Mearns Castle High School

Advanced Higher Chemistry

Stoichiometry

Stoichiometry

This section of Unit 2 relies on the ability to write formulae and balanced equations correctly.

Any reaction in which the substances react completely according to the mole ratios given by a balanced (**stoichiometric**) equation is called a **quantitative** reaction.

When a quantitative reaction takes place, an analysis of the reaction can be undertaken and one unknown value can be determined.
Two chemical methods of analysis are:

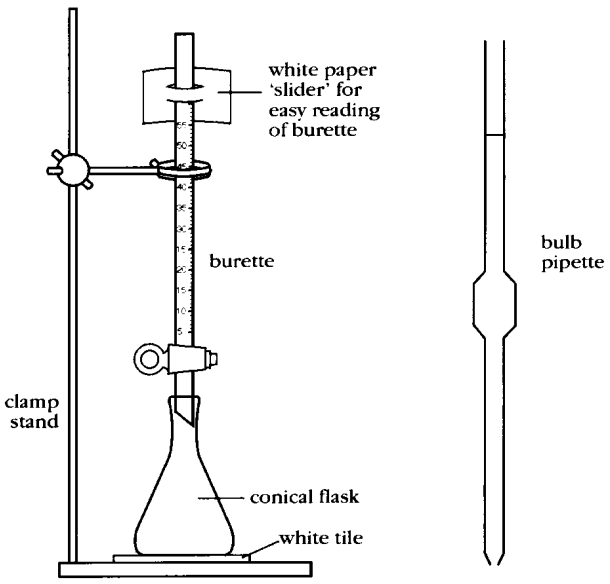
- **volumetric** (involving accurately measured volumes of solutions) and
- **gravimetric** (involving accurate weighing of substances formed in a precipitation).

- there is a third method called **colorimetric**, which involves measuring the colour intensity of a solution and comparing it to solutions of known concentration. This is covered later by a PPA and could also form part of an investigation. Knowledge of this technique is not required but as it is included in a PPA, you could be asked about it in a PPA-based question.

Volumetric analysis
Any volumetric analysis uses a solution of accurately known concentration in a quantitative reaction to determine the concentration of the other solution used in the reaction.
A reaction carried out in this way is called a titration.
There are three main types of titration:

- **acid/base** – an acid or a base being neutralised (already experienced in Int 2)
- **redox** – an oxidising agent and reducing agent reacting together (already experienced in H Grade)
- **complexometric** – formation of a complex of a distinct colour or one which will turn an indicator a specific colour. EDTA is the main reagent in complexometric titrations as it readily forms complexes with many metal ions.
  You may not yet have studied the theory behind how a metal complex forms. It's at the end of Unit 1 "some chemistry of the Periodic Table" All you need to know for the moment is that EDTA will react with a metal ion in the ratio of 1:1.

To carry out a titration, one solution must be pre-prepared accurately using an accurate balance, a standard flask and deionised water.



Solutions to be titrated must be transferred from their container into the conical flask using a pipette.

Titrant solution added to the burette must be ran through the burette to remove any residual liquid (e.g. water from a previous washing) and to get rid of any air bubbles.

You should also choose a starting volume that you can comfortably read.

All of these pieces of glass apparatus have been
used in Int 2 and Higher.

A typical titration setup is shown in the diagram.
Remember also that the pipette must be filled using a pipette filler.
The solution of accurately known concentration is called a **standard** solution. A standard solution can only be prepared from a **primary standard**.
A primary standard is a substance that is readily available and has the following characteristics:

- a high purity (> 99.9%)
  Chemicals are supplied in different grades. Sodium chloride for use in ordinary lab experiments (e.g. conductivity of an ionic solution) would be "standard laboratory grade", but for carrying out experiments requiring a high accuracy, "analytical grade" would be used. It contains far fewer impurities but is more expensive!

- is stable in air and in solution
  Many substances are stable when in solid form but become unstable when made into a solution.
  The most common of these are;
  1) Any alkali – alkalis have a tendency to absorb carbon dioxide from the atmosphere and become carbonates. This of course reduces the concentration of the alkali.
  2) Any iodide solution – iodide ions are quite easily oxidised to iodine. Potassium iodide solution starts off colourless but will turn a shade of yellow after a couple of days. Any dissolved oxygen in the water can cause this.
  3) Any reducing agent is liable to oxidise due to dissolved oxygen.
     Iron (II) will oxidise to iron (III)
     Sulphite solutions will slowly oxidise to sulphates
     Potassium permanganate is also unstable in solution. It reduces to lower manganese compounds which have an undesirable side effect – they stain the glass brown.
  4) Any silver compound – silver compounds are sensitive to light ($Ag^+ + e \longrightarrow Ag$)
     There are also other light-sensitive compounds.

- is readily soluble (usually in water). (obviously!!)

The common primary standards are oxalic acid and anhydrous sodium carbonate for acid/base titrations and ethylenediaminetetraacetic acid disodium salt (EDTA) for complexometric titrations.
There are a large number of reagents used for redox titrations e.g.:
Sodium thiosulphate, iodine solution, potassium permanganate, iron (II) etc.
Once a standard solution has been prepared it can be used to react (is titrated) with a known volume of solution of unknown concentration.

When making up any solution, **deionised water must be used at all times**. Tap water contains small quantities of dissolved compounds (usually calcium) and a small quantity of chlorine.

The point at which the reaction is **just** complete is called the **equivalence point**. An equivalence point must be observed either by a colour change in the reaction at the equivalence point or by the addition of an indicator that changes colour at the equivalence point.
This colour change happens when a certain volume of solution has been added and what is called the end-point of the titration is reached.
Note that there is a difference between end-point and equivalence point. It is often difficult to indicate the equivalence point, but easy to indicate just beyond it (usually one drop from the burette produces the necessary colour change).

One method of carrying out a titration is outlined below:

1. The burette is set up vertically as shown in the diagram on the first page and, after rinsing it with the standard solution, is filled up to zero or any other volume.
2. A pipette is rinsed with the other solution and a known volume put in the conical flask. A few drops of indicator are added if required. The standard solution from the burette is run into the unknown solution while continuously swirling the flask.
3. As the end-point is approached (usually detected by a slight colour change) the solution in the burette is added dropwise until the indicator shows a permanent colour change. At the end-point the reading on the burette is taken again. Subtraction of the first reading from the second reading gives the titre.
4. It is normal to carry out one rough titration and then two accurate titrations, which must be within ± 0.1 ml Results which agree with each other to this level of accuracy are said to be **concordant**, and produces the statement "titrate until concordant results are obtained". These two accurate titrations are then averaged to give the value used in the calculation. Note that the conical flask is placed on a white tile (or piece of filter paper) to make the end-point easier to see and the burette jet must be just inside the flask at all times to avoid missing the flask during swirling.

Acid/base titrations are neutralisation reactions and an indicator is always required, e.g. phenolphthalein or methyl orange.

The choice of indicators

An indicator requires to show the end-point of a titration by a sharp colour change (usually changing with the addition of one drop from the burette.

The choice of indicator for an acid-base titration requires to change colour over a particular pH range, and must be chosen carefully as the end-point of acid-base titrations does not always occur at pH 7.

While you should be able to choose a particular indicator for a titration, most of your experiments will contain the indicator to be used in the instructions.

Here are a few examples. Don't memorise them!! Ones highlighted in bold are commonly used.

There are a large number of websites which will list indicators. One colourful one is [*http://www.ausetute.com.au/indicata.html*](http://www.ausetute.com.au/indicata.html)

Indicator	pH Range in which Colour Change Occurs	Colour Change as pH Increases
Crystal violet	0.0 - 1.6	yellow to blue
Thymol blue	1.2 - 2.8	red to yellow
Orange IV	1.4 - 2.8	red to yellow
Methyl orange	3.2 - 4.4	red to yellow
Bromcresol green	3.8 - 5.4	yellow to blue
Methyl red	4.8 - 6.2	red to yellow
Chlorophenol red	5.2 - 6.8	yellow to red
Bromothymol blue	6.0 - 7.6	yellow to blue
Phenol red	6.6 - 8.0	yellow to red
Neutral red	6.8 - 8.0	red to amber
Thymol blue	8.0 - 9.6	yellow to blue
Phenolphthalein	8.2 - 10.0	colourless to pink
Thymolphthalein	9.4 - 10.6	colourless to blue
Alizarin yellow	10.1 - 12.0	yellow to blue
Indigo carmine	11.4 - 13.0	blue to yellow

Complexometric titrations are based on the formation of a coloured complex by a transition metal ion. EDTA is possibly the most common reagent in complexometric analysis. It complexes with many metal ions in a one-to-one ratio. The theory behind a complexometric titration is:

1) The metal ion solution being titrated forms a coloured complex with the indicator
2) As EDTA is added, it complexes with any free metal ion. This continues until almost all the free metal ions have complexed with EDTA
3) As more EDTA is added now, it "kicks off" the indicator. The free indicator has a different colour from the complexed indicator, so a colour change is observed.

It is important that the quantity of indicator in a complexometric titration is very small otherwise there would be a gradual colour change rather than a sharp one.
There are also some steps which must be taken when using EDTA. It complexes best with metal ions when the pH is 10, so ammonia solution must be added near the end-point.

You are not expected to know the theory of complexometric titrations, but it is probably wrong not to describe it.

Complexometric titrations can be used to determine the concentration of metal ions, such as nickel(II), in solutions with very low concentrations (parts per million).
The choice of indicator is important as different indicators complex with different metal ions, but you are not expected to know which indicator to use.

Redox titrations are based on redox reactions. Redox titrations very often involve potassium permanganate (made up fresh). It reduces from intense purple to almost colourless manganese (II) in acid solution. The end-point is the appearance of a pink colour (free permanganate in the conical flask). Potassium permanganate can be described as self-indicating. One problem with permanganate titrations is that the meniscus in the burette is often difficult to read because of the intense dark colour of the solution, but this is overcome by reading the scale at the top of the meniscus rather than the bottom. Iodine solution has the same problem and solution.

Iodine is another useful substance in redox titrations as it can be easily detected with starch.
If it is formed, it is titrated with sodium thiosulphate. The brown colour turns to a pale yellow and starch is added at this point. Titration continues until the blue-black colour disappears.
If iodine is titrated into the conical flask from the burette, starch is added to the solution in the conical flask. The iodine reduces to iodide ions. When enough iodine has been added to react with all of the solution, the first drop of excess will produce a blue-black colour.

The calculations involving redox titrations require the writing of the overall redox equation from the ion-electron equations in order to establish the mole ratio of the reaction. Calculations can then be carried out in the same way as for acid/base and complexometric titrations.

Volumetric calculations

These calculations can be carried out by a variety of methods, but in Advanced Higher it is always best to work towards calculating the number of moles involved, and then calculating back to masses, ratios or percentages, whatever is asked for.

> *You may recall that in Int 2 you learned a "quick" way of calculating the concentration of an unknown acid or alkali using a formula such as pcv acid = pcv alkali. This formula is fine as far as it goes, but it really only works for acid-alkali titrations and at Advanced Higher you require to handle a greater variety of calculations. You also require to have a greater understanding of stoichiometry as in "what's happening" in order to complete a calculation successfully.*
>
> *At Advanced Higher, you are expected to be able to handle calculations which require several steps e.g. calculation of a percentage by mass from the titration of a sample.*
>
> *Very often, the biggest problem is getting started. If you can overcome this obstacle, you should be able to complete a calculation successfully.*

In all volumetric calculations, you should follow these steps:

1. Establish the mole ratio (i.e. the stoichiometry of the reaction).
   Very often, the balanced equation is given, so establishing the mole ratio is not a problem.

2. Calculate the number of moles from what you know i.e. a volume and a concentration.

3. Calculate the number of moles of the other (unknown) substance

4. If a sample has been titrated, calculate the number of moles in the total volume

5. Calculate the mass, percentage or whatever has been asked.

Worked example

Hydrated iron (II) sulphate ($FeSO_4.\ 7H_2O$) is thought to contain iron (III) as an impurity.
0.97g was dissolved in 50 ml of water and 50 ml of 1 mol l^{-1} sulphuric acid was added.
This solution was made up to 250 ml in a standard flask and 20 ml samples were titrated with 0.005 mol l^{-1} potassium permanganate until the first permanent pink colour was seen.
Calculate the percentage purity of the compound

The equations are:

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

Titration number	Starting Volume (ml)	Final Volume (ml)	Volume Titrated (ml)
Rough	0.0	11.2	11.2
1	11.2	22.2	11.0
2	22.2	33.1	10.9

Average titre = 10.95 ml.

Step 1: Establish the mole ratio of the redox reaction from the redox equations
The ratio is 1 mol permanganate reacts with 5 mol iron (II)

Step 2: Calculate the number of moles from what you know i.e. a volume and concentration
Moles of permanganate can be calculated = $10.9 \times 0.005 \div 1000$
= 5.45×10^{-5}

Step 3: Calculate the number of moles of the other (unknown) substance
Moles of iron (II) in 20 ml sample = moles of permanganate X mole ratio
= $5.45 \times 10^{-5} \times 5$
= 2.725×10^{-4}

Step 4: If a sample has been titrated, calculate the number of moles in the total volume
In this example, total solution = 250 ml and a 20 ml sample was titrated
Moles of iron (II) sulphate in 250 ml = $2.725 \times 10^{-4} \times 250 \div 20$
= 3.406×10^{-3}

Step 5: Calculate the mass, percentage or whatever has been asked.
In this case, percentage purity has been asked.
Mass of iron (II) sulphate in 1g = $3.406 \times 10^{-3} \times 277.9$ (FM)
= 0.9465g
% purity = $0.9465 \div 0.97 \times 100$
= 97.58%

Points to note about the chemistry.

1. Sulphuric acid added to provide excess H^+ ions so that the reduction of permanganate is complete according to the equation.
2. Many ionic compounds contain water locked into their crystal lattices (water of crystallisation). These compounds are said to be **hydrated** and the mass of water must be taken into account when calculating their FM. Ionic compounds which contain no water of crystallisation are said to be **anhydrous**.
3. The RAM of all elements listed in the Data Book for Higher and Advanced Higher are now quoted to one decimal place (it was to the nearest 0.5 in Int 2).

Errors in titrations.
You should be aware that if a titration requires only a small volume to be added from the burette, (say less than 5 ml), you will potentially have a large error.
You can read to an accuracy of ± 0.05 ml. (half of the smallest unit of measure).
If your titration is say 3.4 ml, it could be anywhere between 3.35 and 3.45 ml.
3.35 ÷ 3.4 = 0.985 = 98.5%
3.45 ÷ 3.4 = 1.014 = 101.4%
so your titration could be 1.5% low or 1.4% high. These potential errors are unacceptably high.
If your titration was 13.4 ml, your calculations become
13.35 ÷ 13.4 = 0.996 = 99.6%
13.45 ÷ 13.4 = 1.004 = 100.4%
So your error has been reduced to 0.4% low or 0.4% high. Much more acceptable.
As a guide, you should try to carry out a titration so that you are titrating a *minimum* of 10 ml.
If the solution you are titrating from the burette gives you a very low titration volume, dilute it by whatever factor you require (2, 4, 5, 10 etc) by pipetting a known volume into a standard flask and filling it up to the mark with deionised water.
In any investigation, carrying out a trial titration and reporting that "the titre volume is very small so the titrant was diluted from 0.1 to 0.02 mol l^{-1} and this was the solution used in future titrations" would gain recognition.
Calculation of errors is *not* a specified part of Advanced Higher, but you should be aware that errors exist in *any* quantity that can be measured. The error is always one half of the smallest unit you can measure. In a balance accurate to 0.01g, the error is 0.005g.
There is also human error – judging the point when a colour changes for example.

Gravimetric analysis
In this method of analysis the mass of an element, compound or ion present is determined by changing it into an insoluble substance of known chemical composition that can be readily isolated, purified and weighed.
The accuracy of this method depends on the accuracy of the balance used and the dexterity of the person carrying out the procedure.
Gravimetric analysis frequently involves precipitation followed by filtration followed by drying.
The product must:

- have a low solubility so that all of the product is precipitated
- have a particle size that is not too small to allow easy filtration
- be stable at temperatures of 100 - 105°C to allow it to be dried in an oven.

The accuracy of this method relies on the procedure being carried out very carefully so that all of the material is transferred from the reaction vessel to the filtration apparatus. The apparatus must then be dried and weighed with no further loss of residue during transfer. This is not easy and needs to be carried out with extreme care.
The other common analysis involves heating to change the same substance from one form into another, e.g. dehydration of a hydrated salt to calculate the number of moles of water of crystallisation.

Drying to constant mass
The dryness of any solid can be checked by repeated heating, cooling in a desiccator and weighing until a constant mass is obtained. Successive weighings, at room temperature, should be within 0.01 g of each other.
Both volumetric and gravimetric analyses are included in the practical activities of this unit.
Drying to constant mass is important because some compounds have a natural tendency to absorb water from the atmosphere (sodium carbonate does this) and so must be dried to constant mass before being used to make a primary standard.

Common precipitation reactions found in Advanced Higher are:

Copper (I) thiocyanate	$Cu^{+} + CNS^{-} \longrightarrow CuCNS$
Barium sulphate	$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$
Nickel dimethylglyoxime	
Silver (I) chloride	$Ag^{+} + Cl^{-} \longrightarrow AgCl$

Some compounds require further treatment after the precipitation reaction. Silver chloride requires to be heated with nitric acid in order to coagulate the precipitate to make it easier to filter.

Also note that when a precipitate has been filtered, the filter paper must be weighed and its mass recorded. The filter paper plus precipitate is weighed after drying and its mass recorded. The mass of the precipitate is then calculated.

While the results for titrations are generally presented as a table, the results for gravimetric analysis are more usually presented as "lab report format", an example of which is shown:

Mass of filter paper plus precipitate	=	g
Mass of filter paper	=	g
Mass of precipitate	=	g