AH Chem Skills

1

Weighing By Difference

It is good practice to use a **weighing bottle** when weighing out samples of primary standards. There are various types and the one illustrated is a cylindrical glass container fitted with a ground-glass stopper.

- A clean dry weighing bottle is first weighed empty
- Using a spatula, a sample of the primary standard chemical of mass close to the calculated value is added to the weighing bottle.
- The accurate mass of the weighing bottle and its contents is then measured and recorded.
- The next step is to transfer the sample of the primary standard from the weighing bottle to a clean glass beaker containing some deionised water.
- Gentle tapping on the base of the weighing bottle will ensure that the bulk of the sample is transferred but it is unimportant if traces of the sample remain.
- Finally, the weighing bottle and any residual material are accurately weighed and the mass recorded.
- The accurate mass of the primary standard transferred is the **difference** between the two recorded masses.

Throughout the weighing process it is important that the stopper be removed from the weighing bottle only when necessary. This reduces the time the sample is exposed to the atmosphere and so minimises the chances of it readsorbing moisture.

AH Chem Skills
2

Preparation of a Primary Standard

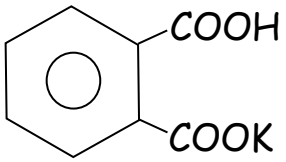
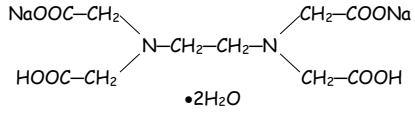
Characteristics of a Primary Standard

A **standard solution** is one of accurately known concentration and it can be prepared directly from a solute if that solute is a **primary standard**. To be suitable as a primary standard, a substance must meet a number of requirements.

- It must have a **high purity**. This is to ensure that the mass of the sample weighed out is composed entirely of the substance itself and nothing else. Were impurities present, then the true mass of the substance present would be less than the measured mass and this would lead to the solution having a concentration less than the calculated value.
- It must be **stable in air and in solution**. If this were not the case then some of the substance would be used up in reacting with chemicals in the air or with the solvent. As a result, the true concentration of the resulting solution would be less than its calculated value.
- It must be **readily soluble in a solvent** (normally water) and its solubility should be reasonably high so that solutions of relatively high concentrations can be prepared.
- It should have a **reasonably large relative formula mass** in order to minimise the uncertainty in the mass of substance weighed out.

As a result of these exacting criteria, there are a limited number of primary standards available. Some examples of acids, bases, oxidising, reducing and complexing agents used as primary standards are outlined in the following table.

Examples of Primary Standards

Type	Primary Standard	Formula
Acid	Hydrated oxalic acid	$(COOH)_2 \bullet 2H_2O$
	Potassium hydrogenphthalate	
Base	Anhydrous sodium carbonate	Na_2CO_3
Oxidising Agent	Potassium dichromate	$K_2Cr_2O_7$
	Potassium iodate	KIO_3
Reducing Agent	Sodium Oxalate	$(COONa)_2$
Complexing Agent	Hydrated Sodium salt of EDTA	

Good Practice in Preparation of a Primary Standard

Chemicals are supplied in various grades of purity but for analytical work **AnalaR** grade primary standards must be used. AnalaR grade *guarantees* high purity.

- sodium hydroxide is commonly used in quantitative analysis but is not used as a primary standard.
    - sodium hydroxide absorbs moisture from the air and dissolves in it to form a very concentrated solution
    - sodium hydroxide in both solid and solution form react with carbon dioxide in air.

This makes sodium hydroxide unstable in air and fails to meet the exacting requirements needed for a primary standard.

Calculate the mass of the primary standard required to give the volume and concentration of the primary standard solution needed.

- The sample of the primary standard must be dried in order to remove any traces of water that may have been adsorbed from the atmosphere. This is particularly important when using older samples of the substance. The water impurity can be removed by placing some of the substance in a crystallising basin and storing it in a desiccator for several hours.
- A **desiccator** is a closed vessel that contains a desiccant (a drying agent) in its base. Desiccants include:
    - phosphorus pentoxide,
    - anhydrous calcium chloride
    - concentrated sulfuric acid
    - self-indicating silica gel (most commonly used)
        - it is blue when dry and turns pink when it absorbs moisture.
- An airtight seal is maintained in the desiccator by lightly greasing the ground-glass surfaces on the lid and base.

Alternatively, primary standards can be dried by heating, although this runs the risk of them decomposing if too high a temperature is used.

- Once the primary standard is dry, the next step in the procedure is to weigh out accurately the approximate mass of substance you need to make the desired solution.
- The words 'accurately' and 'approximate' may sound ambiguous but what it means is that while the mass of the sample of primary standard has to be known accurately, it doesn't need to be exactly that calculated – just close to it.

It is good practice to use a **weighing bottle** when weighing out samples of primary standards. There are various types and the one illustrated is a cylindrical glass container fitted with a ground-glass stopper. The weighing Technique described in Skill 1 previously is used to transfer an exact mass of a substance used as the primary standard.

A balance reading to 0.01 g should be adequate in weighing out samples of primary standards but if greater accuracy is required then a balance reading to three decimal places should be used.

With the sample of the primary standard successfully transferred to the beaker of deionised water, the mixture can be stirred to aid dissolving.

- A glass rod should be used for this purpose and not a spatula since the latter may react with the solution and so contaminate it.
- On removing the stirring rod, make sure that any solution on its surface is washed back into the beaker. A wash bottle can be used to achieve this.

Once the primary standard has dissolved, the resulting solution is carefully poured into an appropriately sized standard (volumetric) flask via a filter funnel placed in the neck of the flask.

- Both the flask and the funnel must be clean but neither need be dry just so long as they are wet with deionised water.
- Using a wash bottle, the interior surface of the beaker should be washed with deionised water and the washings transferred to the flask.
- The washing process should be repeated at least two more times to ensure that all the primary standard has been transferred to the flask.
- Deionised water is then added directly to the flask until the level of the solution is within about 1cm of the graduation mark.
- With the funnel removed, deionised water is carefully added from a dropper until the bottom of the meniscus is level with the graduation mark.
    - During this last operation, a white tile or a piece of white paper should be held behind the neck of the flask so that the meniscus can be seen more clearly.
    - The graduation mark must be at eye level in order to avoid error due to parallax.
- The standard flask should then be stoppered and inverted several times to ensure the solution is thoroughly mixed and is of uniform concentration.
- The solution of the primary standard should finally be transferred to a clean, dry reagent bottle.
    - If the reagent bottle happens to be wet with deionised water, then it must first be rinsed with a little of the standard solution before the bulk of the solution is transferred to it. Were it not rinsed, then the solution would be diluted by the water, making its true concentration slightly less than its calculated value.

Use of Primary Standards in Calculation of Unknown Concentrations

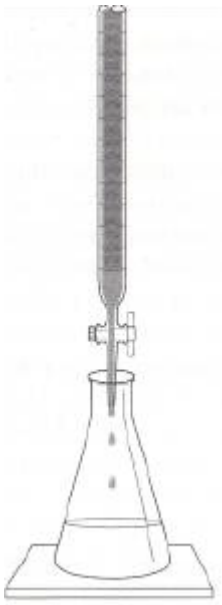
Once a standard solution has been prepared, it can be used to determine the accurate concentration of another solution. This is achieved by **titration** – a procedure whereby one of the solutions is slowly added from a burette to a pipetted volume of the other solution contained in a conical flask. The point at which reaction between the two is just complete is usually detected by adding a suitable indicator to the solution in the flask.

- It is customary, although not essential, to have the standard solution in the burette and the solution of unknown concentration, often referred to as the analyte, in the conical flask.

The practical aspects of a titration are detailed below.

- A clean burette has first to be rinsed with a small portion of the standard solution. This involves tilting the burette almost to a horizontal position and rotating it to make sure the standard solution 'wets' the entire inner surface.
- The burette tip is rinsed by draining the solution through it. It is good practice to repeat the rinsing procedure at least one more time – this ensures that all impurities adhering to the inner surface are washed away.
- The burette is then filled with the standard solution up to the region of the zero mark and the tip is filled by opening the tap for a second or two.
- Transfer a fixed volume of the solution of unknown concentration to a clean conical flask. A rinsed pipette is used.
    - draw a small volume of the analyte solution into the pipette and wetting its inner surface by tilting and rotating it. The 'rinse' solution is allowed to drain through the tip and discarded.
- After repeating the rinsing procedure, the pipette is filled with the analyte solution to a point above the graduation mark. With the pipette held vertically and with the graduation mark at eye level, the solution is allowed to slowly drain from the pipette until the bottom of the meniscus coincides with the graduation mark.
    - Holding a white tile or a piece of white paper behind the stem of the pipette defines the meniscus more clearly.
- With the pipette tip placed well within the conical flask, the analyte solution is run into the flask. When free flow ceases, the tip should be touched against the inner wall of the flask to allow the remaining solution to drain. A few drops of the appropriate indicator are then added to the analyte solution in the flask.
- If the conical flask is wet with deionised water prior to adding the analyte solution to it the solution would be diluted, the number of moles of analyte would be unchanged and this is the critical factor in the calculation
- Before reading the burette, its vertical alignment should be checked both from the front and the side.
    - With a white tile behind the burette and with the eye level with the top of the standard solution, the burette is read from the bottom of the meniscus and the reading recorded.
    - If the solution is dark and coloured, the bottom of the meniscus may not be clearly visible, in which case the reading is taken from the top of the meniscus.

- In reading a burette, it is important that the filter funnel used to fill it has been removed. If it were left in place, some drops of solution could drain from it during the titration, leading to a false titre volume.
- The conical flask containing the analyte solution and indicator is placed underneath the burette, making sure that the tip of the burette is well within the neck of the flask. It is also good practice to have a white tile underneath the flask so that the colour change at the end-point can be seen more clearly.

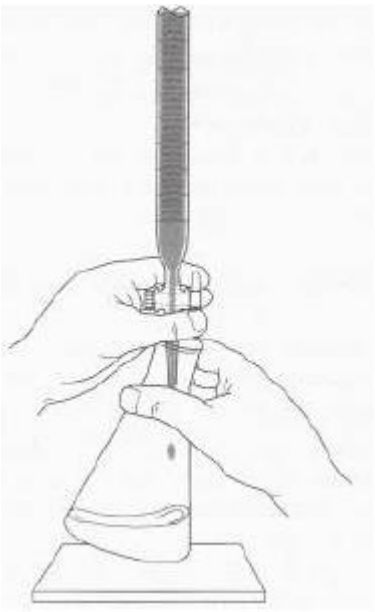


The first titration is usually a rough one and its purpose is to see what the colour change is and to provide an approximate titre volume. In this rough titration, portions of the standard solution, about $1cm^3$ at a time, are run from the burette into the conical flask. During and after the addition of each portion, the contents of the flask should be swirled – this helps the mixing process and gives the reactants time to react.

- These $1cm^3$ additions are continued until the end-point is reached. The final burette reading can then be recorded.
- If the end-point proves difficult to assess, it is worthwhile keeping this rough titrated mixture to aid the detection of end-points in subsequent titrations.

A second but more accurate titration is then performed. A portion of the analyte solution is pipetted into a clean conical flask along with a few drops of indicator. The burette is refilled with the standard solution and the initial reading is recorded.

- Suppose the rough titre volume had been $20cm^3$ then in the second titration it would be safe to add about $18.5cm^3$ of the standard solution without any danger of over-shooting the end-point.
    - Care must be taken to ensure that the rate of delivery is not too fast otherwise the burette may not drain cleanly, leaving drops of solution adhering to the walls of the burette, which in turn would lead to an inaccurate titre volume.
- The titration is completed by adding the standard solution very slowly, drop by drop, while vigorously swirling the contents of the flask. The end-point of the titration is finally reached when the indicator just changes colour.
- The final burette reading should then be recorded.
    - During the titration, should any of the standard solution splash onto the walls of the conical flask then wash it into the mixture with deionised water from a wash bottle. If near the endpoint, you find a drop of the standard solution hanging from the tip of the burette, remove it by touching the tip to the wall of the flask and washing it into the solution.
- The titrations are then repeated until concordant results, i.e. two consecutive titre volumes that are within $0.1cm^3$ of each other, are obtained.



To carry out a titration quickly and efficiently, the recommended method of adding the solution from the burette to that in the conical flask is illustrated below.

- The burette tip is manipulated with the left hand and this leaves the right hand free to swirl the contents of the conical flask as the burette solution is added.
- This technique is likely to feel awkward and clumsy at first but with practice it will become second nature to you.
- Ideally what we try to obtain in a titration is the **equivalence** or **stoichiometric** point.
    - This occurs when the quantity of reagent added from the burette is the exact amount necessary for stoichiometric reaction with the amount of reagent present in the conical flask.
    - In practice, what we actually measure in a titration is the **end-point** and not the equivalence point and there is a subtle difference between the two.

To illustrate the difference, consider the following permanganate/oxalate titration for which the stoichiometric equation for the titration reaction is:

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

Up to and including the equivalence point all the permanganate ions added from the burette are consumed by the oxalate ions in the conical flask and the flask solution remains colourless.

- It is the first trace of a permanent pink colour that marks the end-point of the titration and for this colour to be exhibited extra permanganate ions, beyond those needed to react with the oxalate ions, are required.
- This means the end-point overshoots the equivalence point very slightly and hence the end-point of a titration can never coincide with the equivalence point.

AH Chem Skills
3

Understanding Role of a Control/Blank

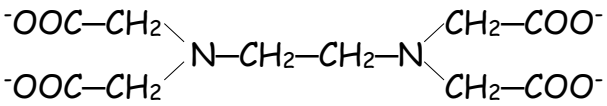
AH Chem Skills

4

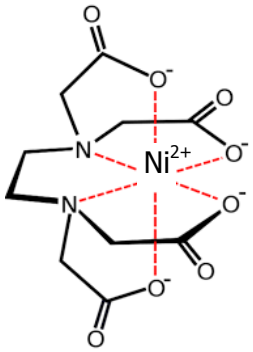
Complexometric Titration

The three main titration types are:

- **acid-base titrations** in which the titration reaction is simply a neutralisation in which H^+ ions are transferred from the acid to the base
- **redox titrations** in which an oxidising agent is titrated against a reducing agent or vice versa
- **complexometric titrations**, which are based on the formation of a complex, i.e. a reaction between metal ions and ligands
    - the ligand molecules or ions use their lone pairs of electrons to bind with metal ions.
    - The most common ligand or complexing agent used in complexometric titrations is **e**thylene**di**amine**te**traacetic **a**cid In alkaline conditions, EDTA has the structure shown above.



The EDTA ion is a hexadentate ligand and forms 1:1 complexes with metal ions. Nickel(II) ions react with EDTA ions to form a complex with the with the octahedral structure shown:



AH Chem Skills
5

Back Titration & Calculation

Most titrations are **direct**, i.e. one reagent is added directly to the other until the end-point is reached. In some situations, however, a direct titration may not be possible, in which case we have to resort to a technique known as a **back titration**.

- This involves adding a known but excess amount of one standard reagent to a known mass of the substance being determined (the analyte).
- After reaction between the two is complete, the excess amount of the standard reagent is determined by titration against a second standard reagent.

Back titrations are used when:

- no suitable indicator is available for a direct titration
- the end-point of the back titration is clearer than that of the direct titration
- the reaction between the standard reagent and analyte is slow
- the analyte is insoluble.

If we wished to determine the percentage calcium carbonate in a sample of impure marble, back titration must be used here since marble is insoluble in water.

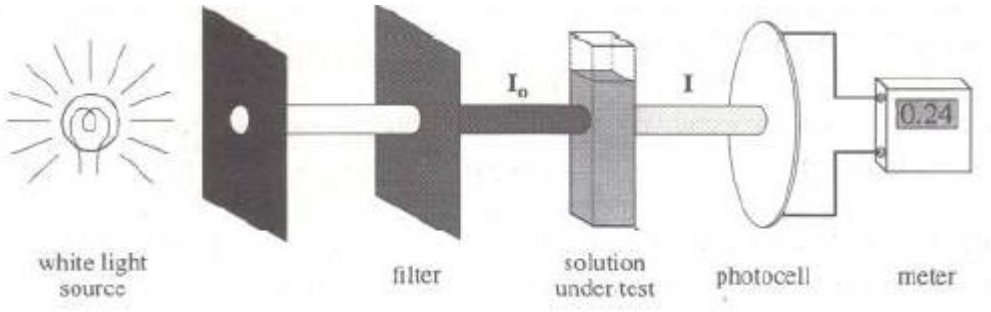
- In practice, a sample of the marble of accurately known mass is treated with a definite amount of hydrochloric acid (the volume & concentration of the acid are accurately known)
- An excess of acid is used and the amount of acid remaining after neutralising the calcium carbonate is determined by titrating the remaining acid against a standardised solution of sodium hydroxide.
- The difference between the initial and excess amounts of hydrochloric acid allows the calculation of how much acid reacted with the marble
- knowledge of the stoichiometry of the calcium carbonate/hydrochloric acid reaction allows the percentage calcium carbonate in the marble sample can be calculated.

Colorimetry

As well as volumetric and gravimetric methods of analysis, there are numerous others that rely on the use of instruments to measure some physical property of the analyte. **Colorimetric analysis** is one such instrumental method. As the name implies, it is used to determine analytes that are **coloured** or can be converted quantitatively into coloured species.
We work with solutions in colorimetry and so it is the concentration of the coloured species in the solution that we wish to determine.
A solution will be coloured if it absorbs some, but not all, wavelengths of the white light passing through it. Those wavelengths that are not absorbed are transmitted through the solution and combine to give the colour we see.

- For example, if a solution absorbs the blue wavelenghts of white light then the light that is transmitted appears yellow (yellow is formed from red and green wavelengths)

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, i.e. 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 from the bulb is first passed through a coloured filter. This can be a piece of coloured glass or a film made of plastic or gelatine that has been impregnated with a dye. Filters come in a range of colours, so how do we decide which one to use? The filter colour must correspond to the colour of light that is **most strongly absorbed** by the solution being analysed.

- If the analyte is an aqueous permanganate solution, it has a purple colour because it absorbs mainly green wavelengths of light (due to the mixing of the remaining red and blue wavelengths)
- When analysing permanganate solutions, the filter used should be green.
- As the beam of white light passes into the green filter only green wavelengths are transmitted and the remaining wavelengths are *filtered* out, i.e. absorbed by the filter.
    - In practice, the filter allows through a narrow band of wavelengths of green light, typically a band of wavelengths covering 40 nm.
- The green light emerging from the filter has an intensity of $\mathbf{I_0}$.
- As it passes through the purple permanganate solution some of it is absorbed and that transmitted will have a lower intensity, namely **I**.

- The transmitted light strikes the 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 by a solution and is related to the intensities of the incident light (I_o) and transmitted light (I) by the relationship:

$$A = \log\frac{I_o}{I}$$

The absorbance (A) is proportional to the concentration of the solution (c) and for **dilute** solutions there is a direct relationship between the two, i.e.

$$\mathbf{A = kc}$$ where k is a constant.

This means that as the concentration of a solution increases, its absorbance increases linearly. To determine its concentration of a solution of potassium permanganate.

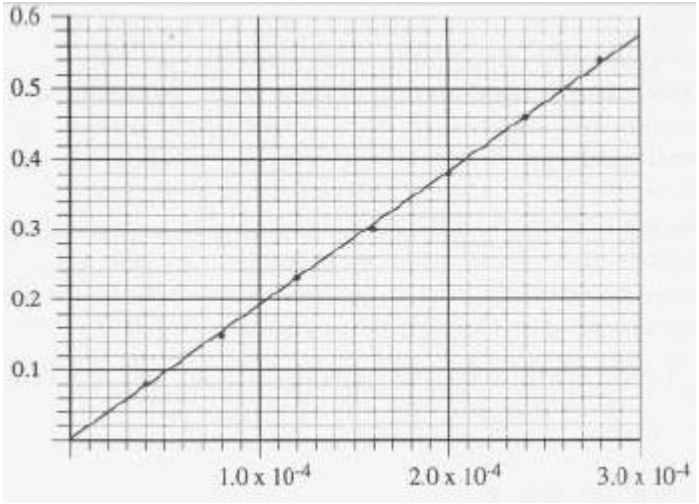
- The colorimeter has first to be calibrated. This is achieved by preparing a series of permanganate solutions of known concentrations by the accurate dilution of a standard permanganate solution.
- The absorbance values of these standard solutions are measured
    - Since permanganate solutions are purple in colour, a green filter is required since green is purple's complementary colour.
    - If more than one green filter is available then the one that gives **maximum absorbance** for the test solution should be selected.
    - Had you not known that green is purple's complementary colour, then you would need to measure the absorbance of the test solution with each of the available coloured filters and choose the one that gave **maximum absorbance**.
- The solution samples are held in containers called **cuvettes** or **cells**. They must be constructed from a material that does not absorb visible radiation – colourless plastic or glass is suitable.

    - Cuvettes come in various shapes but those that have flat faces are preferred to cylindrical ones since they have less tendency to scatter light. A typical cuvette is shown right
    - Two of the opposite faces of a cuvette are ribbed and only these faces should be touched when the cuvette is handled.
- In placing the cuvette in the colorimeter, it is vitally important to make sure that the beam of light emerging from the filter passes through the transparent non-ribbed faces otherwise most of the light would be scattered, which would cause significant error in the absorbance reading.
- It is also important that each time a cuvette is placed in its holder it has exactly the same orientation and is not turned through 180°. This is why some cuvettes, like the one shown, have a mark etched on one of their faces.
- Normally in a colorimetric analysis two cuvettes are used: one for the analyte solution and one for the solvent. They must be optically matched, i.e. have identical absorbing and scattering characteristics so that the difference in absorbance value of the two liquids is entirely due to the analyte and not to the cuvettes.
- If reliable data are to be obtained from a colorimetric analysis, it is critical that the cuvettes are scrupulously clean and handled with extreme care. Any scratches, finger-

marks or other deposits on the transparent faces of a cuvette will scatter and absorb light and result in false absorbance readings.

- One of the optically matched cuvettes is thoroughly rinsed and filled with deionised water (solvent) – this is known as the 'reference' or 'blank'. It is not necessary to fill the cuvette right to the top and risk spillage but sufficient must be added to ensure that the water level will be above the light beam when the cuvette is placed in the colorimeter.
    - At this stage you should check that no solid particles are suspended in the water and that no bubbles of air are present – these would cause serious error since they would scatter light.
- After carefully wiping the transparent faces with a soft tissue, the cuvette is placed in its holder. The colorimeter is then adjusted to give an absorbance reading of zero.
    - In some colorimeters this is done automatically. The reference is removed from the colorimeter but not discarded.
- A second optically matched cuvette is thoroughly rinsed and filled with one of the standard permanganate solutions. It is then prepared and checked in exactly the same way as was the reference. It is placed in the colorimeter and the absorbance measured and recorded.
- Using the same cuvette, the absorbance values of the remaining standard permanganate solutions and the unknown are determined.
- Since most colorimeters are liable to 'drift', it is good practice to re-zero the instrument with the reference in place before measuring the absorbance of each permanganate solution.

The absorbances of the standard permanganate solutions are then plotted against concentration to generate a calibration graph:

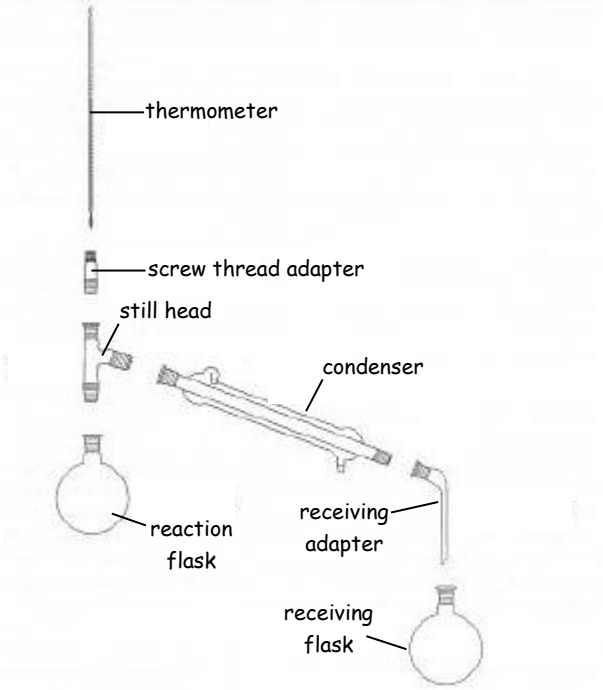


The fact that this is a straight-line plot confirms that, for dilute solutions, absorbance is directly proportional to the concentration of the absorbing species.

Suppose our unknown permanganate solution had an absorbance value of 0.24. We can interpolate from the calibration graph that it must have had a concentration of 1.25×10^{-4} mol l^{-1}. If the absorbance of the unknown had been found to lie outwith the range of the standard solutions, then it must be accurately diluted and its new absorbance measured. Using the calibration graph, the concentration of the diluted solution can be found and then multiplied by the dilution factor to give the concentration of the original solution.

Distillation

If the desired product is present as a **liquid** in the reaction mixture and it is more volatile than the other substances in the mixture, then it is possible to isolate it by **simple distillation**.
The individual items required for such an operation are illustrated and identified in the diagram.
As in the preparation stage, the liquid mixture should occupy about half the volume of the round-bottomed distillation flask.



- The apparatus is then assembled as in the diagram with the distillation flask sitting in a heating mantle and some fresh anti-bumping granules added to the mixture.
- The receiver adapter does not fit tightly into the receiving flask and the receiving flask is open to the atmosphere.

For the accurate measurement of temperature, it is important that the thermometer is positioned correctly.

- It should be arranged such that the top of the bulb is level with the bottom of the still head's side arm.
- The rubber tubing on the lower end of the condenser is attached to the cold-water tap and water is allowed to circulate.
- Before heating commences, the apparatus must be checked to ensure that it is firmly clamped and that all the joints are tight apart from the point where the receiver adapter enters the receiving flask.

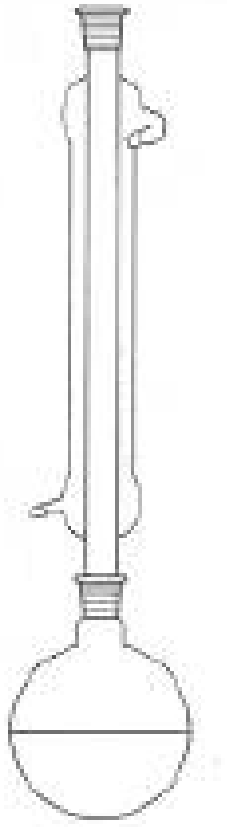
The heating mantle is switched on and the mixture is slowly distilled. Only the liquid that distils over within a certain temperature range should be collected in the receiving flask. The temperature range will be specified in the procedure but it will encompass the temperature at which the pure product boils.
The range is also likely to be wide (20°C or so) to make sure that the maximum amount of desired product is isolated from the mixture.

- If the liquid product is particularly volatile, it is good practice to place the receiving flask in an ice/water bath and to ensure the receiver adapter on the condenser extends well into the flask. Such measures ought to minimise loss of product through evaporation.

There is one slight drawback in using boiling point to characterise our liquid product and it arises from the fact that boiling point varies with atmospheric pressure. The deviation between the observed boiling point and its true value can be quite significant – up to several degrees. Consequently, the number of compounds having a boiling point in the vicinity of the observed value could be very large. However, they are unlikely to be produced in the reaction and so most, if not all, of them can be eliminated.

Heating Under Reflux

As the reaction mixture heats up the more volatile components will boil and their vapours will rise into the condenser. There, they will be cooled, liquefied and returned to the reaction flask. The purpose of the condenser is to prevent the escape of any volatile reactants or products from the apparatus. The operation of boiling a reaction mixture and condensing the vapours back into the reaction flask is known as **heating under reflux** or more commonly as **refluxing**.



- When a reaction mixture is being heated, there is a tendency for it to boil violently as large bubbles of superheated vapour suddenly erupt from the mixture.
- This phenomenon is known as **bumping** and it can be prevented by the addition of a few **anti-bumping granules** to the reaction mixture.
    - They are normally made from pieces of alumina (aluminium oxide) or carborundum (silicon carbide) and have an air-filled porous surface that promotes the formation of a steady stream of tiny bubbles instead of a few large ones.
    - Anti-bumping granules must always be added before heating begins because adding them to a hot mixture is likely to cause it to froth over.
    - If the preparation requires the reaction mixture to be cooled and reheated, then fresh anti-bumping granules must be added before reheating commences. This is because when boiling stops, liquid is drawn into the pores of the granules and renders them ineffective.
- Once the reaction is complete, the heating mantle is switched off and the reaction mixture is allowed to cool. During this time, the condenser must remain in place and the cold water must be kept circulating, otherwise the product may escape from the top of the condenser.
- Sometimes, organic preparations require the addition of a reactant during the course of the reaction. If this is the case, then a two- or three-necked roundbottomed flask can be used, with the reactant being added from a dropping funnel placed in a side neck.

AH Chem Skills
9

Vacuum Filtration Methods

After the preparation stage of a synthesis experiment has been completed, there will often be a bewildering mixture of substances in the reaction flask. Along with the desired product, the mixture is likely to contain:

reactants that were used in excess	other products of the reaction	compounds that are produced as a result of side-reactions	the limiting reactant if the reaction was a reversible one.

The next step in the overall process is to **isolate** or **separate** the compound we set out to prepare from the other components of the mixture. If the desired product is present as a **solid**, then **filtration** provides a fast and convenient way of separating it. This is normally carried out under reduced pressure, which is why the technique is often referred to as **vacuum filtration**. This type of filtration is performed with the aid of a Buchner funnel and flask or Hirsch funnel and filter tube and which is used depends on the amount of solid to be filtered.

Buchner funnel

flask

Hirsch funnel

filter tube

The Buchner and Hirsch funnels each have a plate incorporated in their base that is perforated by a number of small holes.

- The **Buchner flask** is simply a thick-walled conical flask with a short side arm
- the **Hirsch filter tube** is a side-armed pyrex test-tube. The funnel is fitted into the neck of the flask or filter tube by means of a rubber stopper and the flask or filter tube is attached to a water pump via its side arm.

Before filtration, a filter paper is placed on the perforated plate – it should be of such a size that it sits flat on the plate and covers all the holes.

- The filter paper is moistened with a few drops of the liquid present in the mixture and the water pump is turned on. This ensures that the filter paper adheres firmly to the perforated plate and in the subsequent filtration will prevent any solid matter from passing round and under the edge of the paper into the flask.
- The mixture can now be filtered and it is added to the funnel in portions. If the solid is finely divided, then transfer of the bulk of the solid should be delayed to near the end of the filtration, otherwise the pores in the filter paper will become clogged and cause the rate of filtration to slow down.

Inevitably some of the solid product will remain in the reaction flask and if we are to gain maximum yield, it needs to be in the funnel. To do this, some of the filtrate is returned to the reaction flask and the mixture is stirred or swirled and quickly poured into the funnel. This operation is repeated until all the solid is transferred. The product is then washed with two or three portions of a suitable liquid to remove the bulk of the impurities adhering to its surface. The suitable liquid obviously must not dissolve the solid. The product is partially dried by having air drawn through it for several minutes. The crude sample is then ready for purification.

AH Chem Skills
10

Recrystallisation

No matter whether the product was isolated from the reaction mixture by filtration, simple distillation or solvent extraction, it is highly unlikely that the separation would be 'clean'.

- impurities will still be present and these require to be removed from the sample
- method used to purify the product sample depends on its state (solid or liquid)

The simplest and most widely used technique of purifying an organic solid is **recrystallisation**.

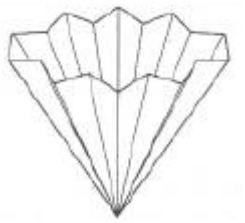
- In a typical recrystallisation procedure, the crude or impure solid is dissolved, by heating, in the minimum volume of a suitable solvent.
- The hot saturated solution that is formed is filtered and allowed to cool, whereupon the solid crystallises out.
- The crop of pure crystals can then be filtered off, leaving the bulk of the soluble impurities in the filtrate or **mother-liquor** as it is more often called.

The success of the recrystallisation process depends largely on the choice of solvent.

- The substance to be purified must not react with the solvent.
- The substance should have a high solubility in the hot solvent and be virtually insoluble in the cold solvent.
- The impurities should, ideally, be completely insoluble in the hot solvent
    - impurities will then be removed when the hot solution is filtered
- Alternatively, the impurities should be completely soluble in the cold solvent
    - impurities remain in the *mother-liquor* and can be separated from the pure solid in the second filtration when the solution is cooled and the pure solid crystallises out.

Solid Recrystallisation Method

- The crude solid is carefully transferred to a clean conical flask.
- A small volume of solvent – sufficient to just cover the solid – is added together with a couple of anti-bumping granules.
- The flask should then be placed on a hot plate and the mixture gently heated until it boils. A hot plate is used since the solvent is likely to be flammable.
- If the solid hasn't all dissolved, then a little more solvent should be added and the mixture heated to boiling once again.
- This process is repeated until all the solid dissolves and then a little excess solvent is added to keep it in solution. Some impurities may be completely insoluble and so care must be taken not to add too much solvent in attempting to dissolve them.
- The next stage in the process is to filter the hot solution through a **'fluted' filter paper**, supported in a glass filter funnel, into a second conical flask.
    - This removes insoluble material – things like dust particles, anti-bumping granules and insoluble impurities. A fluted filter paper is used since it provides a much larger surface area than the usual filter paper cone and makes for a faster filtration.



- Prior to filtering the hot solution, the fluted filter paper, glass funnel and conical flask should be warmed to reduce the risk of crystals separating out on the filter paper and in the stem of the funnel.
- This can be done by heating the filtration equipment in an oven or by adding a little solvent to the conical flask and placing the equipment on a hot plate – as the solvent boils and refluxes, the flask, funnel and filter paper are heated.
- The hot solution is quickly poured through the pre-heated filtration apparatus and provided the operation has been carried out successfully, no crystals should appear at this stage. If they do appear on the filter paper or in the funnel stem, then they must be scraped back into the first flask, re-dissolved and re-filtered. Should any crystals be present in the filtered solution, the flask should be placed back on the hot plate and reheated to dissolve them.
- Once a clear filtered solution has been obtained it is set aside and left undisturbed until it slowly cools to room temperature.
- While it is cooling, the flask should be covered with a watch glass or filter paper to keep out dust particles. Slow cooling of the saturated solution is necessary to promote the formation of **pure** crystals. This is because crystallisation is a selective process and only molecules of the correct shape fit into the growing crystal lattice. Molecules of impurities will have a different shape and won't fit the lattice and as a result they remain dissolved in the mother-liquor.
- If the saturated solution cooled too quickly then the molecules of impurities become surrounded and trapped within the crystals. Not only does the rate of cooling control the purity of the crystals, it also dictates their size: the slower the rate of cooling the larger and purer will be the crystals.
- When the solution has cooled completely, and this could take up to an hour, a good crop of crystals should have appeared in the flask. If none appears then it may be that the solution is not saturated, i.e. too much solvent has been used in the recrystallisation

process. In such a case, some of the solvent can be boiled off in order to concentrate the solution and this can be re-cooled.

- If crystallisation still doesn't occur, there are a number of tactics available to induce the process. One way is to cool the saturated solution by placing the flask in an ice/water bath or in a fridge.
- Alternatively, a minute amount of the crude material or pure compound (if it is available) can be added to the saturated solution. The tiny particles of solid serve as nuclei around which the crystals can grow.
- This method is known as **seeding** and the solid particles that are added are referred to as **seed crystals**.
- Yet another way of inducing crystal formation is to scratch the inside wall of the flask at the liquid surface using a glass rod. The tiny particles of glass that are dislodged act as nuclei for crystal growth.
- When crystallisation is complete, the mixture of crystals and mother-liquor is filtered at the water pump, using a Buchner funnel and flask or Hirsch funnel and filter tube. The crystals are then washed with a small portion of ice cold solvent to remove traces of mother-liquor from their surfaces.
- With the water pump still running, air is drawn through the crystals to dry them partially.
- After transferring the crystals to a pre-weighed clock glass, drying can be continued in an oven at a temperature of at least 20°C below the expected melting point. However, under these conditions many organic solids have a tendency to sublime and so it is probably safer to dry the crystals at room temperature but in a desiccator containing anhydrous calcium chloride or silica gel.
- Once dry, the crystals and clock glass are reweighed.
- This is necessary so that the percentage yield of product can be calculated.

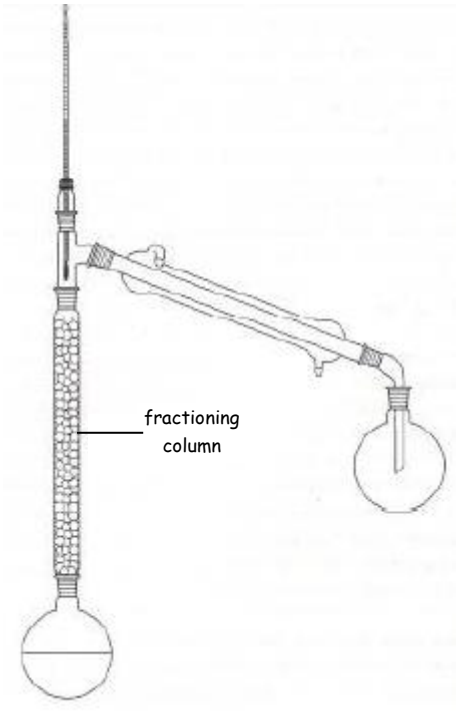
A second crop of crystals can often be extracted from the mother-liquor.

- This is achieved by transferring the mother-liquor from the Buchner flask or filter tube to a conical flask and heating it on a hot plate to drive off about half the solvent.
- On cooling the saturated solution, crystallisation takes place and the crystals are isolated by filtration and washed and dried in the usual way.
- Although the second crop of crystals may not be quite as pure as the first, the advantage of taking a second crop is that the percentage yield will be boosted.

Liquids Method

In a **liquid** product, the most common impurity present is generally water

- The water impurity can be removed using a **drying agent**
    - anhydrous calcium chloride
    - anhydrous magnesium sulphate
- In practice, a small amount of the powdered or granular drying agent is added directly to the crude liquid sample contained in a conical flask.
- The mixture is initially swirled and then left to stand for 10–15 minutes.
- If at this point the liquid is completely clear with no hint of cloudiness then we can assume that the product has been successfully dried.
- The liquid is separated from the drying agent by decanting it or filtering it into a round-bottomed flask.
- The sample is now ready for further purification by **distillation**. The type of distillation to be performed will depend largely on the nature of the remaining impurities and in particular their **volatility**.
    - If they are much less volatile than the desired product then a **simple distillation** will suffice.
    - A few anti-bumping granules are added to the liquid sample in the roundbottomed flask and the apparatus assembled, making sure that the bulb of the thermometer is correctly positioned.
    - Cold water is allowed to circulate through the condenser and the heating mantle is switched on.
- The rate of heating should be adjusted so that the liquid boils gently and the distillation rate is slow – about one or two drops per second.
- The liquid, which distils within a narrow temperature range (about 5°C) that embraces the boiling temperature of the pure product, is collected in a pre-weighed receiving flask.
- The flask and purified product are then reweighed. To minimise loss of product through evaporation the usual precaution of placing the receiving flask in an ice/water bath should be taken.
- If the impurities in the crude liquid sample are volatile then **fractional distillation** rather than simple distillation must be carried out. The procedure is identical to that described above but the apparatus differs slightly in that a **fractionating column** is inserted vertically between the distillation flask and the still head.



- There are various types of fractionating column but the one shown is packed with lots of tiny glass beads. Fractional distillation is a much more effective way of ridding a liquid product of impurities than simple distillation. The liquid mixture goes through a multi-step distillation as it rises up the fractionating column and a much 'cleaner' separation of the components takes place.

AH Chem Skills 11

Determination of Percentage Yield

An organic preparation is incomplete unless the **percentage yield** of pure product has been calculated and reported. Percentage yield is defined as:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

- The actual yield (often shortened to yield) is the mass of pure product obtained in the reaction
- The theoretical yield is the maximum mass that might have been expected
    - Calculated from knowledge of the stoichiometric equation for the reaction and the mass of the limiting reactant, i.e. the one that is not in excess.

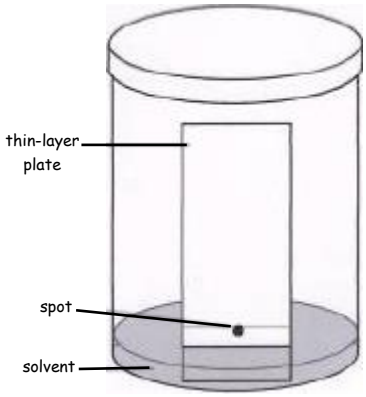
The percentage yield always falls short of 100% but there are many good reasons for this:

- The reaction may be **reversible**, in which case a state of equilibrium will be reached.
    - While we'll never get 100% conversion of reactants into products in a reversible reaction, some tactics can be adopted to maximise the yield
    - We could ensure that the other reactants are used in large excess compared to the limiting one
    - It may be possible to add a reagent that reacts with one of the products.
    - Both measures would encourage the equilibrium position to move to the right and so improve the yield of product.
- **Side reactions** of many kinds may occur
    - The limiting reactant undergoes other reactions in addition to the desired one.
    - Formation of a side product inevitably reduces the yield of the main product
- **Mechanical loss** of the product is likely to occur.
    - During isolation and purification, the product may be transferred from one container to another on numerous occasions
    - some of the product will fail to reach the final container
    - Product loss will also occur in recrystallisation since some will remain in the mother-liquor.
    - Loss can also occur through evaporation and this would be the case if the product was a volatile liquid.
    - While mechanical loss of product cannot be eliminated, good experimental technique will minimise it.

AH Chem Skills
12

Thin-Layer Chromatography

Another powerful tool that is commonly used in identifying a compound is **thin-layer chromatography** (TLC). TLC, like all chromatography techniques, depends 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 pencil line is lightly drawn about 1cm from the bottom of the plate and a small amount of the substance being analysed is dissolved in about $2cm^3$ of a volatile solvent such as propanone or dichloromethane.
- Using a capillary tube, some of this solution is spotted onto the centre of the pencil line and left to dry. This should be repeated two or three more times. It is important that the final spot should be about 1–2 mm in diameter.
- Once the spot is dry the plate is placed in a closed chamber with the lower edge (near the applied spot) immersed in a shallow layer of solvent, i.e. the mobile phase.
    - It is important that the solvent level is below the line with the spot on it
    - The chamber is closed completely to ensure 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.
- The thin-layer plate is removed from the chamber when the solvent front is about 1cm from the top of the plate.
- The position of the solvent front is marked immediately with a pencil before the solvent evaporates.
- The plate should then be left to dry in a fume cupboard.
- If the substance is colourless then its final position on the plate will not be seen but there are a few ways in which this problem can be overcome.
    - One way is to use a plate impregnated with a fluorescent indicator and then expose it to UV light. The plate will glow apart from the spot where the substance is and this can be marked by drawing a pencil circle around it.
    - In another method the dried plate is placed in a closed container containing a few crystals of iodine. The iodine vapour in the container may either react with the substance spot on the plate or adhere to it more strongly than the rest of the plate. Either way, the substance will show up as a brownish spot.

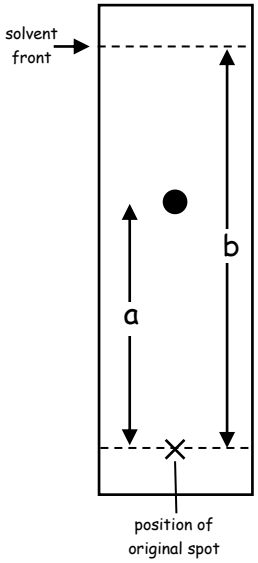
Under a definite set of experimental conditions for a thin-layer chromatographic analysis, a given substance will always travel a fixed distance relative to the distance travelled by the solvent front. This ratio of distances is called the **R_f value**.

- The term R_f stands for '**r**atio to **f**ront' and is expressed as a decimal fraction:

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

The R_f value of a substance can be calculated from its chromatogram:

$$R_f = \frac{a}{b}$$



The R_f value for a substance depends on its structure and is a physical characteristic of the compound, just as a melting point is a physical characteristic. However, identifying a substance purely from its R_f value is unreliable.

In practice, it is more usual to carry out a thin-layer chromatographic analysis with the product you prepared along with a pure sample of the compound you think you prepared. If the resulting chromatogram shows two spots at the same distance from the origin, i.e. with the same R_f value, then the two compounds are identical.

AH Chem Skills
13

Melting Point Determination

Once the desired product of an organic reaction has been separated and purified, the next step is to confirm that it is the compound we had set out to prepare.
If the product is a **solid**, we can determine its **melting point** and compare it with the accepted or literature value.

- If these are in close agreement, we can be fairly sure, although not certain, of the identity of the compound.

The reason for any doubt is that many other compounds will share the same melting point.

- However, the chance of any one of these being formed in the reaction instead of our desired product is extremely remote.

The melting point of a solid is defined as the temperature at which it changes into a liquid.

- In practice, what we measure is the temperature at which it just starts to melt and the temperature at which it has just completely liquefied.
- Measurement of a melting point range rather than a single melting temperature
- when we report the melting point, the temperature range that must be quoted, e.g 148°C –150°C.
- If a substance is pure then it will melt entirely within a range of about 1°C
    - it will have a definite and sharp melting point.
- if a substance is impure the melting point will be indefinite, occuring over several degrees
    - The presence of impurities in a substance lowers its melting point and broadens its melting point range
    - the greater the amount of impurity present the greater will be the depression of the melting point.
- Measuring a melting point not only helps to characterise a substance, but also provides confirmation of its purity.

Method

- A few dry crystals of the substance are placed on a watch glass and crushed to a fine powder using a glass rod or spatula.
- A glass capillary tube – to contain the powdered sample – is prepared by sealing off one end of the tube.
- This is done by touching one end of the tube to the base of a blue Bunsen flame – the glass melts and closes off that end.
- Once the tube has cooled, some of the sample is introduced. This is achieved by pushing the open end of the tube into the sample, trapping some of the powdered solid.
    - The tube is then inverted and while holding it near the base, the sealed end is sharply tapped against the bench.
    - The solid should fall to the bottom of the tube but if it doesn't, gently rub the sides of the tube with a small file.
    - The filling procedure is repeated until there is 1–2 mm (no more) of solid in the tube.

- With the capillary tube filled correctly, we can now measure the melting point of the solid.
- Several types of melting-point devices are available but most contain a metal block in which the capillary tube and a thermometer can be accommodated.
    - The metal block is normally heated electrically and the rate of heating controlled by means of a variable resistor.
    - In addition, the apparatus is likely to have a light to illuminate the sample chamber within the block and an eyepiece containing a small magnifying lens to facilitate observation of the sample.
- With the filled capillary tube and thermometer in place, the temperature of the metal block is raised quite quickly to within 25°C of the expected melting point.
- Thereafter, the temperature is increased very slowly at a rate of about 2°C per minute.
- The thermometer reading is taken when the solid just begins to melt and then again when all the solid has just melted and only a clear liquid is observed.

To obtain an accurate melting point it is vitally important that over the last 25°C or so the temperature of the metal block is raised very, very slowly.

- If it is not, the melting point of the solid will be underestimated, i.e. the measured value will be lower than the true value.
    - This is because the mercury in the thermometer takes time to respond to the rising temperature of the block.
- Consequently, the thermometer reading lags behind the temperature of the block and the more rapid the heating rate, the wider will be the gap between the two.

Knowledge of the melting point of a compound doesn't allow us to identify it with absolute certainty. One way of removing any shadow of doubt is to carry out what is known as the **mixed melting point** technique.

- This involves mixing a pure sample of the compound we have prepared 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 intimate 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.
    - the identity of the compound we have prepared has been confirmed.
    - Had the two compounds not been the same then the melting point of the mixture would have been much lower and the melting range much broader.
    - This results from the fact that each compound would act as an impurity of the other.

.

AH Chem Skills
14

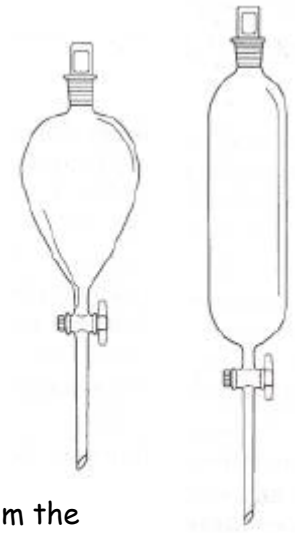
Separating Funnel & Solvent Extraction

On occasions it may not be practicable to isolate the product directly from the mixture by filtration or simple distillation. In such cases we have to resort to another technique known as **solvent extraction**. Suppose, for example, our desired product is present in an aqueous mixture, i.e. water is the solvent.

- The product can be removed or extracted from the mixture by the addition of a second solvent. The choice of the second solvent is critical.
    - It must be **immiscible** with water, i.e. when the two are mixed they form separate layers.
    - The product must not react with the solvent and it must be **more soluble** in it than in water.
- On adding the solvent to the aqueous mixture the product will move out of the aqueous layer and into the solvent layer, from which it can be more readily separated.

Method

The aqueous layer is first transferred to a **separating funnel**, which may be *cylindrical* or *pear-shaped*.



- A portion of solvent, equal to about one-third of the volume of the aqueous mixture, is then added to the funnel.
    - For efficient extraction, the total volume of both liquids should not exceed three-quarters of the funnel's capacity.
- With the stopper held firmly in place, the funnel is inverted and the tap opened to release any pressure build-up caused by the solvent vaporising.
- The tap is then closed and the mixture is shaken for several minutes. This increases the surface area of contact between the two liquids and so speeds up the rate of movement of the product from the aqueous layer into the solvent layer.
    - During the shaking process, it is important to invert the funnel from time to time and open the tap to release the pressure.
- With the funnel supported, the mixture is allowed to settle until the layers have completely separated – there should be a sharp dividing line between the two.
    - The aqueous layer is usually more dense than the solvent layer so the solvent layer will lie above the aqueous layer in the separating funnel.
- With the stopper removed, the lower aqueous layer is drained through the tap into a conical flask.
    - The solvent layer is poured out of the top of the funnel into a separate flask. This avoids contamination with any drops of the aqueous mixture remaining in the stem of the funnel.
- The aqueous layer is then returned to the separating funnel and the above procedure is repeated at least twice using a fresh portion of solvent each time.
- The reason why several extractions are carried out using small volumes of solvent rather than one extraction using a large volume of solvent is that a greater amount of product can be recovered in this way, ie the extraction process is more efficient.
- The solvent extracts are then combined and the solvent is removed by careful distillation, leaving the desired product in the distillation flask.

Stoichiometric Calculations

Exercise 1 - Volumetric Analysis

A standard solution of sodium carbonate was prepared by dissolving 5.06g of the anhydrous solute in water and making it up to 500 cm3. 25.0 cm3 portions of this solution were titrated against hydrochloric acid giving an average titre volume of 19.2cm^3. Calculate the concentration of the acid.

1.8g of iron(II) ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O$, was dissolved in 35cm^3 of distilled water. The solution was then diluted to 50cm^3 using dilute sulphuric acid. The final solution was titrated against potassium permanganate solution and 40 cm3 of the permanganate solution were required to reach the end-point at which all the iron(II) ions had been converted to iron(III) ions. Calculate the concentration of the potassium permanganate solution.

Hardness in water is caused by the presence of calcium and magnesium ions. It can be expressed quantitatively in ppm (parts per million) of calcium carbonate. e.g a water sample with a hardness of 50 ppm would contain the equivalent of 50g of calcium carbonate per million grams of water. In an experiment to determine the hardness of some tap water, a 50.0cm^3 sample was pipetted into a conical flask along with 10cm^3 of a buffer solution and a few drops of Eriochrome Black T indicator. On titration, 9.8cm^3 of 0.0100mol l^{-1} EDTA solution were required to reach the end-point. Calculate the hardness of the tap water in ppm of calcium carbonate assuming that the density of water is 1.00g cm^{-3}.

The percentage of calcium carbonate in a sample of limestone can be determined by back titration as follows: 2.0g of limestone were dissolved in 60.0cm^3 of 0.50mol l^{-1} hydrochloric acid. After the reaction was completed, insoluble impurities were removed by filtration and the amount of unreacted acid was determined by titration with 0.10mol l^{-1} sodium hydroxide solution. On first adding the alkali a white precipitate formed which immediately dissolved in the unreacted acid. 60.0cm^3 of the 0.10mol l^{-1} sodium hydroxide were required to neutralise the unreacted acid.

a) Calculate the number of moles of hydrochloric acid that had reacted with the limestone.

b) Calculate the percentage (by mass) of calcium carbonate in the sample of limestone.

c) What is the white precipitate?

Compound fertilisers are mixtures of chemicals which provide elements essential for plant growth. A certain fertiliser contains ammonium phosphate as the only source of

nitrogen and phosphorus. In an experiment to estimate the percentage nitrogen present in a sample of fertiliser, the following estimation was carried out: 1.40g of the fertiliser was weighed and then heated with 25cm^3 of 2.0mol l^{-1} sodium hydroxide solution. The gas given off was absorbed in 50cm^3 of 0.50mol l^{-1} hydrochloric acid solution. When the reaction was finished, unreacted hydrochloric acid was titrated with 0.1mol l^{-1} sodium hydroxide solution. 50 cm^3 of the alkali were needed for neutralisation.
a) Name the gas given off when the fertiliser is heated with sodium hydroxide.
b) State whether high accuracy is required in measuring the volume of
i) the 2.0mol l-^{1} sodium hydroxide solution
ii) the 0.50mol l-^{1} hydrochloric acid solution
iii) the 0.50mol l-^{1} sodium hydroxide solution
Write the equation for the reaction of the gas referred to in a) with hydrochloric acid.
c) Calculate the number of moles of hydrochloric acid which reacted with the gas.
d) Calculate the percentage (by mass) of nitrogen in the fertiliser.

A metal chloride (6.05g) was dissolved in water and the solution made up to a final volume of 100cm^3. A solution of silver(I) nitrate containing 34.0g l^{-1} was titrated against 20.0cm^3 of the metal chloride solution. The end-point was detected when 50.0 cm^3 of the silver(I) nitrate solution had been added.
a) Calculate the concentration (in mol l-^{1}) of the silver(I) nitrate solution.
b) What mass of metal is present in the metal chloride sample?
c) Use the experimental results to establish that the metal chloride is rubidium chloride. (The relative atomic mass of rubidium is 85.4)

Answers Ex 1. 1. 0.25 mol l-1 2. 0.023 mol l-1 3. 1960 ppm 4. a) 0.024 mol HCl reacted b) 60% c) calcium hydroxide 5. a) ammonia, NH3 b) i) low accuracy (measuring cylinder) ii) high accuracy (pipette) iii) high accuracy (burette) c) NH3 + HCl → NH4Cl d) 0.020 moles HCl e) 20% N by mass 6. a) 0.2 mol l-1 b) 4.275g c) 0.05 mol of metal = 4.275g so 1mol = 85.5g so metal = rubidium

Exercise 2 - Gravimetric Analysis

When nickel(II) ions in solution are reacted with dimethylglyoxime ($C_4H_8N_2O_2$) in ethanol, a red complex of nickel(II) ions and dimethylglyoxime is precipitated. The stoichiometric equation for the reaction is:

$Ni^{2+}(aq) + 2\ C_4H_8N_2O_2 \rightarrow Ni(C_4H_8N_2O_2)_2\ (s) + 2H^+(aq)$

0.2811g of a nickel(II) salt were dissolved in water and completely reacted with dimethylglyoxime. The red precipitate weighed 0.2890g.

a) What is the name given to this type of chemical analysis

b) Calculate the i) mass of nickel(II) ions in the complex

ii) percentage of nickel in the original salt

c) Nickel(II) ions can also be determined by a complexometric titration method.

i) Name a suitable reagent for this method.

ii) Give one advantage and one disadvantage of this method compared with the precipitation method given above.

Before 1947, 'silver' coins were made from an alloy of silver, copper and nickel. To determine the metal composition, a coin weighing 10.00g was dissolved in nitric acid and the resulting solution was diluted to 1000cm^3 in a standard flask. A 100cm^3 portion was treated in the following way.

0.20 mol l^{-1} hydrochloric acid was added to this solution until precipitation of silver(I) chloride was complete. The precipitate was recovered by filtration. It was washed and dried and found to weigh 0.600g.

a) i) Calculate the percentage by mass of silver in the coin.

ii) How could you test that precipitation was complete ?

The filtrate was treated to reduce the copper(II) ions to copper(I) ions.

Ammonium thiocyanate solution was added to precipitate the copper as copper(I) thiocyanate.

$Cu^{2+}\ (aq) + CNS\text{-}(aq) \rightarrow CuCNS(s)$

After filtration, drying and weighing, the precipitate was found to weigh 0.310g.

b) Calculate the percentage by mass of copper in the coin.

Gunmetal is an alloy of mainly copper and tin. The copper constant is sufficiently high to be worth recovering from gunmetal scrap. In order to determine the approximate percentage of copper in a sample, the following estimation was carried out.
0.500g of the gunmetal sample was weighed into a beaker and 50% nitric acid solution was added. When the metal had dissolved, the solution was cooled and diluted. At this stage an insoluble tin compound was formed and this was filtered off.
Sodium carbonate was added to the filtrate and the thick, green, gelatinous precipitate was filtered, washed and dried. The green precipitate was heated strongly in in a crucible until decomposition was complete and a black powder obtained.
Results: mass of crucible + black powder = 26.658g
mass of crucible = 26.101g
a) Write an equation for the decomposition of the green precipitate to the black powder.
b) Calculate the percentage copper in the gunmetal alloy.

A barium salt (4.18g) was heated strongly in a crucible over a Bunsen flame. Only oxygen was evolved during this time and on heating to constant mass and cooling in a dessicator, the residue of barium chloride was found to weigh 2.83g. (The relative atomic mass of barium is 137).
a) Explain what is meant by 'heating to constant mass'.
b) Use the experimental results to establish the formula of the original barium salt.

Ex 2. 1. a) gravimetric analysis b) i) 5.9 x 10-2g ii) 21% c) i) EDTA ii)
quicker (no filtering), less accurate (bigger errors) / difficult end-point
2. a) i) 45.16% ii) once ppt has settled, add some more HCl and watch to
see if more ppt forms or after filtering, add HCl to filtrate and see if more ppt
forms b) 16.2% 3. a) CuCO3 ® CuO + CO2 b) 88.98%
4. a) heating until there is no more change in weight b) BaCl2O6 or
Ba(ClO3)2

1	