Curriculum for Excellence

Advanced Higher Chemistry

Researching Chemistry Notes

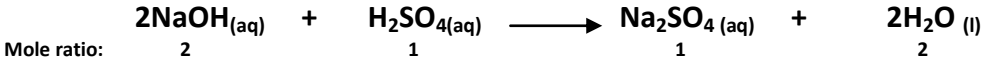
This unit links closely to some of the topics studied in CfE Higher Chemistry. You will study a range of analytical methods including reviewing acid-base and redox titrations and chromatography as well as several new techniques.

As you will use some of these procedures during your individual investigation these notes will be the basis for your initial research into that section of your background chemistry.

These notes have been adapted from the resources developed by the Cross Authority Writing Group for Advanced Higher Sciences

Stoichiometry

A balanced chemical equation is a **stoichiometric** equation. It can be used to calculate the number of moles of the reactants and products in a reaction. Any reaction in which the substances react completely according to the mole ratios given by a balanced (stoichiometric) equation is called a **quantitative reaction.**

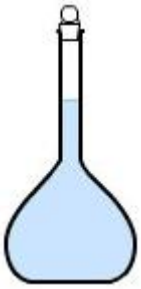


When a quantitative reaction takes place one unknown value can be determined. Two such chemical methods of analysis are **volumetric** (involving accurately measured volumes of solutions) and **gravimetric** (involving accurate weighing of materials).

Volumetric analysis

Any volumetric analysis uses a solution of accurately known concentration in a quantitative reaction to determine the concentration of the other reactant. This procedure is a called a **titration** and usually involves the use of a **standard solution**.

Standard solutions and Primary standards



A solution of accurately known concentration is referred to as a **standard solution**. e.g. A solution of HCl of 1mol l^{-1}.

A **primary standard** is a substance from which a standard solution can be prepared directly.
A primary standard has 4 characteristics:

- available in a high state of purity (>99.9%)
- stable when solid and when in solution so it can be stored indefinitely without change in its composition
- soluble in water
- have a reasonably high formula mass to reduce percentage errors when weighing it out

These are to ensure that when it is weighed out it is an uncontaminated, accurate amount of the material.
Some substances like sodium hydroxide, NaOH, are unable to be used as a primary standard. It absorbs both water and carbon dioxide from the air which would affect its concentration.

Examples of primary standards include sodium carbonate, Na_2CO_3; Oxalic acid, $H_2C_2O_4.2H_2O$; EDTA and Potassium Iodate, KIO_3, potassium hydrogen phthalate, $KH(C_8H_4O_4)$, silver nitrate, $AgNO_3$, potassium dichromate, $K_2Cr_2O_7$.

Preparation of a Standard Solution

1. A calculation is carried out to estimate the approximate mass of the primary standard required to make up a known volume of standard solution.
2. The primary standard is accurately weighed out on a tared electronic balance using a weighing bottle or boat.
3. The solid is transferred to the volumetric flask and the weighing bottle rinsed into the volumetric flask.
4. A volume of distilled water is added to the flask and the mixture swirled until all of the solute has dissolved.
5. Distilled or deionised water is added to the mark (an engraved line on a volumetric flask).
6. The volumetric flask is inverted several times to thoroughly mix the contents.
7. The flask is labelled and set to one side.

(Watch the video and animations) www.youtube.com/watch?v=cckAwavEKA0

http://www.rsc.org/learn-chemistry/resource/res00001457/acid-base-solutions-simulation

Preparation of standard solutions using accurate dilution technique

Often it is necessary to prepare a very dilute solution extremely accurately. This involves the use of standard volumetric glassware to dilute a concentrated (stock) solution in order to prepare a more dilute solution.

For example if you were asked to make a 0.00001 mol l^{-1} solution of NaOH, this would involve weighing out 0.0004g of NaOH accurately. While this may be possible in industry, with the use of very accurate balances, most schools would not have access to such equipment.
However, if a more concentrated solution is made up first, with a much larger mass of sodium hydroxide, this can then be accurately diluted to the correct concentration required.

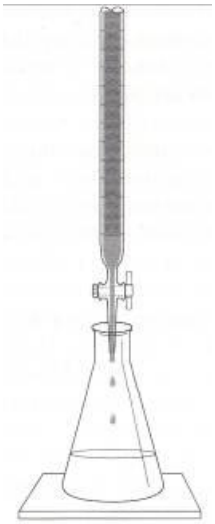
Method

Calculate the mass required to make a litre of a solution that is either 1000 times (or a suitable multiple) more concentrated than the solution required, here this would be 0.4g NaOH.
Weigh this accurately on a balance and make up as stated above for a standard solution. This will now be 0.01 mol l^{-1} NaOH.
Using a 1cm^3 pipette and filler, remove 1cm^3 of this solution and place it in a clean 1 litre standard flask. Use deionised water to make this up to the mark and invert to mix. This solution is now the required concentration; 0.00001 mol l^{-1} NaOH.

Titrations

There are three main types of titration:

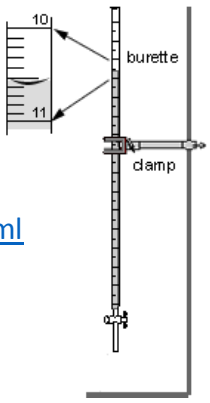
- acid/base (including forward and back titrations)
- complexometric and
- redox (covered in the Higher course)



During a titration a permanent colour change is used to determine the **end point** of the reaction. This is the point at which the completion of the reaction is **observed**. The point at which the reaction is just complete, the **equivalence point**, cannot always be observed. Ideally these points would both be the same.

Titrations should always be repeated until **concordant results** are obtained. These are results within 0.1 or 0.2 cm^3 of each other that are used to calculate an average. Generally a rough titre would not be used for an average as it would not be accurate enough.

Note: Always use a white tile to help identify the colour change at the endpoint.



Look at the following animations:

http://www.labskills.co.uk/free-resources/Titration_SetUp_Free.html
http://www.labskills.co.uk/free-resources/Titration_End_Points_free.html
and this video:
http://www.youtube.com/watch?v=BoxTJGs_XYI

Controls

A control validates a technique and may consist of carrying out a determination on a solution of **known concentration**.
Example:
In an investigation involving Vitamin C the control would involve carrying out the determination of vitamin C (ascorbic acid) using a pure sample of the compound. If the mass of vitamin C (ascorbic acid) you determine matches the mass you started with then this establishes the validity of the procedure and the results. However, if the experimental result deviates significantly from the true value then this could arise from bad technique or not using standardised solutions.

The use of a control is often essential to support the results in an Advanced Higher Investigation. Make sure that you use one, where possible.

Acid- Base titrations and Indicators

In acid base titrations the indicator used will depend on the strength of the acid and base and so the pH of the final salt solution.

indicator	pH range
litmus	5.0 - 8.0
methyl orange	3.1 - 4.4
phenolphthalein	8.3 - 10.0

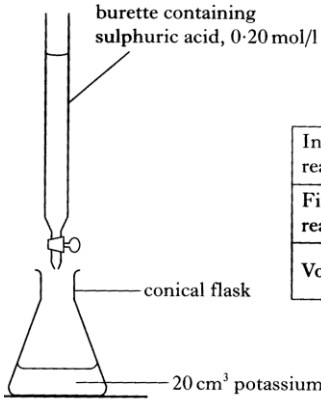
Worked example

1. Calculate the volume of sulphuric acid, concentration 2mol/l, required to neutralise 20cm^3 of 1mol/l sodium hydroxide.

Balanced equation: H_2SO_4 + 2NaOH ⟶ Na_2SO_4 + $2H_20$
Mole ratio: 1 2
n=c v 1 x 0.02
⟵ = 0.02mol
0.01mol
0.02mol of NaOH reacts with 0.01 mol H_2SO_4

Volume of NaOH: v= n/c =0.01/2 = 0.005l or 5cm^3

2. A pupil carried out a titration using the chemicals and apparatus shown below.



	Rough titre	1st titre	2nd titre
Initial burette reading/cm^3	0·5	21·7	0·3
Final burette reading/cm^3	21·7	42·4	20·8
Volume used/cm^3	21·2	20·7	20·5

(a) How would the pupil know when to stop adding acid from the burette?

(b) Calculate the concentration of the potassium hydroxide. [0.412mol l^{-1}]

3. How many moles of $Ca(OH)_2$ will be neutralised by $20cm^3$ of 0.4mol/l H_3PO_4? [0.012]

4. $50cm^3$ of potassium hydroxide requires $60cm^3$ of 1mol/l sulphuric acid for complete neutralisation. How many moles of potassium hydroxide are being neutralised? [0.12]

5. What volume of 0.25mol/l calcium nitrate is required to make by dilution with water $500cm^3$ of a solution with a nitrate ion concentration of 0.1mol/l? [$100cm^3$]

6. What volume of 0.5mol/l sodium carbonate is required to make by dilution with water one litre of a solution with a Na^+ concentration of 0.2mol/l? [$200cm^3$]

Back titration

Substances that are insoluble in water cannot be determined by direct or forward titration. An indirect method like a **back titration** must be used. This involves reacting a known amount of the insoluble substance with an **excess** of a reactant solution of **known concentration**.
As an excess of reactant solution is used, the amount remaining (the excess) can be determined by titrating it against a standard solution; the "back" titration. The difference between the initial and excess amounts (moles) of reactant solution allows the amount of the insoluble substance to be calculated.

Worked example –

1. An **impure** sample of 10g of Mg was reacted with 300cm^3 of 2mol/l HCl(aq).
This solution was added to a 1 litre standard flask, which was made up to the mark with water. A 100cm^3 sample of this solution required 33cm^3 of 1mol/l NaOH to neutralise it.
(This question has been simplified into parts to make it easier for you to follow)

(a) Show that 0.27moles of acid reacted with the Mg.
(b) Calculate the mass of Mg in the sample
(c) Calculate the % purity of the Mg.

(a) Back Titration HCl + NaOH ⟶ NaCl + H_2O
Balanced equation: 1 1

n = cxv 0.033 ⟵ 1 x 0.033
Moles HCl in 100cm^3 0.033 mol

Moles HCl in flask after reaction 0.033 x 10 = 0.33 mol

Initial moles HCl
n= cxv 2 x 0.3 = 0.6 mol

Moles HCl Reacted 0.6 - 0.33 = **0.27 mol**

(b) Balanced equation Mq + 2HCl ⟶ $MgCl_2$ + H_2
Mole ratio: 1 2
Reacting moles 0.135 ⟵ 0.27

Mass of Mg
Mass = nxgfm 0.135 x 24.3 = **3.281g**

(c) % Purity of Mg = $\frac{\text{Mass of Mg}}{\text{Mass of sample}}$ x 100 = $\frac{3.281 \times 100}{10}$ = **32.81%**

Summary of Back Titration steps:

1. Work out the moles of reactant used in total (here, the acid).
2. Calculate the moles of acid unreacted. Usually this will involve calculating the moles of an alkali like NaOH, so=moles of unreacted acid.
3. You may have to multiply this if only a small sample was titrated e.g. 25ml from 250ml: you would have to x10.
4. Calculate the moles of acid reacting=moles total-moles unreacted.
5. Use no.4 to calculate the moles of what you're trying to find out.

Questions

2. An impure sample of 10g $CaCO_3$ was added to 100cm^3 of 2mol/l HCl (aq). This solution was added to a 250cm^3 flask and made up to the mark with water. A 25cm^3 sample of this solution was titrated with 0.5mol/l NaOH where it was found that 10cm^3 was needed to react.

(a) Calculate the moles of acid reacting with the $CaCO_3$ [0.15moles]

(b) Calculate the mass of $CaCO_3$ in the sample [7.5g]

(c) Calculate the % purity of the sample [75%]

Marks

3 Sodium hypochlorite, NaClO, is the active ingredient in household bleach. The concentration of the hypochlorite ion, ClO^-, can be determined in two stages.

In stage 1, an acidified iodide solution is added to a solution of the bleach and iodine is formed.

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

In stage 2, the iodine formed is titrated with sodium thiosulphate solution.

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

$10{\cdot}0\,cm^3$ of a household bleach was diluted to $250\,cm^3$ in a standard flask.

$25{\cdot}0\,cm^3$ of this solution was added to excess acidified potassium iodide solution.

The solution was then titrated with $0{\cdot}10\ mol\,l^{-1}$ sodium thiosulphate using an appropriate indicator.

The volume of thiosulphate solution required to reach the end point of the titration was $20{\cdot}5\,cm^3$.

(*a*) Calculate the number of moles of **iodine** which reacted in the titration. **1**

(*b*) Calculate the concentration, in $mol\,l^{-1}$, of the ClO^- in the original household bleach. **2**

(3)

[(a) 0.001025 moles (b) 1.025 $moll^{-1}$]

Redox titrations (covered at Higher)

These are based on oxidation and reduction reactions. They involve the transfer of electrons from one species to another so it is vital that the ion-electron equations contain equal numbers of electrons. The overall equation is found by adding together the two ion – electron equations so that the electrons cancel out.
A redox reaction always involves an **oxidising agent** (an electron donor which is itself reduced) and a **reducing agent** (an electron acceptor which will be oxidised).

Common oxidising agents are:

- **Acidified Potassium permanganate,** $KMnO_4/H^+$, which is self-indicating. The MnO_4^- ion is purple coloured however, it's reduced form, Mn^{2+} is colourless. At the end point a permanent pale pink colour is observed.
- **Iodine solution**, $I_{2(aq)}$, this requires the use of starch indicator, added close to the end point to produce a clear colour change, (blue/black to almost colourless).
- **Acidified Potassium Dichromate**, $K_2Cr_2O_7^{2-}/H^+$, is also self-indicating; the $Cr_2O_7^{2-}$ ion is orange and the Cr^{3+} ion is green.

Watch the video: http://www.youtube.com/watch?v=GkroZP3oNEw

Worked example

1. In a redox titration, 20ml of $Fe(II)SO_4$ was completely oxidised by 12.5ml of $0.02moll^{-1}$ acidified dichromate solution.

(a) Write a balanced redox equation for the reaction.
(b) Calculate the concentration of the $Fe(II)SO_4$

(a) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ **x6**
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$
Multiply the Fe^{2+} equation by **6** to provide equal numbers of electrons for transfer and add the two ion – electron equations together.

$6\,Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(b) moles $Cr_2O_7^{2-}$ = c x v = 0.02 x 0.0125 = 2.5×10^{-4}

moles Fe^{2+} = moles $Cr_2O_7^{2-}$ **x6** = 2.5×10^{-4} x 6 = 1.5×10^{-3}

concentration of Fe^{2+} = n/v = $\frac{1.5 \times 10^{-3}}{0.002}$ = 0.075 mol l^{-1}

2. The copper (I) ions in a sample of copper (I) sulphate were oxidised using potassium dichromate solution. Write the balanced redox equation for the reaction.

3. The iron (II) ions in a sample of iron(II) sulphate were oxidised using acidified permanganate solution. Write the balanced redox equation for the reaction.

4. Brass is an alloy consisting mainly of copper and zinc. To find the % of copper in a sample of brass, 2.63 g of brass were dissolved in concentrated nitric acid and the solution diluted to 250 cm^3 in a standard flask. Excess potassium iodide was added to 25 cm^3 of this solution, iodine being produced according to the equation

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

The iodine formed was titrated with 0.10 mol l^{-1} sodium thiosulphate solution, $Na_2S_2O_3(aq)$, the volume required for complete reaction being 24.8 cm^3.

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

(a) Which species in the first equation is oxidised?

(b) How could the end point for the titration be made more obvious?

(c) How many moles of sodium thiosulphate were required in the titration?

(d) Calculate the % by mass of copper in the sample of brass. [60%]

5. Excess iron (III) nitrate was added to 40.0 cm^3 of 0.10 mol l^{-1} potassium iodide solution and the iodine formed was titrated with sodium thiosulphate solution. The volume required for complete reaction was 15.0 cm^3. The reaction can be represented by the equation

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

(a) Write the redox equation for the reaction between iron (III) ions and iodide ions.

(b) Calculate the number of moles of iodine produced from the potassium iodide.

(c) Calculate the concentration of the sodium thiosulphate solution. [0.27]

(d) State how you could detect the end point of the titration?

6. Commercial bleaches contain the hypochlorite ion, OCl^- as the bleaching agent. The concentration of this ion can be found by adding a sample of the bleach to excess potassium iodide and ethanoic acid. The iodine released is determined by titrating against standard sodium thiosulphate solution using starch as indicator. The relevant equations are:

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

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

In an investigation, 10.0 cm^3 of a commercial bleach solution was diluted to 250 cm^3 in a standard flask. 25 cm^3 samples were pipetted into conical flasks containing excess potassium iodide and ethanoic acid. Each sample was titrated against 0.1 mol l^{-1} sodium thiosulphate solution using starch as an indicator.
The results of the titration are given below:

Burette reading	**Titre 1 / cm^3**	**Titre 2 / cm^3**	**Titre 3 / cm^3**
Initial	0.00	14.00	27.00
Final	12.90	26.55	39.45

(a) What colour change is observed at the end point?

(b) What is the function of the ethanoic acid?

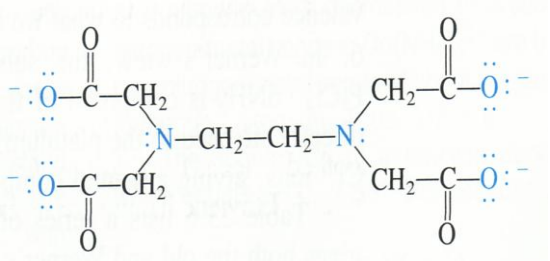
(c) What volume of the sodium thiosulphate solution should be used as the titration value in the calculation?

(d) Calculate the number of moles of hypochlorite ions in 25 cm^3 of the diluted bleach.

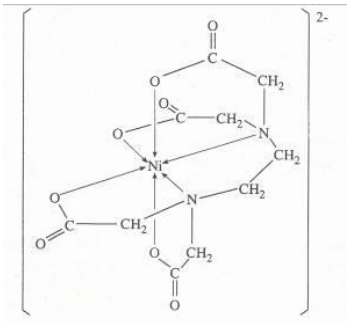
(e) Calculate the concentration in mol l^{-1} of hypochlorite ions in the commercial bleach. [0.625]

Complexometric titrations

These titrations are based on the formation of a complex between a metal ion and a **chelating agent** such as EDTA, ethylenediaminetetraacetic acid.
A chelating agent is a substance whose molecules can form several bonds to a single metal ion. EDTA is a very important **complexometric** reagent that is used to determine the concentration of metal ions in solution.



The $EDTA^{4-}$ ion can form a stable complex with metal ions by the donation of electrons to the central metal ion.



An EDTA complex with nickel.

The end point of titrations involving EDTA is indicated by the colour change in an indicator like **murexide** or **eriochrome black**. These are used because they have one colour when the metal ion is attached to the EDTA (a complex ion) and another when the metal ions are unattached. This happens because the indicators bind less strongly to the metal ions than the EDTA.
At the start of the titration the indicator is bound to the metal ions. As EDTA is added it binds more strongly to the metal ions and replaces the indicator. At the end point the indicator is no longer attached to any of the metal ions, hence the colour change.
Generally EDTA reacts on a **1:1 mole ratio** with metal ions:

$$\text{EDTA} + Co^{2+} \longrightarrow \text{complex ion}$$

Worked example

1. 3.43 g of hydrated nickel(II) sulphate, $NiSO_4.6H_2O$, was dissolved in water and made up to 100cm^3 in a standard flask.
   20.0cm^3 of this solution was titrated against a 0.101 mol l^{-1} solution of EDTA using murexide as an indicator. The results are shown below.

	Rough titre	1st titre	2nd titre	3rd titre
Initial burette reading (cm^3)	0.0	0.0	24.6	0.0
Final burette reading (cm^3)	24.8	24.6	48.8	24.3
Volume of EDTA added (cm^3)	24.8	24.6	24.2	24.3

(a) Calculate the mass of Nickel in the hydrated salt.
(b) Calculate the percentage of nickel present in the hydrated salt.

(a) Balanced equation: EDTA + Ni^{2+} $\longrightarrow$ complex ion
Mole ratio: 1 : 1
moles of EDTA = n = v x c
= 24.25/1000 x 0.101 = 2.449 x 10^{-3} moles EDTA
moles of Ni^{2+} *in 20 cm^3* = 2.45 x 10^{-3}
moles of Ni^{2+} *in 100cm^3* = 0.0122

mass of Ni^{2+} = nxgfm = 0.0122 x 58.7 g = 0.719 g

(b) % yield = $\frac{\text{Mass of nickel}}{\text{Mass of salt}}$ x 100 = 0.719 / 3.43 x 100
= 20.96 % (21%)

Questions

2. 25cm^3 of 0.1mol/l EDTA reacted with 100cm^3 of a calcium ion solution. Calculate the concentration of calcium ions. [2.5 x 10^{-2} mol l^{-1}]

3. Magnesium ions can be determined by titration with EDTA which reacts with Mg ions in a 1mole: 1mole ratio.

0.2g of an impure Mg sample was dissolved in acid. The resulting solution was made up to 2 litres with water. A 25cm^3 sample of this solution was titrated with 0.01mol/l EDTA. The volume of EDTA required was 10cm^3.

(a) Calculate the moles of Mg ions in the original 2 litre sample. 2
(b) Calculate the mass of Mg in the sample and hence calculate the % purity. 2

4. 2.79g of an unknown nickel (II) salt was weighed out and made up to 100cm^3 of solution in a standard flask. 25cm^3 portions were then titrated with 0.10 mol l^{-1} EDTA solution with murexide as an indicator. The average titre achieved was 29.35cm^3.

(a) Calculate the total mass of nickel in the sample. [0.689g]
(b) Calculate the percentage by mass of nickel in the original sample. [24.7%]

Gravimetric Analysis

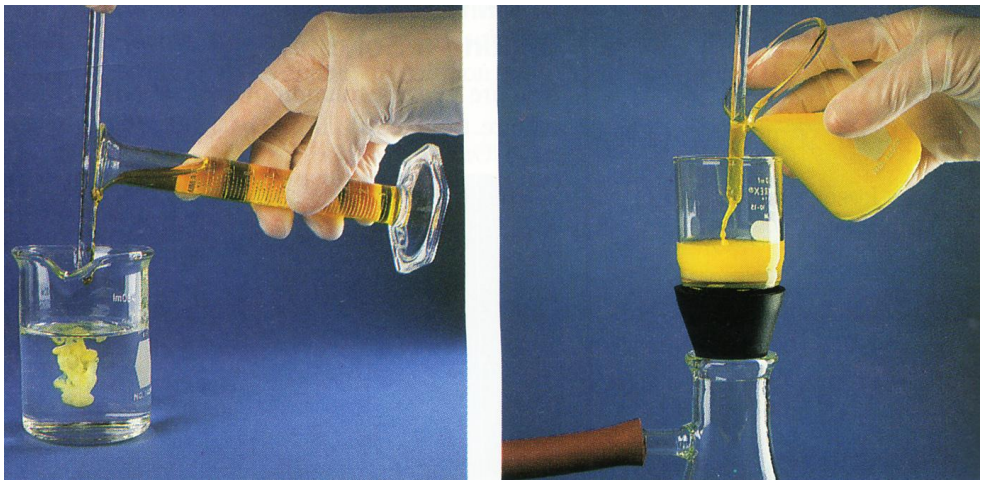
Gravimetric analysis is a quantitative analysis **technique** in which the substance being determined is converted to a solid which can be isolated completely, then purified and accurately weighed. This is done by forming **precipitates** which must be removed by filtration, dried and weighed. As an accurate mass is required the solid the drying and weighing processes are repeated until a **constant mass** is achieved.

A **desiccator** is often used to provide a dry atmosphere in which to cool down hot solids.

Gravimetric analysis is more time consuming than methods like titration because it takes time to allow filter papers and precipitates to dry prior to weighing. However, if properly carried out, gravimetric analysis gives **more accurate results** than volumetric analysis because it is possible to weigh substances more accurately than to measure out volumes. Electronic balances have a lower % error than volumetric glassware such as pipettes, burettes and graduated flasks.

Sometimes the analysis is carried out to find the quantity of water present in a compound for example, "**water of crystallisation**" in copper sulphate, $CuSO_4.5H_2O$. Controlled heating is carried out and the quantity of water and so the mole ratio of water to salt to be calculated from the mass lost. When this type of salt is dried we call it an **anhydrous** salt (without water).

Use your data booklet to check for the solubility of substances. This will allow you to identify insoluble products (precipitates) and add state symbols to equations written. Practise the **accurate use of an electronic balance**.



Worked example

1. An anhydrous salt is known to be a mixture of magnesium chloride and magnesium nitrate.
4.50g of the salt are dissolved in water and the solution made up to 500 cm^3 in a standard flask. A slight excess of silver (I) nitrate solution is then added to 100 cm^3 of this solution and the resulting precipitate recovered by filtration. The precipitate is washed, dried and its mass found to be 2.01g.

(a) Write a balanced chemical equation for the reaction between silver (I) nitrate and the reacting magnesium compound.
(b) Calculate the % by mass of magnesium chloride in the mixture.
(c) How would you check that an excess of silver (I) nitrate had been added?

(a) $2AgNO_3(aq) + MgCl_2(aq) \longrightarrow 2AgCl$ **(s)** $+ Mg(NO_3)_2(aq)$

(b) Mole ratio: 1 : 2
Moles AgCl n= m/gfm = 2.01/143.4 = 0.014mol
Moles $MgCl_2$ 0.007mol ←
Mass *in 100cm³* mol x gfm = 0.007 x 95.3 = 0.667g
Mass *in 500cm³* 0.667 x 5 = 3.335g

(c) By adding the silver nitrate until no more precipitate is formed.

2. 2.68g of hydrated barium chloride was heated until constant mass. The remaining anhydrous salt weighed 2.26g.
Determine the chemical formula of the salt.

Moles of $BaCl_2$ (anhydrous/dry) = mass/gfm = 2.26/208.3 = 0.0108 mol

Moles of water = $\frac{\text{mass of hydrated salt-mass of dry salt}}{\text{gfm of water}} = \frac{2.68 - 2.26}{18} = 0.0233$ mol

Mole ratio = 0.0108 : 0.0233
Simplest ratio = $\frac{0.0108}{0.0108} : \frac{0.0233}{0.0108} = 1 : 2$

Chemical formula: $BaCl_2.2H_2O$

Questions

3. Suggest why Barium ions are added to a solution to determine the quantity of sulphate ions in a solution.

4. A 1.22g sample of $BaCl_2.nH_2O$ was heated to a constant mass of 1.04g.

(a) Calculate the moles of $BaCl_2$ formed.
(b) Hence, calculate the value of n in the formula.
(c) Why must the sample be cooled in a dessicator?

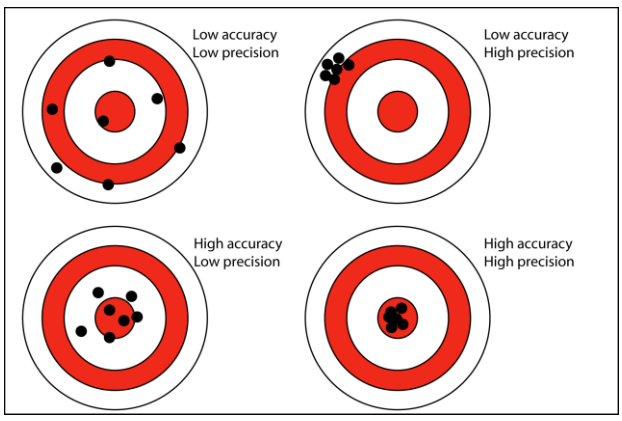
Further Practical Skills and Techniques

You will use these techniques in your individual investigation.
There are more detailed notes on each technique included in the Advanced Higher Practical booklets through the school website. These will be useful to provide greater depth to your **Background Chemistry section**. However the content included here is sufficient for your course notes and the examination.
You should be familiar with using the following equipment and techniques:

- Digital balance
- Buchner or Hirsch or sintered glass funnel
- Glassware with ground glass joints ('Quickfit' or similar)
- Thin layer chromatography apparatus
- Weighing by difference and gravimetric analysis
- Preparing a standard solution
- Using a reference or control or blank determination
- Carrying out a complexometric titration
- Carrying out a back titration
- Using a colorimeter or visible spectrophotometer and carrying out dilution to prepare a calibration graph
- Distilling and Refluxing
- Using vacuum filtration methods
- Recrystallising
- Determining % yield experimentally
- Using thin-layer chromatography
- Using melting point apparatus and mixed melting point determination
- Using a separating funnel and solvent extraction

Throughout each of the key areas you should be aware of and able to apply the following principles:

- Precision
- Accuracy
- Uncertainties
- Units



Accuracy and precision

The terms 'accuracy' and 'precision' are commonly used to mean the same thing but there is a subtle difference in their meanings. An **accurate** measurement or result is defined as one that is in close agreement with the true or accepted value. **Precise** measurements or results are those that are in close agreement with each other.

Errors and Uncertainties

A **quantitive** measurement is incomplete without some idea of the magnitude of the error or uncertainty associated with it. We can define this in terms of the **tolerance** of the piece of equipment used to make the measurement.
Laboratory equipment manufacturers can produce equipment to different levels of accuracy. A "Class A" piece of equipment will be more accurate than a "Class B".
The greater accuracy required from the piece of apparatus the more expensive it is to manufacture.

Example:
A 25 cm^3 class A pipette has a tolerance is **± 0.04 cm^3**. This means that the volume of liquid it delivers will lie somewhere between a lower limit of 24.96 cm^3 and an upper limit of 25.04 cm^3, ie **25.00 ± 0.04 cm^3**, provided the correct procedure is followed in using the pipette.
The tolerance of a piece of equipment is often stamped onto it or it can be looked up.

Pipettes

Capacity	**Uncertainty value (tolerance)**	
	Class A	**Class B**
10 cm^3	±0.02 cm^3	±0.04 cm^3
25 cm^3	±0.03 cm^3	±0.06 cm^3
50 cm^3	±0.05 cm^3	±0.10 cm^3

Burettes

Capacity	**Uncertainty value (tolerance)**	
	Class A	**Class B**
10 cm^3	±0.01 cm^3	±0.02 cm^3
25 cm^3	±0.03 cm^3	±0.05 cm^3

The larger the capacity of the apparatus the larger the error. However if this was expressed as a **percentage** of the total volume, the % uncertainty is in fact **lower** for larger volumes used. This is a good way to minimise errors in your investigation. Make up larger volumes of solutions and use large titres. **Less than 5cm^3** is considered to be not accurate enough as it has a high uncertainty. The tolerance (uncertainty value) of any piece of equipment is half the smallest reading that can be made when using it. If you read a balance or a burette twice (initial and final masses or volumes) while carrying out an experiment, the value is doubled.

Balances

A 2 decimal place balance will read to the nearest 0.01g, half of this is 0.005g, but if 2 readings are taken (initial and final) the tolerance = 2 x 0.005 = 0.01g.

Absolute uncertainties and percentage uncertainties

The absolute uncertainty in a measurement is another way of describing its **actual uncertainty**. For example, the volume of solution contained in a 250 cm^3 class B standard flask has an actual uncertainty of ±0.30 cm^3 and so its absolute uncertainty must be the same, ie ±0.30 cm^3.
It is often useful to describe an uncertainty in terms of a **percentage**.
The percentage uncertainty in a measurement is defined as:

$$\text{Percentage uncertainty} = \frac{\text{absolute uncertainty}}{\text{measurement}} \times 100$$

Hence, the percentage uncertainty in the volume contained in a 250 cm^3 class B standard flask is:

$$\frac{0.30}{250.00} \times 100 = 0.12\%$$

Given the percentage uncertainty in a measurement, we can calculate its absolute uncertainty by rearranging the above expression:

$$\text{absolute uncertainty} = \frac{\text{percentage uncertainty}}{100} \times \text{measurement}$$

Consider, for example, a solution of 0.206 mol l^{-1} sodium hydroxide and let's say the percentage uncertainty in its concentration is 1.6%. The absolute uncertainty in the concentration will be given by:

$$\frac{1.6}{100} \times 0.206 = 0.0033 \text{ mol } l^{-1}$$

So, the sodium hydroxide concentration = 0.206±0.003 mol l^{-1}.

Note: During the Evaluation of your investigation you will be expected to discuss some errors and uncertainties. However you are only required to discuss those related to your greatest error. **Error calculations may not be required in this detail.**

Significant figures

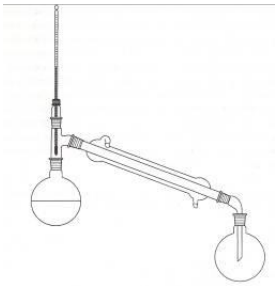
During calculations the use of correct significant figures is important.
The final result must have the **same no. of sig figs** as the measurement with the **lowest** no. of sig figs:

4.1g of NaOH was dissolved in 100ml of water. The solution was transferred to a 250ml std flask. The volume was made up to the mark. Calculate the concentration.

Moles of NaOH= 4.1/40= 0.1025moles
Concentration= 0.1025/0.25 =0.410mol/l Conc= 0.41mol/l (least no. sig figs =4.1g)

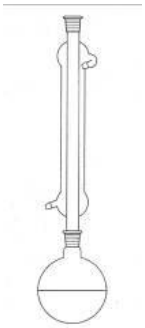
Techniques for Purification and Separation

Distillation



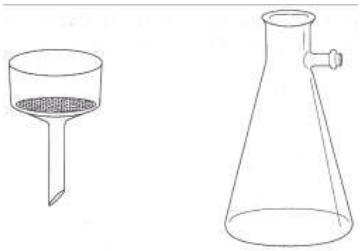
Is used for both the identification and the purification of organic (and other) compounds. The boiling point of a compound can be determined by distillation and used with other information to identify it. Distillation is also used to purify a compound by separating it from a non-volatile or less- volatile material.

Refluxing



The operation of boiling a reaction mixture and condensing the vapours back into the reaction flask is known as **heating under reflux** or **refluxing**. To prevent boiling over a few anti-bumping granules (usually pieces of alumina, aluminium oxide).
The method of often used to allow substances to be heated without loss of volatile or flammable reactants.

Vacuum filtration



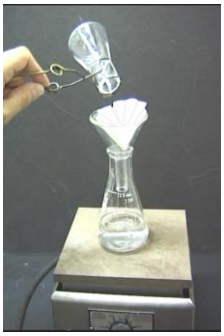
This involves using a Buchner, Hirsch or sintered glass funnel and the filtration is carried out under reduced pressure to provide a faster means of separating the precipitate from the filtrate. The choice of filtering medium depends on the amount and nature of the precipitate to be filtered.

Buchner funnel

Hirsh funnel

What the video: http://www.youtube.com/watch?v=VHAURJD7X7M

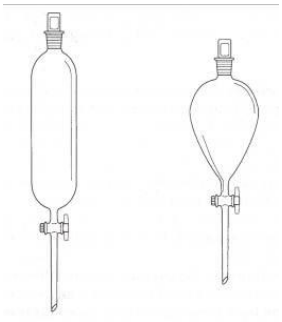
Recrystallisation



Recrystallisation is a technique used to purify solids, based upon **solubility**. The solvent must be carefully selected so that the impure compound is insoluble at lower temperatures, yet completely soluble at higher temperatures.
The impure compound is dissolved gently in the **minimum** volume of **hot** solvent then filtered to remove insoluble impurities. The filtrate is allowed to cool slowly to force crystallisation. The more soluble impurities are left behind in the solvent.

Watch the video: http://www.youtube.com/watch?v=JgMXrmpq1vg

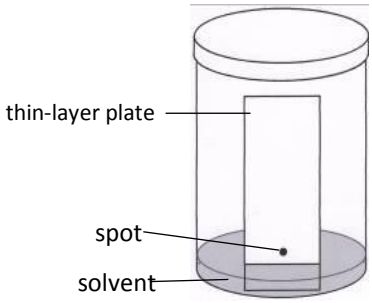
Using a separating funnel



Solvent is based on the relative solubility of a compound in two different **immiscible** liquids, usually water and an organic solvent.
The two solvents form two separate layers in the separating funnel and the lower layer is run off into one container and the upper layer is poured out into another container.
The choice of the solvents is critical. They must be immiscible and the product must not react with the solvent and it must be more soluble in one solvent than the other.
Watch the video: http://www.youtube.com/watch?v=DmvaOb1xb1o

Techniques for Identification

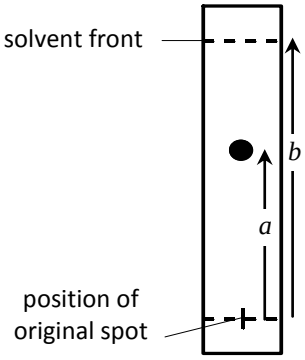
Thin-layer chromatography (TLC)



TLC can be used to assess the purity of a product.
It relies on the distribution of substances between two phases: a **mobile phase** and a **stationary** phase.
TLC uses glass or plastic plates coated with a thin layer of finely ground silica gel or aluminium oxide as the stationary phase. A shallow layer of solvent is the mobile phase.
Using a lid to create a sealed system allows an equilibrium to be set up between the two phases and that the chamber is saturated with solvent vapours. The solvent rises through the stationary phase by capillary action and carries with it the substance being analysed. How far that substance moves depends on how well it binds to the stationary phase and how well it dissolves in the solvent. The more tightly a substance is held to the stationary phase and the less soluble it is in the solvent, the more slowly it moves up the plate.

If the substance is colourless then its final position on the plate will not be seen. A plate impregnated with a fluorescent indicator and then expose it to UV light will show up the substance or treating it with a locating agent like Iodine vapour.
Under a definite set of experimental conditions a given substance will always travel a fixed distance relative to the distance travelled by the solvent front.
This ratio of distances is called the ***R*f value**.

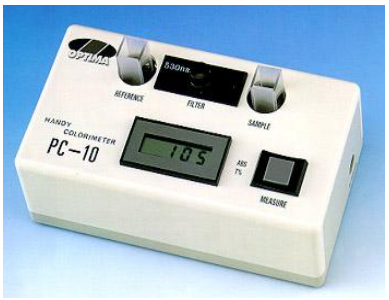
$$R_f = \frac{\text{distance travelled by substance}}{\text{distance travelled by solvent front}} \qquad R_f = \frac{a}{b}$$



Since a pure substance will show up as only one spot on the developed chromatogram, TLC can be used to assess the **purity** of a product prepared in the lab.

Watch the video: http://www.youtube.com/watch?v=tDaKxskUwA0

Colorimetry and Calibration curves



Colorimetry uses the relationship between **colour intensity** of a solution and the concentration of the coloured species present.
A calibration curve must be prepared using solutions of known concentrations (standard solutions). The concentration of the 'unknown' solution is determined from its absorbance and by referring to the calibration curve. The straight line section of the calibration graph should cover the dilution range likely to be used in the determination.

A solution will be coloured if it absorbs some, but not all, parts of the white light passing through it. Those parts that are not absorbed are transmitted through the solution and combine to give the colour we see.
While the colour of a solution depends on the colour of light it absorbs, the intensity of its colour depends on the concentration of the solution: the more concentrated the solution, the darker its colour, ie the more light it absorbs. We can get some idea of the amount of light a coloured solution absorbs by using a colorimeter.

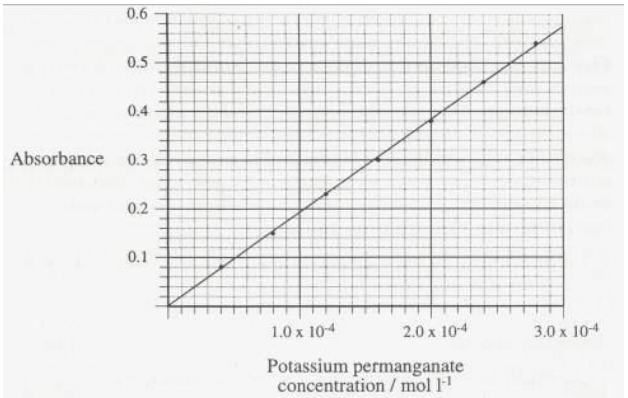
A narrow beam of white light is first passed through a coloured filter. The filter colour must correspond to the colour of light that is most strongly absorbed by the solution being analysed. As the light passes through the solution of unknown concentration some of it is absorbed and some is transmitted. The transmitted light strikes a photocell and generates an electric current that is directly proportional to its intensity. The absorbance (A) is a measure of the extent to which white light is absorbed and is proportional to the concentration of the solution (c).For dilute solutions there is a direct relationship between the two values allowing a calibration curve to be drawn.

The solution samples are held in containers called cuvettes or cells. One cuvette is filled with deionised water (solvent) and is used as a reference' or 'blank' in between all readings taken.

Calibration curves

A **calibration curve** is produced using the absorbance (A) of a range of different concentrations of the solution.
From this the unknown concentration can be determined.

Note: Absorbance (A) has no units.



The straight line on this calibration curve shows that, for dilute solutions, absorbance is directly proportional to the concentration of the permanganate solution.
An unknown concentration can be determined by plotting its absorbance.

Watch the video: http://www.youtube.com/watch?v=0luczWOo0rQ

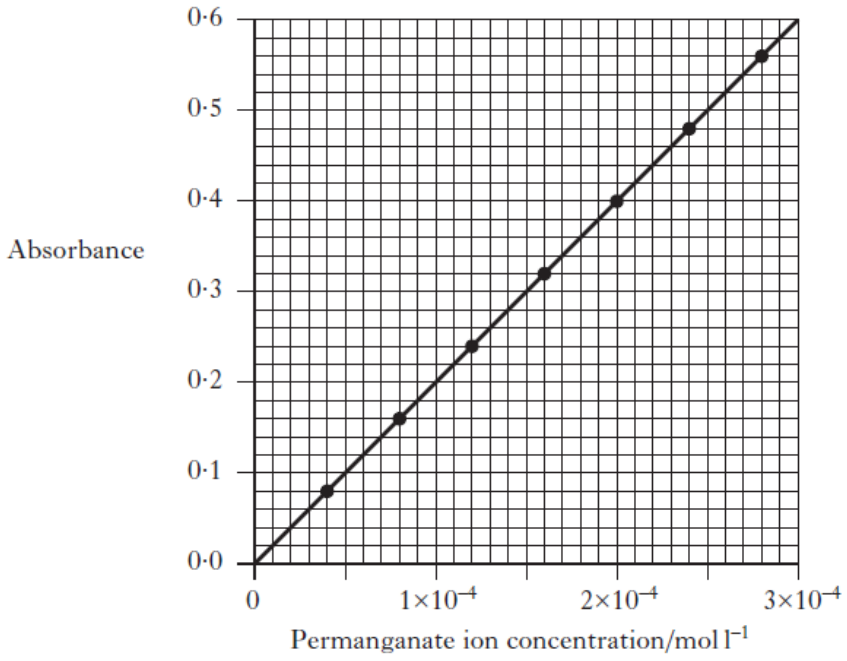
1. The manganese content of an iron nail can be determined by placing the nail in a solution of a strong oxidising agent and then taking the absorbance of the solut1on produced.
During oxidation the manganese is converted into the purple permanganate ion, MnO_4^-. The nail had a mass of 0.31g.

(a) What data must be collected to allow the calibration graph to be drawn? (1)

(b) Which colour of filter or wavelength of light should be used in this procedure? (1)

(c) Following the oxidation to permanganate ions the solution was made up to 100 cm^3 in a standard flask. The absorbance of the solution was measured as 0·35.

Use this information and the following calibration graph to calculate the percentage of manganese in this sample of steel.



3

Determination of melting point and mixed melting point

The melting point of an organic compound is one of several physical properties by which it can be identified. If the product is a **solid**, we can determine its **melting point** and compare it with the accepted or literature value. (However it is possible to have 2 different compounds with the same melting point)
A crystalline substance has a **sharp** melting point, within a very small temperature range of about 1°C. Determination of the melting point can also give an indication of the **purity** of an organic compound. The presence of impurities lowers the melting point and extends the temperature range.

The **mixed melting point** technique involves mixing a pure sample of the compound that has been synthesised and a pure sample of the compound we think we have prepared. Roughly equal amounts of the two compounds are thoroughly ground together and the melting point of the mixture is then measured in the usual way. If the melting point turns out to be sharp and close to the expected value, then the two compounds must be identical.
If our reaction product is a **liquid** rather than a solid then we can measure its **boiling point** using simple distillation to help us identify it.