

## Chapter 11: Measurement and data processing and analysis

### 11.1 Uncertainty and error in measurement and results

All measurement has a limit of precision and accuracy, and this must be taken into account when evaluating experimental results.

- Qualitative data includes all non-numerical information obtained from observations, not from measurement.
- Quantitative data are obtained from measurements and are always associated with random errors/uncertainties determined by the apparatus and by human limitations such as reaction times.
- **Random** errors are caused by:
  - the readability of the measuring instrument
  - the effects of changes in the surroundings, such as temperature variations and air currents
  - insufficient data
  - the observer misinterpreting the reading.
- Random errors make a measurement less precise, but not in any particular direction. They are expressed as an uncertainty range, such as  $25.05 \pm 0.05$  °C.
- The uncertainty of an **analogue** scale is  $\pm$  (half the smallest division).
- The uncertainty of a **digital** scale is  $\pm$  (the smallest scale division).
- **Systematic** errors occur when there is an error in the experimental procedure. Measuring the volume of water from the top of the meniscus rather than the bottom, or overshooting the volume of a liquid delivered in a titration will lead to readings which are too high. Heat losses in an exothermic reaction will lead to smaller observed temperatures changes.
- Experiments are **repeatable** if the same person duplicates the experiment with the same results.
- Experiments are **reproducible** if several experimentalists duplicate the results.
- The **precision** or reliability of an experiment is a measure of the random error. If the precision is high then the random error is small.
- The **accuracy** of a result is a measure of how close the result is to some accepted or literature value. If an experiment is accurate then the systematic error is very small.
- Random uncertainties can be reduced by repeating readings; systematic errors cannot be reduced by repeating measurements.
- Precise measurements have small random errors and are reproducible in repeated trials. Accurate measurements have small systematic errors and give a result close to the accepted value.
- The number of **significant figures** in any answer should reflect the number of significant figures in the given data.
- When data are multiplied or divided the answer should be quoted to the same number of significant figures as the least precise.

- When data are added or subtracted the answer should be quoted to the same number of **decimal places** as the least precise value.
- When adding or subtracting measurements, the total absolute uncertainty is the sum of the absolute uncertainties.
- When multiplying or dividing measurements, the total percentage uncertainty is the sum of the individual percentage uncertainties. The absolute uncertainty can then be calculated from the percentage uncertainty.
- To find the absolute uncertainty in a calculated value for  $ab$  or  $a/b$ :
  - 1 Find the percentage uncertainty in  $a$  and  $b$ .
  - 2 Add the percentage uncertainties of  $a$  and  $b$  to find the percentage uncertainty in the calculated value.
  - 3 Convert this percentage uncertainty to an absolute value.

If one uncertainty is much larger than others, the approximate uncertainty in the calculated result can be taken as due to that quantity alone.

- The **experimental error** in a result is the difference between the recorded value and the generally accepted or literature value.
- **Percentage uncertainty** = (absolute uncertainty/measured value)  $\times$  100%
- **Percentage error** = (accepted value – experimental value)/accepted value  $\times$  100%

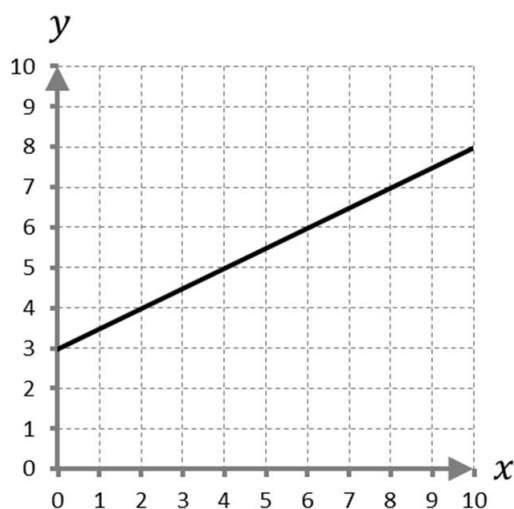
## 11.2 Graphical techniques

Graphs are a visual representation of trends in data.

- Graphical techniques are an effective means of communicating the effect of an independent variable on a dependent variable, and can lead to determination of physical quantities.
- The independent variable is the *cause* and is plotted on the horizontal axis. The dependent variable is the *effect* and is plotted on the vertical axis.
- Sketched graphs have labelled but unscaled axes, and are used to show qualitative trends, such as variables that are proportional or inversely proportional.
- Drawn graphs have labelled and scaled axes, and are used in quantitative measurements.
- **When drawing graphs:**
  - give the graph a title and label the axis with both quantities and units.
  - use the available space as effectively as possible and use sensible scales – there should be no uneven jumps.
  - plot all the points correctly.
  - identify any points which do not agree with the general trend.
  - think carefully about the inclusion of the origin. The point (0, 0) can be the most accurate data point or it can be irrelevant.
- You should be able to give a qualitative physical interpretation of a particular graph. See the next page for examples.
  - The variables are **proportional**.
  - The variables are **inversely proportional**.

- A best-fit straight line does not have to go through all the points but should show the overall trend.
- The equation for a straight line is:  
 $y = mx + c$
- $x$  is the independent variable
- $y$  is the dependent variable
- $m$  is the gradient

- $m = \frac{\Delta y}{\Delta x}$
- $m$  has units
- $c$  is the intercept on the vertical axis



- A systematic error produces a displaced line.
- Random uncertainties lead to points on both sides of the perfect line.
- The gradient of a curve is given by the gradient of the tangent at that point.
- The process of assuming that the trend line applies between two points is called **interpolation**.
- A line is **extrapolated** when it is extended beyond the range of measurement.

### 11.3 Spectroscopic identification of organic compounds

Analytical techniques can be used to determine the structure of a compound, analyse the composition of a substance, or determine the purity of a compound. Spectroscopic techniques are used in the structural identification of organic and inorganic compounds.

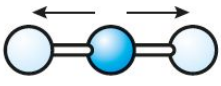
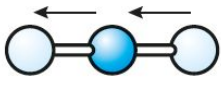
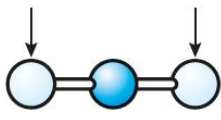
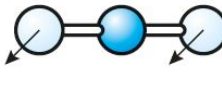
- The **degree of unsaturation** (or **index of hydrogen deficiency**) provides a measure as to the degree of unsaturation of an organic molecule. It relates to how many molecules of hydrogen would in theory be needed to convert an unsaturated molecule to a saturated molecule.
- Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) and infrared spectroscopy (IR) are techniques that can be used to help identify and to determine the structure of compounds.
- The data booklet contains characteristic ranges for IR absorptions (section 26),  $^1\text{H}$  NMR data (section 27), specific MS fragments (section 28) and the formula to determine IHD.

#### Mass spectrometry

- Molecules are hit by fast-moving electrons, forming a positive ion. The ion can fragment. The largest fragment is the **parent ion**.
- A **fragmentation pattern** can provide evidence for the structure of the compound.

#### Infrared spectroscopy

- Energy needed to excite molecules to make them vibrate more occurs in the infrared region of the spectrum.
- IR radiation can cause a bond to stretch or bend. Stretching a bond requires more energy than bending a bond and generally occurs at higher wavenumbers.
- Absorption of particular wavenumbers of IR radiation correspond to particular bonds. Bonds with atoms of small mass absorb at higher wavenumbers than atoms with larger mass. Double bonds occur at higher wavenumbers than single bonds. Characteristic absorption bands can be found in section 26 of the IB data booklet.
- Hydrogen bonding broadens the absorptions.
- The intensity of the absorption depends on the polarity of the bond.
- In a polyatomic molecule such as carbon dioxide it is more correct to consider the molecule stretching and bending as a whole, rather than considering the individual bonds.
- In carbon dioxide, for example, there are four modes of vibration. The symmetric stretch is IR inactive as it produces no change in dipole moment.

			
symmetric stretch inactive As the molecule remains symmetrical, it has no change in dipole.	asymmetric stretch $\approx 2350\text{ cm}^{-1}$ The molecule has a temporary dipole moment when the C=O bond lengths are of unequal length.	two symmetric bends $\approx 670\text{ cm}^{-1}$ The molecule has a temporary dipole moment as it bends away from its linear geometry. The two vibrations are identical, except that one is in the plane of the page and the other is out of the plane of the page.	

- Molecules with several bonds can vibrate in many different ways and with many different frequencies. The complex pattern can be used as a fingerprint to be matched against the recorded spectra of known compounds in a database. A comparison of the spectrum of a sample with that of a pure compound can also be used as a test of purity.

### Nuclear magnetic resonance spectroscopy

- Studies the alignment of protons,  $^1\text{H}$ , (or  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  atoms) in magnetic fields.
- The position of the NMR signal relative to the standard tetramethylsilane is called the **chemical shift** of the proton. Hydrogen nuclei in particular environments have characteristic chemical shifts.
- Tetramethylsilane has 12 hydrogen atoms bonded in the same atypical environment close to a silicon atom. It gives one strong signal away from signals produced in most organic compounds.
- The integrated trace indicates the relative number of hydrogen atoms in the different environments.

## 21.1 Spectroscopic identification of organic compounds

Although spectroscopic characterization techniques form the backbone of structural identification of compounds, typically no one technique results in a full structural identification of a molecule.

### Nuclear magnetic resonance spectroscopy

- Under high resolution individual peaks may split into further peaks due to **spin-spin coupling**. If a proton has  $n$  protons as nearest neighbours its NMR peak is split into  $(n + 1)$  peaks.
- The splitting patterns can be deduced from Pascal's triangle and are summarized below:

Number of chemically equivalent protons causing splitting	Splitting patterns with relative intensities
0	1
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1

- When analysing high-resolution NMR spectra, the following additional points should be noted:
  - Protons bonded to the same atom do not interact with one another as they are equivalent and behave as a group.
  - Protons on non-adjacent carbon atoms do not generally interact with one another.
  - The O—H single peak in ethanol does not split unless the sample is pure, as rapid exchange of the protons between ethanol molecules averages out the different possible spins.

### *X-ray diffraction*

- Used to produce an electron density map of a crystalline solid. This can be related to the atoms which make up the molecule.
- The identity of the atoms can be determined from the pattern in electron densities which are related to an element's electron configuration. Hydrogen atoms are not generally detected as they have only one electron.