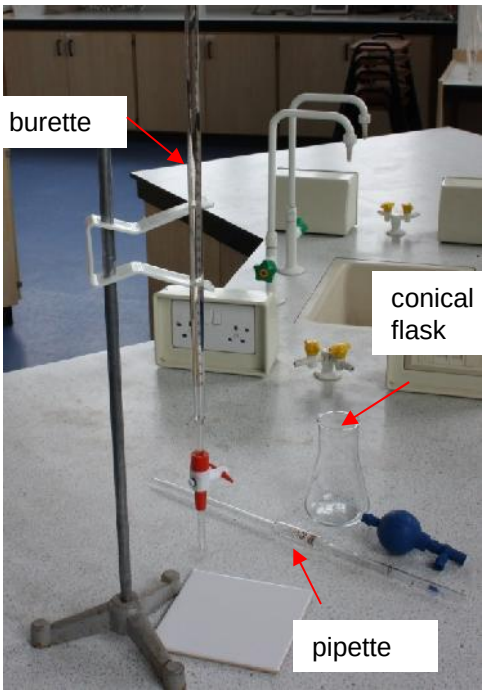
Titrations

Titrations are done often to find out the concentration of one substance by reacting it with another substance of known concentration.

They are often done with neutralisation reactions, but can be done with redox reactions.

One substance (generally the one we don't know the concentration) is put in the conical flask. It is measured using a volumetric pipette.
The other substance is placed in the burette



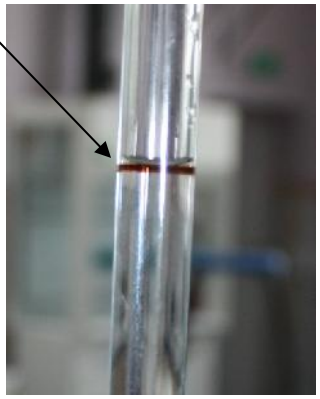
However, the standard phrase: **titrate solution A with solution B** means that A should be in the conical flask and B should be in the burette.

A conical flask is used in preference to a beaker because it is easier to swirl the mixture in a conical flask without spilling the contents.

Method for Titration

Using the pipette

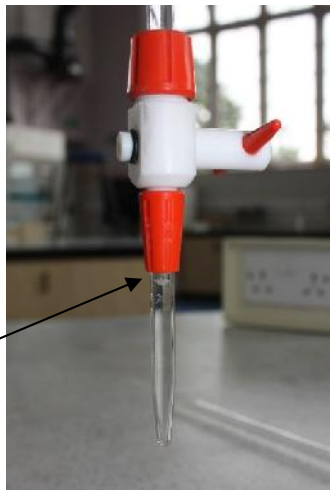
Make sure bottom of meniscus is on line on neck of pipette



•**rinse pipette** with substance to go in it (often alkali).
•**pipette 25 cm^3 of solution A into conical flask.** The volumetric pipette will have a mark on its neck to show the level to fill to. The bottom of the meniscus should sit on this line.
•**touch surface of solution with pipette** (to ensure correct amount is added). A small amount of solution will be left in the pipette at this stage. The calibration of the pipette will take into account this effect. It should not be forced out.

Using the burette

The burette should be rinsed out with substance that will be put in it. If it is not rinsed out the acid or alkali added may be diluted by residual water in the burette or may react with substances left from a previous titration. This would lead to the concentration of the substance being lowered and a larger titre being delivered.



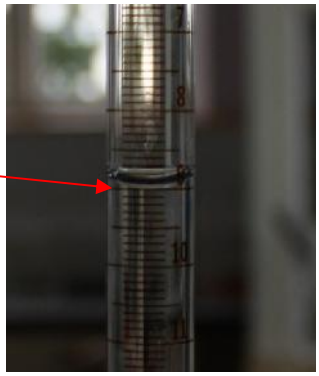
Don't leave the funnel in the burette because small drops of liquid may fall from the funnel during the titration leading to a false burette reading (would give a lower titre volume)

make sure the jet space in the burette **is filled** with the solution and air bubbles are removed.

If the jet space in the burette is not filled properly prior to commencing the titration it will lead to errors if it then fills during the titration, leading to a larger than expected titre reading.

Read the bottom of the meniscus on the burette

This is reading 9.00cm^3



Even though a burette has marking reading to 0.1cm^3, the burette readings should always be given to 2dp either ending in 0.0**0** or 0.0**5**. 0.0**5**cm^3 is the volume of 1 drop of solution delivered from a burette and so this is the smallest difference in readings that can be measured. If the bottom of the meniscus sits on a line it should end with a 0.0**0** as in the above example 9.0**0**cm^3. If the meniscus sits between two lines it should end 0.0**5**. e.g. if the bottom of the meniscus sits between the lines marked 9.1 and 9.2, you should record 9.1**5**

Adding indicator

Add **a few drops of indicator** and refer to colour change at end point

phenolphthalein
If acid is added from the burette the colour change would be pink (alkali) to colourless (acid): end point pink colour just disappears [use with titrations using strong alkalis e.g. NaOH]

Use a white tile underneath the flask to help observe the colour change

Methyl orange

Methyl orange is a suitable indicator for neutralisation reactions where strong acids are used.
It is red in acid and yellow in alkali. It is orange at the end point.

phenolphthalein
Alkali colour

phenolphthalein acid colour

Methyl orange
Alkali colour

Methyl orange
end point

Methyl orange
acid colour

Add solution from burette whilst **swirling the mixture** and **add dropwise at end point**

Distilled water can be added to the conical flask during a titration to wash the sides of the flask so that all the acid on the side is washed into the reaction mixture to react with the alkali.
It does not affect the titration reading as water does not react with the reagents or change the number of moles of acid added.

note burette reading before and after addition of solution
repeats titration until **at least 2 concordant results** are obtained- two readings within 0.1 of each other

A single titration could be flawed. Repeating allows for anomalous titres to be spotted and discounted

Only distilled water should be used to wash out conical flasks between titrations because it does not add any extra moles of reagents

If **2 or 3 values are within 0.10cm^3** and therefore **concordant** or close then we can say results are accurate and **reproducible** and **the titration technique is good and consistent**

Recording results
•Results should be clearly recorded in a table
•Result should be recorded in full (i.e. both initial and final readings)
•**Record titre volumes to 2dp (0.05 cm^3)**

Titration number	1	2	3
Initial burette reading (cm^3)	0.50	2.50	1.55
Final burette reading (cm^3)	24.50	27.00	25.95
Titre (cm^3)	24.00	24.50	24.40

Working out average titre results
Only make an average of the concordant titre results

Average titre = (24.50+ 24.40)/2 = 24.45

Safety precautions

Acids and alkalis are corrosive
(at low concentrations acids are irritants)
Wear eye protection and gloves
If spilled immediately wash affected parts after spillage

If substance is unknown treat it as potentially toxic and wear gloves.

Testing batches
In quality control it will be necessary to do titrations/testing on several samples as the amount/concentration of the chemical being tested may vary between samples.

Titrating mixtures
If titrating a mixture to work out the concentration of an active ingredient it is necessary to consider if the mixture contains other substances that have acid base properties.
If they don't have acid base properties we can titrate with confidence.

Example 1: 23.6cm^3 of H_2SO_4 neutralised 25.0cm^3 of 0.150M NaOH. What is the concentration of the H_2SO_4?
$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Step 1: work out amount, in mol, of sodium hydroxide
amount = conc x vol
= 0.15 x 0.025
= 0. 00375 mol

Step 2: use balanced equation to give moles of H_2SO_4
2 moles NaOH : 1 moles H_2SO_4
So 0.00375 NaOH : 0.001875 moles H_2SO_4

Step 3 work out concentration of H_2SO_4
conc= amount/Volume
= 0.001875 / 0.0236
= 0.0794 mol dm^{-3}

Example 2: A 25.0cm^3 sample of vinegar was diluted in a 250cm^3 volumetric flask. This was then put in a burette and 23.10cm^3 of the diluted vinegar neutralised 25.0 cm^3 of 0.100 M NaOH. What is the concentration of the vinegar in gdm^{-3} ?
$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$

Step 1: work out amount, in mol, of sodium hydroxide
amount = conc x vol
= 0.10 x 0.025
= 0. 00250 mol

Step 2: use balanced equation to give moles of CH_3CO_2H
1 moles NaOH : 1 moles CH_3CO_2H
So 0.00250 NaOH : 0.00250 moles CH_3CO_2H

Step 3 work out concentration of diluted CH_3CO_2H in 23.1 (and 250 cm^3)in moldm^{-3}
conc= amount/Volume
= 0.00250 / 0.0231
= 0.108 mol dm^{-3}

Step 4 work out concentration of original concentrated CH_3CO_2H in 25cm^3 in moldm^{-3}
conc = 0.108 x 10 = 1.08 mol dm^{-3}

Step 5 work out concentration of CH_3CO_2H in original concentrated 25 cm^3 in gdm^{-3}
conc in gdm^{-3} = conc in mol dm^{-3} x Mr
= 1.08 x 60 = 64.8 g dm^{-3}

To turn concentration measured in mol dm^{-3} into concentration measured in g dm^{-3} multiply by Mr of the substance
conc in g dm^{-3} = conc in mol dm^{-3} x Mr
The concentration in g dm^{-3} is the same as the mass of solute dissolved in 1dm^3

Common Titration Equations

$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$HCl + NaOH \rightarrow NaCl + H_2O$

$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

Example 3

950 mg of impure calcium carbonate tablet was crushed. 50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid, an excess, was then added and the mixture was transferred to a volumetric flask. The volume was made up to exactly 100 cm^3 with distilled water. 10.0 cm^3 of this solution was titrated with 11.1cm^3 of 0.300 mol dm^{-3} sodium hydroxide solution.
What is the percentage of $CaCO_3$ by mass in the tablet

1. Calculate the number of moles of sodium hydroxide used

amount = conc x vol
= 0.30 x 0.0111
= 0. 00333 mol

2. Work out number of moles of hydrochloric acid left in 10.0 cm^3
use balanced equation to give moles of HCl
1 mol NaOH : 1 mol HCl
So 0.00333 NaOH : 0.00333 moles HCl

3. Calculate the number of moles of hydrochloric acid left in 100 cm^3 of solution

Moles in 100cm^3 = 0.00333 x10
=0.0333

4. Calculate the number of moles of HCl that reacted with the indigestion tablet.

In original HCl 50.0 cm^3 of 1.00 mol dm^{-3} there is 0.05moles

moles of HCl that reacted with the indigestion tablet. =0.05 -0.0333
=0.0167

5 Use balanced equation to give moles of $CaCO_3$
$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
2 mol HCl : 1 mol $CaCO_3$
So 0.0167 HCl : 0.00835 moles $CaCO_3$

6. work out the mass of $CaCO_3$ in original tablet
mass= amount x Mr
= 0.00835 x 100 = 0.835 g

percentage of $CaCO_3$ by mass in the tablet = 0.835/0.950 x100
= 87.9 %

Uncertainty

Readings and Measurements

Readings
the values found from a single judgement when using a piece of equipment

Measurements
the values taken as the difference between the judgements of two values (e.g. using a burette in a titration)

In general, if uncertainty is not indicated on apparatus, the following assumptions are made:
For an analogue scale-
The uncertainty of a reading (one judgement) is at least ±0.5 of the smallest scale reading.
The uncertainty of a measurement (two judgements) is at least ±1 of the smallest scale reading.
- If the apparatus has a digital scale, the uncertainty is ± the resolution of the apparatus in each measurement

Calculating Apparatus Uncertainties
Each type of apparatus has a sensitivity uncertainty

- balance ± 0.001 g (if using a 3 d.p. balance)
- volumetric flask ± 0.1 cm^3
- 25 cm^3 pipette ± 0.1 cm^3
- burette (start & end readings and end point) ± 0.15 cm^3

Calculate the percentage error for each piece of equipment used by

$$\% \text{ uncertainty} = \pm \frac{\text{uncertainty}}{\text{Measurement made on apparatus}} \times 100$$

e.g. for burette
% uncertainty = 0.15/average titre result x100

To calculate the maximum **total** percentage apparatus uncertainty in the final result add all the individual equipment uncertainties together.

Uncertainty of a measurement using a burette. If the burette used in the titration had an uncertainty for each reading of +/– 0.05 cm^3 then during a titration two readings would be taken so the uncertainty on the titre volume would be +/– 0.10 cm^3 . Then often another 0.05 is added on because of uncertainty identifying the end point colour change

Reducing uncertainties in a titration

Replacing measuring cylinders with pipettes or burettes which have lower apparatus uncertainty will lower the % uncertainty.

To reduce the % uncertainty in a burette reading it is necessary to make the titre a larger volume. This could be done by: increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

To decrease the apparatus uncertainties you can either decrease the sensitivity uncertainty by using apparatus with a greater resolution (finer scale divisions) or you can increase the size of the measurement made.

If looking at a series of measurements in an investigation, the experiments with the smallest readings will have the highest measurement uncertainties.

Reducing uncertainties in measuring mass
Using a balance that measures to more decimal places or using a larger mass will reduce the % uncertainty in weighing a solid.

Weighing sample before and after addition and then calculating difference will ensure a more accurate measurement of the mass added.

Calculating the percentage difference between the actual value and the calculated value

If we calculated an *Mr* of 203 and the real value is 214, then the calculation is as follows:
Calculate difference 214-203 = 11
% = 11/214 x100
=5.41%

If the %**uncertainty** due to the apparatus **<** percentage difference between the actual value and the calculated value then there is a discrepancy in the result due to other errors.

If the %**uncertainty** due to the apparatus **>** percentage difference between the actual value and the calculated value then there is no discrepancy and all the difference between values can be explained by the sensitivity of the equipment.

Errors in Titrations

1) A student carried out an experiment to determine the concentration of ethanoic acid in a solution of vinegar.
   - The student used a measuring cylinder to measure out 25.0 cm^3 of the vinegar solution.
   - This solution was then transferred to a 250 cm^3 volumetric flask and the liquid level was carefully made up to the mark with distilled water.
   - A pipette was used to transfer 25.0 cm^3 portions of the acidic solution to conical flasks.
   - The solution was then titrated with sodium hydroxide solution, concentration 0.100 mol dm^{-3}, using phenolphthalein as the indicator.

   The average titre was 26.5cm^3

a) Suggest, with reasons, how the student's method of preparing the diluted solution could be improved.

b) The maximum total errors for the pipette and the burette in the titration are

   pipette ±0.05 cm^3

   burette ±0.15 cm^3

   These errors take into account multiple measurements.

   Estimate the combined maximum percentage error in using both of these pieces of apparatus.

c) Give two changes you could make to reduce the percentage error in using the burette.

d) State why it is important to fill the space below the tap in the burette with sodium hydroxide before beginning an accurate titration.

e) Give a reason why a 250 cm^3 conical flask is preferred to a 250 cm^3 beaker for a titration.

f) During a titration, a chemist rinsed the inside of the conical flask with deionised water. The water used for rinsing remained in the conical flask.

   (i) Give a reason why this rinsing can improve the accuracy of the end-point.

   (ii) Explain why the water used for rinsing has no effect on the accuracy of the titre.

g) Give a reason why repeating a titration makes the value of the average titre more reliable.

h) Phenolphthalein is an acid. State how the average titre would change if a few cm^3, rather than a few drops, of the indicator were used by mistake in this titration.

i)Vinegar contains other substances which improve flavour. Suggest one reason why these substances could affect the titration with sodium hydroxide.

j) Suggest why the student checks the concentration of the ethanoic acid in several batches of vinegar.

k) Calculate the concentration of the vinegar in the 250 cm^3 flask.

Errors in the method will lead to an inaccurate value of the concentration of acid being calculated. How would the following situations affect the magnitude of the concentration of vinegar calculated? Explain why

i. air lock below tap in burette
ii. air bubble in pipette of vinegar
iii. too much water is added so the meniscus of the diluted acid is above the line on the neck of the volumetric flask
iv. the concentration of the alkali has been incorrectly given. It is actually 0.095mol dm^{-3}
v. The conical flask contains some distilled water before the vinegar is added.
vi. The burette is not rinsed with sodium hydroxide
vii. The pipette was washed with water between titres

2) In a series of titrations a student obtained the following titres (all in cm^3).

Rough	1	2
25.7	25.20	25.35

State what this student must do in order to obtain an accurate average titre in this experiment.

3) A student wanted to test the acidity of a 100cm^3 sample of champagne. She suggested that the 100 cm^3 champagne should be divided into four portions before the titration. Explain how this change increases the reliability and decreases the accuracy of the experiment.

4) A student carried out an experiment to calculate the value of x in $Na_2CO_3.xH_2O$
The correct value of x is 10, making the *M*r of $Na_2CO_3.10H_2O$ is 286.0

a) The maximum percentage error in the experiment that can be due to the apparatus is ±1.0%. If the only error is apparatus error, calculate the minimum value of the *M*r of $Na_2CO_3.10H_2O$ that could be obtained from an experiment.

Use this minimum value of the *M*r to calculate a minimum experimental value for *x*

b) A titration was carried out with a sample of pure washing soda that had been stored for some time. A student obtained a value of 8.6 for the value of *x*. The container from which the hydrated sodium carbonate was taken was labelled $Na_2CO_3.10H_2O$.
Assume that the student carried out the titration and the calculation accurately. State a reason why the number of moles of water of crystallisation is less than 10.