Identifying errors and estimating uncertainties

Types of uncertainty in measurements

Errors in measurements are not mistakes; they are unavoidable differences between measured values and true values. Often, the true value of a particular measurement is not known, so scientists have to assess the degree of uncertainty in their measurements. ‘Measurement uncertainty’ and ‘experimental error’ often mean the same thing, but the term ‘measurement uncertainty’ is preferable. These are not errors or mistakes on the part of the experimenter, but unavoidable variations in results.

There are three kinds of uncertainty in measurements – random errors, systematic errors and zero errors.

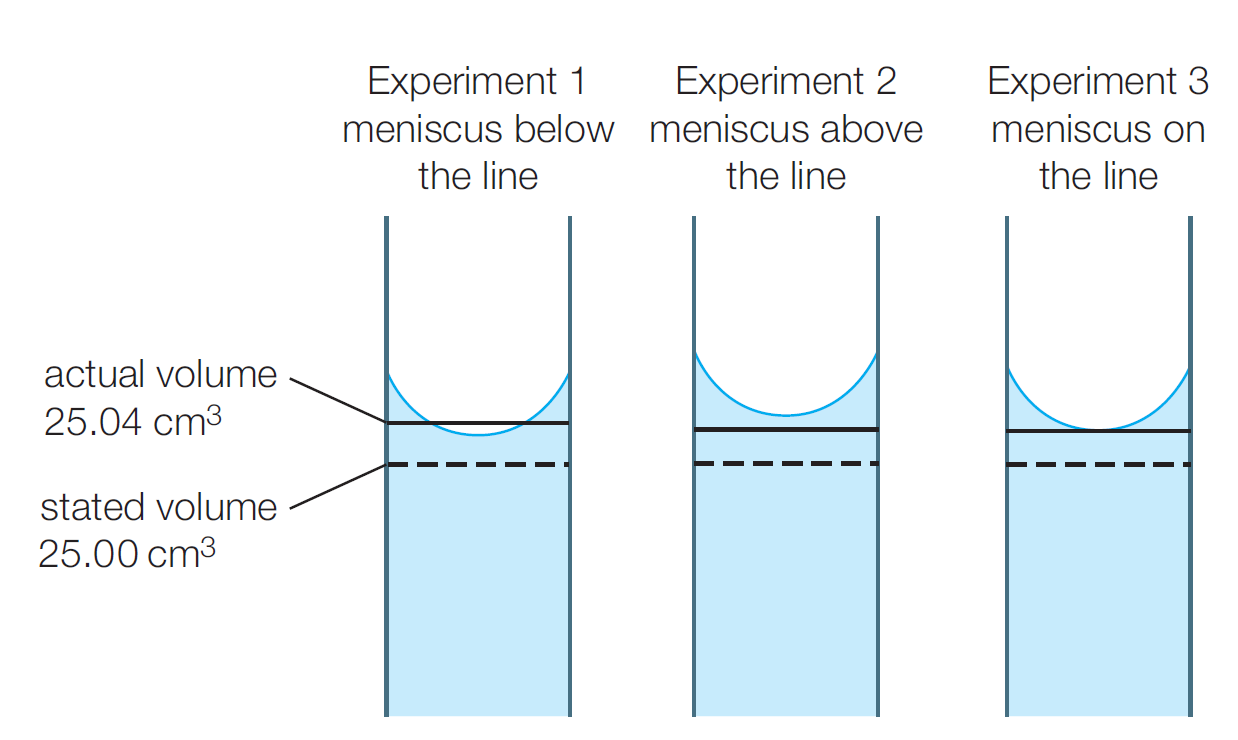
Random errors

Random errors are the uncertainties which arise when a measurement is repeated many times, giving values distributed equally on both sides of the true value. Examples include the slight differences in several measurements of the same length and variations in the timing of an event due to random variations in the moment a stop clock is started and stopped.

Random error can be reduced by taking several measurements and calculating an mean (average) value.

Systematic errors

Systematic errors affect all the measurements using a particular instrument or technique in the same way, making them all higher or all lower than the true value. An example of systematic error arises if the graduation mark on a 25.00 cm3 pipette is actually at 25.04 cm3 (Figure 1).



**Figure 1** Systematic and random errors in the use of a 25.00 cm3 pipette. Every time an analyst uses the pipette, the meniscus is aligned slightly differently with the graduation mark, as in the three experiments. This gives rise to random error. If the graduation mark is actually at 25.04 cm3 and not 25.00 cm3, this will result in a systematic error.

Systematic errors are not reduced by taking repeated measurements and then averaging. However, systematic errors can be corrected by calibration with an accurate instrument or by comparison with a more reliable technique.

Zero errors

Zero errors are a particular form of systematic error caused by measuring instruments that have a false zero. Examples are where the needle on an ammeter fails to register zero when no current flows, or a centigrade thermometer fails to show zero when the temperature is 0 °C.

Sources of measurement uncertainty

Uncertainties in the measurement of quantities such as mass, volume, temperature and time depend on the quality and resolution of the instruments being used. Table 1 below shows the estimated uncertainties involved in the use of various instruments.

**Table 1** The range of uncertainty and overall uncertainty in one reading with various instruments.

|  |  |  |
| --- | --- | --- |
| Instrument | Range of uncertainty in one reading | Uncertainty |
| Balance weighing to 2 decimal places | A reading of, say, 20.01 g could lie anywhere between 20.005 g and 20.015 g, i.e. 0.005 g too low or 0.005 g too high. | ± 0.005 g |
| Balance weighing to 3 decimal places | A reading of, say, 20.001 g could lie anywhere between 20.0005 g and 20.0015 g. | ± 0.0005 g |
| 50 cm3 burette | A reading of 18.10 cm3 could lie between 18.05 cm3 and 18.15 cm3, i.e. 0.05 cm3 too low or 0.05 cm3 too high. | ± 0.05 cm3 |
| 25 cm3 pipette | The volume of the pipette might lie between 24.95 cm3 and 25.05 cm3. | ± 0.05 cm3 |
| 0–100 °C  thermometer | If the readings can be made to every degree, a reading of, say, 55 °C could lie between 54.5 °C and 55.5 °C, i.e. 0.5 °C too low or 0.5 °C too high. | ± 0.5 °C  (± 0.5 K) |

Calculating and combining uncertainties

In most experiments the final results are calculated from a number of measurements. The total uncertainty is determined by combining the individual uncertainties.

Uncertainties when measurements are added or subtracted

When measurements are added or subtracted in calculating a result, the measurement uncertainties can be added to obtain the total uncertainty and percentage uncertainty.

Example

In a thermochemistry experiment, a 0–50 °C thermometer graduated every 0.2 °C was used to take the temperature. The readings before and after a reaction were 19.3 °C and 27.8 °C. What is the uncertainty in the measure of the temperature rise?

Answer

The uncertainty in each of these readings is ± 0.1 °C, so the temperature rise is 8.5 °C and the total uncertainty is ± 0.2 °C.

Hence the temperature rise = 8.5 ± 0.2 °C

Uncertainties when measurements are multiplied or divided

When measurements are multiplied or divided in calculating a result, the values usually have different units. In these cases, the first step is to calculate the percentage uncertainties of the separate measurements.

The percentage uncertainty is given by:

percentage uncertainty = × 100%

For an uncertainty of ± 0.2 °C in a temperature rise of 8.5 °C, the percentage uncertainty is therefore given by:

percentage uncertainty in temperature rise =  × 100% = 2.4%

By using a thermometer with a higher resolution for a thermochemistry experiment, the percentage uncertainty is restricted to only 2.4%. If an ordinary 0–100 °C thermometer is been used, the total uncertainty becomes 1 °C and the percentage uncertainty is then:

percentage uncertainty in temperature rise =  × 100% = 11.8%

The percentage uncertainty in the experiment could also be reduced by planning to have a greater temperature rise. If, for example, the temperature rise had been 15 °C rather than 8.5 °C, then:

percentage uncertainty in temperature rise =  × 100% = 1.3%

The percentage uncertainties are, of course, ratios. They do not have units and are added together to arrive at a total percentage uncertainty for the calculated result.

**TIP**

If planning an experiment, identify the uncertainties likely to make a large percentage contribution to the overall uncertainty. Concentrate on keeping these as small as possible.

Example

Table 2 shows the measurements and calculations from a titration to determine the concentration of a solution of hydrochloric acid. What is the total percentage uncertainty in the calculated value?

**Table 2**

|  |  |  |  |
| --- | --- | --- | --- |
| **Measurement** | **Value** | **Uncertainty** | **Percentage uncertainty** |
| Concentration of the standard solution of NaOH(aq) | 0.100 mol dm−3 | ± 0.001 mol dm−3 | × 100% = 1.0% |
| Volume of hydrochloric acid measured from a pipette | 25.00 cm3 | ± 0.05 cm3 | × 100% = 0.2% |
| Volume of NaOH(aq) from a burette (an initial and a final volume taken and the end-point estimated to ± 0.05 cm3) | 24.00 cm3 | 2 × ± 0.05 cm3  and ± 0.05 cm3  = ± 0.15 cm3 | × 100% = 0.6% |

**Answer**

The concentration of hydrochloric acid calculated from these values = 0.0960 mol dm−3

Total percentage uncertainty = 1% + 0.2% + 0.6% = 1.8%

The total uncertainty in the calculated value =  × 0.096 mol dm−3 ≈ 0.002 mol dm−3

Therefore the concentration of hydrochloric acid = 0.096 ± 0.002 mol dm−3

**TIP**

Do not show the final result with more significant figures than can be justified in the light of the total uncertainty in the calculated value.