Measurement and data processing 11

# Uncertainties and errors in measurements and results

#### Learning objectives

* Understand the difference between quantitative and qualitative data
* Understand the difference between random uncertainties and systematic errors
* Understand the difference between precision and accuracy
* Understand how to quote values with uncertainties
* Understand the difference between significant figures and decimal places

### Qualitative and quantitative data

**Qualitative data** are non-numerical data. These would normally be observations made during an experiment. For instance, when determining the empirical formula of magnesium oxide by burning magnesium in air you might make the following observations:

* the piece of magnesium is grey and not very shiny
* the electronic balance fluctuated as the magnesium was weighed
* the magnesium burned with a bright, white flame
* white smoke escaped as the lid of the crucible was lifted.

These are all pieces of qualitative data.

**Quantitative data** are numerical data. So, for example, all the measurements of mass made during the experiment above constitute quantitative data.

It is not possible to measure the actual, or true, value of a particular quantity. The true mass of a piece of magnesium ribbon could be 0.257 846 368 246 89 g, but we have no way of measuring other than estimate.

#### Random uncertainties

We need to find the mass of a piece of magnesium ribbon 20 cm long .To do this we can measure a piece of magnesium 20 cm long using a ruler on which the smallest division is 1 mm. This is repeated 10 times.

The following data was obtained.

|  |  |
| --- | --- |
| **Reading** | **Mass / g** |
| 1 | 0.27 |
| 2 | 0.28 |
| 3 | 0.28 |
| 4 | 0.27 |
| 5 | 0.27 |
| 6 | 0.27 |
| 7 | 0.26 |
| 8 | 0.28 |
| 9 | 0.28 |
| 10 | 0.27 |

Why repeats on the measurement?

We can not be certain of the measurement measuring only once. Several trials and finding the average minimizes the random errors.

**Why are the readings different for the same measurement?**

This is because of **random uncertainties**.

**Suggest the causes of the random uncertainties on the measurements?**

* slight variations in the length of the strips of magnesium ribbon that we cut because of the limitations of the ruler.
* variations due to air currents in the room on the reading on the electronic balance
* human limitations. There will also be random errors associated with the person doing the measurement. For example in measurement of rate of a reaction experiment, there will always be a delay between noticing the colour change and stopping the stopwatch – this is called **reaction time**.

**What is the quoted value of mass in this experiment?**

 0.27 ± 0.01 g

**Other than repeating the experiment several times in what other ways can the random uncertainties be minimized?**

* careful design of an experiment. For instance, if you plan to carry out an experiment using 0.05 g magnesium and to measure the mass with a two decimal place balance then the uncertainty of the mass will be ± 0.01 g, which is 20% of the mass. If, however, you carry out the experiment with 0.20 g magnesium then the percentage uncertainty due to random error is reduced to 5%.
* Using a more precise measuring instrument. For example, a 0.001g electrical balance to measure 0.050 g Mg.

Discuss whether it’s possible to eliminate the effects of random uncertainties on measurements.

**The random uncertainties can never be completely eliminated**

#### **Estimating the random uncertainties associated with analogue and digital apparatus**

Analogue

 As a rule of thumb, the uncertainty of a measurement is half the smallest division to which you take a reading. uncertainties are usually quoted to only one significant figure.

**Digital instruments**

In general, the uncertainty of a measurement made on a digital instrument should be quoted as ± the smallest division.

Precision and accuracy

**Precision**

Precision relates to the reproducibility of results. If a series of readings is taken with high precision, it indicates that the repeated values are all very close together and close to mean (average) value.

If a single reading is taken, the uncertainty gives us an indication of the precision of the reading – for instance a temperature recorded as ± 0.01 °C is more precise than 21.3 ± 0.1 °C.

It is not really correct to talk about the precision of a single reading, but the term is sometimes used.

For a single reading, a more precise value is a value to more significant figures.

#### **Accuracy**

#### **Accuracy refers to how close a measurement is to the actual value of a particular quantity.**

It is possible for a measurement to have great precision but to not be very accurate

 **Systematic errors and random errors**

A systematic error is an error introduced into an experiment by the apparatus or the procedure. Systematic errors result in a loss of accuracy, i.e. the measured value is further away from the true value. Systematic errors are always in the same direction. Systematic errors can be identified by comparison with accepted literature values.

Suggest ways to reduce systematic errors?

* calibrating the instrument before use
* removing the zero error
* redesign of the experiment

Consider an experiment carried out to measure an enthalpy change of neutralisation by reacting 50 cm3 of 0.10 mol dm−3 sodium hydroxide and 50 cm3 of 0.10 mol dm−3 hydrochloric acid in a beaker. The above experiment gave a calculated heat of neutralisation of −55.8 ± 0.1 kJ mol−1. The accepted literature value for this quantity

is −57.3 kJ mol−1

What is the percentage error in this experiment?. What is the main source of error in the experiment, systematic or the random error?





The percentage error in this experiment is greater than the percentage random uncertainty and the experiment involves some systematic errors.

Suggest some of the possible systematic errors in this experiment

* the beaker is not that well insulated so heat will escape – the measured temperature rise will be less than the actual value
* the reaction does not occur instantaneously and the thermometer does not respond instantaneously and so the measured temperature rise will be less than the actual value.
* the concentration of the sodium hydroxide is less than 0.10 mol dm−3 and so the measured temperature rise will be less than the actual value.

The difference between accuracy and precision

Precision refers to the reproducibility of results (how close repeat readings are to each other and to the mean value), whereas accuracy refers to how close a value is to the true value of the measurement.

####  **Quoting values with uncertainties**

**The uncertainty is usually quoted to one significant figure, and your measurement should be stated so that the uncertainty is in the last significant figure – no figures should be quoted after the uncertainty**

Consider these values value of 1.735 ± 0.1 and 0.065 ± 0.0001. How should these measurement be recorded?

quantity should then be quoted as 1.7 ± 0.1 and 0.0650 ± 0.0001

#### **The uncertainty in a mean value**

There are various more or less complicated ways of quoting the uncertainty in a mean (average) value. What is the mean value for the volume on the table below with uncertainty quoted?

|  |  |
| --- | --- |
| **Reading** | **Volume / cm3** |
| 1 | 21.0 |
| 2 | 21.9 |
| 3 | 22.1 |
| 4 | 21.2 |
| 5 | 20.7 |
| 6 | 21.5 |
| mean value |  |

Two ways

1. Mean and the deviation of the maximum and minimum values from the mean gives 21.4 ± 0.7 cm3.
2. A rough rule of thumb is to take the uncertainty of the mean to be two-thirds of the deviation from the mean. so we could quote our average value as 21.4 ± 0.5 cm3

**Significant figures and decimal places**

* When counting significant figures, we start counting from the left with the first non-zero digit.
* we must count any zeros after the first non-zero digit and after a decimal point.
* If a number such as 500 is quoted as 5.0 × 102 there are two significant figures, and if it is quoted as 5.00 × 102 there are three significant figures.

**What is the difference between significant figures and decimal places?**

|  |  |  |
| --- | --- | --- |
| **Value** | **Number of significant figures** | **Number of decimal places** |
| 23.14 | 4 | 2 |
| 0.012 | 2 | 3 |
| 1.012 | 4 | 3 |
| 100.35 | 5 | 2 |
| 0.001 005 0 | 5 | 7 |
| 50.0 | 3 | 1 |

**In what ways are 5 g, 5.0 g and 5.00 g not the same?**

Precision. They represent the precision of the measuring balance.

**Rounding to the appropriate number of significant figures**

If a number is to be quoted to a certain number of significant figures, then we must look at the next figure after the last one that we wish to quote. If the next figure to the right is five or greater, the last significant figure should be rounded up; if the next figure to the right is less than five then the last significant figure stays the same.

Examples

|  |  |  |
| --- | --- | --- |
|  | **Number of significant figures** | **Rounded value** |
| 27.346 | 3 | 27.3 |
| 27.346 | 4 | 27.35 |
| 0.03674 | 2 | 0.037 |
| 0.03674 | 3 | 0.036 7 |
| 0.399 967 2 | 3 | 0.400 |
| 0.399 967 2 | 4 | 0.4000 |
| 0.399 967 2 | 5 | 0.399 97 |

## **11.1.2 Uncertainties in calculations**

#### Learning objectives

* Quote the result of a calculation involving multiplication/ division or involving addition/ subtraction to the appropriate number of decimal places
* Quote the result of a calculation to the appropriate number of significant figures
* Understand what is meant by absolute uncertainties and percentage uncertainties
* Understand how to combine uncertainties in calculations

**If a calculation involves just adding or subtracting numbers, the final answer should be quoted to the same number of decimal places as the piece of original data that has the fewest decimal places.**

For example, 23.57 − 8.4 = 15.17, but the answer should be quoted as 15.2 because 8.4 has only one decimal place.

**What values should be quoted in the following table**?

|  |  |  |
| --- | --- | --- |
| **Calculation** | **Actual result** | **Value to quote** |
| 23.5 | − | 14.8 | 8.7 | 8.7 |
| 0.786 | + | 0.0367 | 0.8227 | 0.822 |
| 5.234 × 103 | − | 1.2 × 103 | 4.034 × 103 | 4.0 × 103 |

###  **Significant figures and calculations**

**When carrying out calculations involving multiplication and/or division, the general rule is that the final answer should be quoted t o the number of significant figures of the piece of data with the fewest significant figures.**

Sulfuric acid is titrated against 25.00 cm3 of 0.200 mol dm−3 sodium hydroxide solution. 23.20 cm3 of sulfuric acid are required for neutralisation. Calculate the concentration of the sulfuric acid.

 2NaOH(aq) + H2SO4(aq) → Na2SO4(aq) + 2H2O (l)

The volumes are quoted to four significant figures but the concentration is only to three significant figures – therefore the final answer should be quoted to three significant figures.

 

|  |  |  |
| --- | --- | --- |
| **Calculation** | **Actual result** | **Value to quote** |
|  23.5 | × | 14.87 | 349.445 | 349 |
| 0.79 | ÷ | 0.0367 | 21.52588556 | 22 |
| 5.234 × 103 | × | 1.2 × 103 | 6.2808 × 106 | 6.3 × 106 |

#### **Rounding values in calculations**

As a general rule, all numbers should be carried through in a calculation and rounding should only happen when an answer to a particular part of a question is required.

### **Absolute and percentage uncertainties**

An uncertainty can be reported either as an absolute value – e.g. 1.23 ± 0.02 g – or as a percentage value e.g. 1.23 g ± 2%.

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1. **What is the percentage uncertainty in the reading 0.257 ± 0.005 cm? (2%)**
2. **if the final value of a calculation is 0.518 ± 1% what is the absolute uncertainty? (**± 0.005)

### **Propagating uncertainties in calculations**

**Adding or subtracting:** When quantities with uncertainties are added or subtracted, the **absolute** uncertainties are **added**.

Calculate the change in temperature from the following data: (34.16 ± 0.04 °C.)

|  |  |  |
| --- | --- | --- |
|  | **Value** | **Uncertainty** |
| Maximum temperature / °C | 57.58 | ±0.02 |
| Initial temperature / °C | 23.42 | ±0.02 |

***Multiplying or dividing:*** When multiplying or dividing quantities with uncertainties, the **percentage** uncertainties should be added.

What is the absolute uncertainty when 2.57 ± 0.01 is multiplied by 3.456 ± 0.007 and to how many significant figures should the answer be quoted? (8.88 ± 0.05.) absolute uncertainty is to 1sf.

**When multiplying or dividing a quantity with an uncertainty by a pure number, the absolute uncertainty is multiplied/divided by that number so that the percentage uncertainty stays the same.**

**What is 12.12 ± 0.01 multiplied by 3?**

**Sometimes the uncertainty of one quantity is so large relative to the uncertainties of other quantities that the uncertainty of the final value can be considered as arising just from this measurement.**

**The following procedure was used to obtain date in a calorimetry experiment. Weigh out accurately approximately 100 g of water in a polystyrene cup. Measure the initial temperature of the water. Weigh out accurately approximately 6 g of potassium bromide. Add the potassium bromide to the water, stir rapidly until it has all dissolved and record the minimum temperature reached. Use the data below to work out the enthalpy change of solution to the appropriate number of significant figures. (17** ± 2 kJ mol−1)

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**The enthalpy change can be calculated from the heat change given by q= mcΔT**

# 11.2 Graphical techniques

#### Learning objectives

* Understand that graphs are an effective way of communicating the relationship between two variables
* Plot graphs of experimental results and interpret the graphs
* Calculate the gradient and intercept in graphs

**Exam tips:**

* Proportional and directly proportional mean the same thing.
* For a relationship to be proportional the line of best fit must pass through the origin. A straight line not passing through the origin represents a linear relationship.

**Describe the relationships by the following graphs**

 a. Rate of reaction for the reaction A → B. b. Pressure versus volume at constant temperature





c. Volume versus versus temperature at constant pressure for an ideal gas



### **Drawing graphs**

* Make the graph as large as possible. Choose your scales and axes to retain the precision of your data as far as you can and to make the graph as easy as possible to interpret.
* The independent variable (what you change) should be plotted along the horizontal (*x*) axis and the dependent variable (what you measure) should be plotted along the vertical (*y*) axis. For example a graph could be drawn with mass of sodium chloride on the *y*-axis and temperature on the *x*-axis to examine how the solubility of common salt (sodium chloride) is affected by temperature.
* Label the axes with the quantity and units e.g., volume / cm3 or Volume (cm3).
* Plot the points, which may be marked by crosses or by dots in circles.
* Draw a best-fit line (do not join the points!). This may be a straight line or a curve and should represent, as well as possible, the trend in the data. 
* Give the graph a title describing what has been plotted.

### **Gradient and intercept**

* Gradient: it gives the rate of change or can have an important physical meaning

 

Gradient of a curve: is given by drawing a tangent (straight line) to the curve at the desired point and working out the gradient of the tangent as usual.

* The intercepts on the graph can also represent a physical quantity