1) Error Analysis

Apparatus Errors (uncertainty)

Every time you make a measurement with a piece of apparatus, there is a small margin of error (i.e. uncertainty) in that measurement due to the apparatus itself.

For example, no balance can measure an exact mass but a very expensive and high resolution balance may be able to measure a mass to the nearest 0.0001 g, while a cheaper, lower resolution balance may only measure it to the nearest 0.1 g.

Errors such as this are known as apparatus error (uncertainties) and cannot be avoided, although they can be reduced by using the highest resolution equipment available. For example, when measuring out 25 cm^3 of a solution, a pipette is much offers higher resolution than a measuring cylinder.

When you do quantitative experiments (those that require you to measure a quantity), you will have to calculate the total apparatus error from the sum of the apparatus error for each piece of equipment you use to make a measurement.

$$\text{Apparatus error for each piece of equipment} = 100 \times \frac{\text{margin of error}}{\text{quantity measured}}$$

For example, imagine a pupil doing an experiment where she measured out 1.245 g of a base, make it up to 250 cm^3 of solution in a volumetric flask, pipetted 25 cm^3 of that solution into a conical flask, and then found that it reacted with 23.30 cm^3 of acid in a titration using a burette.

Balance	(± 0.001 g)	100 x (0.001/1.245)	= 0.08%
Pipette	(± 0.1 cm^3)	100 x (0.1/25)	= 0.40%
Volumetric flask	(± 0.1 cm^3)	100 x (0.1/250)	= 0.04%
Burette	(± 0.15 cm^3)	100 x (0.15/23.30)	= 0.64%
Total apparatus error			**= 1.16%**

This means that the result of the experiment should be within 1.16% of the correct value.

When experiments are designed, we aim to ensure that the total apparatus error is minimised by working on a suitable scale and with suitable apparatus. A very small titre for example (e.g. 5 cm^3) leads to a very large apparatus error for the burette (3%).

Experimental Errors

When you do an experiment you will make some small errors due to your technique being less than perfect. You can calculate your experimental error as shown:

$$\text{Experimental error} = 100 \times \frac{\text{(real answer – experiment answer)}}{\text{real answer}}$$

If experimental error is smaller than apparatus error, then you have an accurate result. However, if experimental error is larger than apparatus error, then the result is inaccurate.

For example, imagine in the experiment above that the acid concentration was being measured and was found to be 0.0995 mol dm^{-3} compared to the real value of 0.101 mol dm^{-3}.

$$\text{Experimental error} = 100 \times \frac{(0.101 - 0.0995)}{0.101} = \mathbf{1.49\%}$$

The experimental error (1.49%) is greater than the apparatus error (1.16%) meaning that the results are inaccurate.

2) Titrations

Preparation of stock solutions

1) Find the mass of a clean, dry weighing bottle (high precision balance). All masses should be recorded in a table.
2) Measure out the approximate mass of sample (low precision balance). Always take the bottle off the balance when adding sample (to avoid spilling sample on the balance which can both damage the balance and makes the weighing inaccurate).
3) Find the mass of the sample on the high precision balance.
4) Wash the contents of the weighing bottle into a 250 cm^3 volumetric flask using de-ionised water and a clean funnel.
5) Add more de-ionised water and shake well to dissolve.
6) Make up to 250 cm^3 (shake well before and after reaching the mark – make up to mark using a clean teat pipette.

Titrations

1) Wash burette with water and then the solution to be used.
2) Fill the burette, ensuring the bottom part is filled. Make sure you take the funnel out of the burette before doing a titration.
3) Clean pipette first with water (blow out all water with the filler and dry the outside with a cloth) and then with the solution that it going to be measured in it.
4) Transfer 25 cm^3 with pipette into a clean conical flask (drain by gravity and touch the tip under the surface at the end).
5) Add a few drops of indicator to the conical flask.
6) The first titration is rough (unless judged to be accurate) – note the start and end burette readings.
7) Repeat titrations, going dropwise near the end point – washing and swirling (a white tile may help, as may another flask with original colour).
8) Repeat until you have concordant results (two within 0.10 cm^3)
9) Record results to the nearest 0.05 cm^3, e.g. 24.80 cm^3, etc., in a table similar to the one below.

	rough	accurate 1	accurate 2	accurate 3
initial reading (cm^3)	0.10	24.35	0.00	23.90
final reading (cm^3)	24.35	48.40	23.85	28.00
titre (cm^3)	24.25	24.05	23.85	24.10
used in mean	×	✓	×	✓

10) Indicate which results are used in the mean (only use concordant results within the mean).

Cleaning glassware

Weighing bottle	Wash and put in oven to dry (lids should go in the drying rack area).
Volumetric flask	Wash and return to cupboard (with stopper in flask).
Burette	Wash and return to drawer.
Pipette	Wash and return to drawer.
Other glassware	Wash and put back in trays.
Other apparatus	Return to where it came from.

3) Organic preparations

a) The Reaction

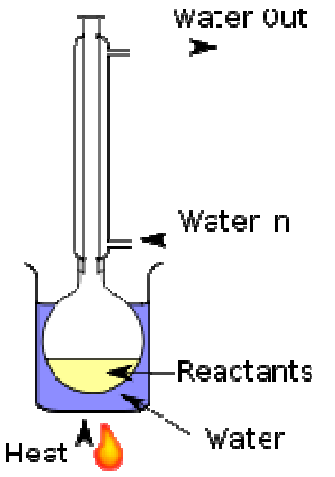
The reactants are measured out either by mass or volume. If volume is used for a liquid, its mass can be calculated from its density.

The reactants are mixed in suitable apparatus. This could be a beaker, a conical flask, or a Quik-Fit flask.

If the reactants need to be cooled, then an ice bath is used.

If the reactants need to be heated, then they are usually refluxed. This allows the reactants (and products) to be heated but not escape from the reaction vessel (as heating causes them to evaporate or even boil). Any escaping vapour condenses and falls back into the flask.

Any bumping granules are placed in the flask to prevent bumping, that is the sudden release of a large bubble of vapour that makes the reaction mixture jump up. The anti-bumping granules produces many small bubbles rather than a large one.



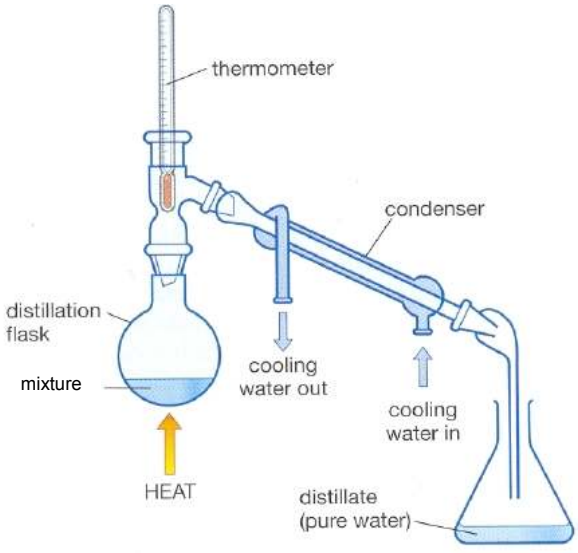
refluxing

b) Separating the product from the reaction mixture

Chemists often talk of "working up" the reaction. This is where the crude (impure) product is separated from the reaction mixture. The method used depends on whether the product is a solid or a liquid.

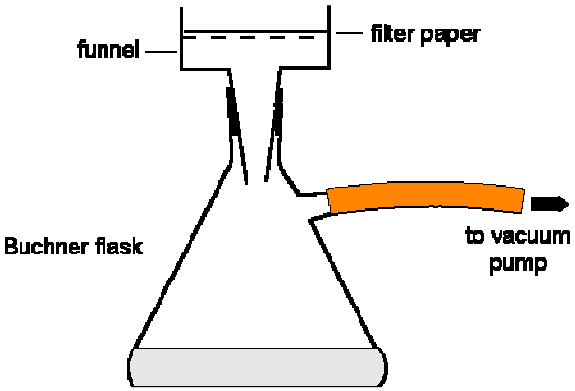
If the product is a liquid:

The product is usually collected by distillation of the reaction mixture. The apparatus is set up for distillation and the chemicals boiling at a range close to that of the product collected (e.g. 15ºC range).



If the product is a solid:

The product is usually collected by filtration from the reaction mixture. Sometimes the product forms as a solid in the reaction, but in other reactions something (e.g. cold water) has to be added to cause the product to form as a solid from solution. The solid is them separated by filtration under reduced pressure using Buchner apparatus.



c) Purifying the product

The product separated will be impure and needs to be purified.

Solids are usually purified by re-crystallisation.

The principle is that the product is dissolved in the minimum amount of a hot solvent to create a solution saturated with the product. Any insoluble impurities can be filtered out (but the apparatus must be heated so the solution does not cool as it is filtered).

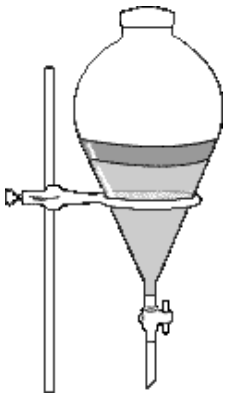
The saturated solution is then allowed to cool slowly, and so the product crystallises out from the solution while any other impurities remain dissolved. Cooling to room temperature may suffice, or an ice bath may be needed. However, if the saturated solution is cooled too quickly, many of the impurities crystallise out as well.

Liquids are usually purified by

a) Putting in a separating funnel with solvents / reagents that do not mix with the product, but in which impurities may dissolve. This usually involves water or water based solutions as most organic compounds are immiscible with water. For example, the product here has been mixed with hydrochloric acid in which any left over reactants would dissolve.

b) If water has been used above, then the product is left to dry by adding a chemical that absorbs water, such as anhydrous sodium sulphate or anhydrous calcium chloride.

c) Finally, the product is distilled again to give a pure product. This time, the product is collected over a much narrower range of temperatures (e.g. 5ºC).

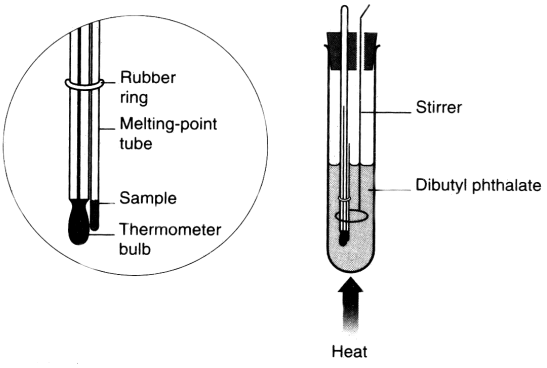


d) Testing the purity of the product

A good test of purity is to see what temperature the product boils or melts at. It will boil / melt over a range of temperatures. The smaller the range (say 2ºC) and the closer this range to the correct value, the purer the product.

For a liquid, the boiling point is usually measured during the final distillation.

For a solid, the melting point is measured by putting a small sample into a capillary tube and strapping it onto a thermometer. The thermometer is placed in a boiling tube half full with dibutyl phthalate and heated, stirring with the rod. Once you know roughly where it melts, the experiment is repeated heating to within 30°C of the melting point and then heating very slowly to measure the exact melting range.

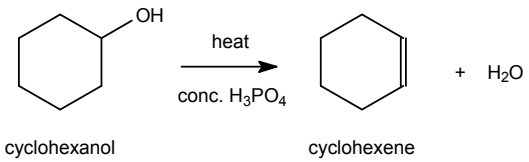


e) Measuring the yield

We also want to know how much product we have made. This is usually recorded as a percentage yield. For example, if a reaction should theoretically make 2 g of a product, but only 0.5 g is formed, then it is a 25% yield.

$$\% \text{ Yield} = \frac{\text{moles of product formed}}{\text{moles of product formed theoretically}} \times 100$$

For example, in the formation of cyclohexene from cyclohexanol. Imagine that 0.45 g of cyclohexene was formed from 1.0 g of cyclohexanol.



Moles cyclohexanol = mass / M_r = 1.0 / 100 = 0.01

Moles cyclohexene theoretically produced = 0.01

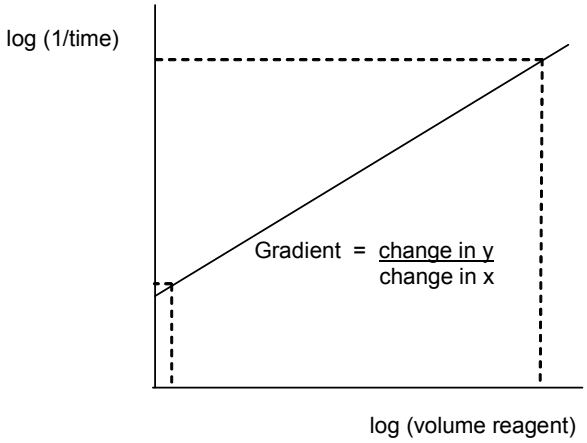
Mass of cyclohexene theoretically produced = moles x M_r = 82.0 x 0.01 = 0.82 g

% Yield = 100 x $\frac{0.45}{0.82}$ = 55 %

4) Kinetics

- The key problem with kinetics practicals is any variation in temperature, as a small change in temperature has a big impact on reaction rate. Controlling the temperature, for example by using a thermostatically controlled water bath, would improve the experiment.
- When recording times, usually the nearest second is appropriate.

- At A2, you may need to plot a log graph to find order with respect to a particular reagent.
  - You should plot log (1/time) on the y axis against log (volume reagent) on the x axis.
  - You should ensure that for each axis you use more than half of the available space.
  - When calculating the gradient, choose two points near opposite ends of the line and remember it is change in y over change in x.
  - Remember that the final order should be a whole number.



5) Test tube observations

- You will often have to carry out test tube reactions and record your observations.
- You must indicate what the reagents were like before mixing and what they were during/after mixing.
- You must clearly state the colour and whether they are solids or solutions.
- Some good examples are shown below:

Reaction	Observation
addition of acidified silver nitrate to a solution of sodium chloride	colourless solution → white precipitate
acidified potassium dichromate (VI) with propan-1-ol	orange solution → green solution
addition of sodium hydrogencarbonate with ethanoic acid	colourless solution → fizzing and colourless solution

6) Calorimetry

If the mass of the water is known (the mass of water = volume of water in grams, e.g. 50 cm^3 of water has a mass of 50 g) and the temperature rise (fall), then the heat released (or absorbed) can be calculated.

- The enthalpy change for a reaction can be found by measuring the temperature change in a reaction.
- The heat energy given out (or taken in) is used to heat (or cool) a known mass of water. We know that it takes 4.18 J of energy to raise the temperature of 1 g of water by 1°C (i.e. 1 K).
- The amount of energy needed to make 1 g of a substance 1°C (1 K) hotter is called the *specific heat capacity* (measured in J g^{-1} K^{-1}).
- The following equation is then used to find the amount of heat energy give out (or absorbed).

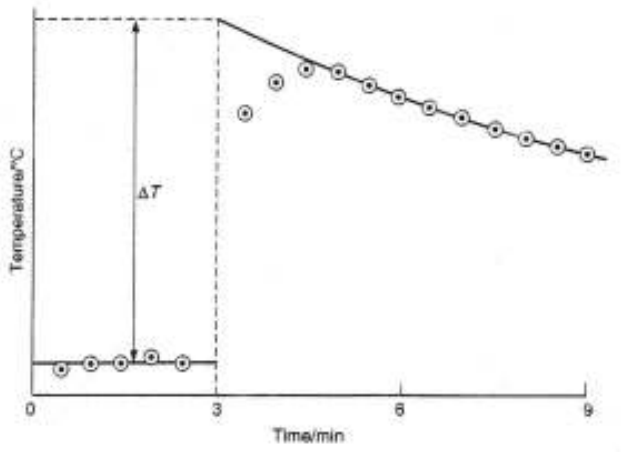
$q = mc\Delta T$

q = heat energy given out (J)
m = mass of substance heated (g)
ΔT = temperature rise (K)
c = specific heat capacity (J g^{-1} K^{-1}) = 4.18 J g^{-1} K^{-1} for water

- To find the enthalpy change in terms of J (or kJ) per mole, the following expression is needed: (***THINK*** kJ per mole!)

$$\text{Enthalpy change (per mole)} = \frac{q}{\text{number of moles reacting}}$$

- For reactions in solution, the reaction is typically done in a supported polystyrene cup (with lid). For combustion reactions, the substance is burned under a copper calorimeter containing water.
- For reactions in solution, if the reaction is very fast, the difference between the starting temperature and the highest temperature recorded is the temperature rise.
- For most reactions in solution, the temperature is recorded every minute (or 30 s) or so and the results plotted on a graph.
- Axes should be chosen so the plot uses more than half of the available space on each axis.
- The graph can be extrapolated back to the time at which the reagents were mixed to find the temperature change.
- **NB – temperatures before the maximum temperature in an exothermic reaction (or minimum temperature for an endothermic reaction) should be <u>ignored</u> when determining the best fit line (which could be a curve or straight line).**



- The main problem with calorimetry experiments is heat loss. This can only be reduced by using a better insulated calorimeter.

7) Significant figures, etc.

- General rule – work to 3 significant figures (unless other rules supercede it)
- General rule – give M_r's to one decimal place (unless other rules supercede it)
- Titrations – give all burette readings to the nearest 0.05 cm^3 (e.g. 26.40 cm^3 not 26.4 cm^3)
- Titrations – give the mean titre to 2 decimal places
- Water of crystallisation – this should be a whole number
- Calorimetry – give all temperatures and the temperature change to the nearest 0.1°C
- Kinetics – record times measured to the nearest second
- Kinetics – order of reactions should be a whole number