

MEASUREMENTS AND ERRORS

- Accuracy** A measure of the closeness of agreement between an individual result and the accepted value. An accurate result is in close agreement with the accepted value.
- Error** The difference between an individual measurement and the true value (or accepted reference value) of the quantity being measured.
- Precision** The closeness of agreement between independent measurements obtained under the same conditions. It depends only on the distribution of random errors (i.e. the spread of measurements) and does not relate to the true value.
- Uncertainty** An estimate attached to a measurement which characterises the range of values within which the true value is said to lie. It is written, for example, as 44.0 ± 0.4 .
- Reliability** The opposite of uncertainty; **high uncertainty = not very reliable** measurement

Accuracy of measurements

Uncertainty is often taken to be **half a division on either side of the smallest unit on the scale**. However, the accuracy of measurements also depends on the quality of the apparatus used (e.g. Grade A or Grade B glassware.)

example If a 100 cm^3 measuring cylinder is graduated in 1 cm^3 divisions.

- Class A - maximum error of half a division (0.5 cm^3)
- Class B - maximum error of a whole division (1 cm^3)

Glassware

When glassware is manufactured there will always be a maximum error. This is usually marked on the glassware.

Temperature Volumetric equipment must not get warm because expansion of the glass will alter the volume; the temperature is marked on the apparatus.

In or out? Apparatus either...

holds an accurate measure **(IN)**

or

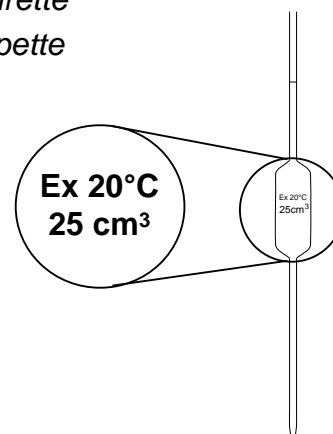
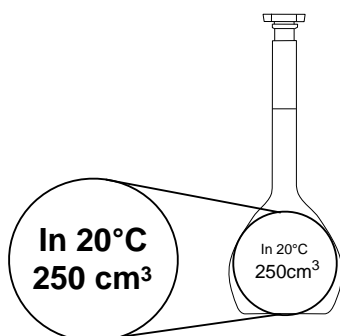
delivers an accurate volume **(EX)**

volumetric flask

burette

measuring cylinder

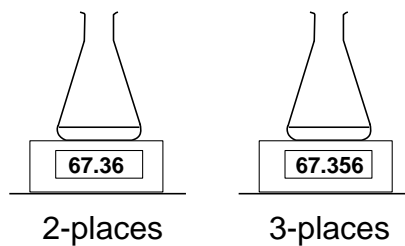
pipette



Reading values

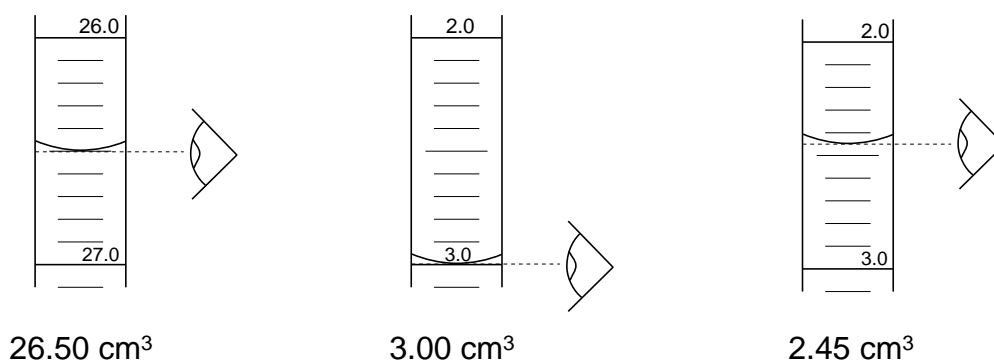
Digital

- top pan balance or pH meter
- record all the digits shown



Non-digital

- burette, measuring cylinder
- record all the figures that are known for certain
- read to half a division
- for a burette, record values to two decimal places ending in a 5 or a 0



Maximum errors

Burette

- graduated in divisions every 0.1 cm³
- maximum error is half a division i.e. ± 0.05 cm³
- burettes are read twice, so the overall maximum error is $2 \times 0.05 = \pm 0.1$ cm³

Pipette

- a 25 cm³ pipette has a maximum error of 0.06 cm³
- like all volumetric equipment it must be used properly

Q.1 Calculate the maximum error of a ...

- 50 cm³ measuring cylinder

cm³

- 10 cm³ measuring cylinder

cm³

Balances

a two-decimal place balance may have a maximum error of 0.005 g

a three-decimal place balance may have a maximum error of 0.0005 g



The significance of the maximum error in a measurement depends upon how large a quantity is being measured. It is useful to quote this error as a **percentage error**.

Percentage Error

- based on two factors
 - maximum error
 - value of measurement
- percentage error =
$$\frac{\text{maximum error} \times 100\%}{\text{value of measurement}}$$
- the smaller the value measured, the greater the percentage error

Volumetric flask (250 cm³)

$$\begin{aligned} \text{maximum error} &= 0.2 \text{ cm}^3 \\ \text{percentage error} &= \frac{0.2 \text{ cm}^3 \times 100}{250 \text{ cm}^3} = \mathbf{0.08\%} \end{aligned}$$

Pipette (25 cm³)

$$\begin{aligned} \text{maximum error} &= 0.06 \text{ cm}^3 \\ \text{percentage error} &= \frac{0.06 \text{ cm}^3 \times 100}{25 \text{ cm}^3} = \mathbf{0.24\%} \end{aligned}$$

Burette

$$\begin{aligned} \text{maximum error} &= 0.05 \text{ cm}^3 \text{ per reading} \\ &0.10 \text{ cm}^3 \text{ per titration (you read it twice)} \\ \text{percentage error} &\text{ depends on the volume delivered} \\ &\text{(the smaller the volume, the bigger the \% error)} \end{aligned}$$

$$\text{for a } 25.00 \text{ cm}^3 \text{ delivery} = \frac{0.10 \text{ cm}^3 \times 100}{25.00 \text{ cm}^3} = \mathbf{0.40\%}$$

$$\text{for a } 15.00 \text{ cm}^3 \text{ delivery} = \frac{0.10 \text{ cm}^3 \times 100}{15.00 \text{ cm}^3} = \mathbf{0.67\%}$$

2-decimal place top-pan balance

$$\begin{aligned} \text{mass of beaker + solid} &= 32.56 \text{ g} & \text{maximum error} &= 0.005 \text{ g} \\ \text{mass of empty beaker} &= 32.16 \text{ g} & \text{maximum error} &= 0.005 \text{ g} \\ \text{mass of solid} &= 0.40 \text{ g} & \text{maximum error} &= 0.01 \text{ g} \\ \text{percentage error} &= \frac{0.01 \text{ g} \times 100}{0.40 \text{ g}} = \mathbf{2.5\%} \end{aligned}$$

3-decimal place top-pan balance

$$\begin{aligned} \text{maximum error over two readings} &\text{ will be } 0.001 \text{ g (2 x 0.0005)} \\ \text{using the above values, percentage error} &\text{ will be } = \mathbf{0.25\%} \end{aligned}$$

Recording volumes during titrations

Burette measurements should be recorded to 2 decimal places with the last figure either 0 or 5.

During a titration, initial and final burette readings should be taken; the titre (actual volume delivered) is calculated by difference. Record titration results in a table as shown below.

	Approx	1	2	3
final volume / cm ³	26.00	26.75	30.85	24.60
initial volume / cm ³	1.00	2.30	6.00	0.25
titre / cm ³	25.00	24.45	24.85	24.35
tick if used to calculate mean		✓		✓

- Mean titres**
- repeat the titrations until there are two **concordant** titres (within 0.10 cm³)
 - take an average of the concordant titres
 - if this is not possible, use the two titres that have the closest agreement

example the two concordant titres are the 1st and 3rd (within 0.1 cm³ of each other)

$$\text{mean (average) titre value} = \frac{24.45 \text{ cm}^3 + 24.35 \text{ cm}^3}{2} = 25.40 \text{ cm}^3$$

$$\text{overall maximum error} = 2 \times 0.05 = 0.10 \text{ cm}^3$$

$$\text{overall percentage error} = \frac{0.10 \text{ cm}^3 \times 100}{25.40 \text{ cm}^3} = \mathbf{0.39\%}$$

There is a case for arguing that the accumulated errors indicate that one decimal place is more appropriate but this should not be used. The maximum error is the worst-case scenario and it is likely that the actual titre will in reality be more accurate than one decimal place.

If concordant titres within 0.05 cm³ of one another are found there is a problem when calculating the mean titre. For example, a student may obtain three recorded titres of 24.45 cm³, 24.85 cm³ and 24.40 cm³.

$$\text{mean titre value} = \frac{24.45 \text{ cm}^3 + 24.40 \text{ cm}^3}{2} = 24.425 \text{ cm}^3$$

This mean titre has a value that is more accurate than the burette can measure. The value of 24.425 cm³ should more correctly be 'rounded' to 24.43 cm³. It would seem very unfair not to credit a mean titre of 24.425 cm³ in this case, especially as the results showed a better concordancy.

In assessed A level practical tasks, the mean of two titres of **25.25 cm³** and **25.20 cm³** will be allowed as **25.2**, **25.20**, **25.25** or **25.225 cm³**.

Errors in procedure

The accuracy of a final result also depends on the procedure used.

For example, in an enthalpy experiment, the measurement of a temperature change may be precise but there may be large heat losses to the surroundings which affect the accuracy of overall result.

Anomalous readings

Where an experiment uses repeated measurements of the same quantity, (e.g. titrations) anomalous readings should be identified. If a titre is clearly outside the range of all other readings, it can be judged as being anomalous and should be ignored when the mean titre is calculated.

If a plotted graph reveals that a value is anomalous, then it too should be ignored.

Introducing rounding errors in multi-step calculations

Example

When 6.074 g of a carbonate is reacted with 50.0 cm³ of 2.0 mol dm⁻³ HCl(aq) (which is an excess), a temperature rise of 5.5 °C is obtained.

[The specific heat capacity of the solution is 4.18 J g⁻¹ K⁻¹]

Heat produced = 50.0 × 4.18 × 5.5 = 1149.5 J = **1.1495 kJ** (by calculator)

Since the least certain measurement (the temperature rise) is only to 2 significant figures the answer should also be quoted to 2 significant figures.

Therefore, the heat produced should be quoted as **1.1 kJ**

If this figure is to be used subsequently to calculate the enthalpy change per mole then a 'rounding' error will be produced. **The 1.1495 kJ value must be used.**

For example, if the carbonate has a molar mass of 84.3 g mol⁻¹, the enthalpy change per mole of carbonate can be calculated from the value above.

Using the calculator value of 1.1495 kJ for the heat produced

enthalpy per mole = 15.95371255 kJ mol⁻¹ = 16 kJ mol⁻¹ (to 2 sig figs)

Using the rounded value of 1.1 kJ for the heat produced,

enthalpy per mole = 15.26671057 kJ mol⁻¹ = 15 kJ mol⁻¹ (to 2 sig figs)

Rounding to 2 sig figs too early produces a 'rounding error'.

References

The Royal Society of Chemistry has produced several very helpful documents on measurements and errors;

www.rsc.org/education/teachers/learnnet/pdf/learnnet/RSCmeasurements_teacher.pdf

www.rsc.org/pdf/amc/brief13.pdf