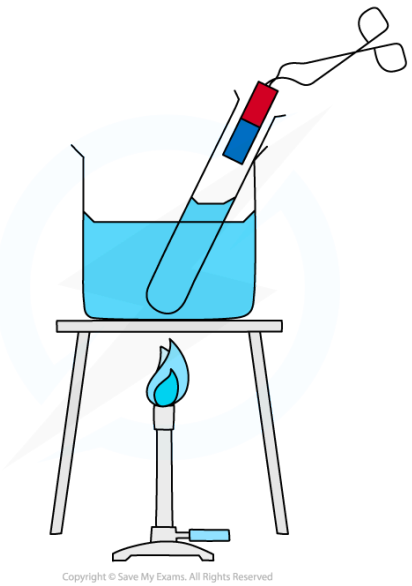
The Positive Results Testing for the Presence of Group 2 ions

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ammonium solution	White precipitate – $Mg(OH)_2$	No change seen	No change seen	No change seen
Excess sodium hydroxide	White precipitate – $Mg(OH)_2$	White precipitate – $Ca(OH)_2$	Slight white precipitate – $Sr(OH)_2$	No change seen
Excess sulfuric acid	Colourless solution	Slight white precipitate – $CaSO_4$	White precipitate – $SrSO_4$	White precipitate – $BaSO_4$

Testing for Ammonium Ions

- About 10 drops of a solution containing ammonium ions, such as ammonium chloride, should be added to a clean test tube
- About 10 drops of sodium hydroxide should be added using a pipette
- The test tube should be swirled carefully to ensure that it is mixed well
- The test tube of the solution should then be placed in a beaker of water, and the beaker of water should be placed above a Bunsen burner, so that it can become a water bath

- As the solution is heated gently, fumes will be produced
- A pair of tongs should be used to hold a damp piece of red litmus paper near the mouth of the test tube, to test the fumes
- The red litmus paper will change colour and become blue in the presence of ammonia gas



Damp red litmus paper turning blue in the presence of ammonia gas

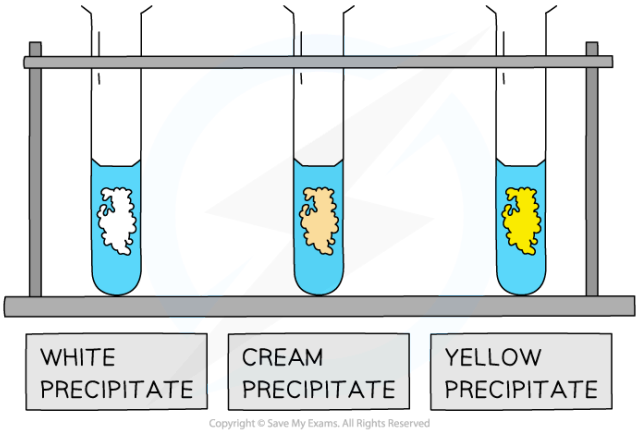
Testing for negative ions

- Simple test tube reactions can be done to identify the following negative ions:
  - Halide ions (X^-)
  - Hydroxide ions (OH^-)
  - Carbonate ions (CO_3^{2-})
  - Sulfate ions (SO_4^{2-})
- If the sample to be tested is a solid, then it must be dissolved in deionised water and made into an aqueous solution

Testing for Halide Ions

- The sample being tested should be added using a pipette to a test tube
- The test tube should be placed into a test tube rack
- A small amount of nitric acid should be added to the sample using a pipette, followed by a small amount of silver nitrate solution
- A precipitate will form, either white, cream or yellow, if a halide ion is present in the sample

Your notes

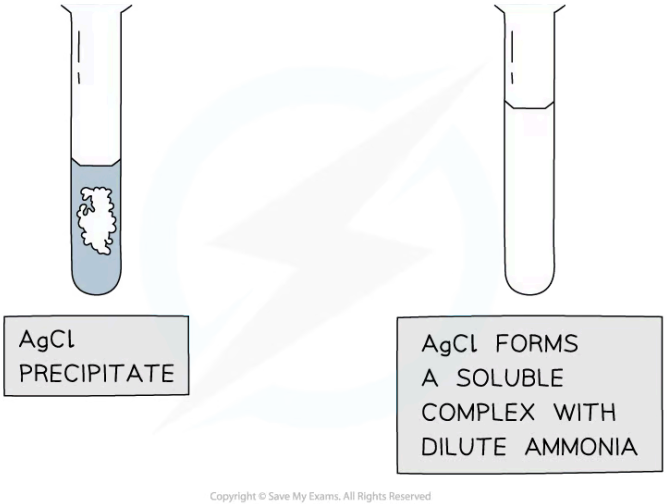


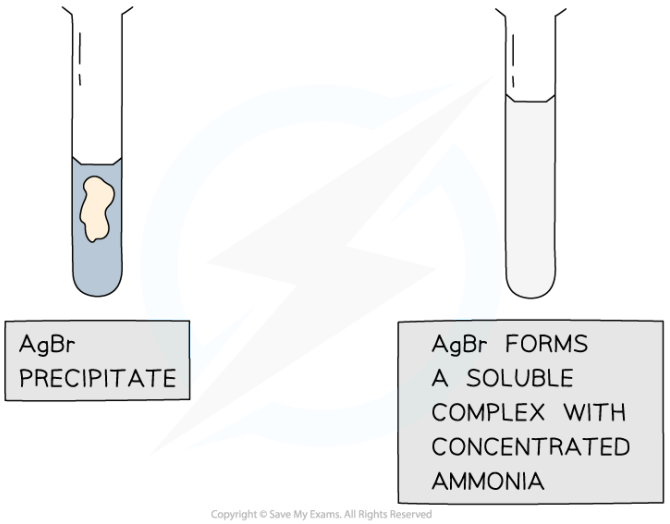
Your notes

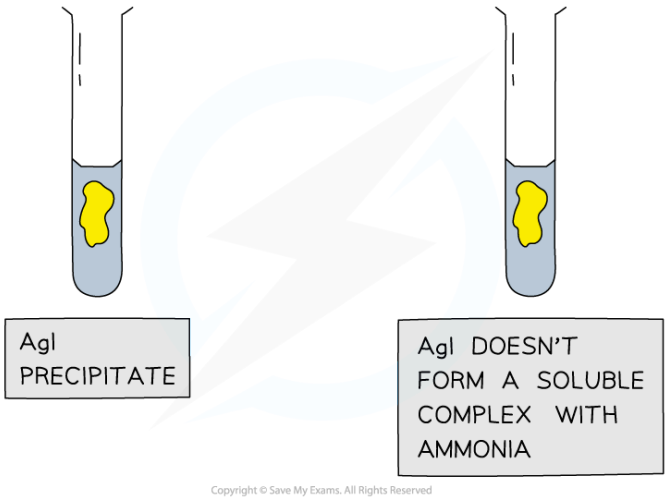
The white, cream and yellow precipitates formed when halide ions react with silver nitrate solution

- The white precipitate will form if chloride ions are present in the sample
  - The white precipitate is AgCl
- The cream precipitate will form if bromide ions are present in the sample
  - The cream precipitate is AgBr
- The yellow precipitate will form if iodide ions are present in the sample
  - The yellow precipitate is AgI

Further test for halides using ammonia solution







Results of the test with ammonia to further distinguish between silver halide precipitates

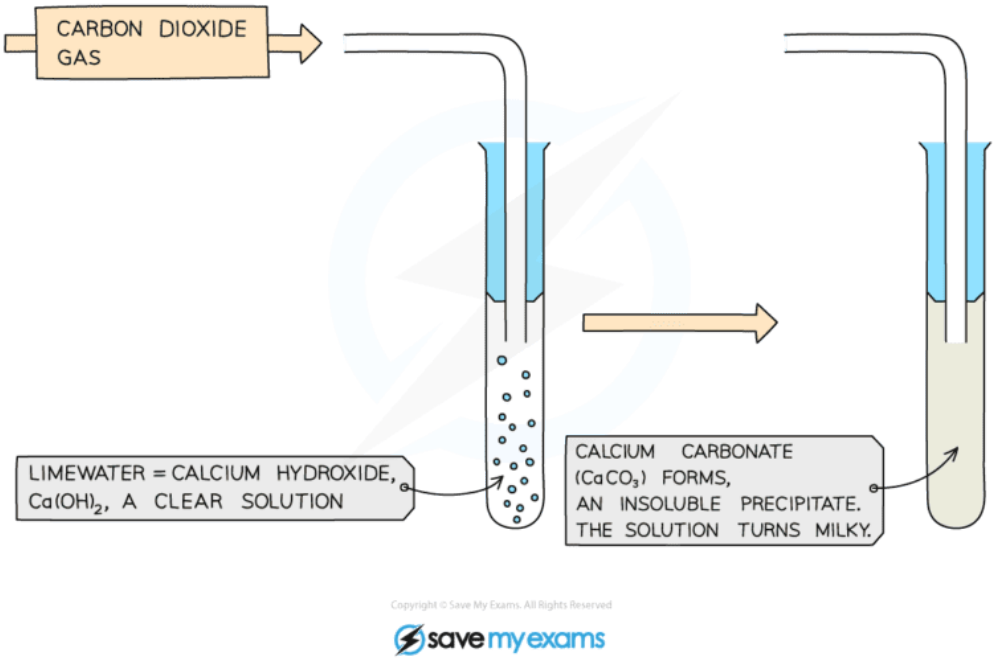
Testing for Hydroxide Ions

- A small amount (around 1 cm^3) of the solution should be added to a test tube using a pipette
- Test the pH of the solution using red litmus paper or universal indicator paper
  - The presence of hydroxide ions will turn the red litmus paper blue and the pH will be clearly alkaline on the universal indicator paper if hydroxide ions are present

Testing for Carbonate Ions

- A small amount (around 1 cm^3) of dilute hydrochloric acid should be added to a test tube using a pipette

- An equal amount of sodium carbonate solution should then be added to the test tube using a clean pipette
- As soon as the sodium carbonate solution is added, a bung with a delivery tube should be attached to the test tube
  - The delivery tube should transfer the gas which is formed into a different test tube which contains a small amount of limewater (calcium hydroxide solution)
- Carbonate ions will react with hydrogen ions from the acid to produce carbon dioxide gas
- Carbon dioxide gas will turn the limewater milky



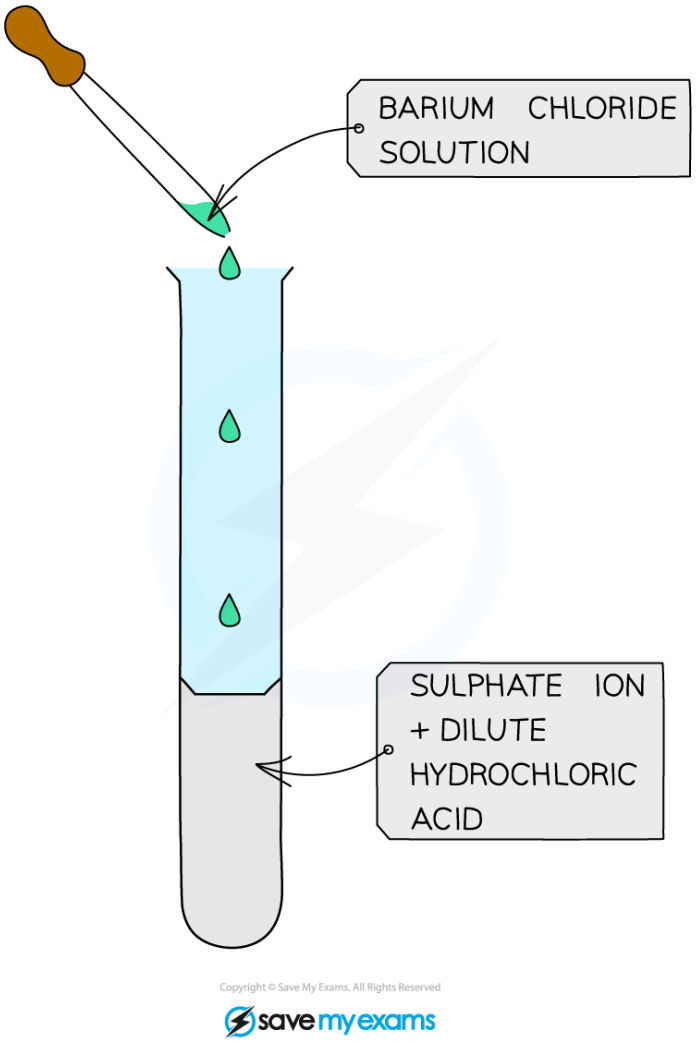
When carbon dioxide gas is bubbled into limewater it will turn cloudy as calcium carbonate is produced

Testing for Sulfate Ions

Acidify the sample with dilute hydrochloric acid and then add a few drops of aqueous barium chloride If a sulfate is present then a **white** precipitate of barium sulfate is formed:

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

Your notes



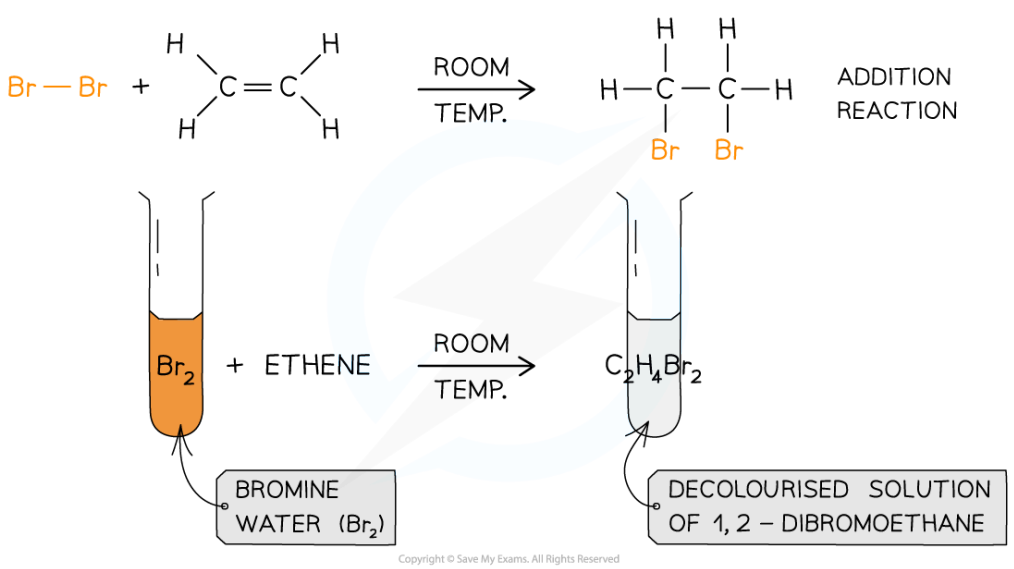
A white precipitate of barium sulfate is a positive result for the presence of sulfate ions

Examiner Tips and Tricks

HCl is added first to remove any carbonates which may be present and would also produce a precipitate and interfere with the results.

Testing for alkenes / saturation

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contain a double bond)
- Br_2 is an orange or yellow solution, called **bromine water**
- The unknown compound is **shaken** with the bromine water
- If the compound is unsaturated, an addition reaction will take place and the coloured solution will decolourise



The bromine water test is the standard test for unsaturation in alkenes

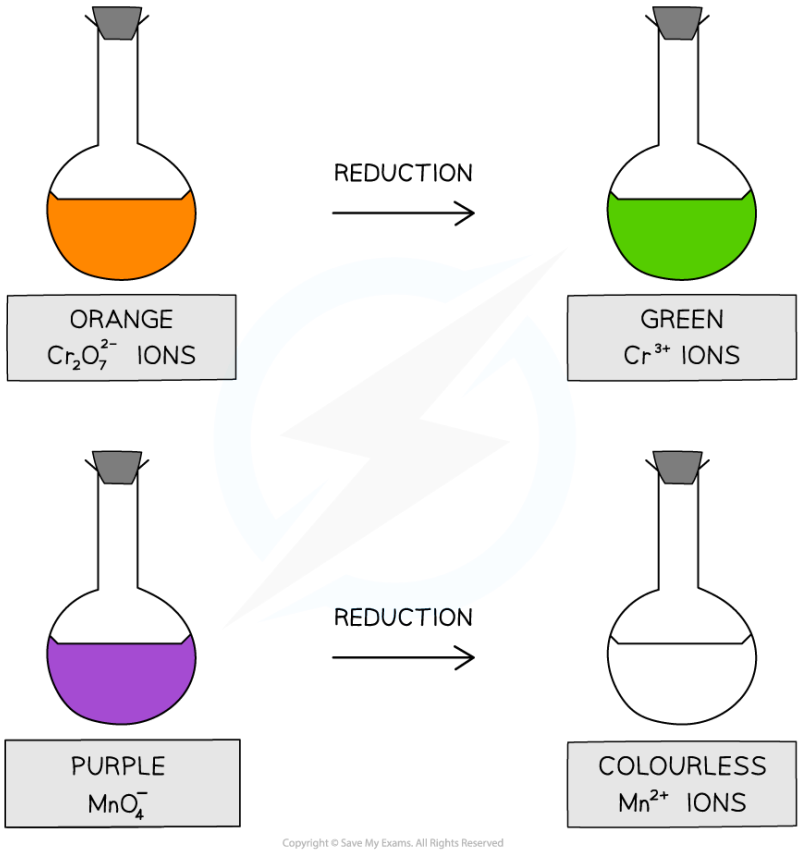
Testing for alcohols

- Phosphorus(V) chloride (PCl_5) can be used as a qualitative test for the presence of an alcoholic -OH group
  - This results in a vigorous reaction at room temperature and does not need heating
  - The evolution of steamy fumes (HCl gas) is a positive result for the presence of the -OH group
- Acidified potassium dichromate(VI) ($K_2Cr_2O_7$) can be used to identify **primary** and **secondary alcohols** from **tertiary alcohols**
  - Acidified potassium manganate(VII) ($KMnO_4$) can also be used

Positive Test Result:

- Primary and secondary alcohols are oxidised to aldehydes and ketones respectively (which can be further tested)
- Primary and secondary alcohols will change acidified potassium dichromate(VI) solution from orange to green
  - They will also cause a colour change from purple to colourless with acidified potassium manganate(VII) solution

Your notes



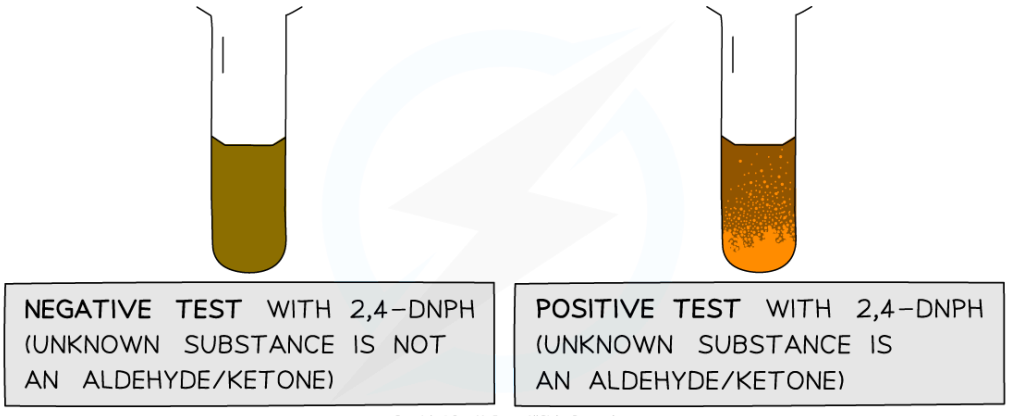
The colour changes associated with testing for primary and secondary alcohols

Testing for carbonyls (general)

- The carbonyl group undergoes a **condensation** reaction with 2,4-dinitrophenylhydrazine

Positive Test Result:

- The **product** formed when 2,4-DNPH is added to a solution that contains an aldehyde or ketone is a **deep-orange precipitate** which can be purified by recrystallisation



Your notes

The test tube on the left shows a negative 2,4-DNPH test and the tube on the right shows a positive test

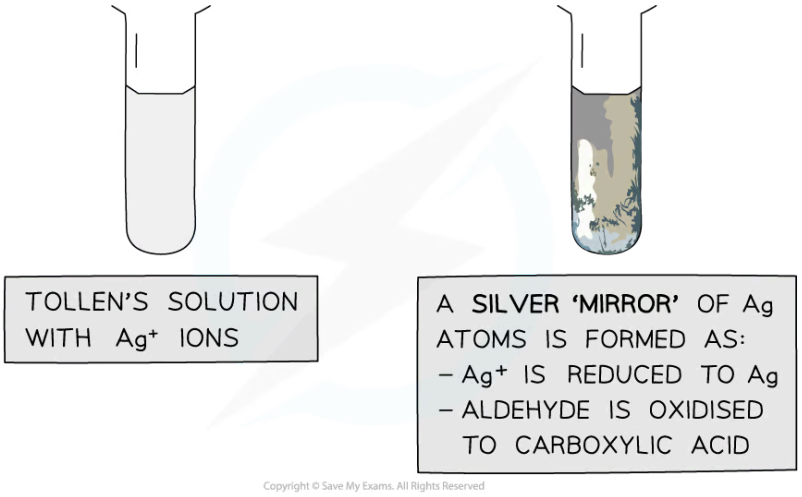
- The **melting point** of the formed precipitate can then be measured and compared to literature values to find out which specific aldehyde or ketone had reacted with 2,4-DNPH

Testing for Carbonyls (aldehyde / ketone specific)

- Tollens' reagent, also known as ammoniacal silver nitrate, is a more specific test-tube reaction that can distinguish between aldehydes and ketones

Positive Test Result:

- When Tollens' reagent is gently warmed with an aldehyde, the silver mirror is formed
  - This is the positive test result
- When Tollens' reagent is gently warmed with a ketone, no silver mirror will be seen, as the ketone cannot be oxidised by Tollens' reagent, so no reaction takes place
  - This is a negative test result



The Ag^+ ions in Tollens' reagent are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to silver atoms

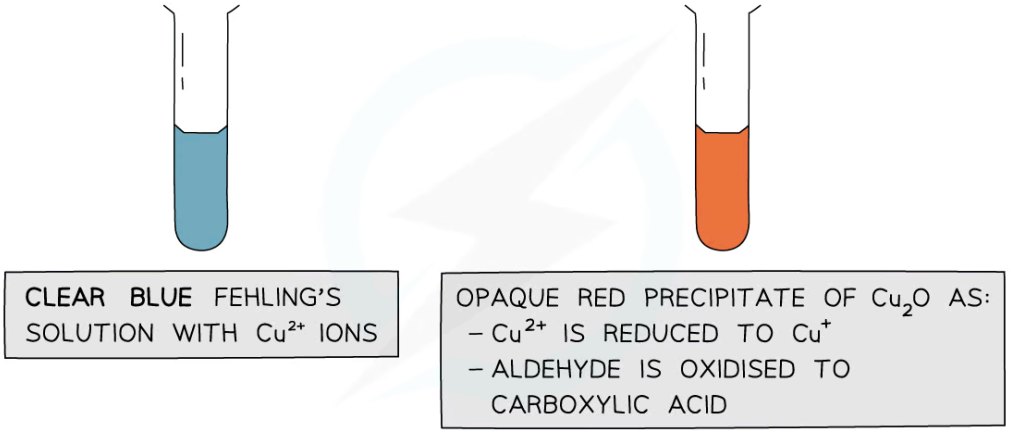
- Fehling's solution (or Benedict's solution) is another specific test-tube reaction that can distinguish between aldehydes and ketones

Positive Test Result:

- When Fehling's solution is gently warmed with an aldehyde, a brick-red precipitate is formed
  - This is the positive test result
- When Fehling's solution is gently warmed with a ketone, no brick-red precipitate will be seen, as the ketone cannot be oxidised by Fehling's solution, so no reaction takes place

Your notes

- This is a negative test result



The copper(II) ions in Fehling's solution are oxidising agents, oxidising the aldehyde to a carboxylic acid and getting reduced themselves to copper(I) ions in the Cu_2O precipitate

Testing for carboxylic acids

- Solid sodium carbonate, Na_2CO_3 (s), or aqueous sodium hydrogen carbonate, $NaHCO_3$ (aq), can be used to test for the presence of a carboxylic acid

Positive Test Result:

- Effervescence / bubbles of gas are seen as carbon dioxide is evolved

Your notes

Your notes

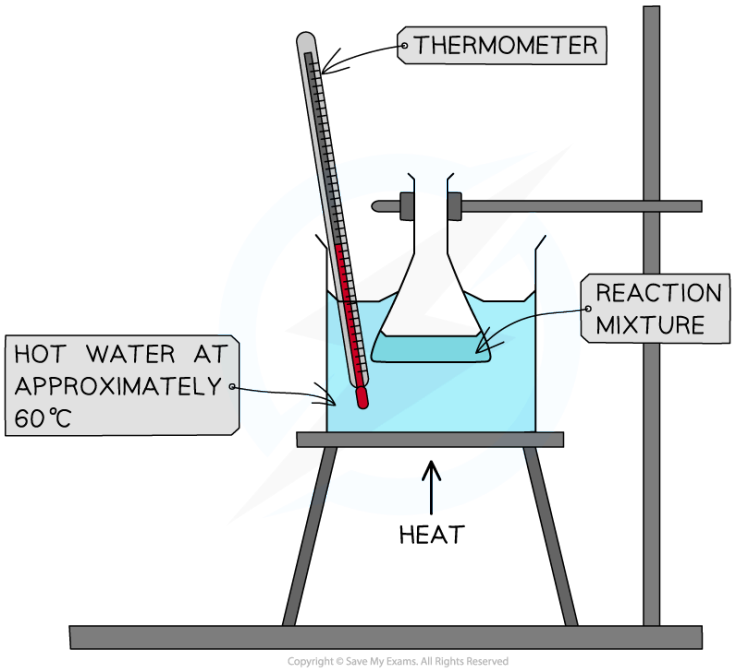
Core Practical 16: Aspirin Preparation

- This practical covers a number of key laboratory skills
  - use appropriate apparatus to record a range of measurements
  - use water bath or electric heater or sand bath for heating
  - use laboratory apparatus for a variety of experimental techniques
  - purify a solid product by recrystallisation
  - use melting point apparatus
  - safely and carefully handle solids and liquids

Synthesis of Aspirin

Key steps in the procedure

- 6.0 g of salicylic acid is added to a conical flask along with 10 cm^3 of ethanoic anhydride and 5 drops of concentrated sulfuric acid
- The mixture is swirled and held in a warm water bath around 60 °C for about 20 minutes
- The flask is then allowed to cool and the contents are added to 75 cm^3 cold water in a beaker at which point the aspirin crystallises out
- The aspirin is recovered using Buchner filtration and left to dry



The preparation of aspirin using a hot water bath

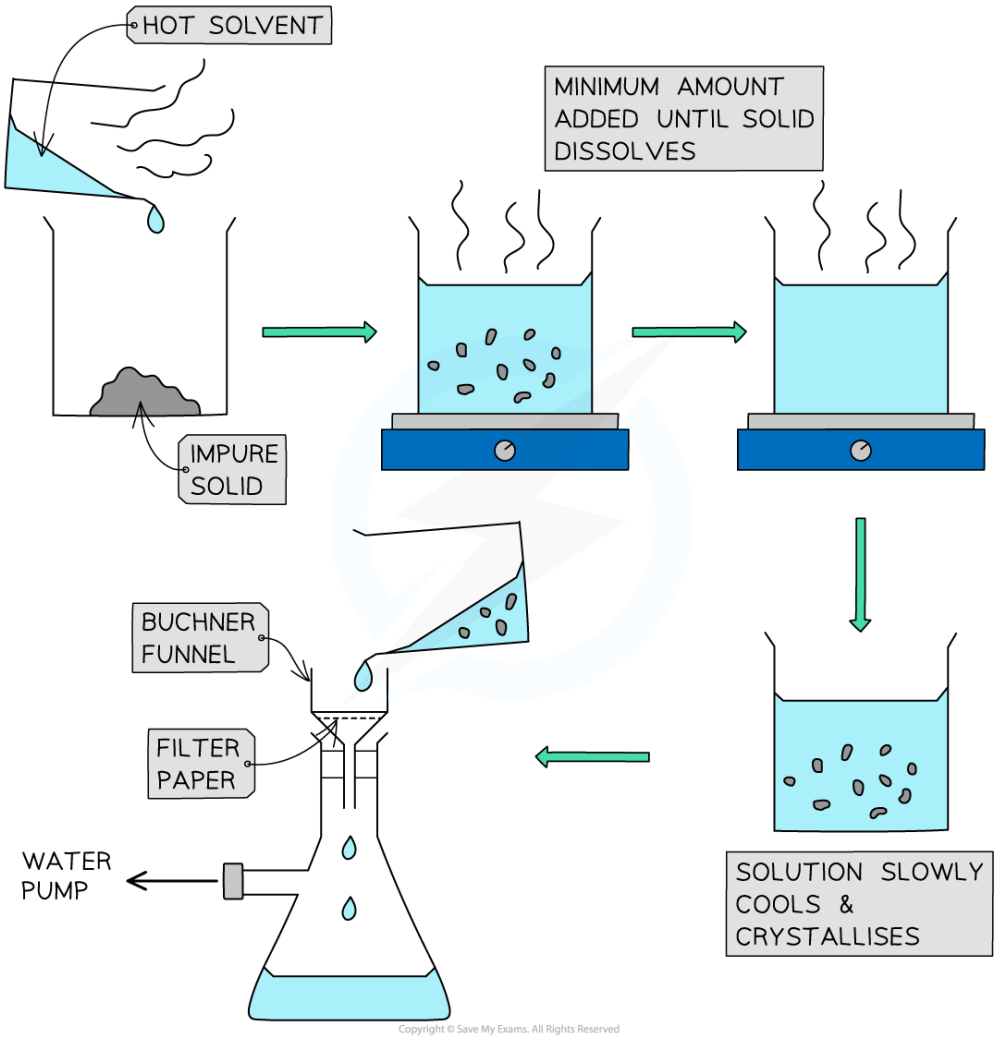
Recrystallisation and melting point test

- The impure aspirin is recrystalised using ethanol, and when the solid has dissolved the solution is poured over 40 cm^3 cold water and recovered using Buchner filtration as before
- The melting point of pure aspirin is 135 °C, so the purity of the product can be assessed

Recrystallisation

- Recrystallisation is used to purify impure solids
- The principle is that a hot solvent is used to dissolve both the organic solid and the impurities and then as the solution cools the solid crystallises out and leaves behind the impurities in the solution
- The key is using the minimum amount of solvent to dissolve the solid and avoid loss of the product
- If any solid impurities remain in the solution, a hot filtration can be carried out
- Once the solution has cooled down to room temperature and crystallised then the product crystals can be recovered by filtration
- This is faster using Buchner apparatus in which filtration occurs under reduced pressure

Your notes



Recrystallisation and Buchner filtration

- After filtration the product is washed with fresh cold solvent and then allowed to dry on filter paper

Examiner Tips and Tricks

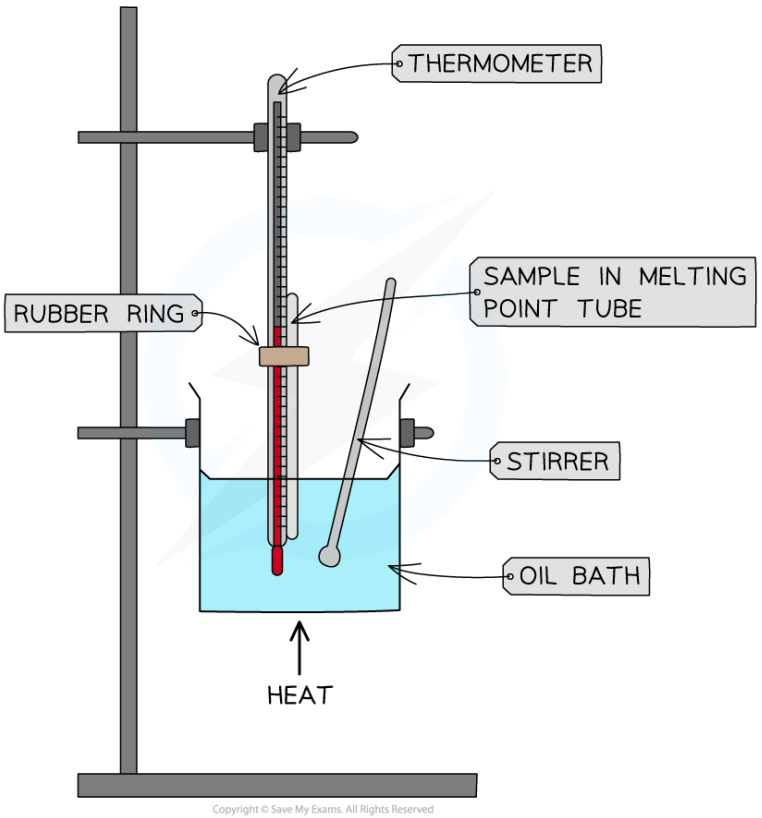
Recrystallisation can be repeated more than once to ensure a very pure product, but each time the yield of product will decrease. Slow cooling results in bigger well defined crystals which are easier to filter and dry.

Melting point analysis

- The melting point of a solid is indicative of its purity and identity
- A melting point can be matched to a known substance as a means of identification or confirmation of a desired product

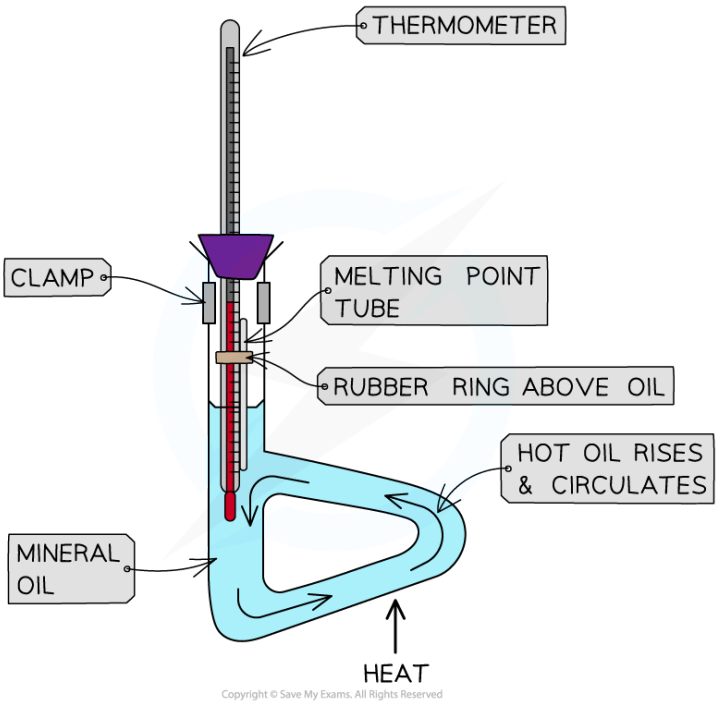
Your notes

- The proximity of a melting point to the actual data book value can express purity
  - Impurities tend to lower the melting point of a solid
- The melting point range also reveals the degree of purity
  - Pure substances have sharp well defined melting points
  - Impure substances have a broad melting point range, i.e. a large difference between when the substance first melts until it completely melts
- The skills needed in performing a melting point test are largely dependent on the specific melting point apparatus you are using
- However, there are some common key skills:
  - Correctly preparing the melting point tubes
  - Heating the tubes very slowly
  - Repeating to get a range of measurements (three would be normal)
- The sample solid must be totally dry and finely powdered - this can be achieved by crushing it with the back of a spatula onto some filter paper or the back of a white tile (this absorbs any moisture)
- Use the first tube to find the approximate melting point range and then repeat using a much slower heating rate

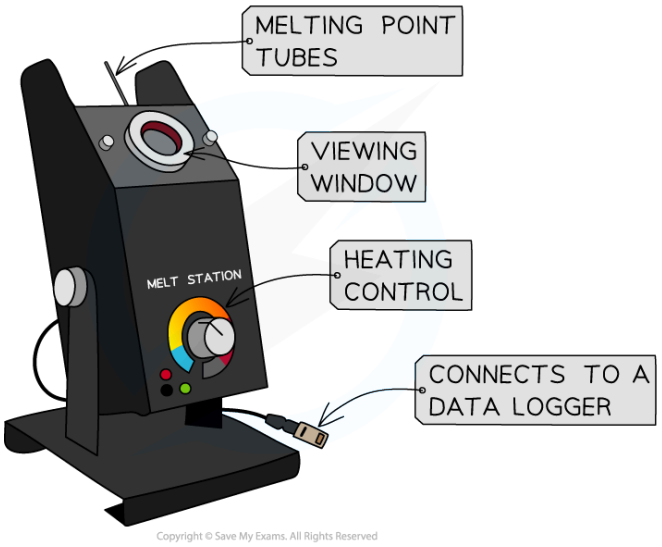


Melting point test using an oil bath

Your notes



Melting point test using a Thiele tube



Melting point test using a melt station

Examiner Tips and Tricks

Always quote a melting point as a range + or - and reference a data book value if you have one.

Your notes