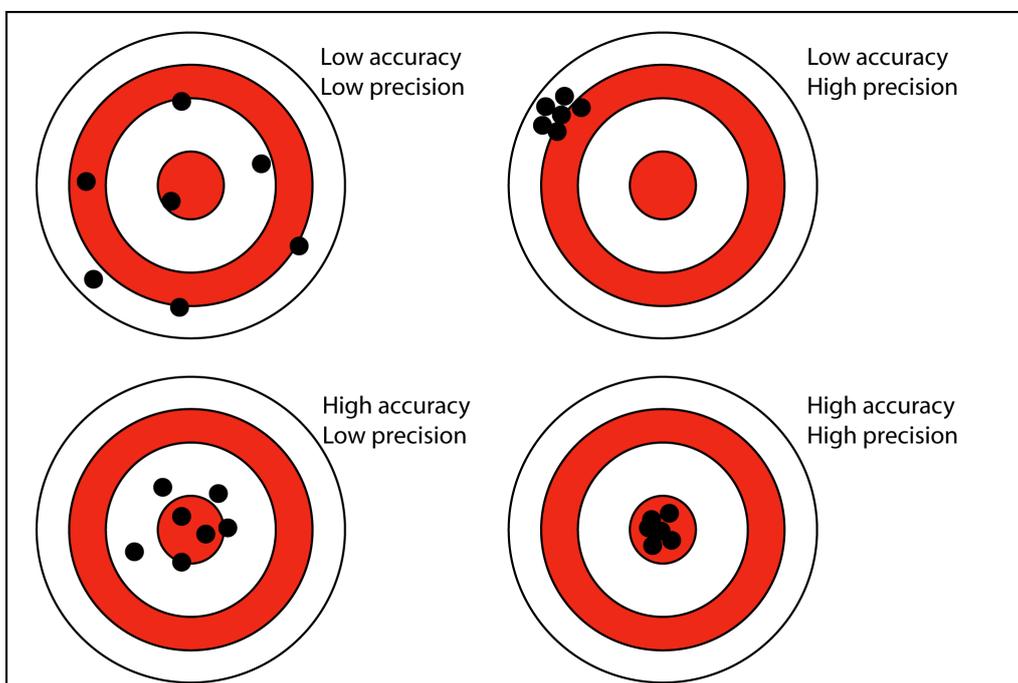


Kelso High School
Revised Advanced Higher

Practical Skills &
Techniques



Book 4: Errors &
Stoichiometry

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Errors

Accuracy and precision

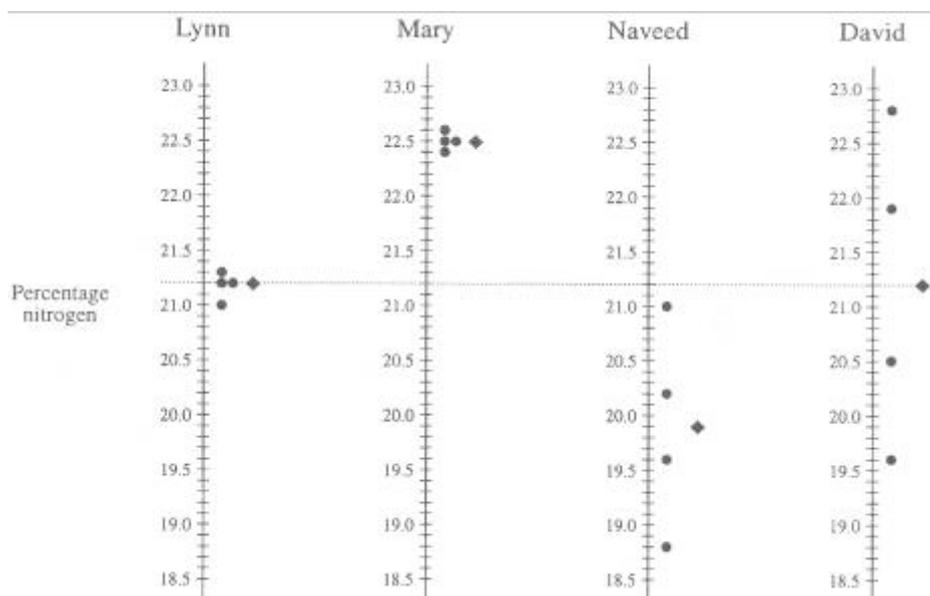
The terms 'accuracy' and 'precision' are commonly used to mean the same thing but there is a subtle difference in their meanings. An **accurate** measurement or result is defined as one that is in close agreement with the true or accepted value. **Precise** measurements or results are those that are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

To illustrate these differences, let's consider an example from analytical chemistry. Suppose four students analysed samples of anhydrous ammonium sulfate in order to determine the percentage by mass of nitrogen and let's say they each performed the procedure four times. Their results are presented in the following table:

Student	Lynn	Mary	Naveed	David
Percentage nitrogen	21.3	22.5	20.2	21.9
	21.2	22.4	19.6	19.6
	21.0	22.6	21.0	22.8
	21.2	22.5	18.8	20.5
Average value	21.2	22.5	19.9	21.2

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In order to analyse these results in terms of accuracy and precision, it is more helpful to present them in a pictorial fashion and this has been done below:



The black dots represent the individual results and the black diamonds indicate the average values. The dotted line shows the true value for the percentage by mass of nitrogen in anhydrous ammonium sulfate, namely 21.2%.

Since Lynn's results are clustered together and in close agreement with one another, we can describe them as precise. For the same reason Mary's results are also precise. In fact, the precision that Mary has achieved is marginally better than Lynn's because the spread in her results is slightly less than in Lynn's – Mary's results range from 22.4% to 22.6% with a spread of 0.2%, while the spread in Lynn's results is 0.3%. Both Naveed and David's results are widely scattered and so are imprecise. The imprecision in David's results is worse than that in Naveed's since the spread in his results (3.2%) is larger than that in Naveed's (2.2%).

As far as accuracy is concerned, all of Lynn's results are reasonably accurate since they deviate only slightly from the true value. Mary's results differ significantly from the true value and are therefore inaccurate and this is despite the fact that they are the most precise. One of Naveed's results, 21.0%, is accurate but the other three are inaccurate. None of David's results is accurate. His average (21.2%), however, is highly accurate – but this is just fortuitous.

In summary, the closer a result is to its true value then the greater is its accuracy and the smaller the spread in a set of results the more precise they are. Furthermore, while it is true to say that a set of accurate results will always be precise, eg Lynn's results, a set of precise results may not always be accurate, eg Mary's results.

Repeatability and reproducibility

When an analyst obtains a set of results by repeating the same analytical procedure and these results are in close agreement then we can describe the results as not only being precise but **repeatable**. The procedure the analyst used can also be described as repeatable. If a second analyst carries out the same analytical procedure and gains a set of results which are precise and close to those obtained by the first analyst, then we can describe both the results and the procedure as **reproducible**. Let's look back at Lynn's results. They are precise and so they must be repeatable but they don't agree with Mary's results and so they cannot be described as reproducible.

Quantifying errors

A measurement is incomplete unless we can provide some idea of the magnitude of the error or uncertainty associated with it. There are various ways of quantifying uncertainty but one convenient method is to define it in terms of the tolerance of the piece of equipment used to make the measurement. Take a 25 cm³ class B pipette, for example. Its tolerance is $\pm 0.06 \text{ cm}^3$ – this means that the volume of liquid it delivers will lie somewhere between a lower limit of 24.94 cm³ and an upper limit of 25.06 cm³, ie $25.00 \pm 0.06 \text{ cm}^3$, provided the correct procedure is followed in using the pipette.

Let's now look at some other pieces of equipment and the uncertainties associated with them.

Pipettes

Capacity	Uncertainty value	
	Class A	Class B
10 cm ³	$\pm 0.02 \text{ cm}^3$	$\pm 0.04 \text{ cm}^3$
20 cm ³	$\pm 0.03 \text{ cm}^3$	$\pm 0.06 \text{ cm}^3$
25 cm ³	$\pm 0.03 \text{ cm}^3$	$\pm 0.06 \text{ cm}^3$
50 cm ³	$\pm 0.05 \text{ cm}^3$	$\pm 0.10 \text{ cm}^3$
100 cm ³	$\pm 0.08 \text{ cm}^3$	$\pm 0.15 \text{ cm}^3$

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Standard (or 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

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

It is important to note that the uncertainty values quoted for burettes are in the volumes delivered by the burettes. For example, if we used a 50 cm³ class B burette in a titration and we found the titre volume to be 24.60 cm³ then the uncertainty in this volume would be ±0.10 cm³.

Balances

Because of the large number of manufacturers and the wide range in specification, it is difficult to be definitive about measurement uncertainties in balances. However, those quoted in the following table are fairly typical.

Readability	Uncertainty value
to 1 decimal place	±0.1 g
to 2 decimal places	±0.01 g
to 3 decimal places	±0.001 g

Absolute uncertainties and percentage uncertainties

The **absolute uncertainty** in a measurement is simply another way of describing its actual uncertainty. For example, the volume of solution

contained in a 250 cm³ class B standard flask has an actual uncertainty of ± 0.30 cm³ and so its absolute uncertainty must be the same, ie ± 0.30 cm³. It is often useful to describe an uncertainty in terms of a percentage. The percentage uncertainty in a measurement is defined as:

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

Hence, the percentage uncertainty in the volume contained in a 250 cm³ class B standard flask is:

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

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

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

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

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

So, the sodium hydroxide concentration = 0.206 ± 0.003 mol l⁻¹.

Combining uncertainties

Normally in an analytical experiment we make a number of measurements and from these we calculate a final result. So how do we combine the uncertainties in the individual measurements to work out the overall uncertainty in the final result? What we do depends on the mathematical operations involved in calculating the results.

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,

$$y = a + b - c$$

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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.

Worked example 1

$$\begin{array}{rcl} \text{Mass of weighing bottle + sodium chloride} & = & 18.54 \text{ g} \\ \text{Mass of weighing bottle} & = & 12.32 \text{ g} \end{array}$$

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

A balance reading to two decimal places has obviously been used and if we look back at page 46 we can see that 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 6.22 g and since the mathematical operation used to derive this result was a subtraction, then

$$\begin{array}{rcl} \text{overall absolute uncertainty} & = & 0.01 + 0.01 \\ & = & 0.02 \text{ g} \end{array}$$

Hence,

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

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 final 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.

Worked example 2

Using a class B pipette, 25.0 cm³ of 0.956 mol l⁻¹ hydrochloric acid was transferred into a 500 cm³ class B standard 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 concentration of the undiluted acid is ± 0.005 mol l⁻¹.

$$\begin{aligned} \text{Concentration of diluted acid} &= \frac{n}{V} \\ &= \frac{\text{concentration of undiluted acid} \times \text{volume of undiluted acid}}{\text{volume of diluted acid}} \\ &= \frac{0.956 \times 0.0250}{0.500} \\ &= 0.0478 \text{ mol l}^{-1} \end{aligned}$$

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 three individual measurements:

- **uncertainty in concentration of undiluted acid**

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

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

- **uncertainty in volume of undiluted acid**

From the table on page 45 we can see that the absolute uncertainty in a 25 cm³ class B pipette is 0.06 cm³.

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

$$\text{percentage uncertainty in volume of undiluted acid} = \frac{0.06}{25.00} \times 100 = 0.24\%$$

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 arrived at the same percentage uncertainty, namely 0.24%.

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- **uncertainty in volume of diluted acid**

From the first table on page 46 we can see that the absolute uncertainty in a 500 cm³ class B standard flask is 0.50 cm³.

$$\begin{aligned}\text{absolute uncertainty in volume of diluted acid} &= 0.50 \text{ cm}^3 \\ \text{percentage uncertainty in volume of diluted acid} &= \frac{0.50}{500.00} \times 100 = 0.10\%\end{aligned}$$

- **overall uncertainty in concentration of diluted acid**

The overall percentage uncertainty in the concentration of the diluted hydrochloric acid is gained by summing those individual percentage uncertainties that we have just calculated:

$$\begin{aligned}\text{percentage uncertainty in concentration of diluted acid} &= 0.52 + 0.24 + 0.10 \\ &= 0.86\% \\ \text{absolute uncertainty in concentration of diluted acid} &= \frac{0.86}{100} \times 0.0478 \\ &= 0.00041 \text{ mol l}^{-1}\end{aligned}$$

Hence,

$$\text{concentration of the diluted hydrochloric acid} = 0.0478 \pm 0.0004 \text{ mol l}^{-1}.$$

Some 'forgotten' uncertainties

The uncertainties we have considered so far have been confined to those that arise from the equipment we use to make measurements. But there are others and although they are quite often overlooked, they may contribute significantly to the overall uncertainty in a result.

One such uncertainty is that in detecting the end-point of a titration, ie in judging the point at which the indicator just changes colour. We ought to be able to estimate the end-point in a titration to within one drop and since the average volume of a drop is 0.05 cm³ then the absolute uncertainty in estimating the end-point will be $\pm 0.05 \text{ cm}^3$. Let's consider an example to gauge the significance of this uncertainty. Suppose a 50 cm³ class A burette was used in a titration and let's say the titre volume was 23.2 cm³. We now know there are two uncertainties associated with this titre volume: one arising from the burette itself, namely $\pm 0.05 \text{ cm}^3$, and the other in estimating the end-point, namely $\pm 0.05 \text{ cm}^3$.

So,

$$\text{overall absolute uncertainty in the titre volume} = 0.05 + 0.05 = 0.10 \text{ cm}^3$$

Hence,

$$\text{titre volume} = 23.2 \pm 0.1 \text{ cm}^3$$

Since the two individual uncertainties are of equal magnitude, that due to estimating the end-point ($\pm 0.05 \text{ cm}^3$) is obviously significant and cannot be ignored.

Even if a 50 cm^3 class B burette – with an uncertainty of $\pm 0.10 \text{ cm}^3$ – had been used, the uncertainty in estimating the end-point ($\pm 0.05 \text{ cm}^3$) would still be a major contributor to the overall uncertainty in the titre volume.

The end-points of some titrations, eg EDTA titrations, are notoriously difficult to judge and in these cases we would be justified in using $\pm 0.10 \text{ cm}^3$ rather than $\pm 0.05 \text{ cm}^3$ as the uncertainty in estimating the end-point.

Another of these ‘forgotten’ uncertainties is that in the relative formula mass (RFM) of a substance.

Consider sodium chloride. If we use relative atomic masses quoted to 1 decimal place (as in the data booklet) then the RFM of sodium chloride is calculated as 58.5. Unless we have information to the contrary, it is reasonable to assume that the uncertainty in the RFM of a substance is ± 1 in the last significant digit.

Hence,

$$\text{RFM of NaCl} = 58.5 \pm 0.1$$

This corresponds to a percentage uncertainty of:

$$\frac{0.1}{58.5} \times 100 = 0.17\%$$

Whether this is significant or not depends on the context in which it is being used. Suppose, for example, 9.83 g of sodium chloride was weighed out by difference on a balance reading to 0.01 g and we wished to find the uncertainty in the number of moles of sodium chloride:

$$\text{number of moles of NaCl} = \frac{9.83}{58.5} = 0.168 \text{ mol}$$

To determine the overall uncertainty in the number of moles of sodium chloride, we need to work out the percentage uncertainties in the mass and RFM of sodium chloride and then add these together:

$$\text{percentage uncertainty in mass of NaCl} = \frac{0.02}{9.83} \times 100 = 0.20\%$$

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Notice that the absolute uncertainty in the mass of sodium chloride is ± 0.02 g. This is because the sodium chloride has been weighed by difference, ie two weighings each of uncertainty ± 0.01 g, giving a total absolute uncertainty of ± 0.02 g:

$$\text{percentage uncertainty in RFM of NaCl} = \frac{0.1}{58.5} \times 100 = 0.17\%$$

So the overall percentage uncertainty in the number of moles of NaCl = $0.20 + 0.17$
= 0.37%

We can see that the individual uncertainties are of the same order of magnitude and so the percentage uncertainty in the RFM of sodium chloride makes a significant contribution to the overall uncertainty in the number of moles of sodium chloride and cannot be ignored.

Had the relative formula mass of the sodium chloride been calculated using relative atomic masses quoted to two decimal places, it would take the value 58.44 and the uncertainty associated with it would be ± 0.01 .

Hence,

$$\text{percentage uncertainty in RFM of NaCl} = \frac{0.01}{58.44} \times 100 = 0.02\%$$

So the overall percentage uncertainty in the number of moles of NaCl = $0.20 + 0.02$
= 0.22%

In this case, the percentage uncertainty in the RFM of sodium chloride is 10 times smaller than that in the mass of sodium chloride and so its contribution to the overall uncertainty in the number of moles of sodium chloride is negligibly small and can be ignored.

In conclusion, if we use a balance reading to 0.01 g and

- relative formula masses quoted to **1** decimal place then the uncertainty associated with the RFM cannot be ignored
- relative formula masses quoted to **2** decimal places then the uncertainty associated with the RFM can be safely ignored.

Relative formula masses quoted to 2 decimal places can be found on reagent bottles and in the catalogues of chemical suppliers.

Worked example 3

A sample of oxalic acid, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (RFM = 126.07), was weighed by difference, giving the following results:

$$\begin{aligned} \text{mass of weighing bottle + oxalic acid} &= 14.21 \text{ g} \\ \text{mass of weighing bottle} &= 12.58 \text{ g} \end{aligned}$$

The sample was dissolved in approximately 25 cm^3 of deionised water contained in a beaker. The resulting solution plus rinsings from the beaker were transferred to a 250 cm^3 class B standard flask. The solution was made up to the graduation mark with deionised water. The flask was stoppered and inverted several times to ensure thorough mixing.

From these data, calculate the concentration of the resulting oxalic acid solution and its absolute uncertainty.

$$\begin{aligned} \text{Mass of oxalic acid} &= 14.21 - 12.58 = 1.63 \text{ g} \\ \text{RFM of oxalic acid} &= 126.07 \\ \text{Number of moles of oxalic acid} &= \frac{1.63}{126.07} = 0.01293 \text{ mol} \\ \text{Concentration of oxalic acid} &= \frac{0.01293}{0.2500} = 0.0517 \text{ mol l}^{-1} \end{aligned}$$

Uncertainty calculation

Working out the mass of oxalic acid involved a **subtraction**. This implies that we must add the **absolute uncertainties** in the mass readings in order to find the uncertainty in the mass of oxalic acid. Since a balance reading to 2 decimal places has been used, the uncertainty in each mass reading must be $\pm 0.01 \text{ g}$.

Hence,

$$\text{absolute uncertainty in mass of oxalic acid} = 0.01 + 0.01 = 0.02 \text{ g}$$

Since the rest of the calculation involved **divisions**, the overall percentage uncertainty in the concentration of the oxalic acid solution is obtained by summing the individual **percentage uncertainties**.

Hence,

$$\text{percentage uncertainty in mass of oxalic acid} = \frac{0.02}{1.63} \times 100 = 1.23\%$$

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Since a 250 cm³ class B standard flask with an uncertainty of ±0.30 cm³ (see page 46) was used, then

$$\text{percentage uncertainty in volume of oxalic acid solution} = \frac{0.30}{250.00} \times 100 = 0.12\%$$

The RFM of oxalic acid has been quoted to 2 decimal places and so its percentage uncertainty (0.008%) is tiny compared with the others – we are therefore justified in ignoring it.

So,

$$\text{percentage uncertainty in concentration of oxalic acid} = 1.23 + 0.12 = 1.35\%$$

and

$$\text{absolute uncertainty in concentration of oxalic acid} = \frac{1.35}{100} \times 0.0517 = 0.00070 \text{ mol l}^{-1}$$

Hence,

$$\text{concentration of oxalic acid} = 0.0517 \pm 0.0007 \text{ mol l}^{-1}$$

Worked example 4

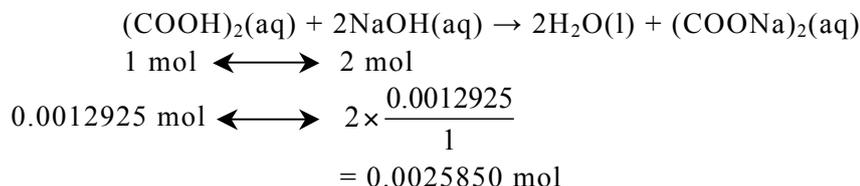
Suppose the oxalic acid solution of worked example 3 had been used to standardise a solution of sodium hydroxide with a concentration of approximately 0.1 mol l⁻¹. This could be achieved by titrating samples of the oxalic acid against the sodium hydroxide solution using phenolphthalein as indicator and let's say the following results were obtained:

<i>Pipette solution</i>	<i>oxalic acid</i>	<i>0.0517 mol l⁻¹</i>	<i>25.0 cm³</i>
<i>Burette solution</i>	<i>sodium hydroxide</i>	<i>~ 0.1 mol l⁻¹</i>	

Titration		Trial	1	2
<i>Burette readings/cm³</i>	<i>Initial</i>	<i>0.6</i>	<i>1.3</i>	<i>0.7</i>
	<i>Final</i>	<i>28.0</i>	<i>28.3</i>	<i>27.6</i>
<i>Titre volume/cm³</i>		<i>27.4</i>	<i>27.0</i>	<i>26.9</i>
<i>Mean titre volume/cm³</i>			<i>26.95</i>	

Calculate the concentration of the sodium hydroxide solution and its absolute uncertainty assuming class B volumetric equipment was used throughout.

$$\text{Number of moles of oxalic acid} = 0.0517 \times 0.0250 = 0.0012925 \text{ mol}$$



$$\text{Concentration of sodium hydroxide} = \frac{0.0025850}{0.02695} = 0.0959 \text{ mol l}^{-1}$$

Uncertainty calculation

Since the calculation to determine the concentration of the sodium hydroxide solution involves only **multiplication** and **division**, the overall percentage uncertainty in the concentration of the sodium hydroxide solution is obtained by adding the individual **percentage uncertainties**.

From the previous example,

$$\text{percentage uncertainty in concentration of oxalic acid} = 1.35\%$$

Since the uncertainty in a 25 cm³ class B pipette is $\pm 0.06 \text{ cm}^3$ (see page 45, then

$$\begin{aligned} \text{percentage uncertainty in volume of oxalic acid solution} &= \frac{0.06}{25.00} \times 100 \\ &= 0.24\% \end{aligned}$$

Since the uncertainty arising from a 50 cm³ class B burette is $\pm 0.10 \text{ cm}^3$ (see page 46, and the uncertainty in estimating the end-point of the titration is $\pm 0.05 \text{ cm}^3$ (see page 50) then

$$\text{absolute uncertainty in titre volume} = 0.10 + 0.05 = 0.15 \text{ cm}^3$$

and

$$\text{percentage uncertainty in titre volume} = \frac{0.15}{26.95} \times 100 = 0.56\%$$

So,

$$\begin{aligned} \text{percentage uncertainty in concentration of sodium hydroxide} &= 1.35 + 0.24 + 0.56 \\ &= 2.15\% \end{aligned}$$

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and

$$\begin{aligned}\text{absolute uncertainty in concentration of sodium hydroxide} &= \frac{2.15}{100} \times 0.0959 \\ &= 0.00206 \text{ mol l}^{-1}\end{aligned}$$

Hence,

$$\text{concentration of sodium hydroxide solution} = 0.096 \pm 0.002 \text{ mol l}^{-1}$$

Stoichiometry – Chemical Calculations

The vast majority of the calculations needed for Advanced Higher Chemistry were met in earlier courses.

The **amount** of a substance is denoted by the symbol '**n**' and it has the units '**mols**'.

One mole is defined as that amount of substance which contains as many elementary entities as there are atoms in exactly 12g of carbon-12 (¹²C).

'elementary entities' can be atoms, molecules or formula units (in the case of ionic compounds).

This number of entities is also known as '**Avogadro's constant**' and is denoted by the symbol '**L**' and it has the units '**mol⁻¹**'.

$$L = 6.02 \times 10^{23} \text{ mol}^{-1}$$

The **Gram Formula Mass** can be used to calculate the *number of moles* present in a particular **mass** of a substance.

Avogadro's constant can be used to calculate the *number of moles* present in a particular **number** of entities present in a substance.

The **Molar Volume** can be used to calculate the *number of moles* present in a particular **volume** of a gas.

The actual volume varies according to temperature and pressure.

At the same temperature and pressure, one mole of any gas occupies the same volume as one mole of any other gas.

The **Concentration** (**mol l⁻¹**) and **Volume** (*in litres*) can be used to calculate the *number of moles* of solute present in a **solution**.

$$C = n / V$$

Any additional knowledge needed for Advanced Higher is likely to be picked up during the practical work. Mole questions in Advanced Higher are likely, therefore, to be placed in the context of a Chemical Analysis.

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

Volumetric analysis involves using a solution of accurately known concentration in a quantitative reaction to determine the concentration of another substance.

A solution of accurately known concentration is known as a **standard solution**.

A standard solution can be prepared directly from a **primary standard**.

A primary standard must have, at least, the following characteristics:

high state of purity (analar reagent)
stability
solubility
reasonably high formula mass

The volume of reactant solution required to **just** complete the reaction is determined by **titration**

The **equivalence point** is the point at which the reaction is **just** complete.

The '**end-point**' is the point at which a change is **observed** and is associated with the equivalence point.

An **indicator** is a substance which changes colour at the end-point.

Acid/base titrations are based on neutralisation reactions

Complexometric titrations are based on complex forming reactions.

EDTA is an important complexometric reagent.

Redox titrations are based on redox reactions. Substances such as potassium permanganate(VII), which can act as their own indicators, are very useful reagents in redox titrations

In **Gravimetric analysis** the mass of an element or compound present in a substance is determined by chemically changing that substance into some other substance of known chemical composition, which can be readily isolated, purified and weighed.

Exercise 1 - Volumetric Analysis

1. 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 19.2 cm³.

Calculate the concentration of the acid.

2. 1.8g of iron(II) ammonium sulphate, Fe(NH₄)₂(SO₄)₂·6H₂O, was dissolved in 35 cm³ of distilled water. The solution was then diluted to 50 cm³ 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.

3. 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 50.0 cm³ sample was pipetted into a conical flask along with 10 cm³ of a buffer solution and a few drops of Eriochrome Black T indicator. On titration, 9.8 cm³ of 0.0100 mol 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 1.00 g cm⁻³.

4. 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 60.0 cm³ of 0.50 mol 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 0.10 mol l⁻¹ sodium hydroxide solution. On first adding the alkali a white precipitate formed which immediately dissolved in the unreacted acid.

60.0 cm³ of the 0.10 mol 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.

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- b)* Calculate the percentage (by mass) of calcium carbonate in the sample of limestone.
- c)* What is the white precipitate ?
5. 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 25 cm³ of 2.0 mol l⁻¹ sodium hydroxide solution. The gas given off was absorbed in 50 cm³ of 0.50 mol l⁻¹ hydrochloric acid solution. When the reaction was finished, unreacted hydrochloric acid was titrated with 0.10 mol l⁻¹ sodium hydroxide solution. 50 cm³ 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 2.0 mol l⁻¹ sodium hydroxide solution
 - ii)* the 0.50 mol l⁻¹ hydrochloric acid solution
 - iii)* the 0.50 mol 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.
6. A metal chloride (6.05g) was dissolved in water and the solution made up to a final volume of 100cm³. A solution of silver(I) nitrate containing 34.0 g l⁻¹ was titrated against 20.0 cm³ of the metal chloride solution. The end-point was detected when 50.0 cm³ 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)

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, NH_3 b) i) low accuracy (measuring cylinder) ii) high accuracy (pipette) iii) high accuracy (burette) c) $NH_3 + HCl \rightarrow NH_4Cl$ 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

1. 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:



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.

2. 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 1000 cm^3 in a standard flask. A 100 cm^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.

EXPERIMENTS



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

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

- 3.** Gunmetal is an alloy of mainly copper and tin. The copper content 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 a crucible until decomposition was complete and a black powder obtained.

<i>Results:</i>	<i>mass of crucible + black powder</i>	= 26.658g
	<i>mass of crucible</i>	= 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.

- 4.** 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 desiccator, 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)** 5.9×10^{-2} g **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)** $\text{CuCO}_3 \rightarrow \text{CuO} + \text{CO}_2$ **b)** 88.98%
4. a) heating until there is no more change in weight **b)** BaCl_2O_6 or $\text{Ba}(\text{ClO}_3)_2$