Chemistry Unit 6: Core Practicals

Core Practical 9A: following the rate of the iodine-propanone reaction by the titrimetric method.

Rates of reaction using a - titrimetric method

Background:

- This uses the continuous method, Which is data from an experiment where the concentration of a substance is followed throughout the experiment.
- To determine the rate of reaction, the data must be plotted (on a concentration-time graph) and the successive half-lives - if the half lives are constant, the reaction is 1st order.

Procedure

Apparatus:

- 50 cm3 of 1 mol dm-3 aqueous propanone
- 50 cm3 of 1 mol dm-3 sulfuric acid
- 50 cm3 of 0.2 mol dm-3 potassium iodide solution
- 0.01 mol dm-3 sodium thiosulfate
- 20 cm3 of starch solution
- Sodium hydrogen carbonate
- 100 cm3 beaker
- 10 cm3 graduated pipette
- Conical flasks
- Stop clocks
- Spatula

Safety:

- Wear eye protection
- Iodopropanone is a lachrymator (irritant to the eyes) so dispose down the sink with lots of water
- Sodium thiosulfate releases SO, and propanone is flammable so ensure room is well ventilated
- Avoid skin contact with reactants and products

Method:

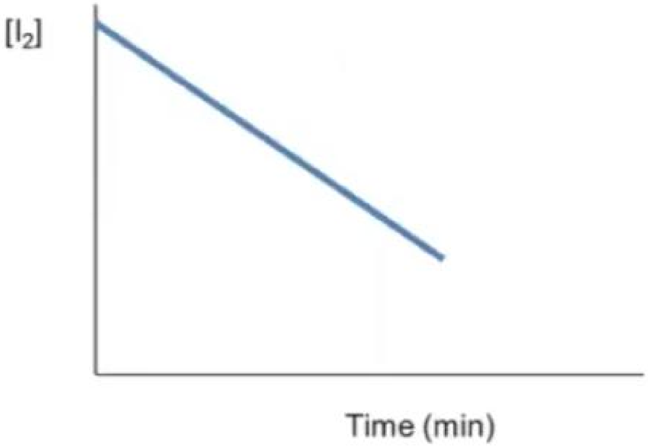
- 25 cm' of 1 mol dm-3 aqueous propanone and 25 cm3 of 1 mol dm-3 sulfuric acid to a beaker. (Acidify the propanone)

- Add 50 cm? of 0.02 mol dm- 3 iodine solution. Start the clock swirl the beaker well to mix. (Ensure all products are mixed)
- Using a 10cm' pipette, withdraw a sample of the mixture and transfer it to a conical flask.
- Add a spatula measure of sodium hydrogencarbonate (quench/ stop the reaction).
- This means the reaction will stop to allow the concentration of the iodine at that time to be measured.
- Record the time at which the sodium hydrogencarbonate is added, the point at which half the reaction mixture is pipettes into the quenching solution.
- Titrate the iodine in the conical flask with 0.01 mol dm-3 sodium thiosulfate solution. When the colour turns a pale yellow add the starch indicator*(If starch is added too early, the iodine-starch complex formed in high concentrations of iodine can delay the reaction, making it difficult to determine the endpoint precisely.*) . The end point is then when the mixture goes from blue to colourless.
- Every 5 minutes withdraw another 10 cm' sample and repeat steps 4/5

CH_3COOH (aq) + I_2 (aq) —> CH_3COCH_2I (aq) + H^+ (aq) + I^- (aq)

Results:

- The results are plotted on a concentration time graph.
- The graph displays the reaction is 0 order with respect to iodine.
- This is due to the half-life of this reaction being independent of the concentration of iodine.



Conclusion:

- This reaction is zero order with respect to iodine.
- However it if first order with respect to the propanone and the acid catalyst
- Therefore the rate equations is:
  Rate = k[CH_3COCH_3(aq)] [H^+ (aq)]
- This means the rate determining step contains only the propanone and hydrogen ion.

calculating the rate = change in concentration/ change in time

PPQ. The concentration of propanone was halved and the experiment repeated in this, explain using the rate equation any difference in the results of the repeat experiment.

- Rate is half the original experiments because propanone is first order.
- The rate is proportional to the concentration of propanone.

PPQ. The titration was Carrie doubt using an indicator and state when it is added. Give all the colour changes involved.

- Starch is the indicator.
- It is added when a pale yellow colour is observed.
- It turn from blue black to colourless at the endpoint

PPQ. At what point should the time be recorded?

- After half the reaction mixture has been pipettes into the quenching solution.

Core Practical 9B: investigating a ‘clock reaction’ (Harcourt-Essen, iodine clock)

Background:

- Use a clock reaction to find the order of reaction with respect to iodine ions or peroxodisulfate ions.
- Clock reactions involve setting up individual experiments and changing the concentration of one reactant at a time.
- Plotting a graph of 1/T against the concentration allows us to determine the shape of the graph and therefore the order of reaction.
- Hydrogen peroxide reacts with iodide ions to form iodine. The thiosulfate ion then immediately reacts with iodine formed in the second reaction.
- When the iodine produced has reacted with all of the limited amount of thiosulfate ions present, excess I_2 remains in a solution.

- Reaction with the starch then suddenly forms a dark blue-black colour.

$$H_2O_2\ (aq) + H^+\ (aq) + 2I^-\ (aq) \longrightarrow I_2\ (aq) + 2H_2O\ (l)$$
$$2S_2O_3^{2-}\ (aq) + I_2\ (aq) \longrightarrow 2I^-\ (aq) + S_4O_6^{2-}\ (aq)$$

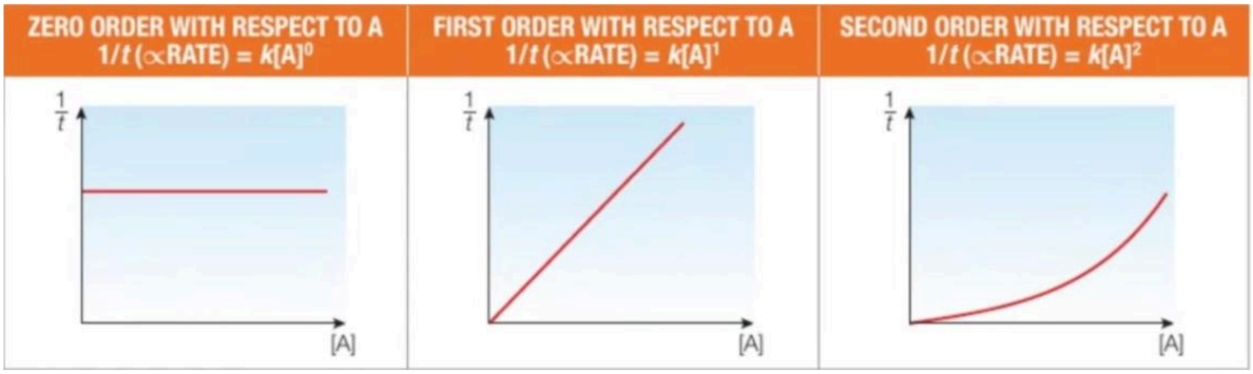
Procedure

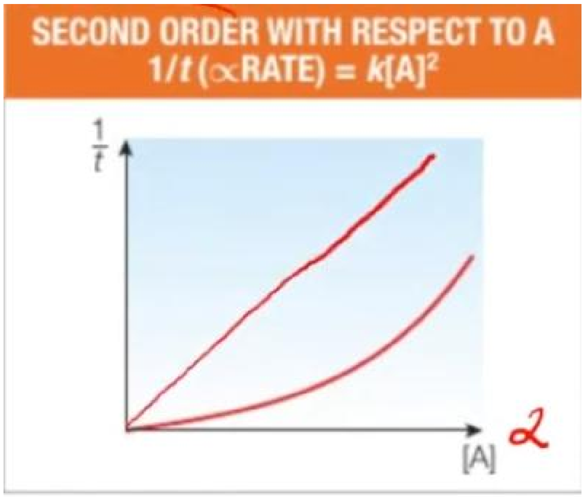
Apparatus:
- 100 cm3 of 0.2 mol dm-3 sodium peroxodisulfate solution
- 100 cm3 of 0.2 mol dm-3 potassium iodide solution
- 50 cm3 of 0.05 mol dm-3 sodium thiosulfate
- 20 cm3 of 1% starch solution
- Distilled water
- 4 × 10 cm3 measuring cylinders
- Pipettes
- White tile
- Nine 100 cm3 beakers
- Stop clock

Safety:
- Wear eye protection
- avoid skin contact with reactants and products

Method:
- Measure 10 cm3 of potassium iodide solution into a small beaker on a white tile
- Add 5 cm3 of sodium thiosulfate solution to the potassium iodide
- Add 10 drops of starch solution to the mixture in the small beaker (top act as an indicator)
- Measure out 10 cm3 of sodium peroxodisulfate solution and pour in to the mixture - start the stop clock
- Stop the clock when the blue colour appears and note the time taken.
- Repeat steps 1-5 using different volumes of sodium peroxodisulfate and potassium iodide ensuring the total volume is 25 cm3 - done by adding distilled water

Results:
- The results for this experiment are plotted into a rate-concentration graph.
- The rate is proportional to 1/time and the order can be determined.





Conclusion:

- The rate of reaction is proportional to 1/ time.
- Using the changes in rates and concentrations we can deduce the order with respect to each reactant.
- If the rate does not change when the concentration of a reactant doubles, then it is zero order.
- If the rate doubles when the concentration doubles then the reaction is in first order.
- If the rate quadruples when the concentration doubles then the reaction is second order.

Errors:

- Inaccurate timing of the appearance of blue colour. Two students could time simultaneously and use an average value.
- Adding starch increases the volume which affects the concentrations of the reactant and thus the amount they change over time.

Core Practical 10: Finding the activations energy of a reaction

Background:

- Use the Arrhenius equation to determine the activation energy of a reactant.
- The Arrhenius equation expresses the rate constant -k= $Ae^{(-Ea/RT)}$
- -gradient = E_a/R

Procedure

Apparatus:

- 70 cm3 of 0.01 mol dm-3 aqueous phenol solution
- 70 cm3 of bromide/bromate solution
- 50 cm3 of 0.5 mol dm-3 sulfuric acid
- Methyl red indicator 3 x 100 cm3 beakers
- 4 x boiling tubes
- 10 cm3 pipette
- Thermometer
- Stop clock
- 2 x 500 cm3 beakers.
- Kettle

Safety:

- Wear eye protection and suitable chemical resistant gloves.
- Avoid skin contact with reactants and products.
- Do not inhale any fumes that may be produced.

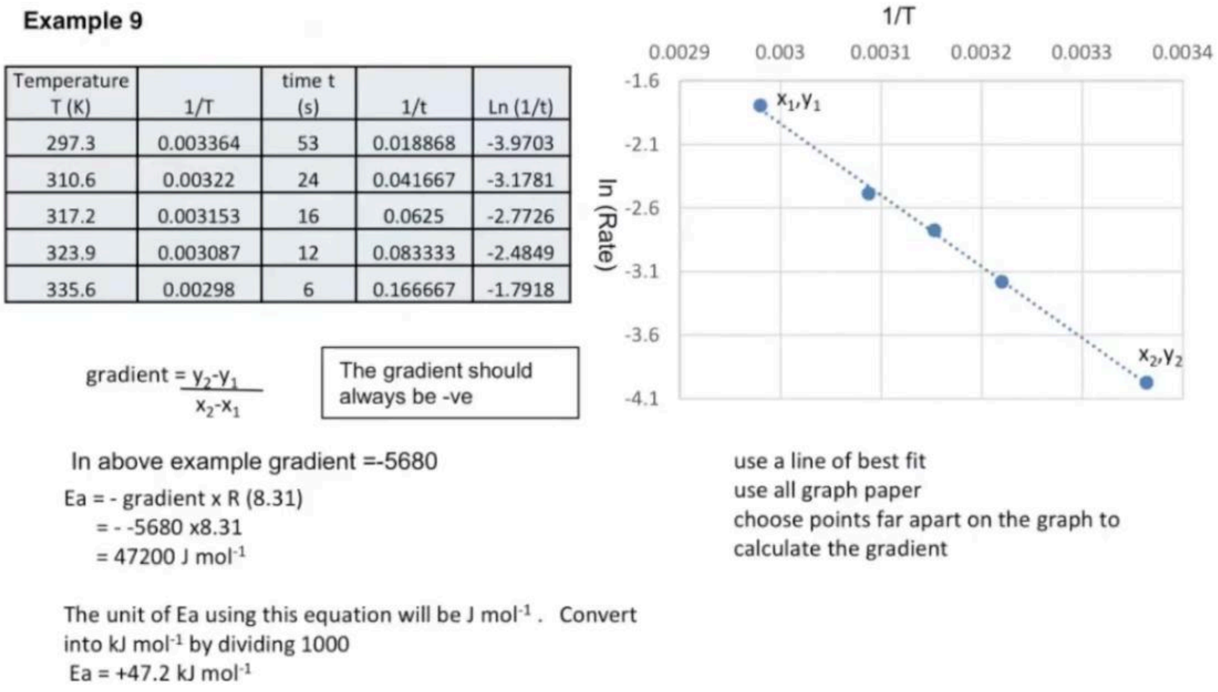
Method:

- Pipette 10 cm3 of phenol solution and 10 cm of bromide/bromate solution into one boiling tube and add four drops of methyl red
- Pipette 5 cm3 of sulfuric acid into another boiling tube
- Use the kettle to create a 70 °C water bath and place the boiling tubes in to it
- When they are the same temperature, combine the two mixtures and start the stop clock
- Leave the boiling tube until the colour of the indicator disappears and stop the stop clock, noting the time
- Repeat at 65 °C, 55 °C, 45 °C, 35 °C, 25 °C and 15 °C

Results:

- Temperatures are converted to kelvin and calculate the reciprocal of each temperature.
- Take the natural logs of each temperature.
- K is equal to constant/ time and take the natural logarithms.
- We can plot a graph of ln t against 1/T and the gradient is equal to E_a/ R

E_a = -gradient x R(8.31)



Example 9

Temperature T (K)	1/T	time t (s)	1/t	Ln (1/t)
297.3	0.003364	53	0.018868	-3.9703
310.6	0.00322	24	0.041667	-3.1781
317.2	0.003153	16	0.0625	-2.7726
323.9	0.003087	12	0.083333	-2.4849
335.6	0.00298	6	0.166667	-1.7918

gradient = $\frac{y_2 - y_1}{x_2 - x_1}$

The gradient should always be -ve

In above example gradient =-5680

Ea = - gradient x R (8.31)

= - -5680 x8.31

= 47200 J mol^{-1}

The unit of Ea using this equation will be J mol^{-1}. Convert into kJ mol^{-1} by dividing 1000

Ea = +47.2 kJ mol^{-1}

use a line of best fit

use all graph paper

choose points far apart on the graph to calculate the gradient

Core practical 11: Finding the k_a value of a weak acid.

Weak acids will partially dissociate.

The K_a can be determined by titrating a known volume of acid against sodium hydroxide then adding a further equal volume of acid and measuring the pH.

Half acid will have been titrated and $K_a = [H^+]$

Apparatus

- 100 cm^3 of 0.1 mol dm^{-3} ethanoic acid solution
- 100 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution
- Data Logger and pH probe
- Stand, clamp and boss for pH probe
- 100 cm^3 burette
- Burette stand
- 250 cm^3 conical flask
- 25 cm^3 pipette and filler
- Phenolphthalein indicator

Safety

- Wear eye protection
- avoid skin contact with reactants and products
- clamping and filling done with care not to crack

Calibrate meter first by measuring **known** pH of a **buffer** solution. This is necessary because pH meters can **lose accuracy on storage**.

- Most pH probes are calibrated by putting the probe in a set buffer (often pH 4) and pressing a calibration button/setting for that pH. Sometimes this is repeated with a second buffer at a different pH.

Method for solution

1. Calibrate the pH meter
2. Pipette 25 cm^3 of 0.1 mol dm^{-3} ethanoic acid solution into a 250 cm^3 conical flask
3. Fill the burette with sodium hydroxide solution
4. Add two or three drops of phenolphthalein to the conical flask
5. Titrate the ethanoic acid with the sodium hydroxide until the mixture just turns pink - swirl to ensure the endpoint is reached (a permanent pink colour)
6. Pipette a further 25 cm^3 of 0.1 mol dm^{-3} ethanoic acid solution in to the conical flask and record the pH of this solution (using pH meter)

Since $[HA] = [A^-]$

$[A^-]$ And $[HA]$ can be cancelled in the expression:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\text{Therefore } K_a = [H^+]$$

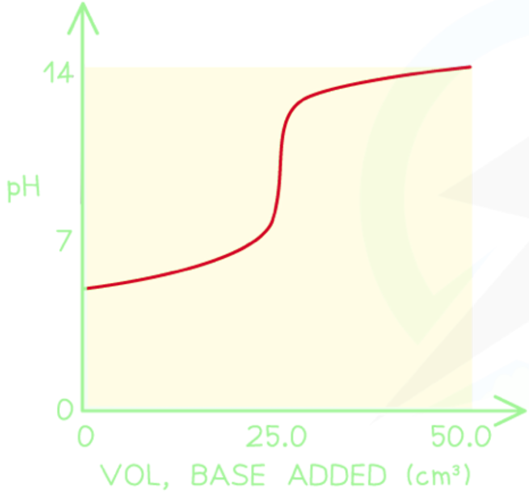
$$pH = -\log[H^+]$$

$$[H^+] = \sqrt{(K_a \times [HA])}$$

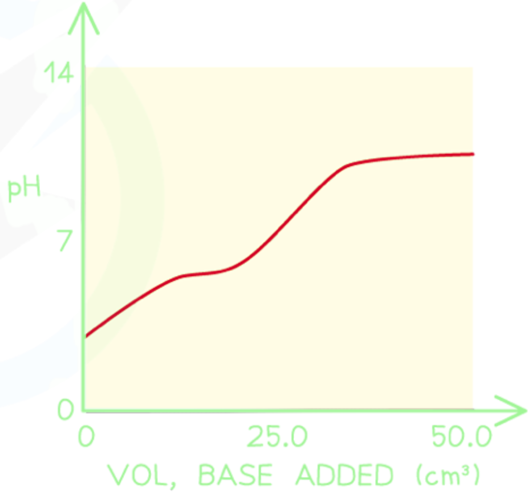
Method for solid

1. Accurately weigh between 0.40 g and 0.50 g of benzoic acid and dissolve it in 50 cm^3 of distilled water
2. Transfer to a 250 cm^3 volumetric flask with washings
3. Put a stopper in the flask and turn upside down to mix
4. Withdraw a sample and place in a small beaker
5. Measure the pH using a calibrated pH meter

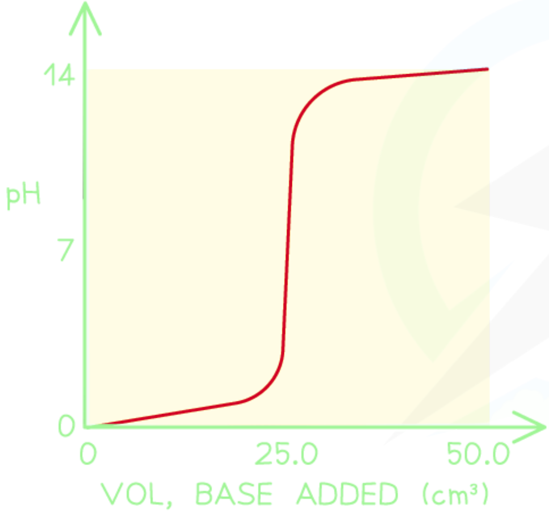
WEAK ACID + STRONG BASE



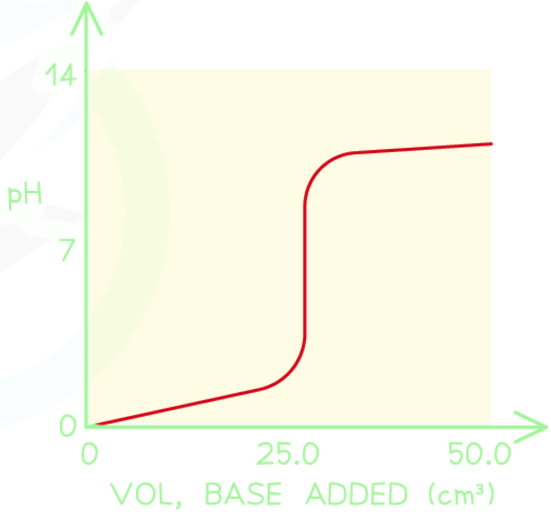
WEAK ACID + WEAK BASE



STRONG ACID + STRONG BASE



STRONG ACID + WEAK BASE



Core Practical 12: investigating some electrochemical cells

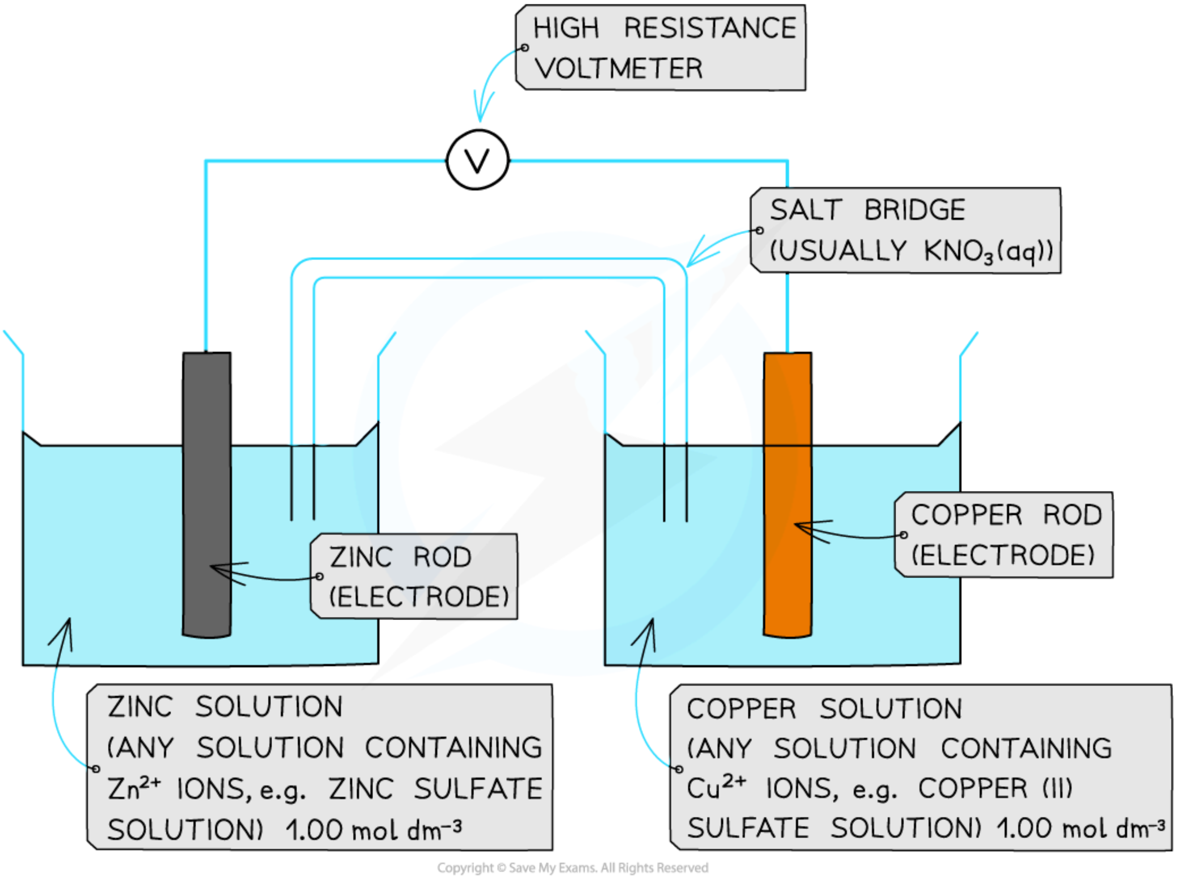
Electrochemical cells used to produce electric current from chemical reactions. Consists of two half-cells (metal electrode in a solution of itself or an inert electrode (platinum) in a solution containing two ions) connected by a salt bridge (filter paper soaked in salt solution) and a high resistance voltmeter.

Apparatus

- 50 cm^3 of 0.4 mol dm^{-3} zinc sulfate and copper(II) sulfate solutions
- 50 cm^3 of 0.1 mol dm^{-3} silver nitrate solution
- 50 cm^3 of 1.0 mol dm^{-3} iron (II) sulfate solution
- Saturated potassium nitrate solution (salt bridge)
- Deionised water
- Strip of zinc, copper, iron and silver
- Sandpaper
- 4 x 100 cm^3 beakers
- Filter paper
- 100 cm^3 measuring cylinder
- High resistance voltmeter
- Wires and crocodile clips

Method

1. Use sandpaper to clean strips of copper and zinc (to get rid of any oxidation on the surface of metal)
2. Pour 50 cm^3 of zinc sulfate solution in to a beaker and stand the strip of zinc metal in the solution
3. Pour 50 cm^3 of copper(II) sulfate solution in to a different beaker and stand the strip of copper metal in the solution
4. Join the two beakers using a salt bridge - filter paper soaked in a saturated solution of potassium nitrate
5. Connect the metal strips to voltmeter using wires and crocodile clips
6. Record the electrode potential of the
    a. [Zn (s) | Zn^{2+} (aq)] and [Cu (s) | Cu^{2+} (aq)] cell
7. Repeat steps 1 to 6 with the following combinations: Zn/Fe, Fe/Cu, Zn/Ag, Cu/Ag



Key points

- Standard conditions are 1 mol dm^{-3} solutions, gases at 100 kPa and 298 K
- The reading on the voltmeter should be positive, if it is negative the electrodes are the wrong way round
- For a thermodynamically feasible process, EMF has to be **positive**
- EMF = E_R - E_L where R is the **right** hand cell (**reduction**) and L is the **left** hand cell (**oxidation**)
- When writing full equations, the reduced equation becomes reversed and the oxidized equation stays the same.

PPQ. Give a reason why potassium hydroxide solution should not be used for the salt bridge.

- Hydroxide ions will react with cations in solutions and form ppt

Core practical 13A: Redox titrations with iron (II) ions and potassium manganate (VII)

Background:

- Be able to calculate the mass in milligrams of iron in an iron tablet.
- Carry out a redox titration involving Fe^{2+} (aq) and MnO_4^-
- Potassium manganate (VII) is a powerful oxidising agent.
- It acts as its own indicator in acidic solutions - as soon as the potassium manganate (VII) is in excess the solution changes from colourless to pink.

Procedure

Apparatus:

- Five iron tablets
- 100 cm3 of 1.5 mol dm-3 sulfuric acid
- 100 cm3 of 0.005 mol dm-3 potassium manganate(VII)
- Distilled water
- 50 cm3 burette.
- 25 cm3 pipette
- Pipette filler
- White tile
- Clamp and stand
- 100 cm3 beaker
- cm3 measuring cylinder
- Two 250 cm3 beakers
- 250 cm3 conical flask
- 250 cm3 volumetric flask and stopper
- Spatula
- Glass rod
- Filter funnel and filter paper
- Pestle and mortar
- Mass balance

Safety

- Wear eye protection and suitable chemical resistant gloves.
- Avoid Skin contact with reactants and products.
- Take care when clamping and filling the burette that it does not crack or topple over.

Method:

- Crush the iron tablets using a mortar and pestle.
- Transfer the crushed tablets to a weighing boat and measure the mass of the tablets/boat. (Weighing by difference)
- Empty the tablets in to a beaker and reweigh the boat
- Add most of the 1.5 mol dm-3 sulfuric acid to the small beaker and stir to dissolve the tablets.
- Filter the solution into the volumetric flask.
- Rinse the beaker with the remaining sulfuric acid and filter the washings into the volumetric flask.
- Fill up to the graduation mark with distilled water and invert to shake.

Titration:

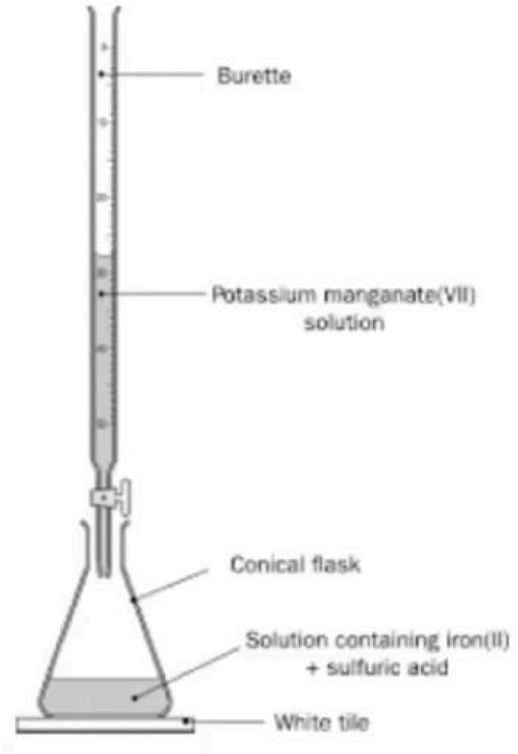
- Pipette 25 cm3 of the iron(II) solution in to a conical flask
- Fill the burette with the potassium manganate(VII) and set up the titration apparatus
- Titrate the iron(II) solution with the potassium manganate(VII) solution until the mixture has just turned pink
- On standing, the pink colour will disappear because there is a secondary reaction - do not add more KMnO4
- Record the titre volume and repeat until you achieve concordat results.
    - (Don't calculate the rough titration (first titration) in the results.) and (concordat results are 0.2 cm3 within each other)

Diagram and come key points:

- In this reaction, the iron (II) ions are reduced and the manganate (VII) ions are oxidised:

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

- The iron (II) reacts with the manganate (VII) in a 5:1 ratio.



PPQ. Give the reason why the titration in step 4 does not require the addition of an indicator and colour change at the endpoint.

- Potassium manganate is a self indicator, it's a self indicating reaction.
- Colourless to pink.

PPQ. If a student decided to take the burette reading from the top of the liquid level rather than from the bottom of the meniscus.

Suggest the effect of this, if any, on the titre value.

- Titre value would be unchanged due to being a difference between the two values

Core Practical 13B: Redox titration with sodium thiosulfate and iodine

Background:

- Calculate the concentration of the oxidising agent potassium iodate (V), KIO_3
- Sodium thiosulfate can be used in a titration with a solution of iodine because it is oxidised as it reacts with iodine.

- Starch is used as indicator as it has a very clear colour (blue-black) in the presence of free iodine and it turns colourless when all sodium thiosulfate Reacts.

Procedure

Apparatus:

- Potassium iodate(V) solution
- 0.05 mol dm-3 potassium iodide solution
- 1.0 mol dm-3 sulfuric acid
- 0.1 mol dm-3 sodium thiosulfate
- Distilled water
- Starch solution
- Pipette and pipette filler
- Burette
- Filter funnel
- Clamp and stand
- White tile
- Conical flask

Safety:

- Wear eye protection and suitable chemical resistant gloves.
- Avoid skin contact with reactants and products.
- Take care when clamping and filling the burette that it does not crack or topple over.

Method:

- Wash the pipette, burette and conical flask with distilled water
- Rinse the pipette with potassium iodate(V) and rinse the burette with sodium thiosulfate (avoids dilution errors)
- Pipette 25 cm3 of potassium iodate(V) solution into a conical flask
- Add 20 cm3 sulfuric acid and 10 cm3 potassium iodide to the flask
- Fill the burette with sodium thiosulfate and set up the titration apparatus
- Titrate the mixture with the sodium thiosulfate until the mixture turns a pale yellow colour and then add 5 drops of starch solution
- Add the sodium thiosulfate dropwise until the blue-black solution turns colourless
- Record the titre volume and repeat until concordant results are seen

Diagram and key points:

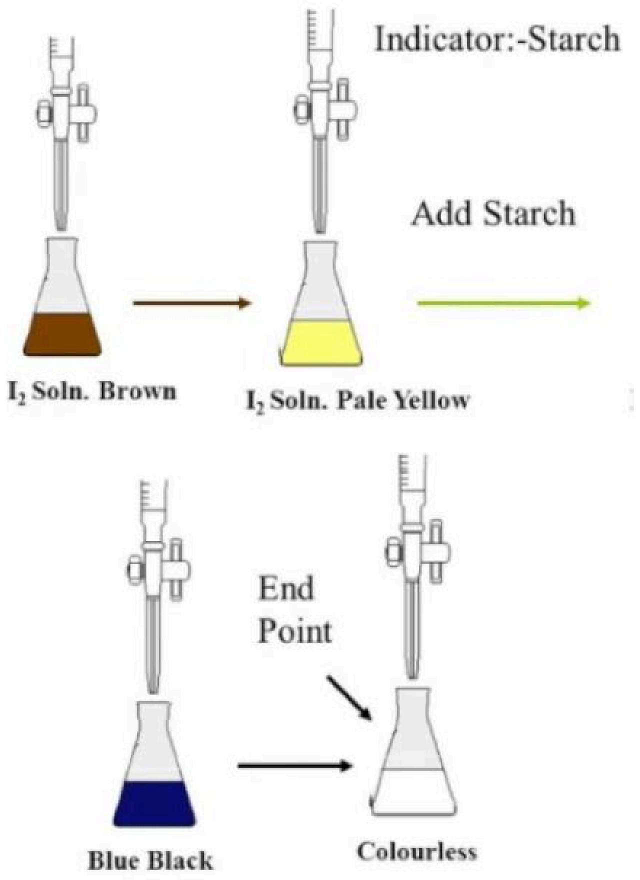
- Thiosulfate ions reduce iodide ions to iodine:

$$2S_2O_3^{2-}\,(aq) \longrightarrow S_4O_6^{2-}\,(aq) + 2e^-$$
$$I_2\,(aq) + 2e^- \longrightarrow 2I^-\,(aq)$$

- The overall reactions:

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

- The thiosulfate reacts in a 2:1 ratio.



Core Practical 14: Preparation of a transition metal complex

Background:

- Prepare a transition metal complex, tetraamminecopper (II) sulfate- 1-water.
- Transition metals undergo different reactions (like redox, deprotonation, ligand exchange and coordination number change)

- For the formation of this transition metal complex, the reaction is a ligand exchange as water ligands are replaced by ammonia or sulfate.

Procedure

Apparatus:

- Copper(II) sulfate pentahydrate
- 10 cm3 ethanol
- 2 cm3 concentrated ammonia solution
- Crushed ice
- Buchner flask and funnel
- Vacuum filtration apparatus
- Filter paper
- Test tube
- 50 cm3 and 100 cm3 beakers.
- 10 cm3 graduated pipette
- Pipette filler
- Spatula and stirring rod
- Mass balance (2 d.p.)

Safety:

- Wear eye protection
- Avoid skin contact with reactants and products
- The ammonia should only be used in a working fume cupboard while wearing suitable chemical resistant gloves
- The water bath must not be heated with a Bunsen burner as the ethanol is highly flammable

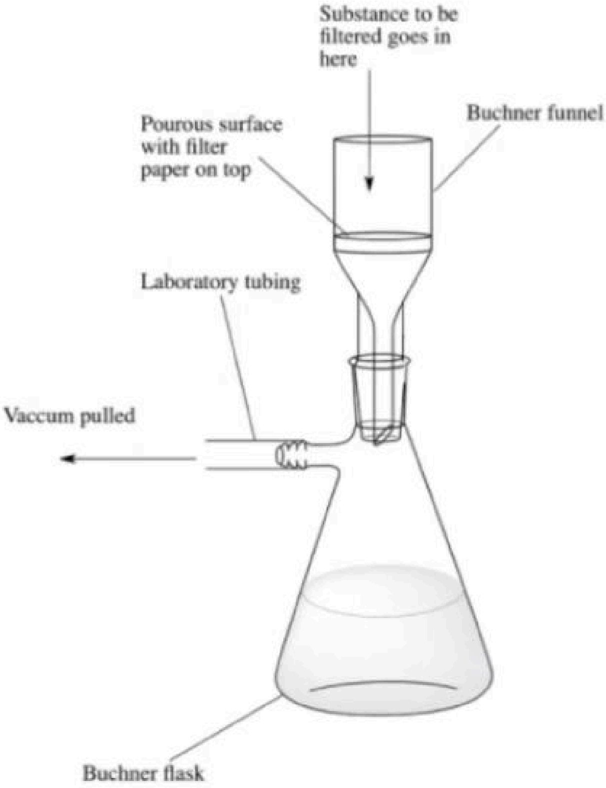
Method:

- Weigh approx. 1.50 g copper(II) sulfate by weighing by difference using a test tube
- Add 4 cm3 water to the test tube using a graduated pipette
- Prepare a water bath, stand the test tube in the water bath and stir gently to dissolve the copper(II) sulfate
- Remove the test tube from the water bath and, using a fume cupboard, add 2 cm3 concentrated ammonia solution to the copper(II) sulfate
- Pour the contents of the test tube into a beaker containing 6 cm3 ethanol, mix well and cool using an ice bath
- Use a Buchner funnel and flask to filter the crystals, wash the test tube using cold ethanol and filter the washings and rinse with cold ethanol

- Scrape the crystals onto a new, dry piece of filter paper and use a 2nd piece of filter paper to dry the crystals. Once dry, measure and record the mass.

Diagram and key points:

- Sometimes the calculated mass is lower or higher than it should be.
    - Losses could be from the reaction not going to completion and product staying in the solution.
    - Gains could be form impure or we crystals.



PPQ. When an excess of concentrated hydrochloric acid is added to copper (II) sulfate dissolved in water, the colour changes from blue to yellow.

Give the formula of the complex ion responsible for the yellow colour.

- $[CuCl4]^{2-}$

PPQ. What would you observe as dilute ammonia is added, drop by drop to another sample of copper (II) sulfate dissolved in water?

- Blue precipitate.

- After adding excess ammonia the precipitate dissolves.
- Forming a deep/ dark blue solution.

Core Practical 15: Analysis of some inorganic and organic unknowns

Chemical tests can be used to identify different molecules or functional groups within in a molecule

Apparatus

- Concentrated hydrochloric acid
- 1.0 mol dm-3 sodium hydroxide
- 1.0 mol dm-3 nitric acid
- 0.1 mol dm-3 silver nitrate solution
- 1.0 mol dm-3 ammonia solution
- 1.0 mol dm-3 dilute hydrochloric acid
- Barium chloride solution
- Limewater
- Bromine water
- Sodium carbonate solution
- Ethanol
- Concentrated sulfuric acid
- Nichrome wire
- Delivery tube
- Bunsen burner and safety mat
- Test tube and bungs
- Distilled water
- Dropping pipette
- Spatula
- Boiling tube
- 250 cm^3 beaker
- 100 cm^3 beaker
- Kettle
- 4 unknown inorganic substances
- 3 unknown organic substances

Method

INORGANIC SUBSTANCES

1. Flame test to identify cations
2. Sodium hydroxide test to identify cations
3. Silver nitrate test to identify halide ions
4. Barium nitrate test to identify sulfate ions
5. Hydrochloric acid test to identify carbonate ions
6. Use the results to identify each unknown inorganic substance

ORGANIC SUBSTANCES

7. Bromine water test for alkenes
8. Tollens/Fehling's/Potassium dichromate(VI) for aldehydes
9. Hydrochloric acid or ethanol test for carboxylic acids
10. Use the results to identify each unknown organic substance

Flame test to identify cations

Method

- Dip the loop of an **unreactive** metal wire such as nichrome or platinum in concentrated acid, and then hold it in the blue flame of a Bunsen burner until there is no colour change
- This cleans the wire loop and avoids **contamination**
    - This is an important step as the test will only work if there is just **one type** of ion present
    - Two or more ions means the colours will mix, making identification erroneous
- Dip the loop into the solid sample and place it in the edge of the **blue** Bunsen flame
- Avoid letting the wire get so hot that it glows red otherwise this can be confused with a flame colour

Explanation for the occurrence of the flame

- In a flame test the heat causes the electron to move to a higher energy level
- The electron is unstable at this energy level so falls back down
- As it drops back down from the higher to a lower energy level, energy is emitted in the form of visible light energy with the wavelength of the observed light

Metal ion	Colour observed
Li^+	Scarlet red
Na^+	Yellow
K^+	Lilac
Rb^+	Red
Cs^+	Blue
Mg^{2+}	No flame colour
Ca^{2+}	Brick red
Sr^{2+}	Red
Ba^{2+}	Apple green

Sodium hydroxide test for cations

Testing for Ammonium ion

- 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

Overall equation:

$$NH_4Cl\ (aq) + NaOH\ (aq) \rightarrow NH_3\ (g) + H_2O\ (l) + NaCl\ (aq)$$

Ionic equation:

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

- 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

Ammonia gas test

NH_3 can be tested for as it will form a white smoke if reacted with fumes of hydrogen chloride (from concentrated hydrochloric acid)

- The white smoke formed is ammonium chloride

$$NH_3\ (g) + HCl\ (g) \rightarrow NH_4Cl\ (s)$$

Testing for carbonate ions

- 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

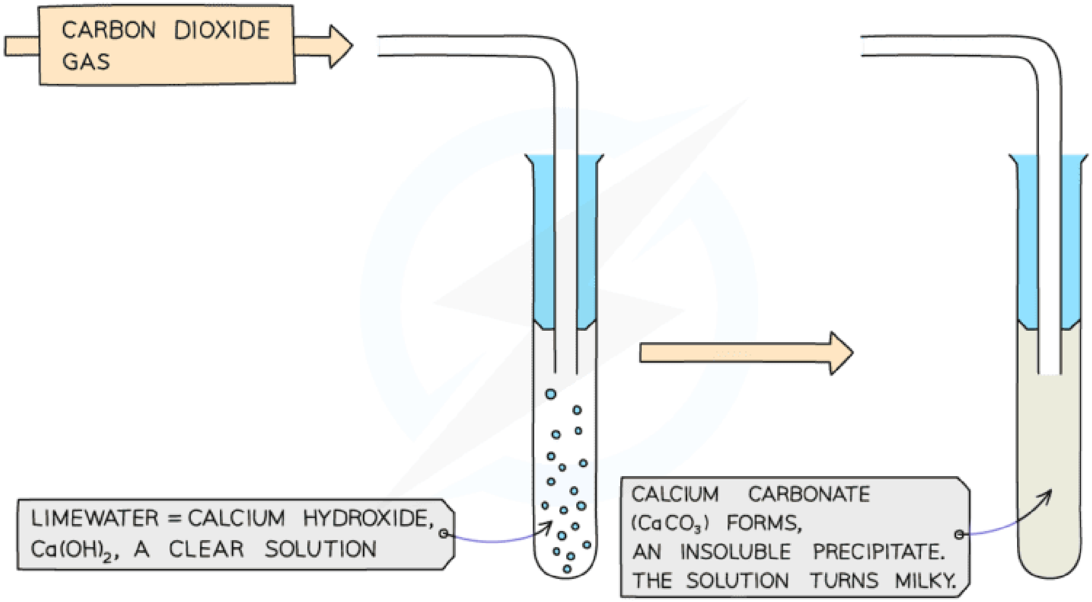
Overall equation:

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

Ionic equation:

$$2H^+\ (aq) + CO_3^{2-}\ (aq) \rightarrow CO_2\ (g) + H_2O\ (l)$$

- 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**



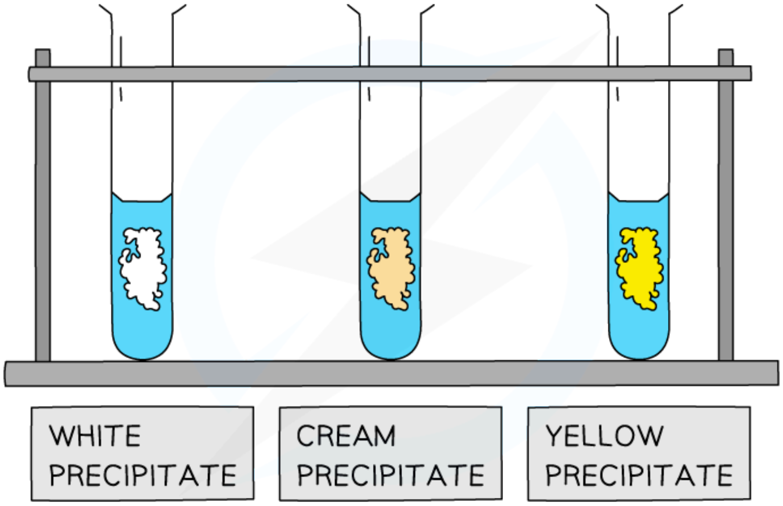
Test for sulfate ions

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:

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

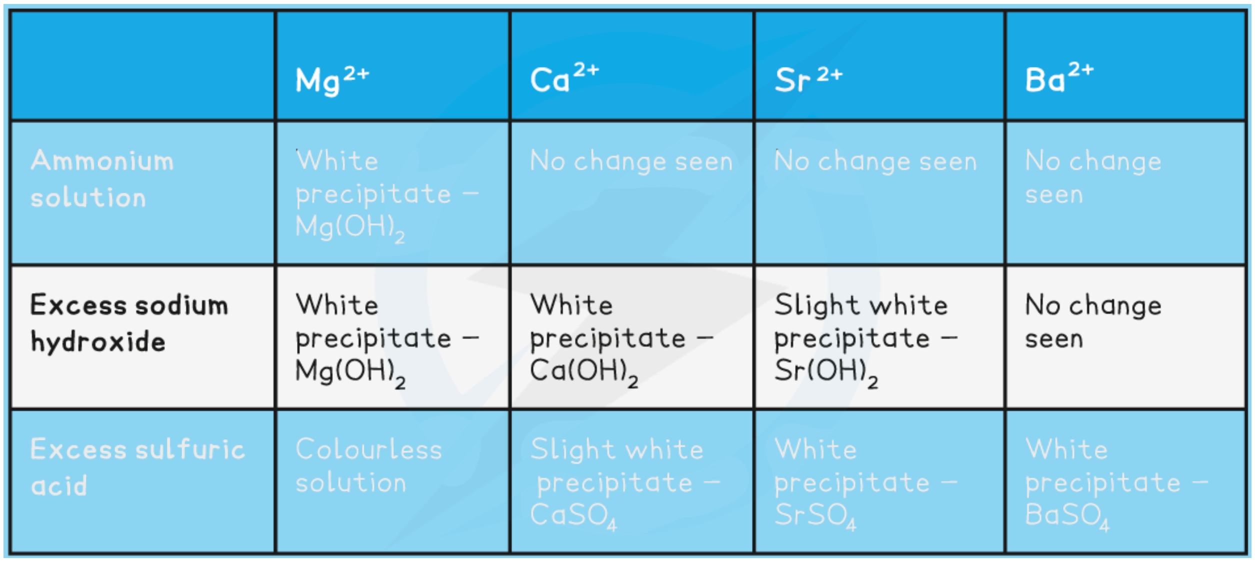
Silver nitrate test for halides



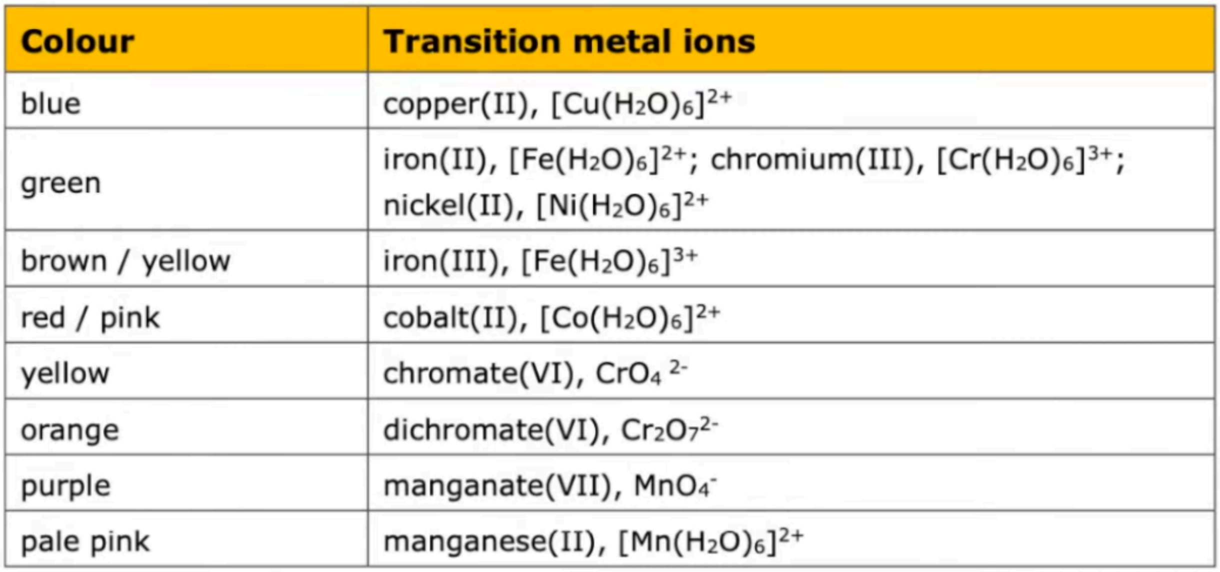
Further test with Ammonia solution

silver halide	In Dilute Ammonia	In conc. Ammonia
AgCl	soluble	soluble
AgBr	insoluble	soluble
AgI	insoluble	insoluble

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 – $BaSO_4$



Colour	**Transition metal ions**
blue	copper(II), $[Cu(H_2O)_6]^{2+}$
green	iron(II), $[Fe(H_2O)_6]^{2+}$; chromium(III), $[Cr(H_2O)_6]^{3+}$; nickel(II), $[Ni(H_2O)_6]^{2+}$
brown / yellow	iron(III), $[Fe(H_2O)_6]^{3+}$
red / pink	cobalt(II), $[Co(H_2O)_6]^{2+}$
yellow	chromate(VI), $CrO_4{}^{2-}$
orange	dichromate(VI), $Cr_2O_7{}^{2-}$
purple	manganate(VII), $MnO_4{}^{-}$
pale pink	manganese(II), $[Mn(H_2O)_6]^{2+}$

Addition of sodium hydroxide solution

When dilute, aqueous sodium hydroxide is added to an aqueous solution of a metal ion a precipitate of the insoluble hydroxide may be formed e.g. $Cr(OH)_3$.

Some precipitates will dissolve in excess sodium hydroxide to give a solution containing a complex ion e.g. $[Cr(OH)_6]^{3-}$.

When carrying out these tests students should be told to add aqueous sodium hydroxide, drop-by-drop, until there is no further change.

Metal ion solution	Observation on adding aqueous NaOH	Observation on adding excess aqueous NaOH
chromium(III), $[Cr(H_2O)_6]^{3+}$	green precipitate	precipitate dissolves to give a dark green solution
manganese(II), $[Mn(H_2O)_6]^{2+}$	pale brown precipitate, turning darker brown on exposure to air	precipitate is insoluble
iron(II), $[Fe(H_2O)_6]^{2+}$	green precipitate, turning brown on exposure to air	precipitate is insoluble
iron(III), $[Fe(H_2O)_6]^{3+}$	red-brown precipitate	precipitate is insoluble
cobalt(II), $[Co(H_2O)_6]^{2+}$	blue precipitate, turning pink on standing	precipitate is insoluble
nickel(II), $[Ni(H_2O)_6]^{2+}$	green precipitate	precipitate is insoluble
copper(II), $[Cu(H_2O)_6]^{2+}$	blue precipitate	precipitate is insoluble
zinc(II), $[Zn(H_2O)_6]^{2+}$	white precipitate	precipitate dissolves to give a colourless solution
Group 2 cations: $Mg^{2+}(aq)$, $Ca^{2+}(aq)$, $Ba^{2+}(aq)$	white precipitate	precipitate is insoluble
Group 1 cations: $Na^{+}(aq)$, $K^{+}(aq)$	no precipitate	–

Addition of ammonia solution

When dilute, aqueous ammonia is added to an aqueous solution of a transition metal ion a precipitate of the insoluble hydroxide is formed. e.g. $Cu(OH)_2$.

Some precipitates will dissolve in excess ammonia to give a solution containing a complex ion e.g. $[Cu(NH_3)_4(H_2O)_2]^{2+}$

When carrying out these tests students should be told to add aqueous ammonia, drop-by-drop, until there is no further change.

Metal ion solution	**Observation on adding aqueous NH_3**	**Observation on adding excess aqueous NH_3**
chromium(III), $[Cr(H_2O)_6]^{3+}$	green precipitate	precipitate dissolves to a give a green solution
manganese(II), $[Mn(H_2O)_6]^{2+}$	off-white precipitate, turning brown on exposure to air	precipitate is insoluble
iron(II), $[Fe(H_2O)_6]^{2+}$	green precipitate turning brown on exposure to air	precipitate is insoluble
iron(III), $[Fe(H_2O)_6]^{3+}$	red-brown precipitate	precipitate is insoluble
cobalt(II), $[Co(H_2O)_6]^{2+}$	blue precipitate	precipitate dissolves to a brown solution
nickel(II), $[Ni(H_2O)_6]^{2+}$	green precipitate	precipitate dissolves to give a blue solution
copper(II), $[Cu(H_2O)_6]^{2+}$	blue precipitate	precipitate dissolves to a deep blue solution
zinc(II), $[Zn(H_2O)_6]^{2+}$	white precipitate	precipitate dissolves to give a colourless solution

Silver nitrate solution

Aqueous silver nitrate is used to test for the presence of halide ions in solution.

Anions such as carbonate that would form precipitates with silver nitrate are removed by adding dilute nitric acid before the silver nitrate.

The identity of the halide may be confirmed by adding aqueous ammonia to the silver halide.

Anion	Precipitate		Addition of aqueous ammonia	
	Colour	Formula	Dilute	Concentrated
chloride, Cl^-	White	AgCl	soluble	—
bromide, Br^-	Cream	AgBr	insoluble	soluble
iodide, I^-	pale yellow	AgI	insoluble	insoluble

Barium chloride solution

Aqueous barium chloride forms precipitates with a number of anions but is usually used as the test for the sulfate(VI), SO_4^{2-} anion.

When dilute hydrochloric acid is added to the anion solution before the addition of aqueous barium chloride then only the sulfate(VI) anion will form a precipitate.

Anion	Precipitate		Addition of dilute hydrochloric acid
	Colour	Formula	
sulfate(VI), SO_4^{2-}	white	$BaSO_4$	precipitate is insoluble
sulfate(IV), SO_3^{2-}	white	$BaSO_3$	precipitate dissolves
carbonate, CO_3^{2-}	white	$BaCO_3$	precipitate dissolves

Concentrated sulfuric acid

When a few drops of concentrated sulfuric acid are added to a solid halide the observed products may be used to identify the halide ion.

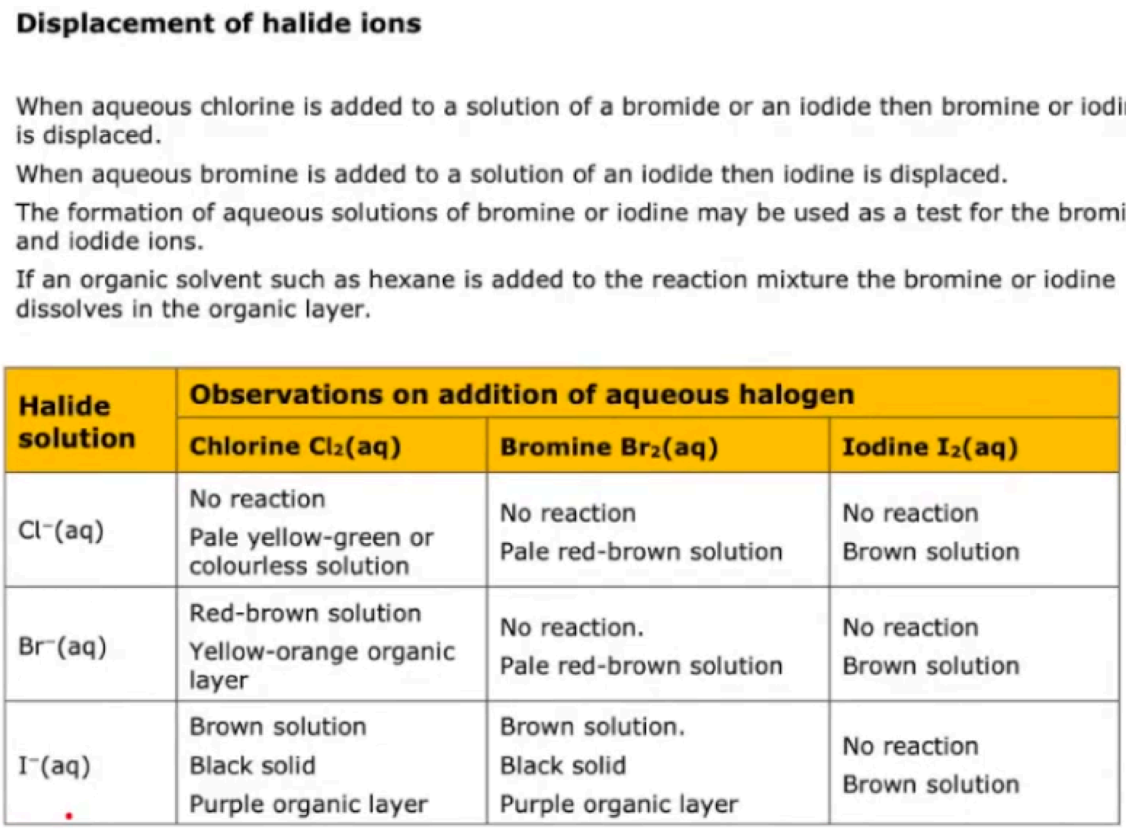
The test must be carried out on a small scale and in a fume cupboard.

The gaseous products in brackets will not be observed since they are colourless.

No attempt should ever be made to smell the products of these reactions.

Solid halide	Observations with concentrated sulfuric acid	Observed reaction products
chloride, Cl^-	steamy fumes	HCl
bromide, Br^-	steamy fumes, brown vapour	HBr, Br_2, (SO_2)
iodide, I^-	steamy fumes, purple vapour, black solid, yellow solid	HI, I_2, S, (H_2S)

Results – Inorganic Tests



Displacement of halide ions

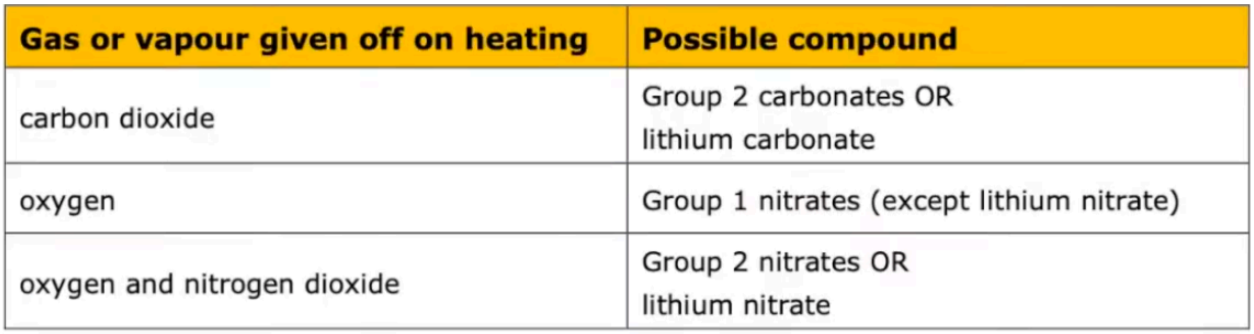
When aqueous chlorine is added to a solution of a bromide or an iodide then bromine or iodine is displaced.

When aqueous bromine is added to a solution of an iodide then iodine is displaced.

The formation of aqueous solutions of bromine or iodine may be used as a test for the bromide and iodide ions.

If an organic solvent such as hexane is added to the reaction mixture the bromine or iodine dissolves in the organic layer.

Halide solution	**Observations on addition of aqueous halogen**		
	Chlorine $Cl_2(aq)$	**Bromine $Br_2(aq)$**	**Iodine $I_2(aq)$**
$Cl^-(aq)$	No reaction Pale yellow-green or colourless solution	No reaction Pale red-brown solution	No reaction Brown solution
$Br^-(aq)$	Red-brown solution Yellow-orange organic layer	No reaction. Pale red-brown solution	No reaction Brown solution
$I^-(aq)$	Brown solution Black solid Purple organic layer	Brown solution. Black solid Purple organic layer	No reaction Brown solution



Gas or vapour given off on heating	**Possible compound**
carbon dioxide	Group 2 carbonates OR lithium carbonate
oxygen	Group 1 nitrates (except lithium nitrate)
oxygen and nitrogen dioxide	Group 2 nitrates OR lithium nitrate

Testing for Alkenes / saturation

- 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

Testing for alcohols

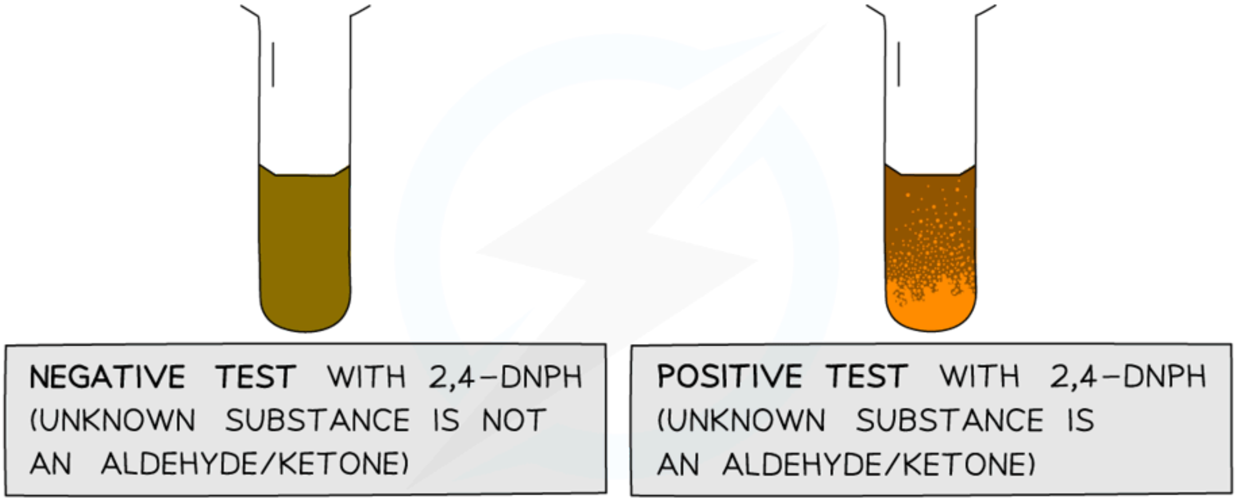
- Phosphorus(V) chloride (PCl_5) can be used as a qualitative test for the presence of an alcoholic -OH group
  - This results in a vigorous reaction at room temperature and does not need heating
  - The evolution of steamy fumes (HCl gas) is a positive result for the presence of the -OH group
- Acidified 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

($K_2Cr_2O_7$) positive result is Orange —> Green
($KMnO_4$) positive result is Purple —> Colourless

Testing for carbonyls

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

- 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



- 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

Test for aldehyde

Tollen’s reagent

when warmed with aldehyde a silver mirror is formed

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

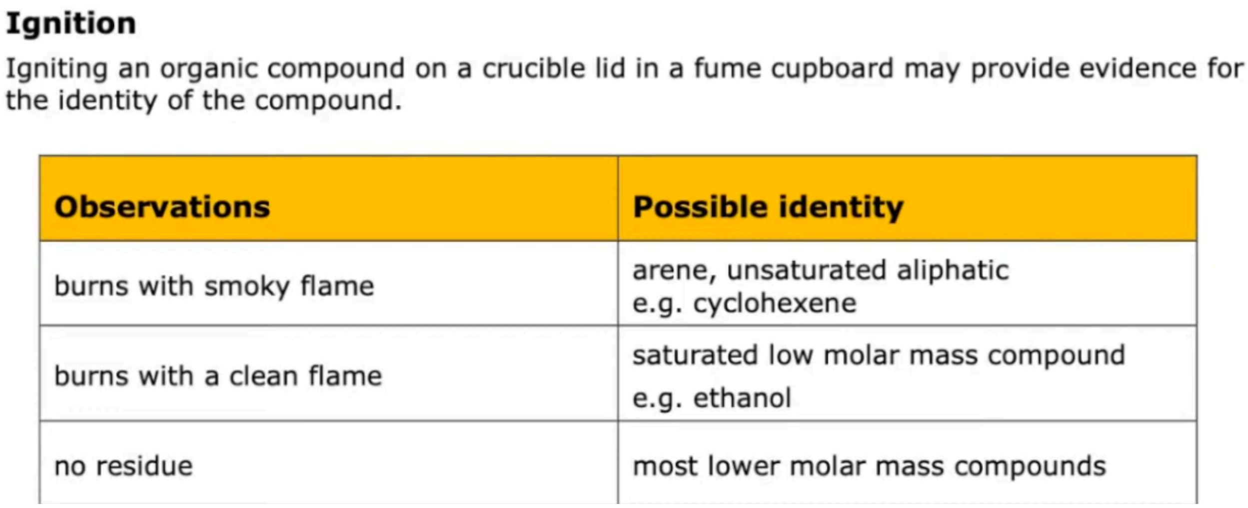
When warmed with aldehyde solution turns brick red

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

Test 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

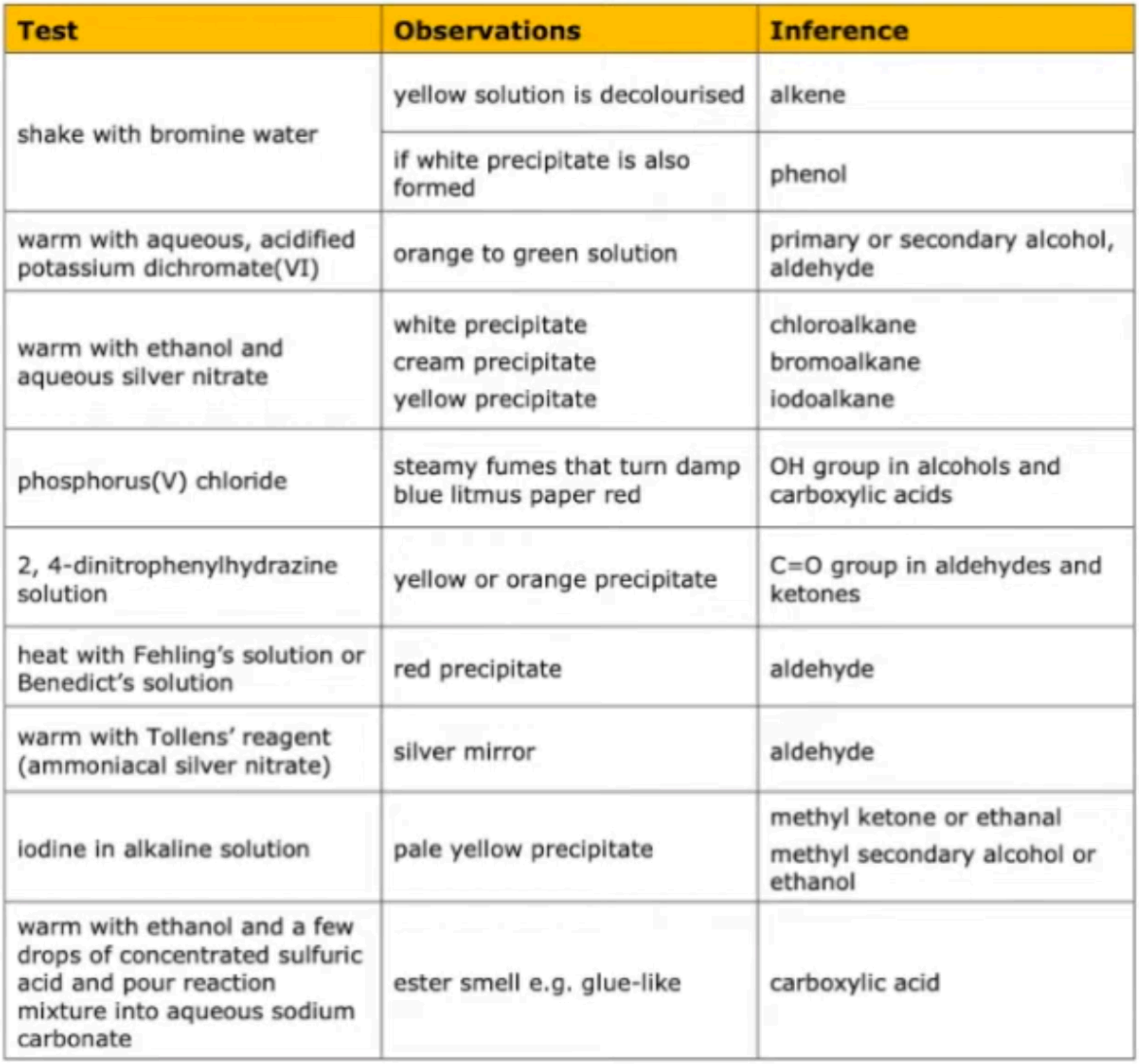
- Effervescence/bubbles of gas seen as carbon dioxide is evolved.



Ignition

Igniting an organic compound on a crucible lid in a fume cupboard may provide evidence for the identity of the compound.

Observations	Possible identity
burns with smoky flame	arene, unsaturated aliphatic e.g. cyclohexene
burns with a clean flame	saturated low molar mass compound e.g. ethanol
no residue	most lower molar mass compounds



Test	Observations	Inference
shake with bromine water	yellow solution is decolourised	alkene
	if white precipitate is also formed	phenol
warm with aqueous, acidified potassium dichromate(VI)	orange to green solution	primary or secondary alcohol, aldehyde
warm with ethanol and aqueous silver nitrate	white precipitate cream precipitate yellow precipitate	chloroalkane bromoalkane iodoalkane
phosphorus(V) chloride	steamy fumes that turn damp blue litmus paper red	OH group in alcohols and carboxylic acids
2, 4-dinitrophenylhydrazine solution	yellow or orange precipitate	C=O group in aldehydes and ketones
heat with Fehling's solution or Benedict's solution	red precipitate	aldehyde
warm with Tollens' reagent (ammoniacal silver nitrate)	silver mirror	aldehyde
iodine in alkaline solution	pale yellow precipitate	methyl ketone or ethanal methyl secondary alcohol or ethanol
warm with ethanol and a few drops of concentrated sulfuric acid and pour reaction mixture into aqueous sodium carbonate	ester smell e.g. glue-like	carboxylic acid

Core Practical 16: Preparation of aspirin

Background:

- Perform and explain the reactions of acid anhydrides.
    - An acid anhydride is a compound that has two acyl groups bonded to the same oxygen.
- To synthesise aspirin from 2-hydroxybenzoic acid.
    - The aspirin is formed in the presence of a catalyst such as sulfuric or phosphoric acid

Procedure

Apparatus:

- 10 cm^3 ethanoic anhydride
- 2 g 2-hydroxybenzoic acid
- 1cm^3 concentrated sulfuric acid
- Distilled water
- Ethanol
- Ice
- 10 cm^3 measuring cylinders
- Condenser
- Small pear-shaped flask
- Stand, clamp and boss
- 250cm^3 beakers
- Dropping pipette
- Bunsen burner, tripod, gauze and safety mat
- Mass balance (2 d.p.)
- Buchner funnel, flask and suction pump
- Melting point apparatus

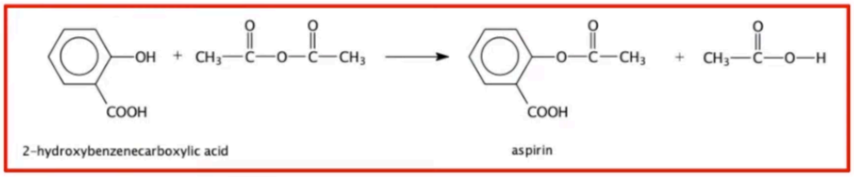
MEthod

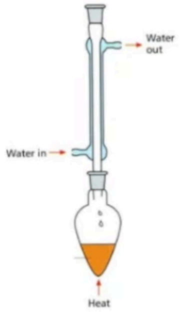
- Weigh 2 g of 2-hydroxybenzoic acid and put it in a pear-shaped flask. Clamp the flask and suspend it in a beaker of water
- Add 5 cm^3 ethanoic anhydride to the flask as well as 5 drops of concentration sulfuric acid and fix a condenser on to the flask
- In a well-ventilated room, use a Bunsen burner to carefully warm the mixture in a water bath whilst gently swirling to dissolve the solid
- After 10 minutes, remove the flask from the hot water bath. Add 10 cm^3 crushed ice and some distilled water to break down the unreacted ethanoic anhydride
- Stand the flask in a beaker of water until precipitation begins to appear. Filter the product using a Buchner funnel and wash the crystals with the minimum amount of iced water

Recrystallisation of Aspirin

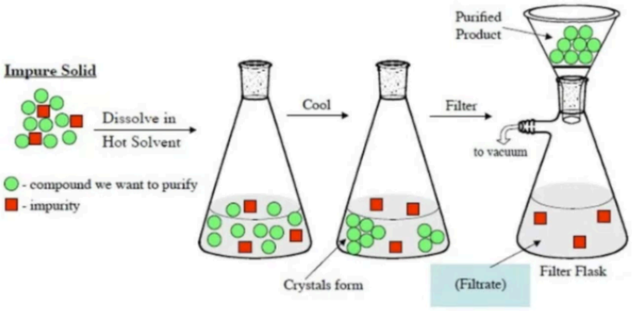
1. Set up a water bath ready with boiling water. Put the crystals in a boiling tube and add some water then put the tube in the water bath and dissolve the crystals in the **minimum volume** of hot water.
2. If there are any insoluble impurities, carry out a **fast filtration** with pre-heated glassware. (Hot filtration)

3. **Cool** the solution, slowly at first (and then in an ice bath if necessary) until crystals reappear.
4. Filter off the crystals under suction and wash with a small amount of **cold water**.
5. Part dry the crystals by pressing between filter papers and then place them in a warm oven to dry thoroughly.
6. When dry, measure the melting point and yield of the aspirin.

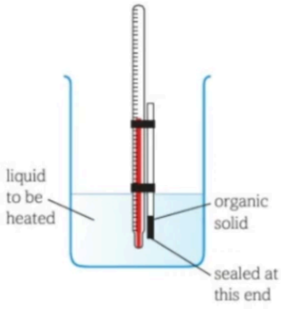




Heating under reflux



Recrystallisation



Melting point determination

PPQ

June 2023

(b) State why, in the silver nitrate test on **P**, the nitric acid was not needed in this case. Justify your answer by considering the role of nitric acid in the silver nitrate test.

(2)

Acid is added to remove ions such as carbonate ions that would form a precipitate with silver nitrate, but chromium (III) carbonate is not present since it would not dissolve to form green solution with NaOH.

X = Acyl Chloride

(ii) A student prepared an ester using **X** and a suitable compound.

Explain why the student added aqueous sodium hydrogencarbonate to the reaction mixture to allow the presence of an ester to be detected.

(2)

To react with traces of acid to allow the fruity smell of ester to be detected.

(a) State why the sulfuric acid and propanone concentrations are both much larger than the iodine concentration.

So that the concentration of acid and propanone remain approximately constant and the rate is affected only by concentration of iodine.

(b) State why sodium hydrogencarbonate is used in Step **3**.

To neutralize the acid to quench the reaction.

(c) Name the indicator that would be used for the titration in Step **4**, stating the colour **change** that would be seen at the end-point of the reaction.

Starch solution, turns from dark blue black to colourless

(ii) State why the volume of thiosulfate may be used for plotting the graph rather than the concentration of iodine.

(1)

Volume of thiosulphate is directly proportional to the concentration of iodine

(a) An ice bath is a mixture of ice and water in a beaker.

Suggest an advantage of using an ice bath in Steps **1** and **3** rather than a beaker containing only ice cubes. Justify your answer.

(1)

Larger surface area so more effective cooling

Step **7** Recrystallise the methyl 3-nitrobenzoate using ethanol as the solvent.

(d) Describe the stages in the recrystallisation of methyl 3-nitrobenzoate in Step **7**, stating which stages are required to remove the insoluble and soluble impurities. Only outline details of the method are required.

(4)

A description that makes reference to the following points:		
• dissolve (solid) in the **minimum** (volume) of **hot** ethanol	**(1)**	Allow solvent for ethanol Ignore warm
• (hot) (gravity) filtration to remove insoluble impurities	**(1)**	
• cool (solution) to precipitate the solid / methyl 3-nitrobenzoate	**(1)**	Allow crystallise
• (suction) filtration to remove the soluble impurities	**(1)**	Ignore any washing comments

(e) The crystals must be dried before the melting temperature can be determined. Methyl 3-nitrobenzoate cannot be dried by the addition of a solid drying agent such as anhydrous calcium chloride.

(i) Suggest why the addition of a solid drying agent is not suitable to dry methyl 3-nitrobenzoate.

(1)

An answer that makes reference to the following point:

- difficult to separate the solid drying agent from the product

(g) The melting temperature range of methyl 3-nitrobenzoate is given in a data book as 78–80 °C.

Suggest a melting temperature **range** for a sample of the methyl 3-nitrobenzoate **before** recrystallisation. Justify your answer.

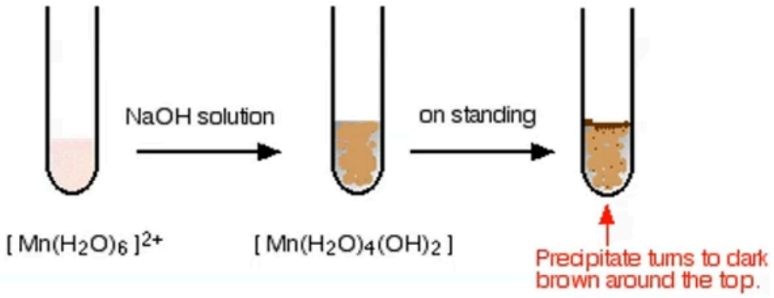
(2)

An answer that makes reference to the following points:	
• any melting temperature range of 4 or more degrees **and** higher figure 70-79°C and lower figure no lower than 65°C	**(1)**
• impurities make the melting temperature range lower **and** wider	**(1)**

Jan 2024

	Test	Observation	Inference	
(iv)	Dilute aqueous sodium hydroxide was added drop-by-drop to 4 cm^3 of **D** until there was no further change	An off-white precipitate formed which did not dissolve in excess but darkened when left to stand	The cation in **D** is *Mn^{2+}*	(1)

Mn^{2+} + NaOH → white precipitate insoluble in excess → darkens when left to stand



(c) A sample of **Y** gave a positive result when warmed with an alkaline solution of iodine.

(i) Give **two** observations of a positive result from this test.

Yellow precipitate

Antiseptic smell

(b) The student was told that sulfur dioxide is toxic and that cylinders of the gas are not recommended for use in schools.
The student was advised to prepare it within the reaction mixture from sodium sulfate(IV) and hydrochloric acid.

(i) Suggest why sulfur dioxide is advised to be prepared in this way. (1)

Gas is likely to escape from the cylinder, while in the reaction it will be used up as it is made.

(ii) Information about the experiment is shown.

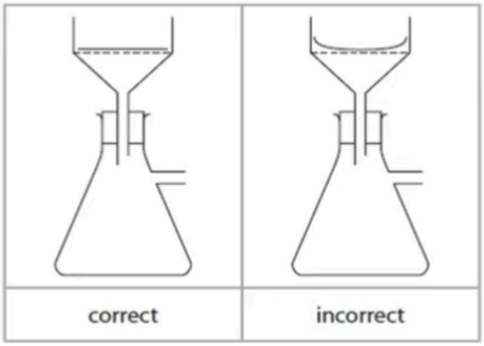
- $25.0\,cm^3$ of $0.0200\,mol\,dm^{-3}$ ammonium vanadate(V) was reduced by tin
- $20.00\,cm^3$ of $0.0100\,mol\,dm^{-3}$ potassium manganate(VII) was required to oxidise the vanadium back to its original oxidation state
- the manganate(VII) half-equation is
  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Deduce the vanadium ion oxidation state after the reduction by tin.
You must show your working.

(4)

No. of moles of Vanadate (V) = c x v = 0.02 x (25/1000) = 0.0005 mole
No. of moles of manganate = c x v = 0.01 x (20/1000) = 0.0002 mole
No. of moles of electrons gained = 0.0002 x 5 = 0.001 mole
No. of moles of electrons lost by vanadate = 0.001/0.0005 = 2
Vanadium is reduced by 2 electrons.
Vanadate (V) was reduced to Vanadium (III)

(i) The filter paper used should fit in the funnel and lie flat on the base of the Büchner funnel rather than curl up the sides of the funnel.



Explain why it is important to place the filter paper in this way.

(2)

Filter paper should be flat to close the holes . The curled up sides may allow solid to pass through and be lost.

Step **4** Collect the impure sample of phenylethanamide by filtration under reduced pressure.

(ii) Explain why the solid collected in Step **4** is washed with **a small volume** of **cold** water.

(2)

To wash away soluble impurities without dissolving the phenylethanamide solid.