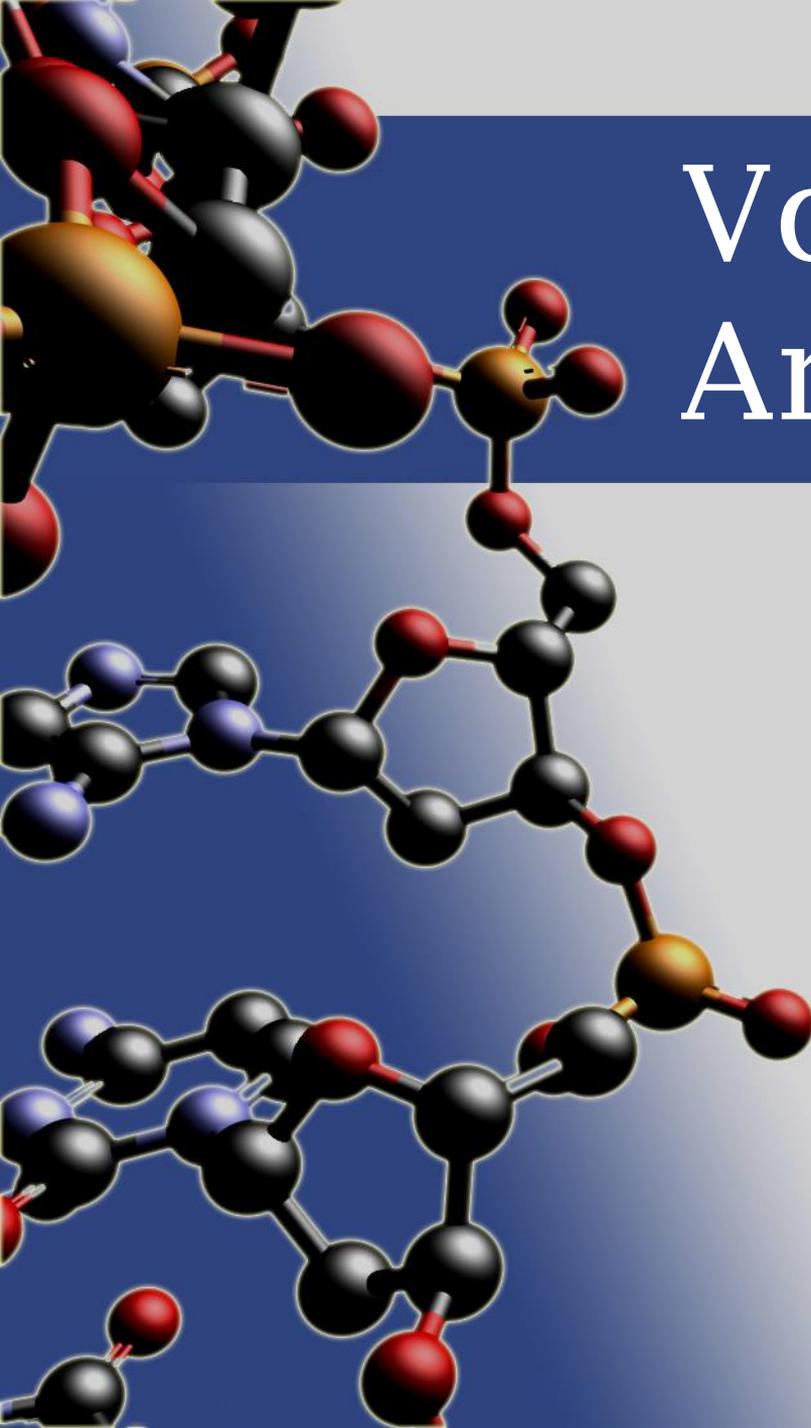# Volumetric Analysis

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Volumetric Analysis

Introduction

The Equipment

The Terms

The Process

Calculations

Introduction

- Often in chemistry we need to work out the concentration of a solution. There are a number of methods we could use, but they all involve working out the amount of the substance in a certain volume.

- Volumetric analysis involves using volumes of liquids to analyse a concentration. To do this we need the following things:
  - A chemical of a known concentration that will react with our 'unknown' concentration chemical
  - An indicator that will tell us when all the chemical has been reacted
  - A number of pieces of equipment that we can use to measure volume accurately

Volumetric Analysis

- Is a method that involved chemical reactions between substances in aqueous solutions.

- The amount, in mol, of the substance being analysed is determined by measuring the volume of the test solution required to react completely with a volume of solution with a known concentration.

- This method is usually faster and more convenient than gravimetric analysis.

Concentration

- Concentration is the measure of the amount of solute in a specified volume of solvent.

- Concentration is usually expressed as molar concentration, or molarity.

- C = n/V or re-arranged we can use n = CV

The Equipment

- Volumetric analysis involves a few pieces of equipment:

    Pipette – for measuring accurate and precise volumes of solutions

    Burette – for pouring measured volumes of solutions

    Conical flask – for mixing two solutions

    Wash bottles – these contain distilled water for cleaning equipment

    Funnel – for transfer of liquids without spilling

    Volumetric flasks – a flask used to make up accurate volumes for solutions of known concentration

The Process - Preparation

- Two solutions are used:
  - The solution of unknown concentration;
  - The solution of known concentration – this is also known as the **standard solution**
- Write a balanced equation for the reaction between your two chemicals
- Clean all glassware to be used with distilled water. The pipettes and burettes will be rinsed with the solutions you are adding to them

Preparation of Standard Solutions

- A solution with an accurately known concentration is a standard solution

- A standard solution can be prepared from a primary standard by dissolving an accurately known mass to make up an accurately known volume of solution. Volumetric flasks are used to obtain precise volumes.

- What is a primary standard?

Primary Standards

- Substances that are so pure that the amount of substance, in mole, can be calculated accurately from their mass are called primary standards.

- A primary standard should:

- Be readily available
- Be available in a pure form
- Not readily react with the atmosphere
- Be easily stored
- Have a high molar mass
- Be inexpensive

- Examples: sodium carbonate, sodium borate, hydrated oxalic acid.

Making a Standard Solution

- A standard solution can be prepared from a primary standard by dissolving an accurately known mass to make up an accurately known volume of solution.

- Precise volumes of solutions are obtained using volumetric flasks.

1. Place weighed sample in volumetric flask.
2. Half fill with water, shake to dissolve the sample.
3. Add water to the calibration line, shake again.

Primary Standards

- Why do we not use common acidic and basic substances as standard solutions?

- Because KOH, NaOH, HCl and H_2SO_4 are either impure or their exact concentration may not be specified. The bases tend to absorb water as they react with carbon dioxide in the air.

1 Place weighed sample in volumetric flask.

2 Half fill with water. Shake to dissolve the sample.

3 Add water to the calibration line. Shake again.
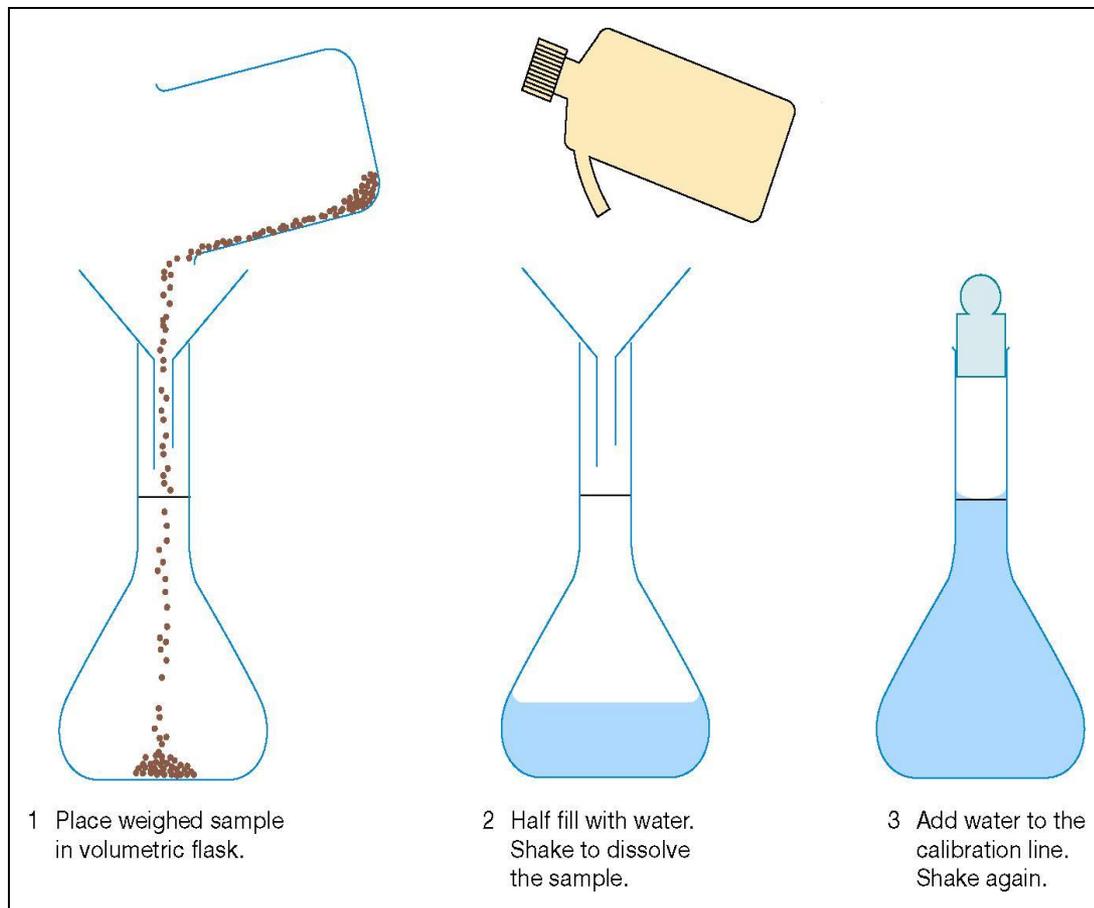
Preparation of a standard solution

- The burette is attached to a clamp stand above a conical flask
- The burette is filled with one of the solutions (in this case a yellow standard solution)
- A pipette is used to measure an aliquot of the other solution (in this case a purple solution of unknown concentration) into the conical flask
- Prepare a number of flasks for repeat tests
- Last, an indicator is added to the conical flask
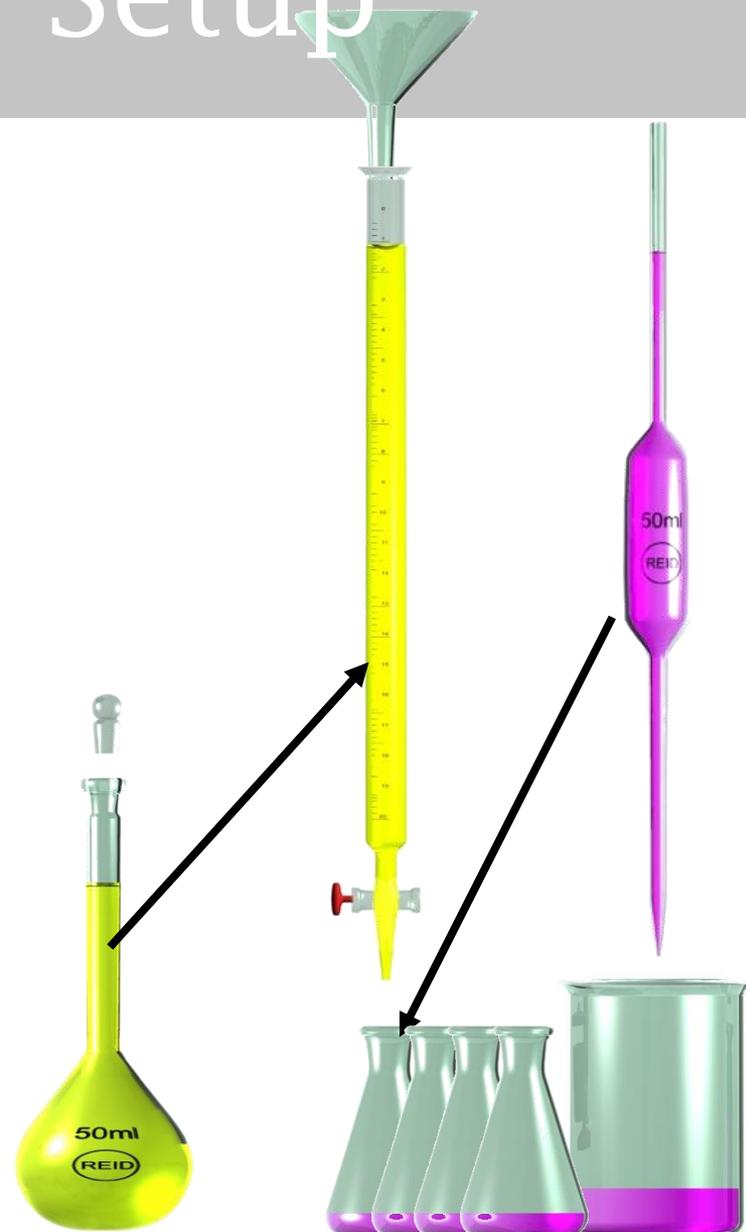
Process – The Titration

- Read the initial level of liquid in the burette
- Turn the tap to start pouring out liquid of the burette into the flask. Swirl the flask continuously. When the indicator begins to change colour slow the flow.
- When the colour changes permanently, stop the flow and read the final volume. The volume change needs to be calculated (and written down). This volume is called a titre
- Repeat the titration with a new flask now that you know the 'rough' volume required. Repeat until you get precise results
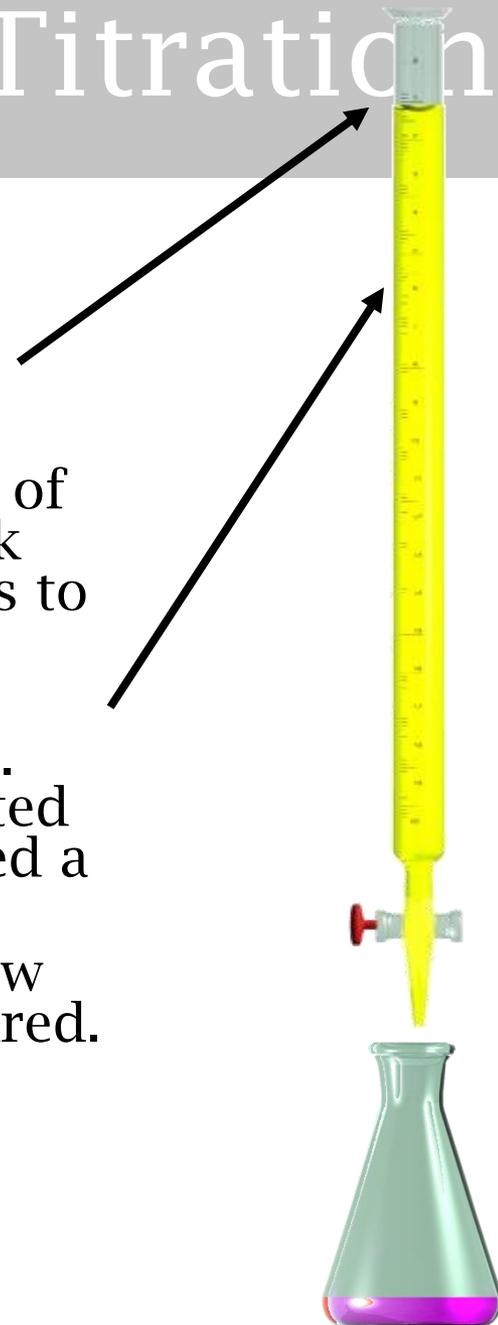
- We will have a number of titres for each solution we analysed. The first thing we do is to calculate the mean (average) titre:

Titres   = 12.6ml 13.0ml 13.1ml 12.9ml

Mean   = Sum of the titres / number of titres
               = (13.0 + 13.1 + 12.9) / 3
               = 13.0ml

- Why did we discard the 12.6ml reading?
- Concordant titres – three titres that differ by a **_maximum 0.10mL_** between the lowest & highest reading

1. Write down the balanced equation e.g.

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

2. Write down everything else we know. This will be:
   a. Volume of liquid in the pipette
   b. Mean titre (from burette)
   c. The concentration of the standard solution
   d. Was the standard solution in the pipette or in the burette?

3. Now calculate the **amount** in the standard solution you used. Use the $n = cV$ formula. **Remember:** the millilitres must always be converted into litres for this formula!

4. Now that you know how many moles of the standard you used, look at the balanced equation. Would you need more or less of the 'unknown' substance in a balanced reaction?

   - If more, then how much more – two times, three times?
   - If less, then how much less – half as much, one third?

   We can calculate the amount of the unknown:

   - We multiply if we need more i.e. 2x, 3x, …etc
   - We divide if we need less i.e. ½ = divide by 2, …etc

5. Now we have the **volume** and **amount** of the 'unknown' substance. We can now rearrange our $n = cV$ formula to $c = n/V$

- Remember:
  - All the calculations must be in litres (not millilitres)
  - The final value must have units (mol L^{-1} or M) written after it

Example:

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

2. - Standard solution = NaOH (in burette) = $0.1 mol L^{-1}$
   - Unknown concentration = H_2SO_4 (from 20ml pipette)
   - Titres = 12.6ml, 13.1ml, 13.0, 12.9ml
   - Average titre = (13.1+13.0+12.9) / 3 = 13.0ml

3. Amount of NaOH = cV = 0.1 x (13/1000) = 0.0013mol

4. Amount of H_2SO_4 = half of NaOH = 0.0013/2 = 0.00065mol

5. Concentration H_2SO_4 = n/V = 0.00065/(20/1000) = 0.325 M

$$HCl \ + \ NaOH \rightarrow NaCl \ + H_2O$$

Titres: 12.1mL, 12.3mL, 12.1mL, 12.0mL

Known solution details: HCl in the burette,
                Concentration = 0.522 M

Unknown solution details: NaOH
                                15mL aliquots

Calculations:

Answer: 0.4199M

Titrations

- Key terms to remember:
- **Aliquot** – volume measured out by the pipette
- **Standard solution** – pure substances with known concentrations
- **Titre** – the volume of solution added from the burette
- **End point** – signalled by a change in colour of an indicator (indicators are chosen so they change colour as close as possible to the equivalence point)
- **Equivalence point** – the point in the reaction which the reaction is just complete (the reactants are in their exact mole proportions)
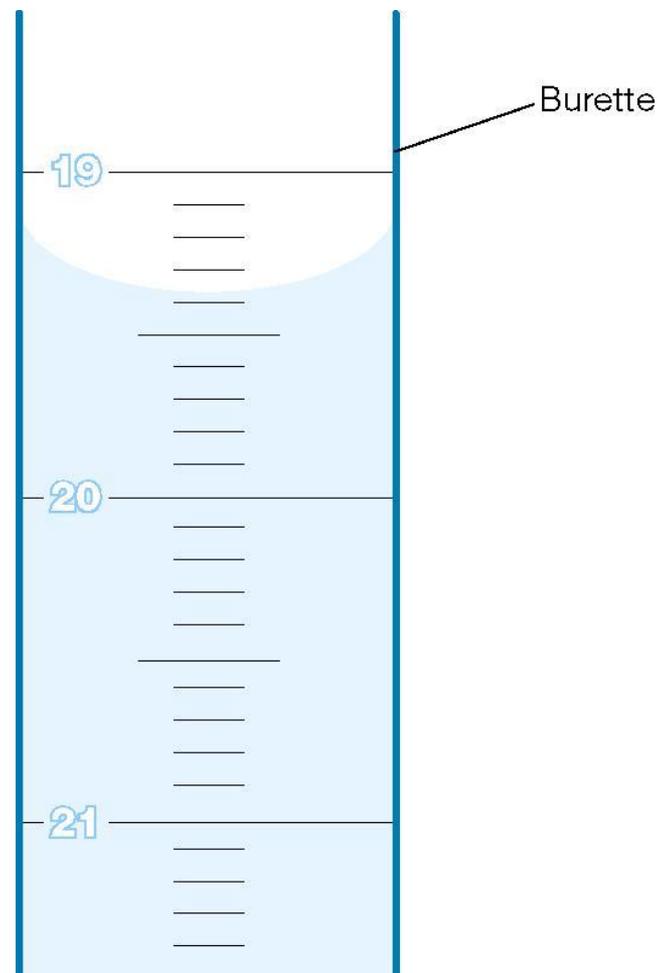
Types of Volumetric Analysis:

- Acid base (neutralisation)

- Redox (oxidation & reduction)

- Back titrations

Use of pipette equipment

Graduation line

A pipette must always be filled using a safety pipette filler. When the pipette is filled correctly, the meniscus sits on the graduation line. Remember burette titres are read going DOWN.

Burette

19

20

21

Measurement Errors

- Experimental error in the lab can either be systematic or random.

- *Systematic* errors result from an equipment fault, for example a measuring cylinder or burette is incorrectly marked.

- *Random* errors are human errors that result from varied reading off the markings on equipment. By repeating measurements these can be reduced.

Accuracy

- The accuracy with which the volumes of the aliquot and titre are measured depends on the calibration of the pieces of equipment used.

- Analytical pipettes deliver fixed, accurate volumes of liquid.

Errors & Uncertainties

- There are always errors associated with measurements made during experimental work.

- Typical uncertainties associated with volumetric analysis are:

  - 20.0mL pipette ± 0.05mL

  - Burette ±0.02mL for each reading

  - 250.0mL volumetric flask ±0.03mL

Errors & Uncertainties cont...

- Burettes are usually calibrated at 0.1mL intervals.
- The meniscus is usually read to the bottom curve and the volume can be estimated to the nearest 0.02mL
- If the meniscus lies exactly on a line, it should be recorded to the second decimal place to indicate this.
- It is usual to keep repeating titrations until three concordant titres are obtained, that means three titres differing by a maximum of 0.1mL from highest to lowest.
- This is because the volume of one single drop from a burette is 0.05mL, so taking the average of three results assumes that they will be no more than one drop over or under the accurate titre.

Indicators used for acid-base titrations

- An **indicator** is a substance that undergoes a change in colour when the end-point of a titration is reached
- **An acid-base indicator is itself a weak acid (or its conjugate base)**
- Methyl orange as an indicator. It changes from red (at pH 3.1) to orange-yellow (at pH 4.4)

pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Common indicators used in VCE Chemistry

TABLE 4.1 Common indicators

Indicator	Colour of acid form	Colour of base form	pH range
Phenolphthalein	Colourless	Pink	8.2–10.0
Methyl orange	Pink	Yellow	3.2–4.4
Bromothymol blue	Yellow	Blue	6.0–7.6