

Kirkcaldy High School



Chemistry

Advanced Higher

Unit 4 - Researching Chemistry

NOTES

Course Overview

Contents

The Advanced Higher Chemistry Course is split into four units. *Italic* shows the contents of this notes booklet.

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Atomic orbitals, electronic configurations and the periodic table

Transition Metals

Unit 2 - Physical Chemistry

Chemical Equilibrium

Reaction Feasibility

Kinetics

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Unit 4 - Researching Chemistry

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Assessment

- There is a **final exam** for Advanced Higher Chemistry. It lasts for 3 h and contains 110 marks scaled to a total of 120. There are.
 - 25 marks of multiple-choice questions
 - 85 marks of written answer questions
- There is a **Project** to write for Advanced Higher Chemistry.
 - The Assignment is **externally marked** by an SQA marker (NOT your teacher)
 - The Assignment contains **25 marks**, but these are scaled to 40 marks such that the assignment is worth one quarter of the total marks.
 - You have unlimited **time to research** and gather data for your Assignment.
 - It must contain data and analysis from experiments you have carried out.

(a) Weighing by difference and gravimetric analysis

When we weight samples in chemistry, we can either “tare” the balance or “weigh by difference.

Taring

When an empty vessel (*e.g.* beaker, weighing boat) is placed on a balance, the balanced can then be “tared” (set to zero) such that the reading is only the substance being measured.

Weighing by Difference

Weighing by difference is when the empty vessel (*e.g.* beaker, weighing boat) is weighed, substance added and then weighed again. The mass of the substance is the difference between the two.

i.e.

$$\text{mass of substance} = \text{mass of vessel with substance} - \text{mass of empty vessel}$$

Gravimetric Analysis by Precipitation/Filtration

For this method, the product must have :

- A low solubility so that all the product is precipitated
- A particle size large enough for filtration
- Be stable at temperatures of 100-105⁰C so that it can be dried in an oven.

This process has to be carried out carefully to ensure all material is transferred and all apparatus dried and weighed with extreme care.

In gravimetric analysis, the mass of an element or compound present in a substance is determined by changing that substance into another of known chemical composition that can be readily isolated, purified and weighed.

To use gravimetric analysis we need:

- The equation
- The reaction to proceed to completion.
- The accuracy of this method depends upon the dexterity of the person carrying out the procedure.

e.g.

An anhydrous salt is known to be a mixture of magnesium chloride and magnesium nitrate. To determine the composition of the mixture the following procedure was carried out. 4.5 g of the salt was dissolved in water and the solution made up to 500 cm³ in a standard flask. A slight excess of silver(I) nitrate was then added to 100 cm³ of this solution and the resulting precipitate recovered by filtration. The precipitate was washed dried and its mass found to be 2.01 g.

Calculate the percentage by mass of magnesium chloride in the mixture.

A displacement reaction will take place on addition of the silver nitrate to produce the insoluble silver chloride.

We can calculate the number of moles of silver(I) chloride, AgCl produced.

$$n = \frac{m}{\text{GFM}}$$
$$n = \frac{2.01}{107.9 + 35.5}$$
$$n = \frac{2.01}{143.4}$$

$$n = 0.0140 \text{ moles of Ag}$$

MgCl₂. To calculate moles of Mg need to divide by 2.

$$n = \frac{0.0140}{2} = 0.007 \text{ moles}$$

0.007 moles in 100cm^3 . The original sample was $500\text{ cm}^3 = 0.007 \times 5 = 0.035$ moles.

$$m = n \times \text{GFM}$$

$$m = 0.035 \times (24.3 + (35.5 \times 2))$$

$$m = 0.035 \times 95.3$$

$$m = \underline{3.336\text{ g}}$$

$$\% \text{ mass} = \frac{3.336}{4.5} \times 100 = \underline{74.1\%}$$

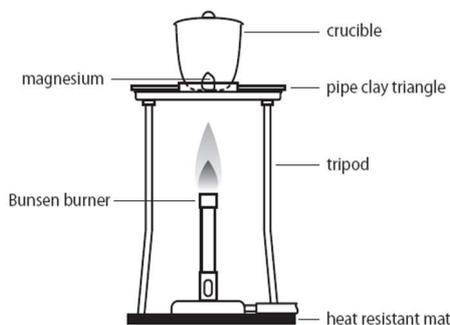
Gravimetric Analysis by Heating

The other common gravimetric method involves heating to change one substance into another.

e.g.

Gravimetric Determination of Water in Hydrated Barium Chloride.

Barium chloride forms crystals which include a certain number of molecules of H_2O per formula unit of BaCl_2 . This is called “water of crystallisation”, and occurs with many ionic compounds. *e.g.* copper sulfate is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

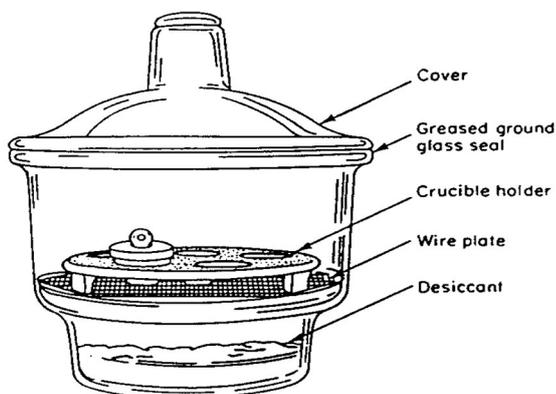


The water of crystallisation can be driven off by strong heating. This results in a weight loss, from which the quantity of water per mole of compound can be found.

A crucible is weighed empty, then with barium chloride in it.

It is heated gently for 2 minutes and then strongly for 10 - 15 minutes.

It is allowed to cool in a desiccator and is then weighed. A desiccator allows the crucible to cool down without absorbing any more moisture.



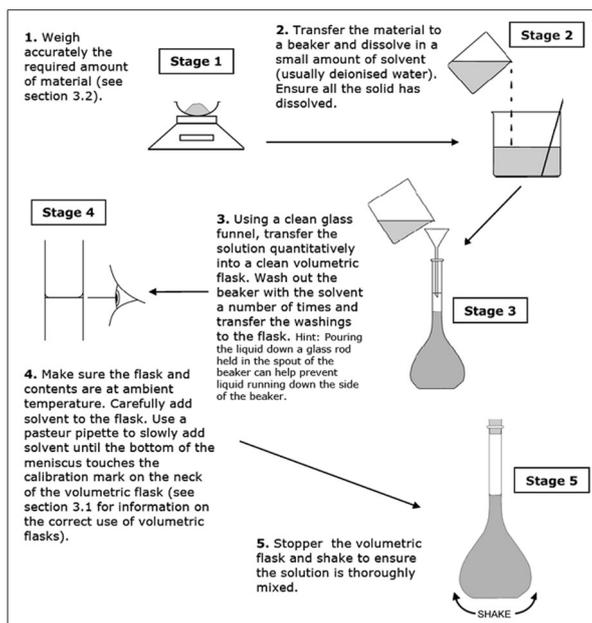
There should be a weight loss. It is then heated again for about 4 minutes, cooled in a desiccator and reweighed. This process is continued until two successive weights are within 0.002 g of each other. This is called 'heating to constant mass'

The weight loss is water. The moles of water can be calculated.

The solid left behind is anhydrous barium chloride. Its mass is found by subtracting the mass of the empty crucible. The moles of the anhydrous compound can then be calculated. The ratio of moles of water to moles of anhydrous barium sulfate can then be found.

(b) Preparing a Standard Solution

A standard solution is a solution of accurately known concentration i.e. one in which contains a known weight of reagent in a definite volume of solution.



A standard solution is always prepared from a primary standard.

A primary standard is a substance which must have the following characteristics:

- High purity (>99.9%)
- Stable in air and in solution (allows storage)
- Reasonably high formula mass (reduces error)
- Readily soluble (usually in water)

The most common primary standards in use are:

- Oxalic acid and anhydrous (no water) sodium carbonate for acid /base titrations.
- EDTA (ethylenediaminetetracetic acid) for complexometric titrations
- Potassium iodate or potassium dichromate for redox titrations

Certain substances are unsuitable for use as primary standards, such as sodium hydroxide. This is because it is hygroscopic which means that it will absorb moisture from the air which can affect the properties of the compound i.e. the viscosity or boiling point can be affected.

(c) Using a reference or control or blank determination

A control in chemistry is often a check to make sure the technique you're using works. For example, if you were trying to find the mass of vitamin C in a sample of fruit juice by volumetric analysis, you would most likely carry out the experiment on a sample with a known quantity of vitamin C in it. If the experiment gives you the result you expect then you can claim it is a valid technique.

A "blank" is a common aspect of spectroscopic techniques such as IR Spectroscopy and colourimetry. Say you are measuring the light absorbance of a compound dissolved in water, you would measure the absorbance of water first and then subtract that from the absorbance of the water with the compound to find the absorbance of the compound.

i.e.

absorbance of compound = absorbance of compound in water - absorbance of water

(d) Carrying out a Complexometric Titration

Complexometric titrations are based on the formation of a coloured complex by a transition metal ion. EDTA is generally used as it forms complexes with metal ions in a 1:1 ratio. This technique can be used to determine the concentration of metal ions in solution. Its use can be limited though as appropriate indicators are not always available as the indicator has to complex with the metal ion to produce a different colour.

Example Complexometric Determination of Nickel Using EDTA

The object of the experiment is to find the % of Ni in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

Part 1: Making up the nickel ion solution.

- A known mass of nickel sulphate is dissolved in a little water in a beaker and added to a graduated flask. The beaker is rinsed out several times with water and the washings added to the flask. The level is then made up to the mark on the flask. Then the flask is turned upside down a few times to ensure mixing.

Part 2: Titration

- The burette is rinsed with the EDTA solution.
- The pipette is rinsed with the nickel solution.
- 20 cm^3 of nickel solution is added to a conical flask; it is diluted with water to about 100 cm^3 . Murexide indicator is added, with some NH_4Cl solution. About 15 cm^3 of EDTA is added, then the solution is made alkaline by adding 10 cm^3 of concentrated ammonia solution. Addition of EDTA is continued until the end point (appearance of blue - violet colour).
- The end point in this titration can be difficult to see, and this would be a source of error in the experiment.

(e) Carrying Out a Back Titration

Back titration is a technique used to find the number of moles of a substance by reacting it with an excess volume of reactant of known concentration. The resulting mixture is then titrated to work out the number of moles of excess reactant. From the initial number of moles of that reactant the number of moles used in the reaction can be determined, making it possible to work back to calculate the initial number of moles of substance under test. A back titration is useful when trying to work out the quantity of substance in an insoluble solid.

A control experiment validates a technique and may consist of carrying out a determination on a known solution of known concentration.

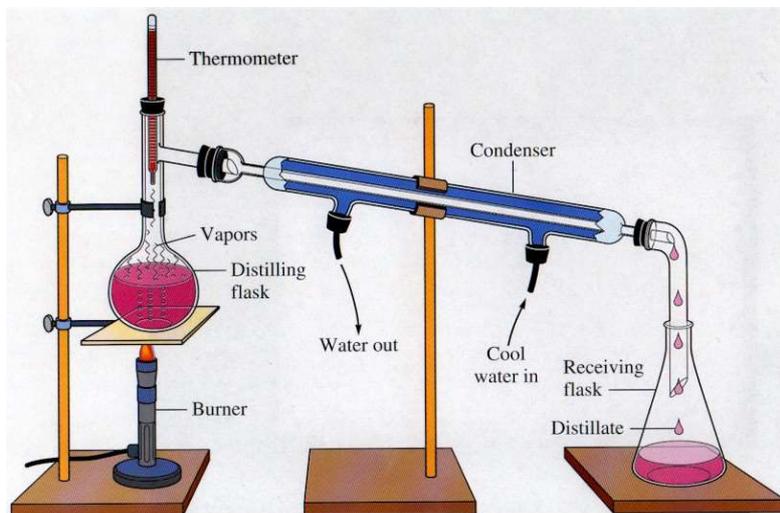
Aspirin is an analgesic medicine which is insoluble in water and the quantity in a tablet has to be determined by a 'back titration' method. This involves treating an accurately known mass of aspirin with a definite amount of sodium hydroxide. The alkali first catalyses the hydrolysis of the aspirin to ethanoic and salicylic acids and then neutralises these acids. An excess of alkali has to be used and the amount remaining after reaction is determined by titrating it against a standard solution of sulfuric acid.

(f) Using a colorimeter or visible spectrophotometer and carrying out dilution to prepare a calibration graph

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.

(g) Distilling

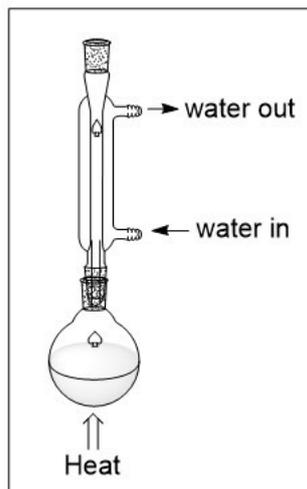
In the modern chemistry lab, distillation is a powerful tool, both for the identification and purification of organic compounds. The boiling point of a compound is well defined and thus is one of the physical properties of a compound which is identified.



Distillation is used to purify a compound by separating it from a non-volatile or less volatile material.

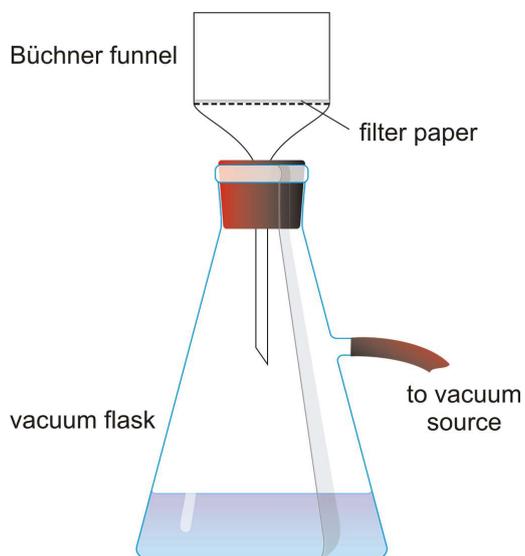
(h) Refluxing

Refluxing is a technique used to apply heat energy to a chemical reaction mixture over an extended period. The liquid reaction mixture is placed in a round bottomed flask along with anti-bumping granules with a condenser at the top. The flask is heated vigorously over the course of the chemical reaction. Any vapours given off are immediately returned to the reaction vessel as liquids when they reach the condenser.



(i) Using Vacuum Filtration Methods

Using a Buchner, Hirsch or sintered glass funnel. These methods are carried out under reduced pressure and provide a faster means of separating the precipitate from the filtrate. The choice of filtering medium depends on the quantity and nature of the precipitate.



(j) Recrystallising

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

(k) Determining Percentage yield Experimentally

Theoretical yield - the expected quantity of product from a known mass of reactant, which is calculated from the balanced equation.

Actual yield - the quantity of product actually obtained, which is usually less than the theoretical yield

The actual yield is usually less than the theoretical yield because:

- The reaction has not gone to completion
- Other reactions may have occurred which compete with the reaction
- Separation of the desired product may be difficult
- The product may be impure or some may be lost on purification

Industrial processes require a high percentage yield and a high purity of product. Therefore unconverted reactants are often recycled for further reaction. *Eg.* Haber process to produce ammonia, hydration of ethene to produce ethanol.

Calculation of percentage yield

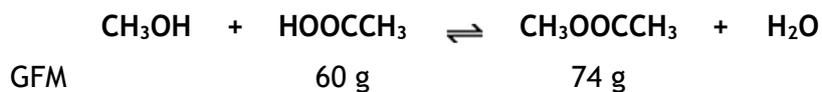
$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

OR:

$$\text{Actual yield} = \frac{\text{Percentage yield}}{100} \times \text{Theoretical yield}$$

e.g.

A sample of methyl ethanoate weighing 6.9 g was obtained from a reaction mixture containing 9.0 g ethanoic acid, excess methanol and a small volume of conc. sulfuric acid. Calculate the percentage yield of ester using the following equation:



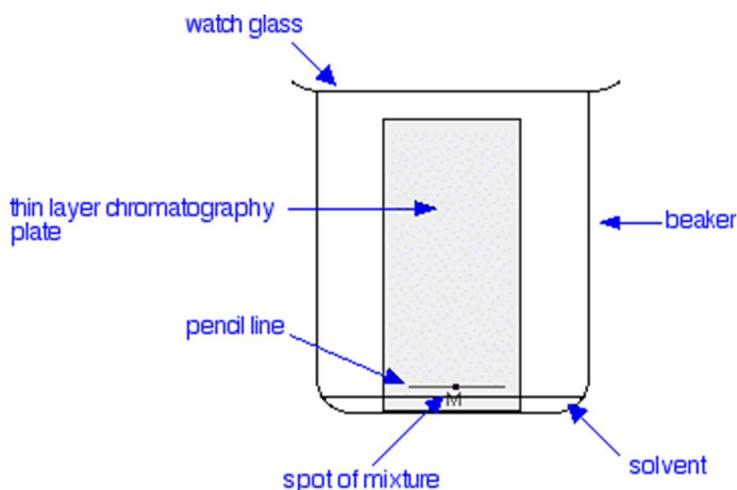
Calculate theoretical yield:

$$\begin{array}{ccccccc} \text{CH}_3\text{OH} & + & \text{HOOCCH}_3 & \rightleftharpoons & \text{CH}_3\text{OOCCH}_3 & + & \text{H}_2\text{O} \\ n & = & \frac{m}{\text{GFM}} & & & & \\ & & \frac{9}{60} & & & & \\ & & 0.15 \text{ moles} & \begin{array}{l} \times 1 \\ \rightarrow \end{array} & 0.15 \text{ moles} & & \\ m & = & & & n \times \text{GFM} & & \\ & & & & 0.15 \times 74 & & \\ & & & & 11.1 \text{ g} & & \end{array}$$

$$\text{Percentage yield} = \frac{6.9}{11.1} \times 100\% = \underline{62.2\%}$$

(I) Thin-Layer Chromatography (TLC)

Thin Layer Chromatography is similar to paper chromatography, but it uses a fine film of silica or aluminium oxide spread over glass or plastic. The silica or aluminium oxide is the stationary phase. A suitable solvent is the mobile phase.



The R_f values are then calculated in the same way as for paper chromatography.

If an experiment is carried out under similar conditions, it will always have the same R_f value. (Allowing for experimental error)

If the spots obtained are colourless, then sometimes a fluorescent substance can be added to the stationary phase so that in the presence of UV light the spots appear as darker patches. The other method is to spray it with another chemical e.g. ninhydrin which is used in the identification of amino acids.

Thin Layer Chromatography is used to determine the purity of a substance prepared in the lab. It can be used in this way as a pure product will only show as one spot whilst if impurities were present there would be more.

Other Chromatographic Techniques

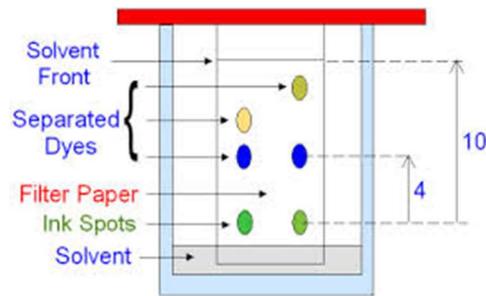
Chromatography is a separation process. It depends upon the partition of substances between two phases, one stationary and one mobile.

The separation occurs because the substances in the mixture have different partition co-efficients between the stationary and mobile phases.

Paper Chromatography

Paper chromatography involves spotting a piece of paper with the sample mixture which is to be separated. The bottom of the paper is then placed in a pool of solvent which is drawn up the paper. This is the mobile phase and the water held in the paper is the stationary phase.

When the paper is removed from the solvent, the various parts of the mixture will have moved different distances along the paper.



The separation relies on many factors:

- Solvent
- Rate of flow of solvent over the paper
- Solubility of the components in the mixture in the solvent
- The partition of the components between the moving solvent and the water bound to the surface of the paper.

For each of the components in the mixture, the partition coefficient remains constant. It is the difference between the partition coefficient of each component that separates them.

A common reference calculated in paper chromatography is the R_f value. This is the distance the component has travelled compared to the distance the solvent has travelled.

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

It is a useful figure which remains constant as long as all the conditions are reproduced exactly.

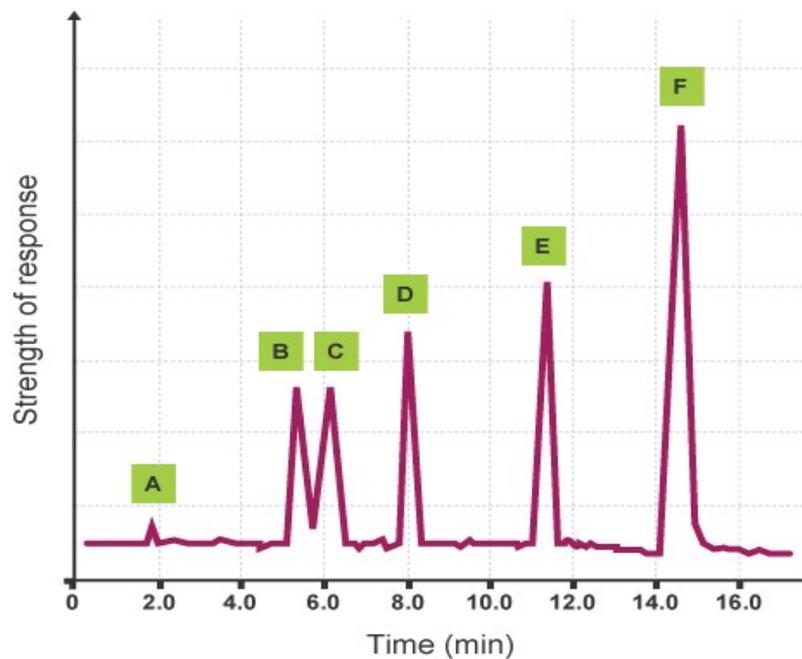
Gas-Liquid Chromatography

In gas-liquid chromatography the stationary phase is a high boiling point liquid which is held on an inert solid support of relatively small particle size.

The mobile phase of gas chromatography is a gas, usually called the carrier gas.

The stationary phase is packed into a thin tube called a column which is usually between 1-3 metres long. This is then housed in an oven so that the material being analysed can be made into a gas. This then passes through the column along with the carrier gas where separation takes place in a similar way to paper chromatography. At the other end of the column the carrier gas passes through a detector which measures any changes in the composition. The signal from the detector is recorded and translated into peaks which represent the individual components of the sample. The time taken for the peak to appear after injection is called the retention time and is used as a reference to identify components. If conditions remain constant the retention time will be the same for a given compound.

The gas used depends upon the method of detection and the area under the peaks is proportional to the amount present.



(m) 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. A crystalline substance has a sharp melting point falling within a very small temperature range. Determination of the melting point can also give an indication of the purity of an organic compound, as the presence of impurities lowers the melting point and extends its melting temperature range.

Since impurities lower the melting point, the technique of mixed melting point determination can be used as a means of identifying the product of a reaction

(n) Using a separating funnel and solvent extraction

Liquids which do not mix with each other are said to be immiscible.

If a solute is added to two immiscible liquids and the solute is soluble in both, then some of the solute will dissolve in both liquids. It will distribute itself in a definite ratio which we call the Partition Co-efficient.

The partition co-efficient is a measure of the distribution of a solute between two immiscible solvents and is simply a specific case of equilibrium.

The size of a partition co-efficient will vary as it depends upon:

- The solute
- The nature of the two immiscible liquids
- The temperature
- It is independent of the amount of solute or volume of solvent.

The partition co-efficient is a measure of the distribution of a solute between two immiscible solvents and is simply a specific case of equilibrium.

Partition co-efficients can therefore be calculated in much the same way as the equilibrium constant.

i.e.

$$K = \frac{[\text{solute X}]_{\text{solvent A(organic)}}}{[\text{solute X}]_{\text{solvent B(aqueous)}}$$

e.g. Iodine dissolves in both potassium iodide and trichloromethane (both these liquids are immiscible.)

The partition coefficient would be defined as;

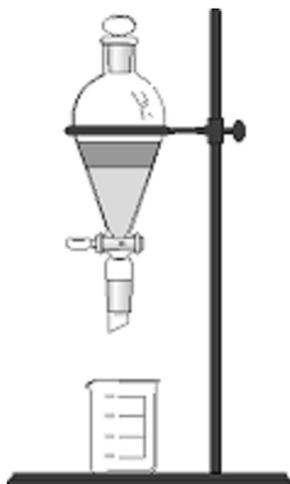
$$K = \frac{[I_2]_{CHCl_3}}{[I_2]_{KI}}$$

Solvent Extraction is an application of the partition co-efficient of a solute between two liquids *i.e.*

solvent extraction is a practical example of using the partition co-efficient.

Solvent extraction is the process used to purify a compound by using its different solubility between two solvents.

This technique is used in organic chemistry for purification, processing perfumes and in the nuclear industry for the separation of plutonium and uranium in spent fuel.



Solvents are used to 'selectively' separate out the components of a mixture.

The two components of the mixture must have different partition co-efficients in the solvent A and B. The two solvents will form two separate layers. The bottom layer is run off and separated from the top layer. When all the top layers, for example, are combined and the solvent evaporated, virtually pure solute would be obtained. The quantity of solute obtained depends upon the partition co-efficient and how many times the process is repeated. A larger number of smaller extractions will yield more solute than one larger extraction.

Decaffeinated Coffee

Caffeine is removed from coffee using solvent extraction. It was previously extracted using dichloromethane (CH_2Cl_2) as the solvent but this was found to be toxic so it is now removed by using an environmentally friendly solvent, supercritical CO_2 . Supercritical has the ability to behave as both a liquid and a gas at a temperature of 31°C and a pressure of 73atm . The gas state is able to penetrate the green coffee beans whilst the liquid properties allow it to dissolve out about 98% of the caffeine. The extracted caffeine is then recycled into soft drinks and medicines.

(o) Carrying Out Stoichiometric Calculations

Stoichiometry involves the numerical relationships between reacting substances. I.e. how many moles of each reactant are required for the reaction to go to completion?

Stoichiometry is used in quantitative analysis which involves looking at the amount of reactants required and amount of products made rather than just what they are.

What we know as a balanced equation is more correctly called a balanced stoichiometric equation (i.e. one in which the mole ratios have been considered).

A quantitative reaction is one in which the substances react completely according to the mole ratios given by the balanced (stoichiometric) equation.

Revision - Basic skills required in stoichiometry

Writing and naming of compounds

e.g. Barium Phosphate: $\text{Ba}_3(\text{PO}_4)_2$

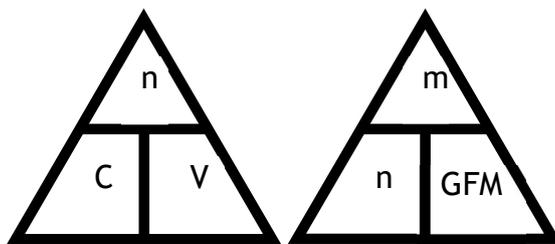
Potassium Permanganate: KMnO_4

Using relative atomic mass

e.g. $\text{Al}_2(\text{SO}_4)_3$

$$\text{GFM} = (2 \times 27) + [(32 + 64) \times 3] = 342 \text{ g}$$

Mole Calculations



e.g. Calculate the concentration of the solution containing 16 g of CuSO_4 dissolved in 250 cm^3 of solution. Need to use both equations. 'n' is common to both so we need to use the information given in one of the triangles to work out this value.

$$n = \frac{m}{\text{GFM}}$$

$$n = \frac{16}{(63.5+32.1+(4 \times 16))}$$

$$n = \frac{16}{159.6}$$

$$n = 0.1 \text{ moles}$$

$$C = \frac{n}{V}$$

$$C = \frac{0.1}{0.25}$$

$$C = \underline{0.4 \text{ mol l}^{-1}}$$

Calculations across Chemical Equations

e.g. Calculate the mass of carbon dioxide produced when 4g of methane burns.

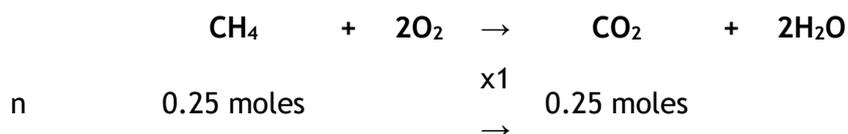
1. Write and balance equation



2. Calculate number of moles:

$$\begin{array}{ccccccc} & \text{CH}_4 & + & 2\text{O}_2 & \rightarrow & \text{CO}_2 & + & 2\text{H}_2\text{O} \\ & \text{m} & & & & ? & & \\ n & = & & \frac{\text{m}}{\text{GFM}} & & & & \\ & = & & \frac{4}{(1 \times 12) + (1 \times 4)} & & & & \\ & = & & \frac{4}{16} & & & & \\ & = & & 0.25 \text{ moles} & & & & \end{array}$$

3. Use the mole ratio to calculate the number of moles of the unknown (x1 here as 1:1 mole ratio).



4. Use the equation again to calculate the mass of the unknown

$$\begin{array}{ccccccc} & \text{CH}_4 & + & 2\text{O}_2 & \rightarrow & \text{CO}_2 & + & 2\text{H}_2\text{O} \\ m & = & & & & n \times \text{GFM} & & \\ & = & & & & 0.25 \times ((12 \times 1) + 16 \times 2) & & \\ & = & & & & 0.25 \times 44 & & \\ & = & & & & \underline{11 \text{ g}} & & \end{array}$$

Excess Calculations

e.g.

Calculate the mass of ammonia gas which is produced when 1.32 g of ammonium sulfate is heated with 1 g of sodium hydroxide.

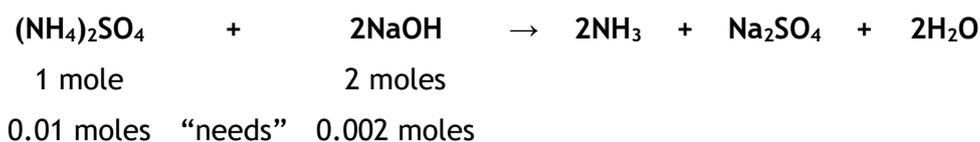


Need to calculate which reactant is in excess first so we know which reactant will limit the amount produced.

1. To do this we first need to calculate the moles of each reactant.

$$\begin{array}{rcc} & (\text{NH}_4)_2\text{SO}_4 & + & 2\text{NaOH} & \rightarrow & 2\text{NH}_3 & + & \text{Na}_2\text{SO}_4 & + & 2\text{H}_2\text{O} \\ n & = & \frac{m}{\text{GFM}} & & & \frac{m}{\text{GFM}} & & & & \\ & & \frac{1.32}{132.1} & & & \frac{1}{40} & & & & \\ & & 0.01 \text{ moles} & & & 0.025 \text{ moles} & & & & \end{array}$$

2. Mole ratio of reactants



We have 0.025 mole of NaOH which means that some will be left over, therefore NaOH will be in excess.

3. It then becomes a calculation from equation where we ignore the reactant which is in excess.

$$\begin{array}{rcc} & (\text{NH}_4)_2\text{SO}_4 & + & 2\text{NaOH} & \rightarrow & 2\text{NH}_3 & + & \text{Na}_2\text{SO}_4 & + & 2\text{H}_2\text{O} \\ n & 0.01 \text{ moles} & & & \times 2 & 0.02 \text{ moles} & & & & \\ & & & & \rightarrow & & & & & \\ m & = & & & & n \times \text{GFM} & & & & \\ & = & & & & 0.02 \times 17 & & & & \\ & = & & & & \underline{0.34 \text{ g}} & & & & \end{array}$$

Molar Volume

e.g.

Calculate the volume (in l) of carbon dioxide would be produced by completely reacting 60 g of carbon with oxygen? (molar volume is 24 l)



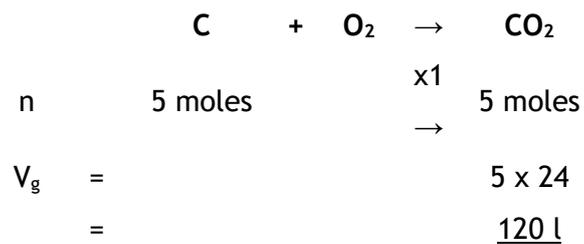
1. We need to calculate the number of moles of carbon present

$$\begin{aligned} \text{C} + \text{O}_2 &\rightarrow \text{CO}_2 \\ n &= \frac{m}{\text{GFM}} \\ &= \frac{60}{12} \\ &= 5 \text{ moles} \end{aligned}$$

2. Mole ratio



3. We know that 1 mole has a volume of 24litres



Volumetric Analysis Calculations

Calculating Concentrations

A molar solution is a solution which contains 1 mole of solute dissolved in 1 litre of solution.

$$C = \frac{n}{V}$$

e.g.

Calculate the molar concentration of the solution obtained when 5.35 g of potassium iodate (KIO_3) is dissolved in 250 cm^3 of solution.

1. Calculate the number of moles of KIO_3

$$n = \frac{m}{\text{GFM}}$$
$$n = \frac{5.35}{39.1 + 126.9 + (3 \times 16)}$$

$$n = \frac{5.35}{214}$$

$$n = 0.025 \text{ moles}$$

2. Calculate the concentration of KIO_3

$$C = \frac{n}{V}$$

$$C = \frac{0.025}{0.25}$$

$$C = \underline{0.1 \text{ mol l}^{-1}}$$

Calculating Dilutions

When a concentrated solution is diluted the number of moles of solute in the solution does not change, only the volume of solvent.

Because of this we can use the relationship:

$$C_1V_1 = C_2V_2$$

Where C_1, V_1 are the concentration and volume of the concentrated solution and C_2V_2 apply to the diluted solution.

e.g. What volume of 0.5 mol l^{-1} sodium carbonate is required to make by dilution with water, one litre of a solution with a $\text{Na}^+_{(\text{aq})}$ concentration of 0.2 mol l^{-1} ?

$$\begin{aligned}C_1V_1 &= C_2V_2 \\0.5 \times V_1 &= 0.2 \times 1 \\V_1 &= \frac{0.2}{0.5} \\V_1 &= 0.4 \text{ l}\end{aligned}$$

However question asked for Na^+ , the formula for sodium carbonate is Na_2CO_3 . There are two Na^+ present so we need to divide our volume by 2.

$$\frac{0.4}{2} = \underline{0.2 \text{ litres}}$$

Complexometric Titration

Example

A 50 cm³ aqueous sample containing iron(III) required 21.675 cm³ of 0.240 mol l⁻¹ EDTA for complete reaction. What is the concentration of iron in the sample in mol l⁻¹?

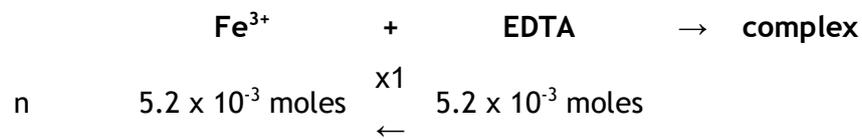
Metals react with EDTA in the ratio of 1:1



1. Calculate number of moles of EDTA

$$\begin{aligned} \text{Fe}^{3+} + \text{EDTA} &\rightarrow \text{complex} \\ n &= \frac{CV}{1} \\ &= 0.24 \times 0.021675 \\ &= 5.2 \times 10^{-3} \text{ moles} \end{aligned}$$

2. Use the mole ratio

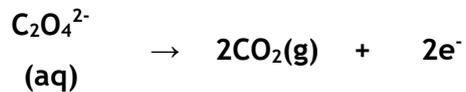


3. Calculate the concentration

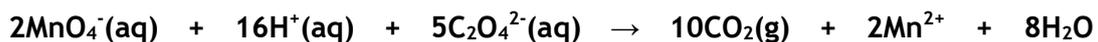
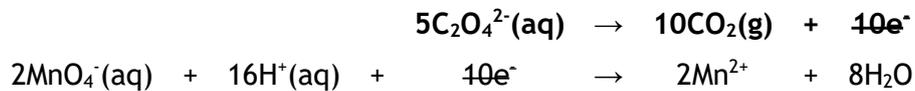
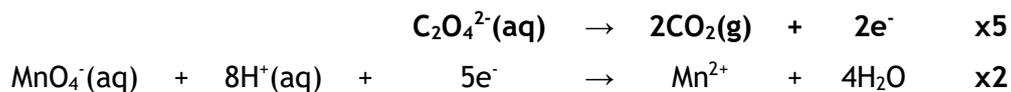
$$\begin{aligned} \text{C} &= \frac{n}{V} \\ &= \frac{5.2 \times 10^{-3} \text{ moles}}{0.05} \\ &= \underline{0.104 \text{ mol l}^{-1}} \end{aligned}$$

Redox Titration

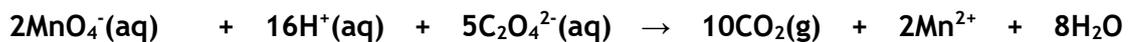
e.g.
25 cm³ of an acidified solution of potassium oxalate, K₂C₂O₄, was heated to 80 °C and titrated with a standard solution of 0.02 mol l⁻¹ potassium permanganate, KMnO₄. The end-point was reached when 22.5 cm³ of KMnO₄ was added. Calculate the concentration of the potassium oxalate used in the titration.
The ion-electron equations involved in the reaction are;



1. Need a redox equation- need to balance and cancel out the electrons:

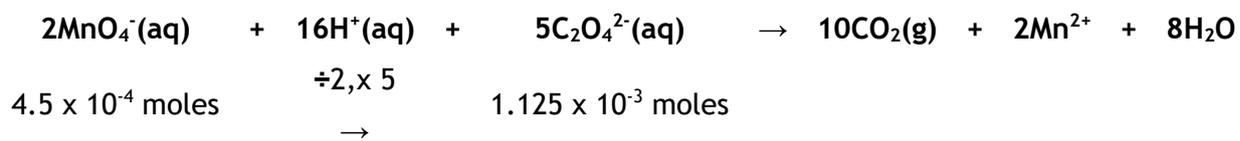


2. Number of moles of permanganate



$$\begin{aligned} n &= CV \\ &= 0.02 \times 0.0225 \\ &= 4.5 \times 10^{-4} \text{ moles} \end{aligned}$$

3. Mole ratio



4. Calculate concentration

$$\begin{array}{ccccccc} 2\text{MnO}_4^- (\text{aq}) & + & 16\text{H}^+ (\text{aq}) & + & 5\text{C}_2\text{O}_4^{2-} (\text{aq}) & \rightarrow & 10\text{CO}_2 (\text{g}) + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \\ C = & & & & \frac{n}{V} & & \\ = & & & & \frac{1.125 \times 10^{-3}}{0.025} & & \\ = & & & & 0.045 \text{ mol} & & \\ & & & & \text{l}^{-1} & & \end{array}$$

Volumetric Analysis

e.g.

A 1.1 g sample of steel containing manganese was dissolved in nitric acid. The manganese(II) ions formed were then oxidised to permanganate ions. The resulting purple solution was made up to 100 cm³ in a standard flask.

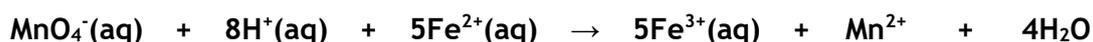
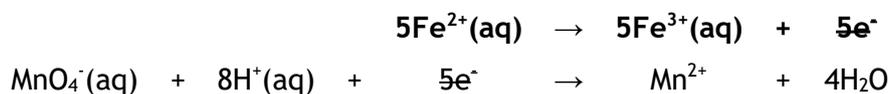
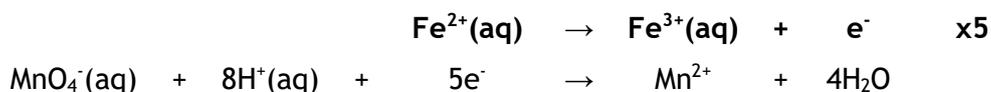
In a titration, a 25 cm³ portion of the permanganate solution was reduced by 30.1 cm³ of 0.002 mol l⁻¹ iron (II) sulphate solution.

Write the redox equation for the reaction

Calculate the number of moles of permanganate ions in the 25 cm³ titrated sample.

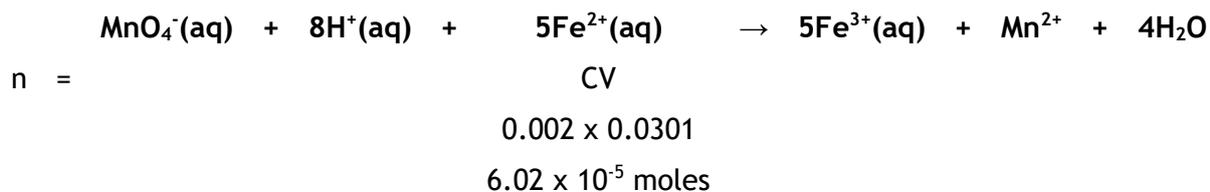
Calculate the percentage by mass of manganese in the original sample of steel.

(a) Write the redox equation for the reaction

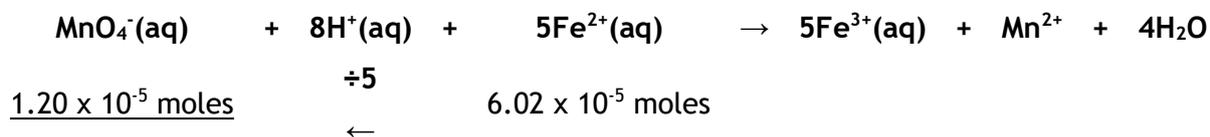


(b) Calculate the number of moles of permanganate ions in the 25 cm³ titrated sample.

Number of moles of iron



Mole ratio



(c) Calculate the percentage by mass of manganese in the original sample of steel.

$$m = n \times \text{gfm}$$

$$m = 1.204 \times 10^{-5} \times 54.9$$

$$m = 0.00066 \text{ g}$$

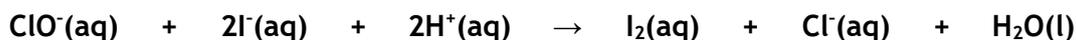
0.00066 in 25 cm³, in 100cm³, 4 x 0.00066 = 0.00264 g

$$\% \text{mass} = \frac{0.00264}{1.11} \times 100 = \underline{0.238 \%}$$

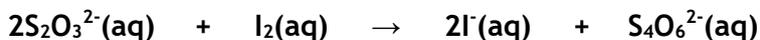
e.g.

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.



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



10.0 cm³ of a household bleach was diluted to 250 cm³ in a standard flask.

25.0 cm³ of this solution was added to excess acidified potassium iodide solution.

The solution was then titrated with 0.10 mol l⁻¹ sodium thiosulfate using an appropriate indicator.

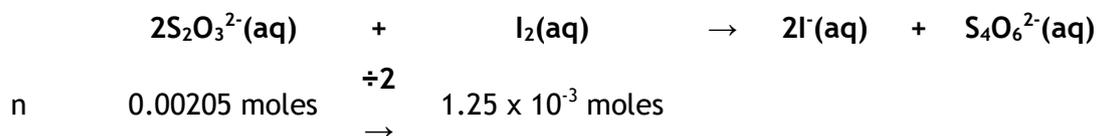
The volume of thiosulfate solution required to reach the end point of the titration was 20.5 cm³.

1. Calculate the number of moles of iodine which reacted in the titration.
2. Calculate the concentration, in mol l⁻¹, of the ClO⁻ in the original household bleach.
3. Calculate the number of moles of iodine which reacted in the titration.

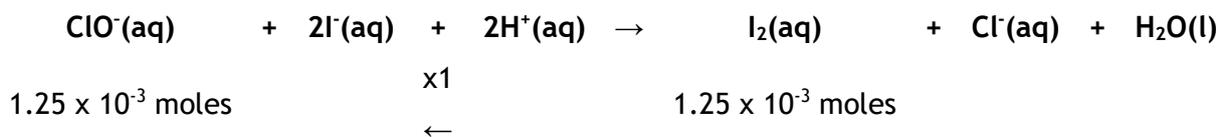
Number of moles of thiosulfate

$$\begin{aligned} & 2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^{\ominus}(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq}) \\ n &= CV \\ &= 0.1 \times 0.0205 \\ &= 0.00205 \text{ moles} \end{aligned}$$

Mole ratio to iodine



3. Calculate the concentration, in mol l⁻¹, of the ClO⁻ in the original household bleach.



$$0.001025 \text{ in } 25 \text{ cm}^3 \rightarrow 10 \times 0.001025 = 0.01025 \text{ in } 250 \text{ cm}^3$$

Original sample was 10 cm³

$$\begin{aligned} C &= \frac{n}{V} \\ C &= \frac{0.01025}{0.01} \\ C &= \underline{1.025 \text{ mol}} \\ & \quad \underline{\text{l}^{-1}} \end{aligned}$$

(p) Volumetric Analysis

The technique of volumetric analysis uses a solution of accurately known concentration (the standard solution) in a quantitative reaction to determine the concentration of another substance.

The following conditions must be satisfied:

- The reaction goes to completion.
- The stoichiometric equation is known
- A suitable indicator or method to show the end-point of the reaction is known.
- A reaction carried out in this way is a titration.

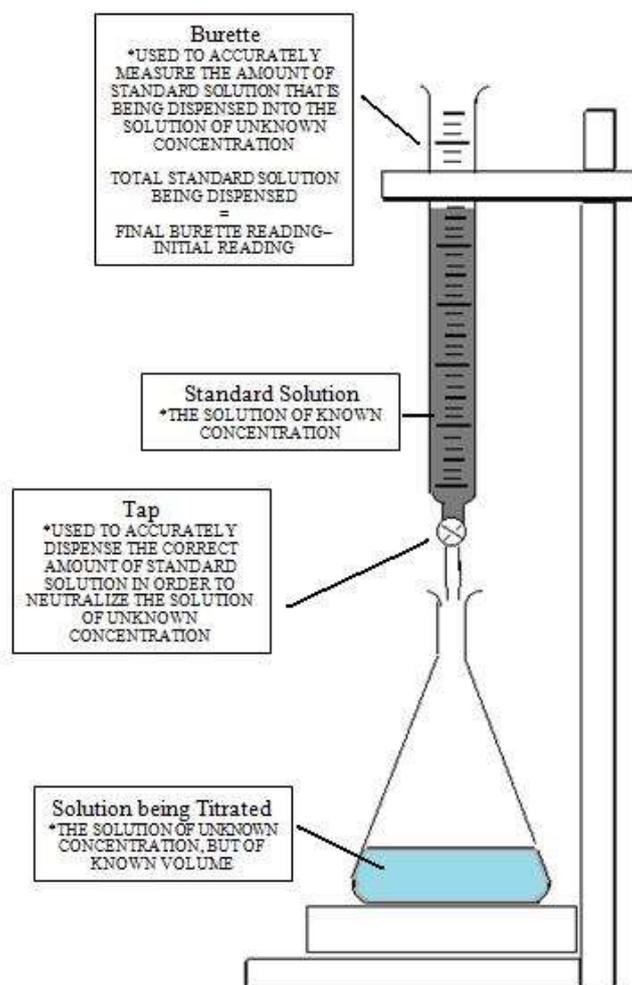
Correct Titration Procedure

A known volume of the solution of unknown molarity is pipetted into a clean titration flask, to which a few drops of suitable indicator are added. The burette is then filled with the solution of known molarity (standard solution) and the meniscus is set at zero, ensuring that the jet below the tap does not contain air.

A rough titration is carried out first. The titre is added 1cm^3 at a time whilst the solution in the flask is gently swirled. This will give an end-point in the range of 1cm^3 e.g. $25\text{-}26\text{cm}^3$.

The whole procedure is then repeated but this time approx 25cm^3 can be added at one time until the indicator changing colour marks the end-point.

This accurate titration is then repeated until concordant results are obtained and an average is calculated. Concordant results are within 0.1cm^3 of each other.



The advantages of this type of analysis are speed and accuracy.

Acid/Base Titrations

Acid/base titrations are neutralisation reactions and an indicator is always required. The choice of indicator is very important as it must cover the pH range over which the change takes place.

Redox Titrations

Redox titrations are based on redox reactions. The two most common systems in use are ones which use potassium permanganate and iodine as oxidising agents.

Using Potassium Permanganate

Potassium manganate (VII) - potassium permanganate is widely used in redox titrations as it can act as its own indicator. It becomes decolourised in a redox reaction and therefore is able to indicate the end-point. The colour change associated with KMnO_4 in a redox reaction is;

Purple → Clear (pale pink)

(MnO_4^- titrations are sometimes difficult to read due to the dark colour- remedied by reading top of meniscus rather than the bottom).

Using Iodine

Iodine will produce a blue/black colour in the presence of starch, it can therefore be used as an indicator.



Other systems used

Other oxidising systems used are cerium (IV) Ce^{4+} and more commonly dichromate $\text{Cr}_2\text{O}_7^{2-}$. The dichromate also acts as its own indicator as its colour changes from orange to green.

(q) Scientific Precision and Uncertainties

Precision: Refers to how well experimental data and values agree with each other in multiple experiments.

Precise Results

If experiments can be repeated several times and their values are numerically similar then your results are said to be precise.

If the same experimenter obtains these numerically similar values then the experimental procedure is said to be repeatable.

If a number of different experimenters obtain these numerically similar values then the experimental procedure is said to be reproducible.

Accuracy

The accuracy of a measurement is how close a result comes to the true value.

Determining the accuracy of a measurement usually requires calibration of an analytical method with a known standard.

Experimental errors arise as a result of;

- The limitations in accuracy in the apparatus being used.
- Limited or inexperience in the experimental technique being employed.
- Operational error.

Types of Errors

Systematic errors

An error repeated in each measurement made by the experimenter. This type of error can be considered in any calculation.

Random Errors

These are made by the experimenter. This type of error is minimised by repeated measurements and averaging.

Uncertainties

Uncertainty of measurements results from the scale or digital readings not being an exact or precise measurement.

Measuring Uncertainties

Equipment	Accuracy of Measurement
Digital Balance (one decimal place)	0.1g
Digital Balance (two decimal place)	0.01g
Digital Balance (three decimal place)	0.001g
Measuring Cylinders (25cm ³)	0.5cm ³
Graduated Pipette (25cm ³ grade B)	0.06cm ³
Burette (50cm ³ grade B)	0.1cm ³
Volumetric Flask (250cm ³ grade B)	0.3cm ³
Stopwatch (Digital)	0.01s (Reaction Time 0.09)
Thermometers (alcohol)	0.2 ^o C

$$\text{Percentage Error} = \frac{\text{Uncertainty}}{\text{Actual Measurement Made}} \times 100$$

Digital Balance

Consider measuring the mass of 1g of a substance

Digital Balance (one decimal places):

$$\% \text{ Error} = \frac{0.1}{1} \times 100 = \underline{10 \%}$$

Digital Balance (two decimal places):

$$\% \text{ Error} = \frac{0.01}{1} \times 100 = \underline{1 \%}$$

Digital Balance (three decimal places):

$$\% \text{ Error} = \frac{0.001}{1} \times 100 = \underline{0.1\%}$$

Consider measuring a 10g mass of substance using a digital balance to two decimal places

Digital Balance (two decimal places).

$$\% \text{ Error} = \frac{0.1}{10} \times 100 = \underline{0.01\%}$$

Consideration of the mass to be measured and the digital balance chosen to be used can have a major effect on the percentage error associated with this element of experimental work.

Volume

Measuring Cylinders:

25 cm³ using a 25 cm³ class B measuring cylinder

Class B measuring cylinders can be read to an accuracy of 0.50 cm³

$$\% \text{ Error} = \frac{0.50}{25} \times 100 = \underline{2.0\%}$$

Pipette:

Capacity	Uncertainty value	
	Class A	Class B
10 cm ³	±0.02 cm ³	±0.04 cm ³
20 cm ³	±0.03 cm ³	±0.06 cm ³
25 cm ³	±0.03 cm ³	±0.06 cm ³
50 cm ³	±0.05 cm ³	±0.10 cm ³
100 cm ³	±0.08 cm ³	±0.15 cm ³

Graduated pipette:

Measuring 25 cm³ using a 25 cm³ graduated class B pipette

25 cm³ graduated class B Pipettes can be read to an accuracy of 0.06cm³

$$\% \text{ Error} = \frac{0.06}{25} \times 100 = \underline{0.24\%}$$

Burettes:

Capacity	Uncertainty value*	
	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
50 cm ³	±0.05 cm ³	±0.10 cm ³

Measuring 25 cm³ using a 50 cm³ graduated class A burette

25 cm³ graduated class A burettes can be read to an accuracy of 0.05 cm³

$$\% \text{ Error} = \frac{0.05}{25} \times 100 = \underline{0.2 \%}$$

Measuring 25cm³ using a 50cm³ graduated class B burette

25cm³ graduated class B burettes can be read to an accuracy of 0.10cm³

$$\% \text{ Error} = \frac{0.10}{25} \times 100 = \underline{0.4 \%}$$

Consideration of the volume to be measured and the apparatus chosen to be used can have a major effect on the percentage error associated with this element of experimental work.

Volumetric Flasks:

Capacity	Uncertainty value	
	Class A	Class B
50 cm ³	±0.06 cm ³	±0.12 cm ³
100 cm ³	±0.10 cm ³	±0.20 cm ³
250 cm ³	±0.15 cm ³	±0.30 cm ³
500 cm ³	±0.25 cm ³	±0.50 cm ³
1000 cm ³	±0.40 cm ³	±0.80 cm ³

250cm³ graduated class B Volumetric Flasks can be read to an accuracy of 0.30 cm³

Percentage error associated with a 250 cm³ graduated class B volumetric flasks is;

$$\% \text{ Error} = \frac{0.30}{250} \times 100 = \underline{0.4 \%}$$

Time

Time often displayed to the nearest 0.01 s.

So for 10s

$$\% \text{ Error} = \frac{0.01}{10} \times 100 = \underline{0.1 \%}$$

Note

Reaction Time is the limiting factor in time measurements - Reaction Time quoted as 0.09 s.

So for 10s

$$\% \text{ Error} = \frac{0.09}{10} \times 100 = \underline{0.9 \%}$$

Temperature

Temperature measured using a school laboratory mercury/alcohol thermometer is usually measure to accuracy of 0.2 °C. (Student must determine the accuracy of the thermometer).

For a temperature of 20 °C

$$\% \text{ Error} = \frac{0.2}{20} \times 100 = \underline{1.0 \%}$$

For a temperature of 50 °C

$$\% \text{ Error} = \frac{0.2}{50} \times 100 = \underline{0.4 \%}$$

Note: The percentage error for this temperature change is $1.0 + 0.4 = 1.4\%$

Absolute Uncertainties - Combined Uncertainties

Addition and subtraction

For calculations involving addition and/or subtraction, we use the absolute uncertainties in the individual measurements and simply add them to obtain the overall absolute uncertainty.

Hence, for the calculation,

$$y = a + b - c$$

the absolute uncertainty in y is given by:

$$u_a + u_b + u_c$$

where u_a , u_b and u_c are the absolute uncertainties in the individual measurements a , b and c respectively.

e.g.

- mass of weighing bottle + sodium chloride = 18.54 g
- mass of weighing bottle = 12.32 g

From these data, calculate the absolute uncertainty in the mass of sodium chloride transferred from the weighing bottle.

A balance reading to two decimal places has obviously been used therefore the absolute uncertainty associated with each of the mass readings must be 0.01 g.

The mass of sodium chloride transferred from the weighing bottle is $18.54 - 12.32 = 6.22$ g and since the mathematical operation used to derive this result was a subtraction, then

$$\text{overall absolute uncertainty} = 0.01 + 0.01$$

$$\text{overall absolute uncertainty} = 0.02 \text{ g}$$

Thus,

$$\text{mass of sodium chloride transferred} = 6.22 \pm 0.02 \text{ g}$$

$$\% \text{ Error} = \frac{0.02}{6.22} \times 100 = \underline{0.32 \%}$$

Multiplication and Division

For calculations involving multiplication and/or division, we use the percentage uncertainties in the individual measurements. These are again added to give the overall percentage uncertainty in the result.

Hence, for the calculation,

$$y = \frac{a \times b}{c}$$

the percentage uncertainty in y is given by:

$$\%u_a + \%u_b + \%u_c$$

where $\%u_a$, $\%u_b$ and $\%u_c$ are the percentage uncertainties in the individual measurements a , b and c respectively.

e.g.

Using a class B pipette, 25.0 cm³ of 0.956 mol l⁻¹ hydrochloric acid was transferred into a 500 cm³ class B volumetric flask. The solution was made up to the graduation mark with deionised water.

Calculate the concentration of the diluted acid and its absolute uncertainty given that the absolute uncertainty in the 0.956 mol l⁻¹ hydrochloric acid is ± 0.005 mol l⁻¹.

$$\begin{aligned} \text{Concentration of diluted acid} &= \\ &= \frac{\text{concentration} \times \text{volume of undiluted acid}}{\text{volume of undiluted acid}} \end{aligned}$$

$$\text{Concentration of diluted acid} = \frac{0.956 \times 0.250}{0.5}$$

$$\text{Concentration of diluted acid} = \underline{0.0478 \text{ mol l}^{-1}}$$

You'll have noticed in this case that the calculation of the result involves the mathematical operations multiplication and division. So, to calculate the absolute uncertainty in the concentration of the diluted acid we need first to work out the percentage uncertainty in each of the individual measurements.

$$\text{absolute uncertainty in concentration of undiluted acid} = 0.005 \text{ mol l}^{-1}$$

$$\text{percentage uncertainty in concentration of undiluted acid} = \frac{0.005}{0.956} \times 100 = \underline{0.52 \%}$$

From table on page 42 we can see that the absolute uncertainty in a 25 cm³ class B pipette is 0.06 cm³.

Hence,

$$\text{absolute uncertainty in volume of undiluted acid} = 0.06 \text{ cm}^3$$

$$\text{percentage uncertainty in volume of undiluted acid} = \frac{0.06}{25} \times 100 = 0.24 \%$$

You may be wondering why we expressed the volume of undiluted acid in litres when calculating the concentration of the diluted acid and yet in working out the percentage uncertainty, this volume has been quoted in cm³. It's purely a matter of convenience - we could equally well have expressed the volume of undiluted acid in litres and had we done so, we would have arrived at the same percentage uncertainty, namely 0.24 %.

From the second table on page 43 we can see that the absolute uncertainty in a 500 cm³ class B volumetric flask is 0.50 cm³.

Hence,

$$\text{absolute uncertainty in volume of diluted acid} = 0.50 \text{ cm}^3$$

$$\text{percentage uncertainty in volume of diluted acid} = \frac{0.5}{500} \times 100 = \underline{0.1 \%}$$

The overall percentage uncertainty in the concentration of the diluted hydrochloric acid is gained by summing these individual percentage uncertainties.

Thus,

$$\text{percentage uncertainty in concentration of diluted acid} = 0.52 + 0.24 + 0.10 = 0.86\%$$