Summary – continued

boiling point increases as chain length increases

HOMOLOGOUS SERIES – series of compounds with the same functional group, in which each member differs from the next by a $-CH_2-$ group.

functional group – atom or group of atoms that gives an organic molecule its characteristic chemical properties

position

members of a series have similar chemical properties

complete products: CO_2, H_2O

incomplete products: CO, C, H_2O

primary – group attached to carbon that is attached to **one** other carbon

secondary – group attached to carbon that is attached to **two** other carbons

tertiary – group attached to carbon that is attached to **three** other carbons

combustion

C_nH_{2n+2}

alkanes – hydrocarbons with only single bonds

C_nH_{2n} for compounds with one double bond

alkenes – contain one or more C=C bonds

$C_nH_{2n+2}O$

alcohols – contain a hydroxyl group: $-OH$

esterification – a carboxylic acid and an alcohol join to form an ester

are **unsaturated**

with $Cr_2O_7^{2-}/H^+$ colour change from orange to green

Primary and secondary alcohols can be oxidised using acidified $K_2Cr_2O_7$ or $KMnO_4$.

decolorise bromine water

addition reaction – molecule X–Y is added either side of a C=C bond

with MnO_4^-/H^+ colour change from purple to colourless

HL electrophilic addition mechanism

A primary alcohol is oxidised first to an **aldehyde** and then to a **carboxylic acid** $C_nH_{2n}O_2$.

Secondary alcohols are oxidised to **ketones**.

HL ketones can be reduced to secondary alcohols

hydrogenation – H_2 is added, forms an alkane

hydration – H_2O is added, forms an alcohol

addition polymerisation – alkene monomers join together in polymer chain

Aldehydes and ketones are **carbonyl compounds** – they contain a C=O group.

react with halogens in presence of sunlight or UV light through free radical substitution

substitution – an atom or group is replaced by another atom or group

HL Aldehydes and carboxylic acids can be reduced to primary alcohols.

HL steric effects prevent S_N2 mechanism

more stable carbocation

Nucleophile – molecule or negative ion with a lone pair of electrons which is attracted to regions of low electron density.

rate not affected by nature or concentration of nucleophile

faster with protic polar solvents

Cl_2 splits into chlorine free radicals.

free radical – a species with an unpaired electron

tertiary halogenoalkane

HL S_N1 mechanism two steps

secondary halogenoalkane

homolytic fission – each atom gets one electron from the bond that splits

The free radicals react with the alkane molecules to form **halogenoalkanes**.

Undergo **nucleophilic substitution**. The nucleophile replaces the halogen.

S_N2 mechanism one step

primary halogenoalkane

faster with aprotic polar solvents

contains a halogen atom as functional group

stereospecific

reactions rate: R–I > R–Br > R–Cl > R–F
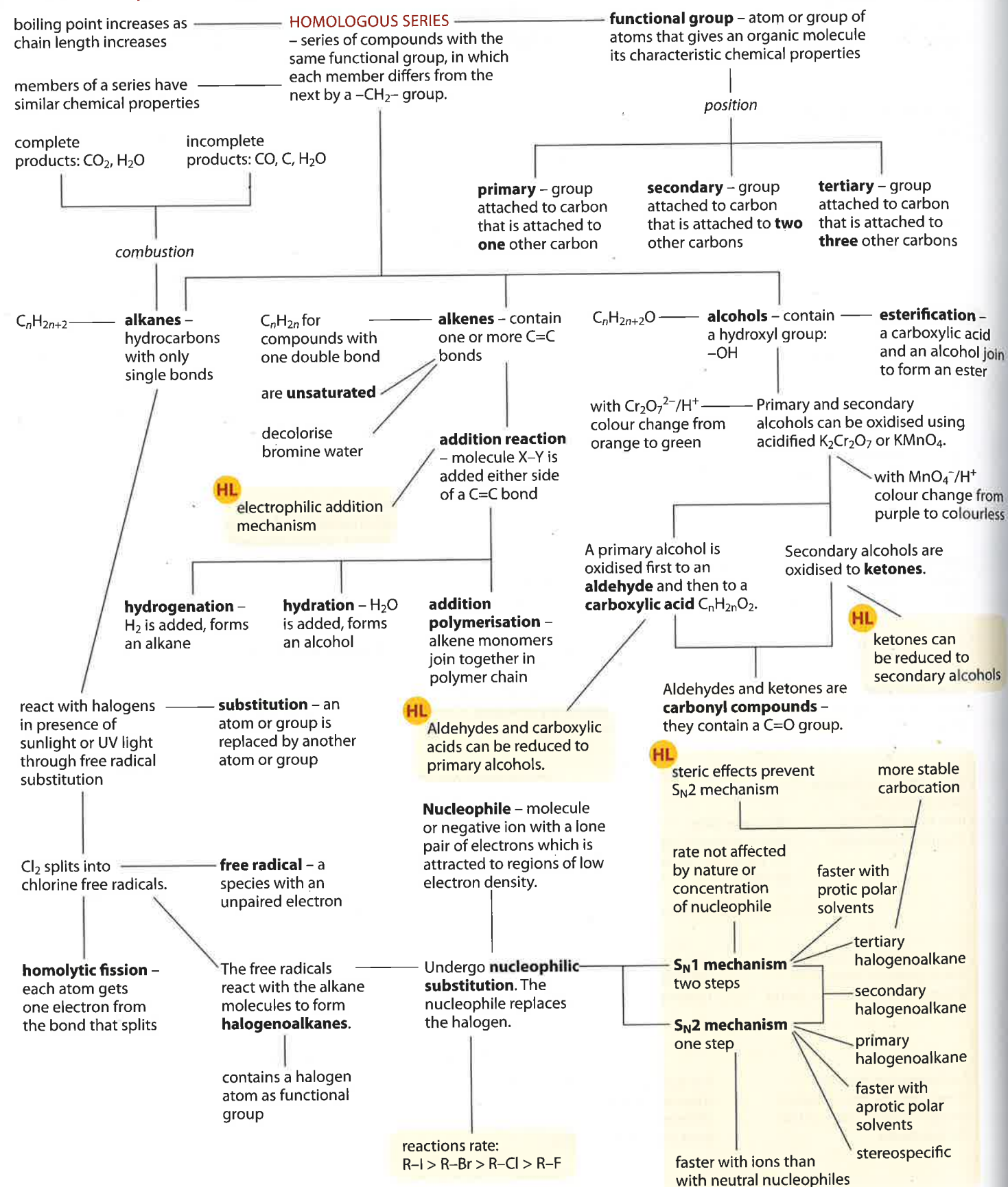
faster with ions than with neutral nucleophiles

Measurement and data processing 11

11.1 Uncertainties and errors in measurements and results

11.1.1 Uncertainties in measurements

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 crucible was dirty
- 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.

Measurements in science

Although in mathematics it is possible to have pure numbers and to write a number to any number of decimal places, in chemistry we are concerned with real quantities obtained by making measurements in a laboratory.

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 actually measuring that. The best we can ever get is an estimate. If we put the piece of magnesium on an electronic balance that gives values to one decimal place, we might measure 0.3 g. If we had a balance that could measure to three decimal places, then we might get 0.258 g. Neither of these values is the true mass of the piece of magnesium ribbon.

Consider the following argument.
Experimental data can never provide a true value for a quantity. The knowledge we get from science is ultimately obtained from experimental data. The knowledge we obtain from science is never true.

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

Figure 11.1 This electronic balance reads to two decimal places.

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

Table 11.1 The results obtained from weighing ten strips of magnesium ribbon.

The effect of random uncertainties can be reduced by repeating the measurements more often.

The random uncertainties can never be completely eliminated.

The effects of random uncertainties should mean that the measurements taken will be distributed either side of the mean – i.e. fluctuations will be in both directions.

Random uncertainties

Suppose 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. The strip of magnesium ribbon is cut from a roll and weighed on an electronic balance that reads to two decimal places. Suppose that mass of the first strip of magnesium ribbon is 0.27 g (Figure **11.1**). We then cut and measure nine more strips in the same way from the same roll, and the results are shown in Table **11.1**.

The first thing we should notice is that not all the readings are the same. This is because of **random uncertainties**.

Random uncertainties are caused by the limitations of the measuring apparatus and other uncontrollable variables that are inevitable in any experiment.

There are several sources of random uncertainty, even in this simple procedure. Firstly, there will be slight variations in the length of the strips of magnesium ribbon that we cut because of the limitations of the ruler that we use to measure it, the thickness of the scissors etc.; secondly, when we measure the mass using the electronic balance, there could be variations due to air currents in the room, the heating effects of the current in the circuits, friction between various mechanical parts etc.

We can give an indication of the size of the random uncertainty by quoting the measured value along with an uncertainty. For instance, the mass of a piece of magnesium ribbon 20 cm long could be quoted as 0.27 ± 0.01 g, where '± 0.01 g' is the uncertainty in the measurement. This means that we are reasonably confident that the mass of a piece of magnesium ribbon 20 cm long is somewhere between 0.26 g and 0.28 g. If we kept cutting strips from this roll we would expect each mass to lie between 0.26 g and 0.28 g.

Taking more repeats gives a more reliable mean value. If we had just taken one measurement in the above example, we could have obtained 0.26 g, 0.27 g or 0.28 g as the value of the mass of the strip of magnesium. If, however, we take the reading 100 times and work out the mean value, we should get a value that more closely represents the true mean.

The effect of random uncertainties can also be minimised by 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%.

No matter to how many decimal places a piece of measuring apparatus is able to measure a quantity, there will always be an uncertainty in the value.

Estimating the random uncertainties associated with measuring apparatus

Analogue instruments

As a rule of thumb, the uncertainty of a measurement is half the smallest division to which you take a reading. This may be the division on the piece of apparatus used or it may be an estimate if the divisions are sufficiently far apart that you are able to estimate between them.

For instance, the smallest division on the 100 cm^3 measuring cylinder shown in Figure **11.2** is 1 cm^3; however, the divisions are sufficiently far apart that we can probably estimate between these divisions to the nearest 0.5 cm^3. We can thus estimate that our actual value is greater than 68.75 and less than 69.25. The uncertainty is half the smallest division, i.e. 0.25 cm^3, or 0.3 cm^3 to one significant figure (uncertainties are usually quoted to only one significant figure). We can therefore quote the reading as $69.0 \pm 0.3 \text{ cm}^3$, i.e. the volume of water is somewhere between 68.7 and 69.3 cm^3.

Digital instruments

On an electronic balance reading to two decimal places, the smallest division is 0.01 g, so the uncertainty associated with this is ± 0.005 g. So if a particular reading is taken as 2.46 g, this means that the value is somewhere between 2.455 g and 2.465 g.

However, the balance will have been zeroed beforehand and this zero value also has an uncertainty associated with it. That is, when the reading on the balance is 0.00 g it indicates a value between -0.005 and $+0.005$ g. The largest possible value of the measured mass would be from -0.005 to 2.465 g, i.e. 2.47 g, and the smallest possible value is from 0.005 to 2.455 g, i.e. 2.45 g. So, the uncertainty of this measurement is ± 0.01 g, and the measurement should be quoted as 2.46 ± 0.01 g.

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

Human limitations

There will also be random errors associated with the person doing the measurement. Imagine an experiment in which a student is measuring the time taken for a reaction mixture to change colour in order to determine the rate of reaction. If the student is using a digital stopwatch that can measure to 1/100 second then the above discussion would lead to an uncertainty of ± 0.01 s. However, if you actually try doing this experiment there will always be a delay between noticing the colour change and stopping the stopwatch – this is called **reaction time**. In this case, you should estimate the uncertainty of the measurement of time and not just use that from the stopwatch. A suitable uncertainty for this experiment might be ± 0.5 s or ± 1 s.

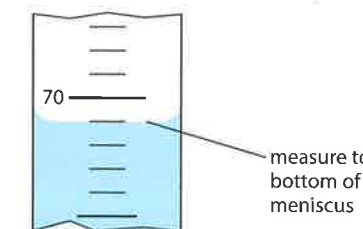70 — measure to bottom of meniscus

Figure 11.2 Measuring a liquid volume.

Note: this is only an estimate, so if you quoted this value as 69.0 ± 0.5 cm, this would not be incorrect.

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 the mean (average) value.

Consider the values in Table **11.2**. The results in the first column could be reported as $21.2 \pm 0.1 \, cm^3$, whereas the second column would yield $21.4 \pm 0.7 \, cm^3$. The larger uncertainty in the second set of readings indicates the greater spread of the values, i.e. lower precision.

If a single reading is taken, the uncertainty gives us an indication of the precision of the reading – for instance a temperature recorded as $21.33 \pm 0.01 \, °C$ is more precise than $21.3 \pm 0.1 \, °C$. In the first case, repeat values of the quantity would be expected to mostly lie between 21.32 and 21.34 °C, whereas in the second (less precise) case, the values would be expected to lie between 21.2 and 21.4 °C.

The uncertainties here are worked out from the range of the data, i.e. looking at how far the maximum and minimum values are from the mean.

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.

Extension

Standard deviation is often used to give an idea of the precision of a set of measurements. The larger the standard deviation, the less precise the measurements.

Reading	Temperature/°C	Temperature/°C
1	21.2	21.0
2	21.3	21.9
3	21.1	22.1
4	21.3	21.2
5	21.1	20.7
6	21.2	21.5
mean value	21.2	21.4

Table 11.2 Measurements of the same quantity using two different pieces of apparatus: the first set of readings is more precise than the second set, because the values in the first set are much closer to each other and to the mean value.

Accuracy

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

In the example discussed above the true value of the temperature was 19.57 °C – although a value of $21.33 \pm 0.01 \, °C$ is quite precise, it is not very accurate because it is not very close to the true value.

In this case, there appears to be some sort of **systematic error** with the procedure (for instance, perhaps the thermometer was not originally calibrated properly). In this case, repeating the readings will not improve the accuracy of the measurements because all the values would be expected to be around $21.33 \pm 0.01 \, °C$.

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

Systematic 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. For instance, you might measure the mass of some sodium chloride using a balance that has not been calibrated recently and the balance might always record a mass that is 1.00 g too high. The actual value of the mass is 23.25 g, but the balance reads 24.25 g. No matter how many times this reading is repeated, the mass will always be 1.00 g too high.

The above experiment could probably have been improved by using several different balances and taking an average of the values from all of them. (However, this is still no guarantee of greater accuracy because each might have a systematic error associated with it!)

Consider an experiment carried out to measure an enthalpy change of neutralisation by reacting $50 \, cm^3$ of $0.10 \, mol \, dm^{-3}$ sodium hydroxide and $50 \, cm^3$ of $0.10 \, mol \, dm^{-3}$ hydrochloric acid in a beaker.

Systematic errors can be identified by comparison with accepted literature values. The above experiment might give a calculated heat of neutralisation of $-55.8 \pm 0.1 \, kJ \, mol^{-1}$. The ± 0.1 indicates the uncertainties due to random errors. The accepted literature value for this quantity is $-57.3 \, kJ \, mol^{-1}$. We can use the **percentage error** to compare the experimental value with the accepted literature value.

The effect of a systematic error cannot be reduced by repeating the readings.

$$percentage \ error = \frac{|\,experimental \ value - accepted \ value\,|}{|\,accepted \ value\,|} \times 100$$

$|value|$ indicates the modulus of the value; i.e. ignore the overall sign

In this case, the percentage error $= \dfrac{|\,55.8 - 57.3\,|}{57.3} \times 100 = 2.6\%$

The percentage uncertainty due to random uncertainties is

$$\frac{0.1}{55.8} \times 100 = 0.2\%$$

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

Some of the systematic errors in this experiment could be:
- 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.

These systematic errors can be reduced by changing the way the experiment is carried out, for instance by using an insulated container

with a lid in which to do the reaction or by checking the concentration of the sodium hydroxide by titration against a standard solution of an acid.

When compared to the literature value, if the percentage error is smaller than that due to random errors then the experiment has worked well as a way of obtaining a value for this particular quantity. If the random errors are, however, quite large then the experiment can be further refined by using more precise measuring apparatus and/or taking more repeat measurements.

If the percentage error is larger than the percentage uncertainty due to random errors then this suggests that there are systematic errors in the experimental procedure – these must be eliminated as far as possible to obtain a more accurate value for the measured quantity. In the case of systematic errors redesign of the experiment must be considered.

If your experiment involves finding a value for a quantity for which no literature value exists, it can be very difficult to spot systematic errors.

The difference between accuracy and precision

As we have seen, 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. The difference between accuracy and precision can be seen in Figure **11.3**.

Similarly, think about a tennis player serving the ball (Figure **11.4**). If he can hit nearly the same spot each time then he is serving with a great deal of precision. If this spot is not in the service box, however, then the serve is not very accurate. In this case (and in the case of scientific experiments) precision without accuracy is useless – it doesn't win any points!
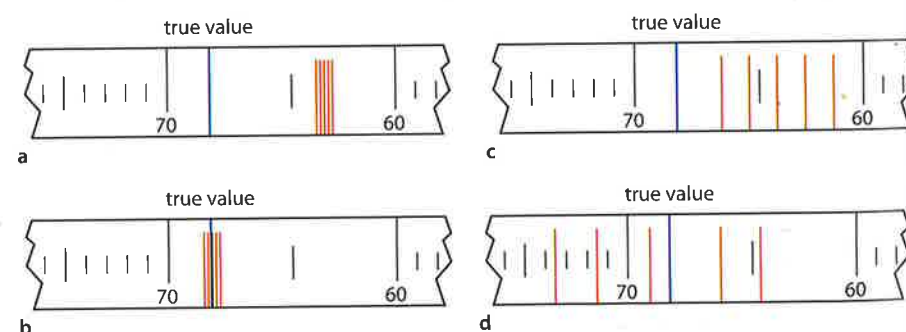
Figure 11.3 a A set of readings (shown in red) with high precision but poor accuracy; **b** a set of readings with high precision and high accuracy; **c** a set of readings with low precision and low accuracy; **d** a set of readings with low precision and high accuracy. In this last set, the accuracy is high because the mean value is close to the true value. However, it is a poor set of data and the high accuracy is probably more a case of luck than good experimental design!

Figure 11.4 Like a game of tennis, the goal of a scientific experiment is high precision and high accuracy.

The Hubble Space Telescope, a collaborative project of NASA and the European Space Agency (ESA), was launched in 1990 but it was very soon noticed that there was a problem with the mirror because the quality of the images was not as high as expected. Although the mirror was shaped to a high degree of precision (very small uncertainty), the device used to control the shape was not constructed correctly, which resulted in a systematic error in the shape of the mirror. This problem was corrected in a subsequent space mission. Time for using the Hubble telescope and data it collects has been made available to scientists throughout the world and has contributed enormously to our understanding of astronomy.

Test yourself

1 The table shows data from five trials of two separate experiments. Which set of values is more precise?

Trial	Experiment	
	A	**B**
1	1.34	1.37
2	1.48	1.22
3	1.40	1.58
4	1.27	1.18
5	1.38	1.44

2 A series of experiments was carried out to determine the value for a particular quantity. The results are shown in the table. The literature value of this quantity is 47.0 J. Which experiment produced the most accurate value?

Experiment	Value/J
1	45.276
2	48
3	44.2
4	49.57

Quoting values with uncertainties

Consider a value of 1.735 ± 0.1 obtained from an experiment.

The uncertainty is in this decimal place, so no figures should be quoted beyond it. This quantity should then be quoted as 1.7 ± 0.1. Table **11.3** shows some more examples.

With 363.2 ± 8, the random uncertainties mean that the value is known only to within 8 either way – the 0.2 is meaningless. With 0.0650 ± 0.0001, the final zero is required because the uncertainty is in the fourth decimal place. If the value were quoted as 0.065, this would imply that the value lies between 0.0645 and 0.0655 rather than between 0.0651 and 0.0649, and therefore there would be a loss of precision.

The uncertainty in a mean value

There are various more or less complicated ways of quoting the uncertainty in a mean (average) value. Consider the data given in Table **11.4**. One way of quoting the mean is as $21.4 \pm 0.7 \, cm^3$. Here we are taking the uncertainty as the deviation of the maximum and minimum values from the mean. The largest value is $22.1 \, cm^3$, which is $0.7 \, cm^3$ greater than the mean value, and the smallest value is $20.7 \, cm^3$, which is $0.7 \, cm^3$ smaller than the mean value. However, if we have a large number of readings, quoting the uncertainty based on the range is probably pessimistic, because most of the values would be expected to lie closer to the mean than that.

A rough rule of thumb is to take the uncertainty of the mean to be two-thirds of the deviation from the mean. For example, with the data in Table **11.4**, the deviation from the mean is $\pm 0.7 \, cm^3$ and two-thirds of this is approximately $0.5 \, cm^3$ – so we could quote our average value as $21.4 \pm 0.5 \, cm^3$ and be reasonably confident that, if we make any further measurements, most of them will lie between 20.9 and $21.9 \, cm^3$.

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.

Measured value ± uncertainty	Value you should quote
151.3 ± 0.2	151.3 ± 0.2
157.47 ± 0.1	157.5 ± 0.1
0.06500 ± 0.0001	0.0650 ± 0.0001
363.2 ± 8	363 ± 8
363.2 ± 20	360 ± 20
363.2 ± 100	400 ± 100

Table 11.3 Measured values with uncertainties and how they should be quoted.

Reading	Volume / cm³
1	21.0
2	21.9
3	22.1
4	21.2
5	20.7
6	21.5
mean value	21.4

Table 11.4 The same quantity has been measured six times and the average taken.

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

Table 11.5 The difference between significant figures and decimal places.

Value	Number of significant figures	Rounded value
27.346	3	27.3
27.346	4	27.35
0.03674	2	0.037
0.03674	3	0.0367
0.399 967 2	3	0.400
0.399 967 2	4	0.4000
0.399 967 2	5	0.399 97

Table 11.6 Rounding to the appropriate number of significant figures.

Significant figures and decimal places

When counting significant figures, we start counting from the left with the first non-zero digit. For example, 0.012 has two significant figures because we do not count the first two zeros. 0.001 005 0 has five significant figures because we do not count the first three zeros but we must count any zeros after the first non-zero digit and after a decimal point (Table **11.5**).

Problems come when numbers are quoted as 500, for example, because this could represent one, two or three significant figures. This ambiguity is avoided by quoting the number in standard form. If it is quoted as 5.0×10^2 there are two significant figures, and if it is quoted as 5.00×10^2 there are three significant figures.

> The number could also be quoted with an uncertainty, e.g. 500 ± 1, so that it is clear that the value is known to three significant figures.

It is important to realise that 5 g, 5.0 g and 5.00 g are not the same. 5 g implies that the mass is between 4.5 and 5.5 g; 5.0 g implies that the mass is between 4.95 and 5.05 g; 5.00 g implies that the mass is between 4.995 and 5.005 g. A value of 5 g measured using a two decimal place electronic balance must be quoted as 5.00 g and not 5 g, otherwise there will be a loss of precision in your results.

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. Some examples of rounding to the appropriate number of significant figures are shown in Table **11.6**.

Recurring decimals such as $0.\dot{3}$ should never be used in chemistry, as they imply infinite precision. A value should always be rounded to the appropriate number of significant figures, e.g. as 0.33 or 0.333.

? Test yourself

3 Copy and complete the table:

Measured value ± uncertainty	Value you should quote
71.7 ± 0.2	
3.475 ± 0.01	
0.065 06 ± 0.001	
63.27 ± 5	
593.2 ± 30	
783.28 ± 100	

4 State the number of significant figures for each of the following numbers:
   a 2.78   d 3.95×10^4
   b 0.057   e 80.00
   c 0.003 480

5 Round each of the following numbers to three significant figures:
   a 6.7863   d 8.2457×10^5
   b 0.000 079 835 e 1.78339×10^{-3}
   c 0.004 999 31

11.1.2 Uncertainties in calculations

Decimal places and 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.

Other examples of calculations are shown in Table **11.7**.

Calculation			Actual result	Value to quote
23.5	−	14.8	8.7	8.7
0.786	+	0.0367	0.8227	0.823
5.234×10^3	−	1.2×10^3	4.034×10^3	4.0×10^3

Table 11.7 Some examples of calculations involving addition and subtraction.

Significant figures and calculations

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

Example

Sulfuric acid is titrated against $25.00 \, cm^3$ of $0.200 \, mol \, dm^{-3}$ sodium hydroxide solution. $23.20 \, cm^3$ of sulfuric acid are required for neutralisation. Calculate the concentration of the sulfuric acid.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$
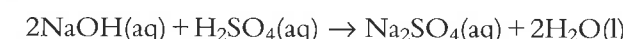
The volumes are quoted to four significant figures but the concentration is only to three significant figures – therefore the final answer should be quoted to three significant figures.

Carrying all the numbers through in the calculation gives an answer of $0.107 758 6 \, mol \, dm^{-3}$ so the concentration of the sulfuric acid should be quoted as $0.108 \, mol \, dm^{-3}$.

Other examples of calculations are shown in Table **11.8**.

Calculation			Actual result	Value to quote
23.5	×	14.87	349.445	349
0.79	÷	0.0367	21.52588556	22
5.234×10^3	×	1.2×10^3	6.2808×10^6	6.3×10^6

Table 11.8 Some examples of calculations involving multiplication or division.

- 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

'25.00' implies that the volume is somewhere between 24.995 and $25.005 \, cm^3$.

$$\frac{c_1 V_1}{n_1} = \frac{c_2 V_2}{n_2}$$

Rounding values in calculations

When carrying out multi-stage calculations, it is important to avoid rounding errors that could, after several stages, introduce large inaccuracies into the calculation. 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 $\pm 2\%$.

The **percentage uncertainty** is worked out using the equation:

$$\text{percentage uncertainty} = \frac{\text{absolute uncertainty}}{\text{value}} \times 100$$

For example, for 0.257 ± 0.005 cm:

$$\text{percentage uncertainty} = \frac{0.005}{0.257} \times 100 = 2\%$$

The absolute uncertainty can be worked out from the percentage uncertainty using the equation:

$$\text{absolute uncertainty} = \frac{\text{percentage uncertainty}}{100} \times \text{value}$$

For example, if the final value of a calculation is $0.518 \pm 1\%$:

$$\text{absolute uncertainty} = \frac{1}{100} \times 0.518 = 0.005 \text{ (to one significant figure)}.$$

Therefore the final answer is 0.518 ± 0.005.

Propagating uncertainties in calculations

Adding or subtracting

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

Worked example

11.1 Calculate the change in temperature from the following data:

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

change of temperature = maximum temperature − initial temperature

change of temperature = $57.58 - 23.42 = 34.16\,°C$

The uncertainty in the change of temperature is obtained by adding the uncertainty in the initial temperature to the uncertainty in the maximum temperature:

uncertainty in change of temperature = $0.02 + 0.02 = 0.04\,°C$

Therefore the change of temperature is quoted as $34.16 \pm 0.04\,°C$.

That this is appropriate can be seen by subtracting the minimum possible value for the initial temperature $(23.42 - 0.02 = 23.40)$ from the maximum possible value for the final temperature $(57.58 + 0.02 = 57.60)$ and vice versa.

Multiplying or dividing

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

Worked example

11.2 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?

$2.57 \times 3.456 = 8.881\,92$

Percentage uncertainties:

$$\frac{0.01}{2.57} \times 100 = 0.39\% \qquad \frac{0.007}{3.456} \times 100 = 0.20\%$$

total percentage uncertainty = $0.39 + 0.20 = 0.59\%$

To work out the absolute uncertainty of the final value, it is multiplied by its percentage uncertainty:

$$\text{absolute uncertainty} = \frac{0.59}{100} \times 8.88192 = 0.05 \text{ (to one significant figure)}.$$

The absolute uncertainty is in the second decimal place, and therefore no figures should be quoted beyond that. The final answer should be quoted as 8.88 ± 0.05.

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.

So, if 12.12 ± 0.01 (percentage uncertainty = 0.083%) is multiplied by 3, the answer is 36.36 ± 0.03 (percentage uncertainty = 0.083%). If 2.00 ± 0.03 (percentage uncertainty = 1.5%) is divided by 3, the answer is 0.67 ± 0.01 (percentage uncertainty = 1.5%).

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.

This will be considered in the next worked example.

Worked example

11.3 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.

mass of polystyrene cup/g	5.00 ± 0.01
mass of polystyrene cup + water/g	105.23 ± 0.01
initial temperature of water/°C	21.1 ± 0.1
minimum temperature of water/°C	19.0 ± 0.1
mass of weighing boat/g	0.50 ± 0.01
mass of weighing boat + potassium bromide/g	6.61 ± 0.01

The specific heat capacity of water $= 4.18 \, J \, g^{-1} \, °C^{-1}$.

mass of water $= (105.23 \pm 0.01) - (5.00 \pm 0.01) = 100.23 \pm 0.02 \, g$

percentage uncertainty of mass of water $= \dfrac{0.02}{100.23} \times 100 = 0.02\%$

mass of KBr $= (6.61 \pm 0.01) - (0.50 \pm 0.01) = 6.11 \pm 0.02 \, g$

percentage uncertainty of mass of KBr $= \dfrac{0.02}{6.11} \times 100 = 0.3\%$

change in temperature of water $= (21.1 \pm 0.1) - (19.0 \pm 0.1) = 2.1 \pm 0.2 \, °C$

percentage uncertainty of temperature change $= \dfrac{0.2}{2.1} \times 100 = 9.5\%$

The percentage uncertainty of the change in temperature is much larger than the other two uncertainties and therefore we can assume that the uncertainty of the final value is also going to be about 9.5%.

heat taken in $= mc\Delta T = 100.23 \times 4.18 \times 2.1 = 879.82 \, J$

number of moles of KBr $= \dfrac{6.11}{119.00} = 0.0513 \, mol$

enthalpy change $= \dfrac{879.82}{0.0513} = 17150 \, J \, mol^{-1} = 17.150 \, kJ \, mol^{-1}$

We must now consider to how many significant figures the answer can be quoted. We will take the percentage uncertainty of the final answer as 9.5% and must work out 9.5% of 17.150.

absolute uncertainty $= \dfrac{9.5}{100} \times 17.150 = 2$ (to one significant figure).

Therefore, the enthalpy change of solution should be quoted as $17 \pm 2 \, kJ \, mol^{-1}$.

Working out the total percentage error as $(0.02 + 0.3 + 9.5)\%$ would have made no difference to the final value or uncertainty.

Nature of science

Scientific work often involves the collection of quantitative data, but scientists must always be aware of the limitations of their data. When publishing, for instance, a value for the relative atomic mass of sulfur, to how many decimal places can the value be quoted?

Scientists often repeat experiments to reduce random uncertainties but the effects of systematic errors can be more difficult to spot, especially when reporting the value of a quantity for the first time, because there is nothing with which to compare it.

? Test yourself

6 Copy and complete the table:

0.345 ± 0.001	+	0.216 ± 0.002	=	
23.45 ± 0.03	−	15.23 ± 0.03	=	
0.0034 ± 0.0003	+	0.0127 ± 0.0003	=	
1.103 ± 0.004	−	0.823 ± 0.001	=	
1.10 ± 0.05	+	17.20 ± 0.05	=	

7 Copy and complete the table:

Value	Percentage uncertainty %
27.2 ± 0.2	
0.576 ± 0.007	
4.46 ± 0.01	
$7.63 \times 10^{-5} \pm 4 \times 10^{-7}$	

8 a What is the absolute uncertainty when 2.13 ± 0.01 is multiplied by 4.328 ± 0.005? Give the final answer to the appropriate number of significant figures.

b What is the absolute uncertainty when 48.93 ± 0.02 is divided by 0.567 ± 0.003. Give the final answer to the appropriate number of significant figures.

9 Use the equation $E = mc\Delta T$ and the values in the table to calculate the energy released, to the appropriate number of significant figures, when a sample of a solution cools:

Mass of solution (m)	$43.27 \pm 0.01 \, g$
Temperature change (ΔT)	22.8 ± 0.2
Specific heat capacity (c)	$4.2 \, J \, g^{-1} \, °C^{-1}$

11.2 Graphical techniques

A graph is a very useful way of presenting the relationship between two quantities. Consider a graph of rate of reaction against concentration.
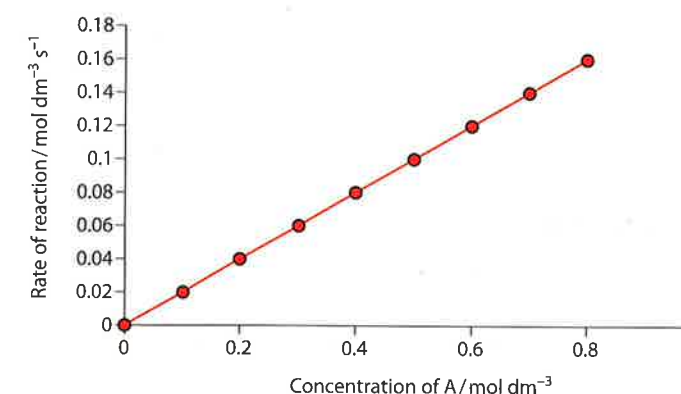
Figure 11.5 Rate of reaction against concentration for A → B.

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
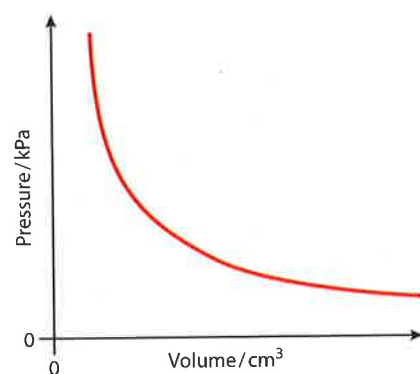- Calculate the gradient and intercept in graphs

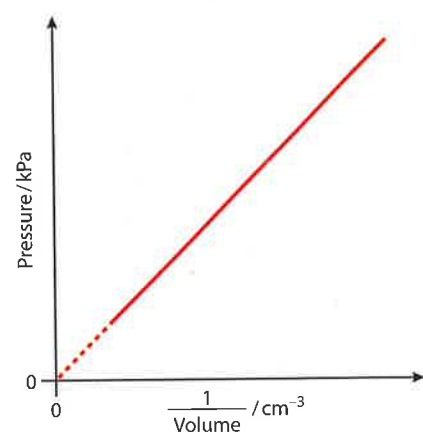**Figure 11.7** Pressure versus volume at constant temperature.

Figure 11.8 Pressure versus $\frac{1}{\text{volume}}$.

$$y = mx + c$$

The relationship between volume and pressure, shown in Figure **11.7**, is an inversely proportional one:

$$\text{pressure} \propto \frac{1}{\text{volume}}$$

This means that doubling the volume causes the pressure to be halved, and vice versa.

That this is indeed an inversely proportional relationship can be confirmed by plotting pressure against $\frac{1}{\text{volume}}$. Because pressure is proportional to $\frac{1}{\text{volume}}$, this graph should produce a straight line through the origin (Figure **11.8**).

The graph in Figure **11.9** shows that the rate of reaction increases as the concentration of A increases. The relationship between the two quantities is, however, not immediately obvious, other than that it is not a
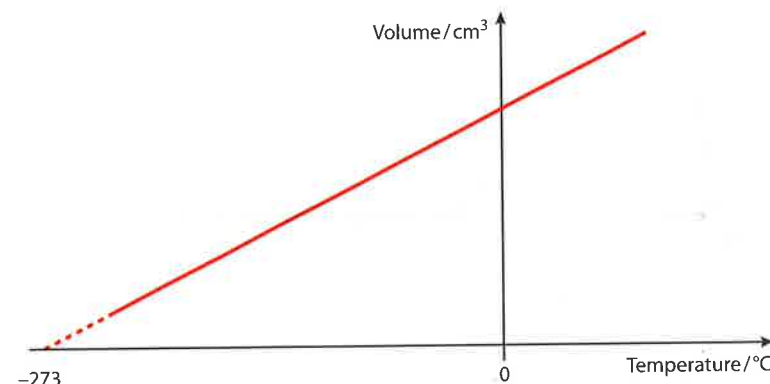
Figure 11.6 Volume versus temperature at constant pressure.

proportional relationship and that the rate of reaction more than doubles when the concentration of A doubles.

We can further analyse these data by trying out some relationships between the rate of reaction and concentration. If we try plotting the rate of reaction against (concentration of A)^2 (Figure **11.10**), we get a straight line through the origin.

The proportional relationship indicated by the straight line through the origin tells us that rate is proportional to (concentration of A)^2.

If this graph had not resulted in a straight line, we could have tried plotting rate against (concentration of A)^3 and so on until a proportional relationship was obtained.

Drawing graphs

There are several general rules for drawing graphs.
1 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
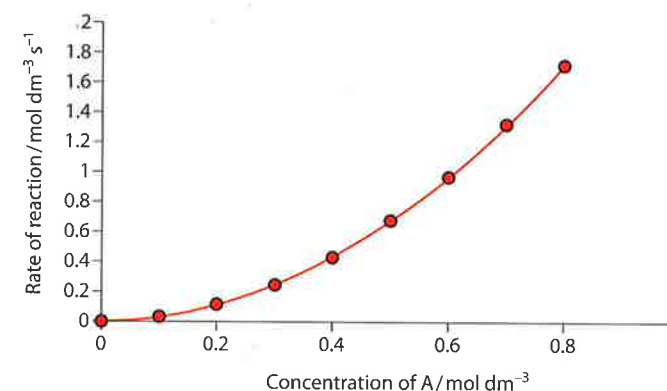
Figure 11.9 Rate of reaction against concentration of A.
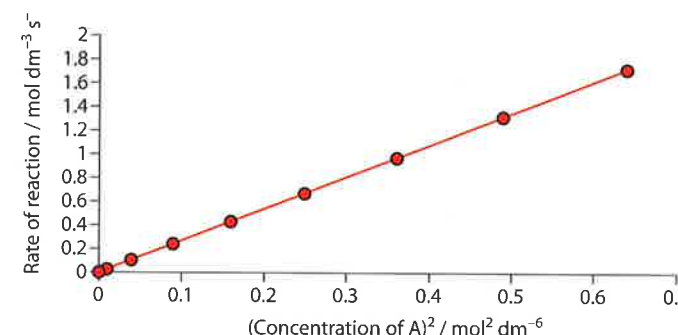
Figure 11.10 Rate of reaction against (concentration of A)^2.

as easy as possible to interpret. A graph would usually be expected to fill most of a piece of graph paper. Suppose the data in Table **11.9** were collected in an experiment.

Choosing a scale for the temperature in which the smallest square is one unit would make it very difficult to plot 23.12 precisely. Ideally, if possible, one small square should represent one unit of the last significant figure of your data, i.e. 0.01 °C in this case. This may not be possible with the size of the piece of graph paper available, however!

Time / s	Temperature / °C
0	23.12
30	25.56
60	28.78
90	29.67
120	30.23

Table 11.9 Sample data.
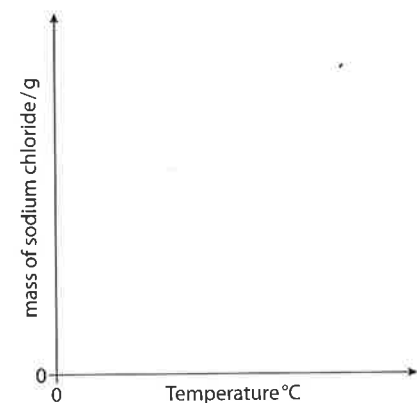
Figure 11.11 The dependent variable goes on the y-axis and the independent variable on the x-axis.

If the volume to be plotted is $23.0\,cm^3$, dividing by cm^3 gives the number 23.0, which will be plotted on the graph.

The graphs shown here are for continuous data – that is, the quantities plotted can take any value. When discrete data are plotted a best-fit line should not be drawn, and points may be joined or the data could be plotted as a bar chart.

If the pressure to be plotted is $5.34 \times 10^5\,Pa$, then dividing that by $10^5\,Pa$ means that the number can be plotted on the graph as 5.34.

$$gradient = \frac{change\ in\ y}{change\ in\ x}$$

2 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 instance, you are given the task of investigating how the solubility of common salt (sodium chloride) is affected by temperature. You could carry out a series of experiments varying the temperature (independent variable) to determine what mass of salt (dependent variable) dissolves in a fixed volume of water at each temperature. A graph could now be drawn with mass of sodium chloride on the y-axis and temperature on the x-axis – Figure **11.11**.

Another graph could then also be drawn of the processed data – in this case solubility could be plotted on the y-axis and temperature on the x-axis.

3 Label the axes with the quantity and units. There are various conventions for laying out the units. One way that is commonly used is to have the quantity divided by the units, e.g. volume/cm^3 and pressure/$10^5\,Pa$. You could also put the units in brackets, e.g. volume (cm^3) and pressure (Pa).

4 Plot the points, which may be marked by crosses or by dots in circles.

5 Draw a best-fit line (do not join the points!). This may be a straight line or a curve (Figure **11.12**) and should represent, as well as possible, the trend in the data. The points should be evenly distributed about the line. A line of best fit is very much a matter of judgement and no two lines of best fit drawn by different people will be identical.

6 Give the graph a title describing what has been plotted.
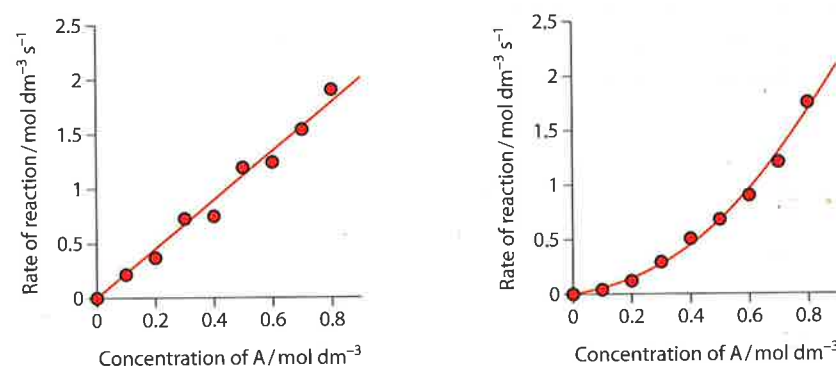
Figure 11.12 Best-fit lines.

Deriving quantities from graphs

The gradient (slope) is one of the most important quantities that can be derived from a graph. A gradient gives us an idea how much one quantity (the dependent variable) is affected by another quantity (the independent variable). If the gradient is large, a small change in the independent variable has a large effect on the dependent variable. Sometimes the gradient can also have an important physical meaning – e.g. if a graph of the amount of a reactant or a product of a chemical reaction against time is plotted, the gradient represents the rate of the reaction.
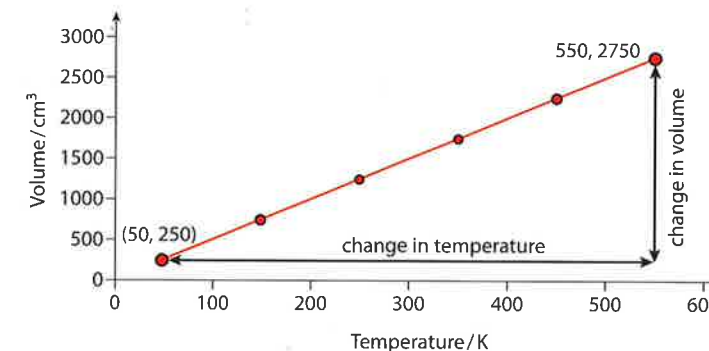
Figure 11.13 Volume versus temperature for a fixed mass of an ideal gas.

Consider the graph of the volume of a fixed mass of gas against temperature shown in Figure **11.13**.

When determining the gradient from a straight-line graph, a triangle is drawn as shown in Figure **11.13**, and the change in the quantity on the vertical axis is divided by the change in the quantity on the horizontal axis. The triangle should be made as large as possible to minimise any uncertainties caused by reading from the graph.

$$gradient = \frac{change\ in\ volume}{change\ in\ temperature} = \frac{2750 - 250}{550 - 50} = 5$$

The units of the gradient are obtained by dividing the units of volume (y-axis) by the units of temperature (x-axis), i.e. cm^3/K or $cm^3\,K^{-1}$ in this case. Therefore the gradient (slope) of the line is $5\,cm^3\,K^{-1}$.

Another important quantity that can be obtained from a graph is the intercept on the y-axis. An example of a calculation involving determination of the gradient and intercept is given on page **268** (in Topic **6**).

Finding the gradient of a curve

A curved line has a constantly changing gradient, and therefore we can work out the gradient only at specific points. This is done by drawing a tangent (straight line) to the curve at the desired point and working out the gradient of the tangent as usual.

In this graph the tangent is drawn at the initial point (Figure **11.14**) and the initial rate of reaction is the gradient of this tangent.

$$gradient = \frac{70 - 0}{32 - 0} = 2.2\,cm^3\,s^{-1}$$

The initial rate of reaction is therefore $2.2\,cm^3\,s^{-1}$.

Nature of science

The idea of the correlation between variables can be tested experimentally and the results displayed on a graph.

It is important that the public have an understanding of certain scientific issues and graphs can often provide a convenient way of presenting data and showing a correlation between factors. Scientists, however, have a responsibility to ensure that their data are reported fairly and accurately – incomplete graphs or graphs without scales can be misleading for example.
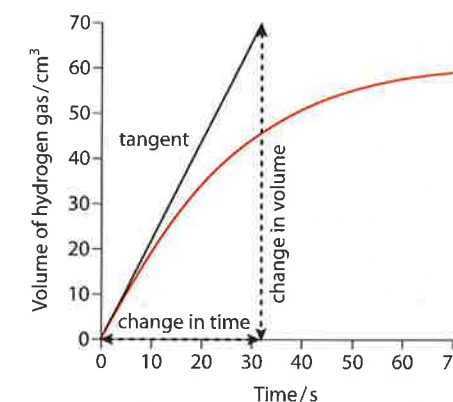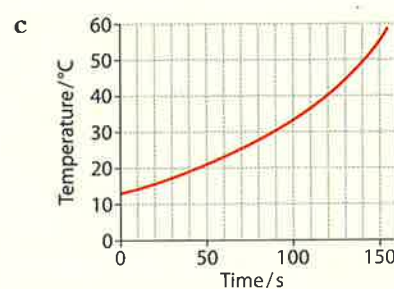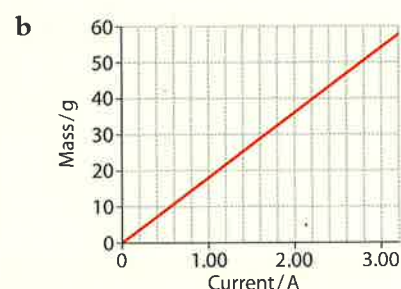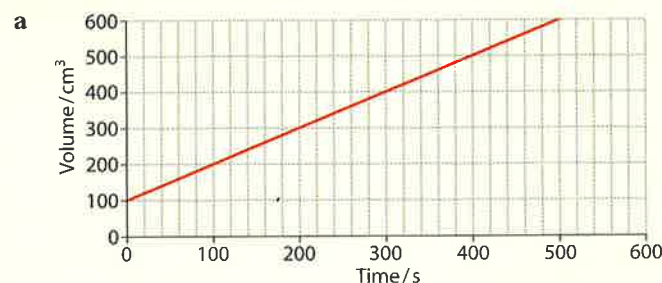

Figure 11.14 Calculating a gradient.

A tangent should be drawn as large as possible to minimise uncertainties caused by reading values off the graph.

10 Describe the relationship between the two variables shown in each of the following graphs.

a

b

c

11 Calculate the gradients, with units, for the graphs in question **10a** and **b**.

11.3 Spectroscopic identification of organic compounds

Determination of the number of multiple bonds/rings in a molecule

If we compare the molecular formulas of some organic compounds, we can see the relationship between the formula and the number of multiple bonds/rings present – Table **11.10**.

It can be seen that:

> **for every two hydrogen atoms fewer than in the alkane with the same number of carbon atoms, there is one double bond or ring present** (*double bond equivalent*)

So, a molecule with the formula C_4H_8 has two hydrogen atoms fewer than the parent alkane (C_4H_{10}) and can contain one double bond or one ring. C_4H_6 has four hydrogens fewer than in the alkane and therefore has two double bond equivalents – which could mean that there are two double bonds, one triple bond, two rings (not possible with four carbon atoms) or one ring and one double bond present.

The number of double bond equivalents is sometimes called the *degree of unsaturation* or *the index of hydrogen deficiency* (*IHD*).

Molecule				
Name	butane	but-1-ene	but-1-yne	cyclobutane
Molecular formula	C_4H_{10}	C_4H_8	C_4H_6	C_4H_8
Double bond equivalents	0	1	2	1
IHD	0	1	2	1

Table 11.10 The formulas of some compounds containing four carbon atoms.

We can extend the idea to compounds containing atoms other than carbon and hydrogen.

The rule works in the same way with compounds containing oxygen atoms – so C_2H_6O has the same number of hydrogens as ethane (C_2H_6) and contains no double bonds (IHD = 0), whereas C_4H_8O has two hydrogens fewer than butane and contains either one double bond or one ring (IHD = 1).

When a compound contains a halogen atom, we simply count this as a hydrogen atom and work out the number of double bond equivalents – so in $C_4H_8Cl_2$ we replace the Cl atoms with hydrogen atoms to make C_4H_{10}, which has the same number of hydrogen atoms as butane and therefore there are no double bond equivalents (IHD = 0).

The most complicated situation you are likely to meet is when a compound contains nitrogen atoms. To work out the number of double bond equivalents, we must subtract one hydrogen for every nitrogen atom and then calculate as above.

Worked example

11.4 Work out the index of hydrogen deficiency for C_3H_5N and suggest a possible structure for the molecule.

Subtracting 1 (because there is one nitrogen atom present) from the number of hydrogen atoms gives us C_3H_4. This has four hydrogens fewer than the parent alkane (C_3H_8) and so there are two double bond equivalents – therefore IHD = 2.

Possible structural formulas are $CH_3CH_2C\equiv N$, $HC\equiv CCH_2NH_2$ etc.

> An IHD can also be worked out using an equation. In a molecule with the formula $C_cH_hN_nO_oX_x$, where X is a halogen atom, the IHD is given by:
> $$IHD = \frac{1}{2} \times [2c + 2 - h - x + n]$$

Exam tip
Benzene (C_6H_6) has an IHD of 4 because it contains one ring and the equivalent of three double bonds.

? Test yourself

12 Work out the index of hydrogen deficiency for each of the following:

a C_3H_6 c C_6H_9Cl e C_6H_6
b $C_4H_8O_2$ d $C_5H_{12}N_2$

Structure determination using infrared spectroscopy

Infrared spectroscopy is a very useful tool when determining the structure of an organic compound. In an infrared spectrometer, electromagnetic radiation in the range $400{-}4000\,cm^{-1}$ is passed through a sample. The printout of the spectrum then shows which frequencies (wavenumbers) are absorbed.

Infrared spectra are always looked at with the baseline (representing 100% transmittance/zero absorbance of infrared radiation) at the top. So the troughs (usually called 'bands'; sometimes 'peaks') represent wavenumbers at which radiation is absorbed (Figure **11.15**).

An infrared spectrum can be used to determine which bonds are present in a molecule. In the infrared spectrum of propanone there are two bands in the region above $1500\,cm^{-1}$, corresponding to absorptions by the C–H bond and the C=O bond.

The segment of the spectrum below $1500\,cm^{-1}$ is called the 'fingerprint region' and is characteristic of the molecule as a whole. Comparison of the fingerprint region of a spectrum with infrared spectra in databases can be used to identify molecules. For example, butanone and propanone both

Wavenumbers (cm^{-1}) are used in infrared spectroscopy. This represents the number of wavelengths per cm. Wavenumbers are proportional to frequency and to energy.

Even at absolute zero, the atoms in a molecule are vibrating relative to each other. Just as the electrons in an atom or molecule can exist only in certain energy levels (the energy of an electron is quantised), the vibrational energy of a molecule is quantised. This means that the vibrational energy of a molecule can take only certain allowed values. So a molecule can exist, for instance, in either the level with vibrational energy V_1 or that with V_2. The molecule can absorb a certain frequency of infrared radiation to move it from the lower vibrational energy level to the higher one. In the higher energy level, the molecule vibrates more violently – with a bigger amplitude.

Figure 11.15 The infrared spectrum of propanone – CH_3COCH_3.

Bond	Functional group/class of compound	Characteristic range of wavenumber / cm^{-1}
C–Cl	chloroalkane	600–800
C–O	alcohol, ether, ester, carboxylic acid	1000–1300
C=C	alkene	1610–1680
C=O	aldehyde, ketone, carboxylic acids, ester	1700–1750
C≡C	alkyne	2100–2260
O–H	hydrogen bonded in carboxylic acids	2400–3400
C–H	alkane, alkene, arene	2840–3100
O–H	hydrogen bonded in alcohols, phenols	3200–3600
N–H	primary amine	3300–3500

Table 11.11 The characteristic ranges of wavenumbers at which some bonds vibrate.

show very similar bands in the region above $1500\,cm^{-1}$, because they have the same functional group (C=O), but they can be distinguished using their fingerprint regions, which are very different.

To a good approximation, the various bonds in a molecule can be considered to vibrate independently of each other. The wavenumbers at which some bonds absorb are shown in Table **11.11**.

The precise wavenumber at which infrared radiation is absorbed by a particular functional group depends on the adjacent atoms. So a C=O bond in a ketone absorbs at a slightly different frequency to a C=O bond in an ester.

We can use infrared spectra to identify the bonds present in molecules but we cannot always distinguish between functional groups. For example, using Table **11.11** we could identify the presence of C=O in a molecule but would not be able to distinguish between an aldehyde and a ketone.

Consider the infrared spectrum of butanoic acid, shown in Figure **11.16**. To identify the bonds present in the molecule, we first of all look at the region above $1500\,cm^{-1}$.
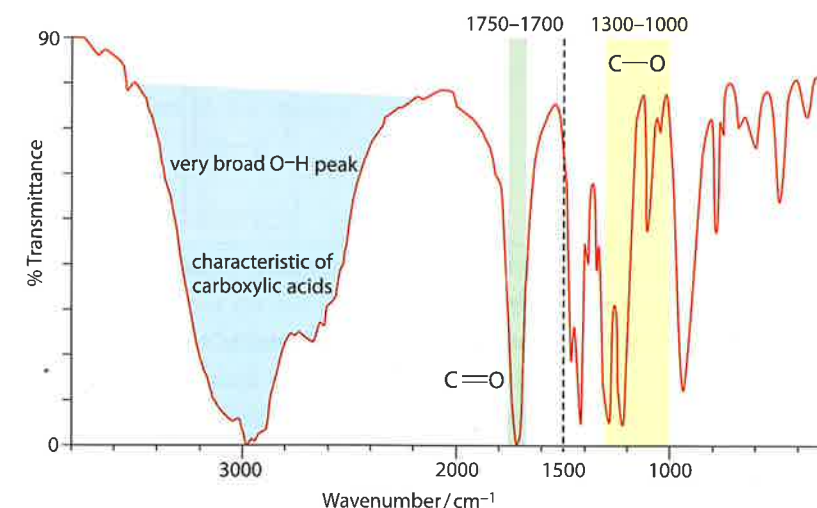
Exam tip
A table of infrared absorption frequencies is given in the IB Chemistry data booklet. The values in that table differ slightly from those given here – you will use the values in the data booklet for the examination.

The broadness of the O–H band is due to hydrogen bonding between molecules. If the infrared spectrum of a carboxylic acid in the gas phase is examined, the O–H absorption band is much narrower.

Figure 11.16 The infrared spectrum of butanoic acid – $CH_3CH_2CH_2COOH$.

The C–H stretch also occurs in the region around 3000 cm^{-1} but this is usually significantly obscured by the broad O–H absorption.

We now need to match up the wavenumbers of bands in the spectrum with the wavenumbers given in Table **11.11**. The presence of an absorption band in the 1700–1750 cm^{-1} region suggests that there is a C=O bond in the molecule. The very broad absorption band between about 2400 and 3400 cm^{-1} is due to the O–H bond – a very broad band in this region is characteristic of carboxylic acids.

The functional group of a carboxylic acid has a C–O bond, and so we should now look in the fingerprint region to confirm the presence of an absorption in the region 1000–1300 cm^{-1}, which is indeed the case. If there were no band in this region, we would have to review our hypothesis that the molecule is a carboxylic acid.

The region below 1500 cm^{-1} contains many absorptions due to C–C bonds and C–H bonds and is difficult to interpret. We usually look only at the fingerprint region to confirm the presence of a particular vibration once we have a good idea of the structure of the molecule. For example, a band in the 1000–1300 cm^{-1} region does not confirm the presence of a C–O bond in a molecule – but the absence of a band in this region means that a C–O bond is not present. For example, in the infrared spectrum of propanone (Figure **11.15**) there are peaks in the 1000–1300 cm^{-1} region but no C–O bond.

The infrared spectrum of propan-1-ol is shown in Figure **11.17**.

Again, by comparison of the bands with the values in Table **11.11**, we can identify an O–H absorption (about 3350 cm^{-1}) and a C–H absorption (about 2900–3000 cm^{-1}). Evidence for a C–O bond should also be present and we can see that there is a band in the region 1000–1300 cm^{-1}.
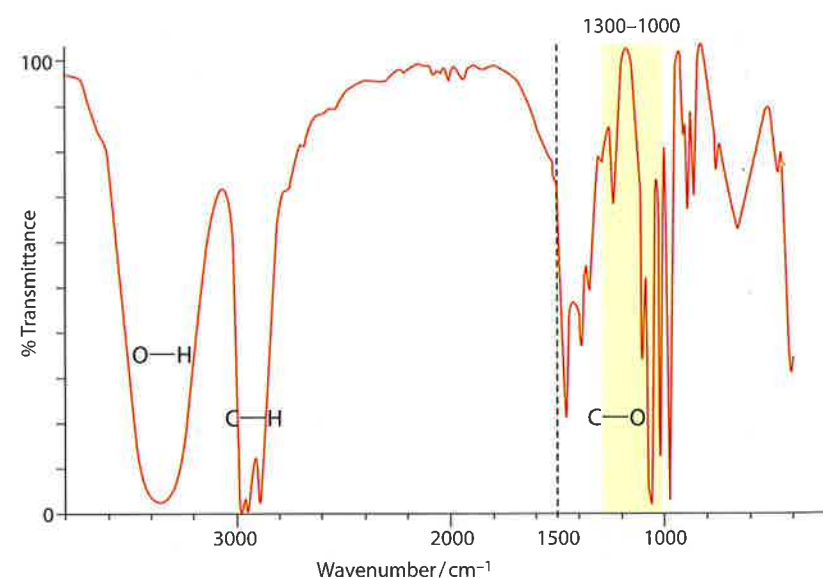
Figure 11.17 The infrared spectrum of propan-1-ol, CH$_3$CH$_2$CH$_2$OH.

Worked example

11.5 The infrared spectrum shown is for one of these compounds below.

Identify the compound and explain how you arrive at your choice.
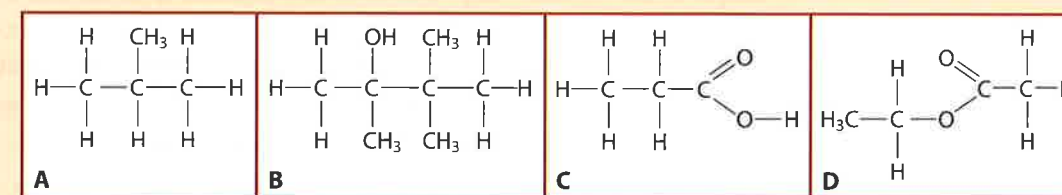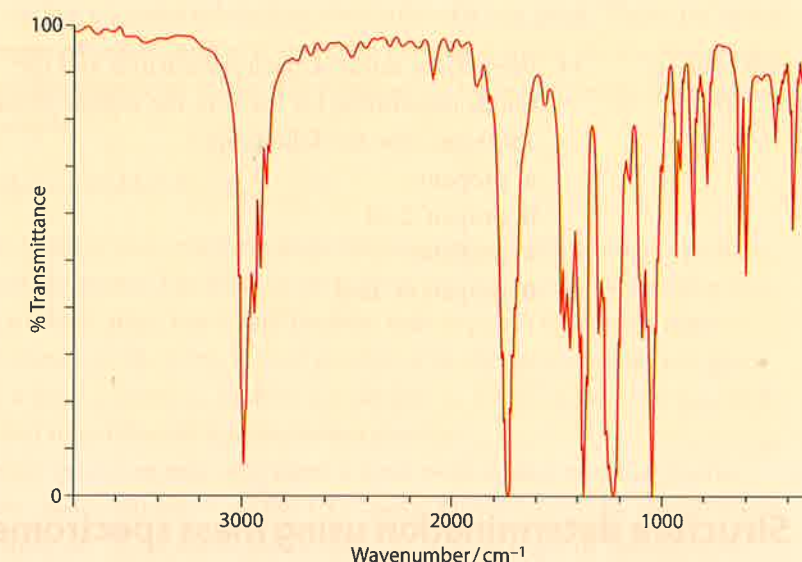
Looking in the region above 1500 cm^{-1}, we can identify an absorption band around 2840–3100 cm^{-1} that is due to a C–H bond, and an absorption in the region 1700–1750 cm^{-1} that is due to a C=O bond. This eliminates molecules **A** and **B** because neither contains a C=O bond.

C is a carboxylic acid, which would be expected to have a very broad O–H absorption band in the region 2400–3400 cm^{-1}. This band is not present so the spectrum cannot be for molecule **C**.

This means that we are left with molecule **D**. Molecule **D** contains C–H bonds and C=O bonds and should give rise to a band in the region 1000–1300 cm^{-1} because it contains a C–O bond – the spectrum shows that there is an absorption in this region.

Nature of science

Sciences use models routinely to provide a framework in which we can understand process on the atomic/molecular level. Our interpretation of infrared spectra is based on a simple model in which the bonds in different functional groups are assumed to vibrate completely independently of each other and absorption of infrared radiation causes the promotion of the bond to a higher vibrational energy level.

Understanding and knowledge in many areas of Chemistry has developed enormously as more and more sophisticated analytical

instruments became available throughout the twentieth century and into the twenty-first century. This has allowed chemists to work out the structures of simple molecules fairly routinely and to also derive the structures of some very complex systems such as proteins.

? Test yourself

13 Which of the following compounds will have an infrared absorption band in the 1700–1750 cm^{-1} region?
   A but-2-ene
   B propanal
   C CH_3COCH_3
   D $CH_3CH_2CH_2CH_2Cl$
   E CH_3COOCH_3
   F $CH_3CH_2CH(OH)CH_3$
   G CH_3CH_2COOH

14 Predict the infrared absorption bands and the bonds responsible for them in the region above 1500 cm^{-1} for the following:
   a propane
   b propan-2-ol
   c propene
   d propanoic acid

Structure determination using mass spectrometry

A sample of the organic compound to be investigated is injected into a **mass spectrometer**. First, it is bombarded with high-energy electrons to produce positive ions. These pass on through the mass spectrometer where they are separated according to mass (actually the mass : charge ratio) and detected.

When a sample of propane (C_3H_8) is introduced into a mass spectrometer, $C_3H_8^+$ positive ions are produced:

$$C_3H_8(g) + \underset{\text{high-energy electron}}{e^-} \rightarrow \underset{\text{molecular ion}}{C_3H_8^+(g)} + 2e^-$$

The ion produced when just one electron is removed from a molecule is called the **molecular ion**, M^+.

> The peak in the spectrum at the highest mass (m/z value) corresponds to the molecular ion and indicates the relative molecular mass of the molecule (Figure **11.18**).

> The mass of an electron is negligible.

> The mass spectrometer sorts molecules according to their mass : charge (m/z or m/e) ratio. We assume here that only 1+ ions are formed so that the mass : charge ratio is equal to the mass.

Figure 11.18 The mass spectrum of propane – $CH_3CH_2CH_3$.

We can deduce from Figure **11.18** that the relative molecular mass of the compound being investigated is 44. It is important to note that the molecular ion peak is not necessarily the biggest peak in terms of abundance, but it has the highest m/z value.

It can be seen from the mass spectrum of propane in Figure **11.18** that there are lots of peaks other than the molecular ion peak. These are called the **fragmentation pattern** and arise because a molecule can break apart into smaller fragments when it is bombarded by high-energy electrons – for example:

$$C_3H_8^+ \rightarrow C_2H_5^+ + CH_3$$

All the positive ions resulting from fragmentation will produce a peak in the mass spectrum. The peak at m/z 29 in the mass spectrum of propane is due to the $C_2H_5^+$ ion. Only positive ions can pass through a mass spectrometer, so the CH_3 radical produced in this process does not give rise to a peak. However, there is a peak due to CH_3^+ at m/z 15, which is produced in a different fragmentation process.

A mass spectrum may also show a peak with a mass one unit higher than the molecular ion – an $(M+1)^+$ peak. This is caused by the presence of an atom of ^{13}C in some molecules. ^{13}C is an isotope of carbon – its natural abundance is low at 1.1%.

> Only positive ions give peaks in a mass spectrum.

Fragmentation patterns

We can think of fragmentation in two ways – we can look at:
- the ion formed when a molecular ion breaks apart
- the group lost from a molecular ion.

Look at the mass spectrum of propanoic acid in Figure **11.19**. The molecular ion peak occurs at m/z 74, so the relative molecular mass is 74.

There is a peak in the spectrum at m/z 57, which corresponds to the loss of OH (mass 17) from the molecular ion. So the fragment responsible for the peak at m/z 57 is ($C_2H_5COOH^+ - OH$), or $C_2H_5CO^+$.

> **Exam tip**
> The fragmentation pattern in a mass spectrum can be very complicated and you should not try to identify every single peak.

> Molecules can undergo fragmentation in many different ways – they can also undergo rearrangement as they fragment.
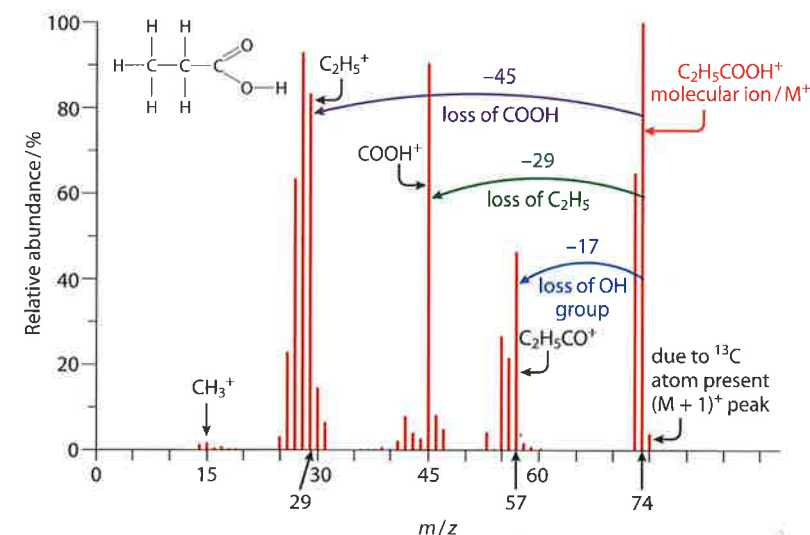
Figure 11.19 The mass spectrum of propanoic acid – CH_3CH_2COOH.

Fragment	Mass of fragment ion	Possible inference
CH_3^+	15	
OH^+	17	alcohol / carboxylic acid
$C_2H_5^+$ / CHO^+	29	
CH_3O^+ / CH_2OH^+	31	methyl ester / ether / primary alcohol
CH_3CO^+	43	ketone with C=O on second C
$COOH^+$	45	carboxylic acid
$C_6H_5^+$	77	arene

Table 11.12 Formulas of some common fragment ions. Peaks are also be formed when fragments are lost from a molecule – in this case the m/z value of the peak will be the relative molecular mass minus the mass of the fragment.

The peak at m/z 45 corresponds to the loss of 29 mass units from the molecular ion. C_2H_5 is a group with mass 29 and so we can deduce that C_2H_5 is lost from $C_2H_5COOH^+$ to form the $COOH^+$ ion.

The peak at m/z 29 is due to the $C_2H_5^+$ ion, which is formed by loss of COOH from $C_2H_5COOH^+$.

The formulas of some common fragment ions are shown in Table **11.12**.

The mass spectrum of chloroethane is shown in Figure **11.20**.

The relative molecular mass of chloroethane can be calculated to be 64.5, but it can be seen that there is no peak at 64.5. The relative atomic mass of chlorine, 35.45, arises because chlorine has two isotopes – ^{35}Cl and ^{37}Cl, with an abundance ratio of 3:1. So some chloroethane molecules contain a ^{35}Cl atom and others have a ^{37}Cl atom – therefore we get molecular ion peaks at m/z 64 ($C_2H_5{}^{35}Cl^+$) and m/z 66 ($C_2H_5{}^{37}Cl^+$).
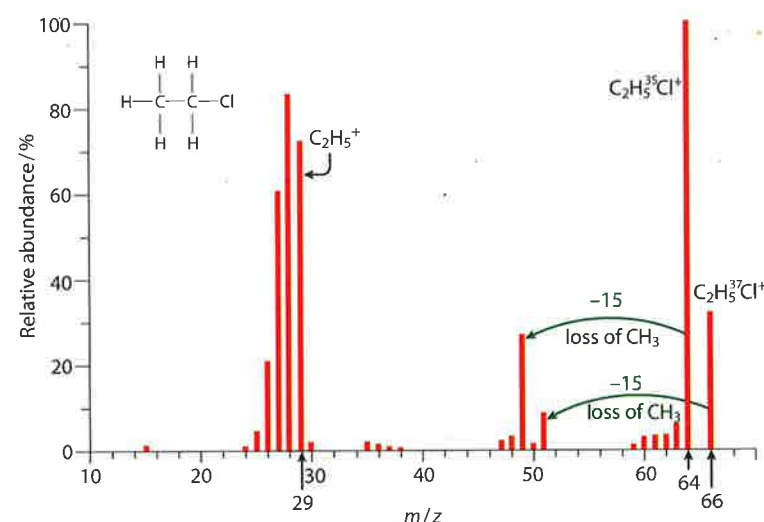
Figure 11.20 The mass spectrum of chloroethane – CH_3CH_2Cl.

Structure determination using nuclear magnetic resonance spectroscopy

A hydrogen nucleus has a property called **spin**. A spinning nucleus acts like a tiny bar magnet. This bar magnet can either align itself with (lower energy) or against (higher energy) an externally applied magnetic field. Energy in the **radio frequency** range of the electromagnetic spectrum can be used to cause a hydrogen nucleus to change its orientation relative to the applied magnetic field. It is these changes in energy state that occur in nuclear magnetic resonance (NMR) spectra. In analysing NMR spectra, we are looking at absorptions due to ^1H nuclei (usually just called **protons**) – this technique provides information about the environments of protons in molecules.

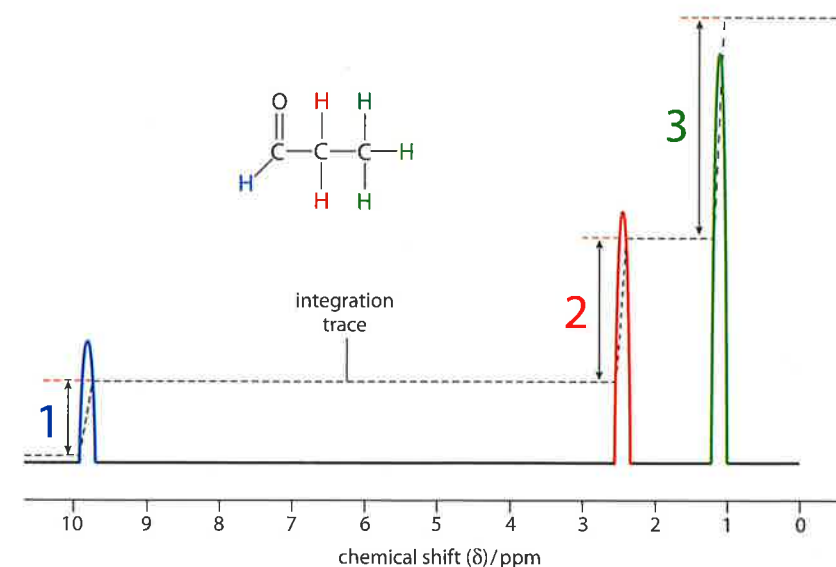The low-resolution NMR spectrum of propanal is shown in Figure **11.21**.

In all the discussion in this section, 'proton' refers to the nucleus of a hydrogen (^1H) atom.

Only nuclei with an odd value for the mass number and/or atomic number have the property of spin.

Figure 11.21 The low-resolution NMR spectrum of propanal – CH_3CH_2CHO. The integration trace allows us to work out the ratio of the numbers of protons in each environment.
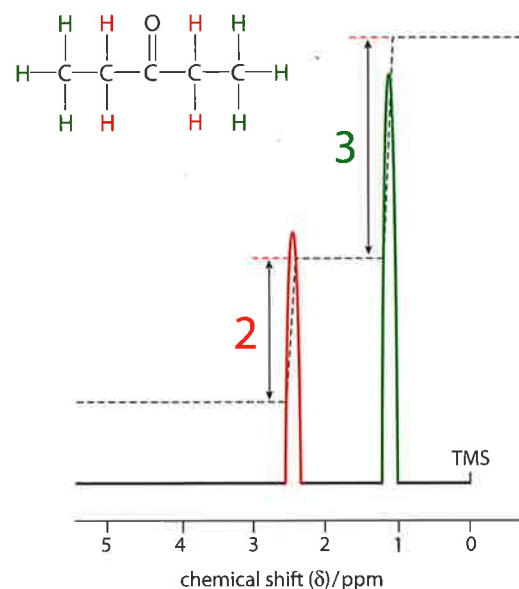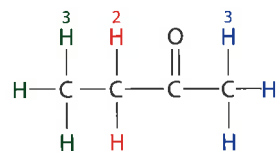
Figure 11.22 – $CH_3CH_2COCH_2CH_3$.

Figure 11.23 Butanone showing the different environments for protons.

It can be seen that there are three peaks in the spectrum – these correspond to three different chemical environments for the protons (hydrogen atoms) in one molecule of the aldehyde. The protons in the different environments are coloured differently in Figure **11.21**. Hydrogen atoms joined to the same carbon atom are said to be chemically equivalent (or just 'equivalent').

It can also be seen from Figure **11.21** that the peaks have different sizes. The area underneath a peak is proportional to the number of hydrogen atoms in that environment. So, the area under the red peak is twice (2 H in this environment) the area under the blue peak (1 H in this environment); and the area under the green peak (3 H in this environment) is three times that under the blue peak.

An NMR spectrometer can also work out the area under each peak to produce an **integration trace**. The vertical heights of the steps in the integration trace are proportional to the number of hydrogen atoms in each environment.

The horizontal scale on an NMR spectrum is the **chemical shift**, which is given the symbol δ and has units of parts per million (ppm). This quantity gives information about the environments that the protons (hydrogen atoms) are in – protons in different chemical environments have different chemical shifts.

The number of different hydrogen (proton) environments and the relative numbers of hydrogen atoms in each

To work out the number of hydrogen environments, you must first decide whether or not the molecule is symmetrical. If the molecule is not symmetrical then the hydrogen atoms on the different atoms in the carbon chain will be in different chemical environments.

The NMR spectrum for pentan-3-one (Figure **11.22**) shows two peaks (not counting any due to TMS – see page **536**).

There are only two different chemical environments for the hydrogen atoms in pentan-3-one because the molecule is symmetrical. The six hydrogens shown in green are equivalent – all in the same chemical environment; and the four hydrogens shown in red are also equivalent to each other.

The heights of the steps in the integration trace are in the ratio 2:3 because there are four hydrogen atoms in one environment and six hydrogen atoms in the other.

Butanone has three different environments for its protons (Figure **11.23**) and the ratio of the numbers of hydrogens in each environment is 3:2:3.

There are only three peaks in the NMR spectrum of propan-2-ol (Figure **11.24a**) because the molecule is symmetrical. The six hydrogens in the two CH_3 groups are equivalent. The ratio of the numbers of protons in each environment is 6:1:1. In general, the hydrogen atoms in CH_3 groups that are attached to the same carbon atom will be equivalent, so that there are only two environments in 2-methylpropan-2-ol (Figure **11.24b**). Table **11.13** shows some further examples.
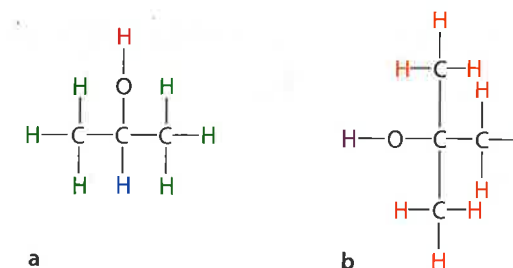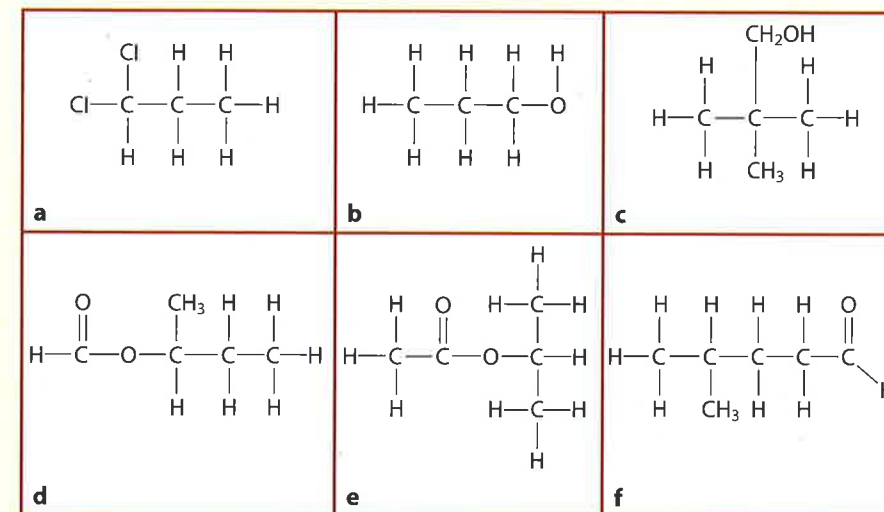

Figure 11.24 Proton environments: **a** propan-2-ol; **b** 2-methylpropan-2-ol.

	No. of different chemical environments for H	Ratio of no. of H atoms in each environment
	3	3:1:2
	5	3:1:1:2:3
	4	3:1:1:6

Table 11.13 Proton environments.

? Test yourself

17 Suggest the numbers of peaks and the ratio between the areas under the peaks in the NMR spectrum of each of the following:

Learning objectives

- Understand how chemical shifts can provide information about the structure of organic molecules
- Use high-resolution ^{1}H NMR to determine the structure of molecules
- Understand how to use information from a combination of spectroscopic techniques to determine the structure of molecules.
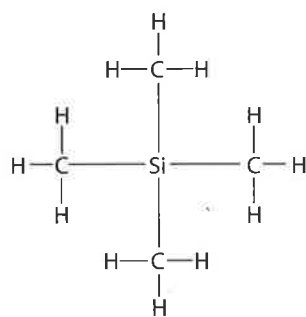

Figure 11.25 Tetramethylsilane.

TMS is a reference standard used to fix the chemical shift scale. A small amount of TMS is added to the sample before the NMR spectrum is recorded.

Another way of saying this is that the chemical shift for a particular hydrogen depends on the number of alkyl groups that are attached to the carbon to which it is bonded.

11.4 Spectroscopic identification of organic compounds (HL)

Chemical shift

The horizontal scale on a nuclear magnetic resonance spectrum is the **chemical shift**, which is given the symbol δ and has units of parts per million (ppm). Chemical shift data provide information about the environments that protons (hydrogen nuclei) are in – protons in different chemical environments have different chemical shifts.

Chemical shift values are measured relative to tetramethylsilane (TMS) (Figure **11.25**).

The protons in TMS are assigned an arbitrary chemical shift of 0.00 ppm – all chemical shifts are measured relative to this.

TMS was chosen as the standard because it has 12 protons all in the same environment and so gives a strong signal when only a small amount is added. Also the chemical shift of the protons in TMS is at a lower value than the protons in virtually all organic molecules – therefore TMS fixes the lower end of the chemical shift scale. The position of the chemical shift is also such that it is well away from the chemical shifts of protons in nearly all organic molecules – so the TMS signal does not overlap with the protons signals that we are interested in. Other reasons for using TMS are that it is non-toxic and inert.

Some typical values for the chemical shifts of protons in different environments are given in Table **11.14**.

The values in Table **11.14** are approximate and can vary depending on any groups attached. For example, it makes a difference how many other hydrogen atoms are attached to the carbon atom to which the hydrogen of interest is attached. However, in most cases, we can assume that the ranges given in the table include all possibilities, and we just look at the environment of the proton rather than the number of hydrogen atoms in that environment. So we can assume that the chemical shift of a hydrogen on a carbon next to the C=O group of an aldehyde or ketone comes in the range 2.1–2.7 no matter how many other hydrogens are attached – Figure **11.26** shows this clearly.
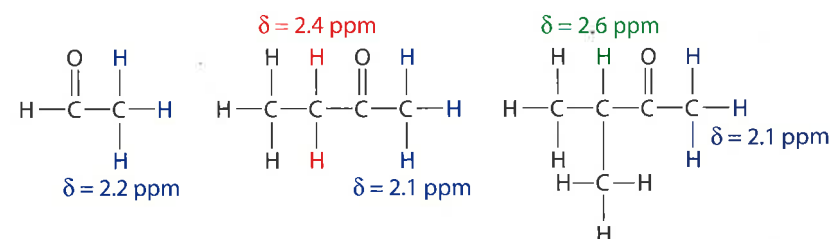

Figure 11.26 Chemical shifts are influenced by the number of hydrogen atoms on a particular carbon atom but the range in the Table **11.14** includes all possibilities.

Type of proton	Chemical shift / ppm	Comments
	0.9–1.7	H on a carbon chain but not next to any other functional groups
	2.0–2.5	H on a C next to C=O of an ester
	2.1–2.7	H on a C next to C=O of an aldehyde or ketone
	2.3–3.0	H on a C attached to a benzene ring
X is a halogen	3.2–4.4	H attached to a C that also has a halogen atom attached
	3.3–3.7	H attached to a C that has an O attached
	3.7–4.8	H on a C next to C–O of an ester
R—O—H	0.5–5.0	H attached to O in an alcohol
	6.7–8.2	H attached to a benzene ring
	9.4–10.0	H attached to C=O of an aldehyde
	9.0–13.0	H on an O in a carboxylic acid

Table 11.14 Chemical shifts for protons in different environments.

Exam tip
The representation of groups and chemical shifts here is different from those in the IB Chemistry data booklet. You should practise using those as well.

When using a table of chemical shift values, you must try to find the best match to the proton environments in the molecule you are analysing. So in the spectrum of propanal (Figure 11.27), the H (blue) attached directly to the C=O group would be expected to have a chemical shift in the range 9.4–10.0 ppm; in fact the peak for this proton occurs at a chemical shift of 9.8 ppm.
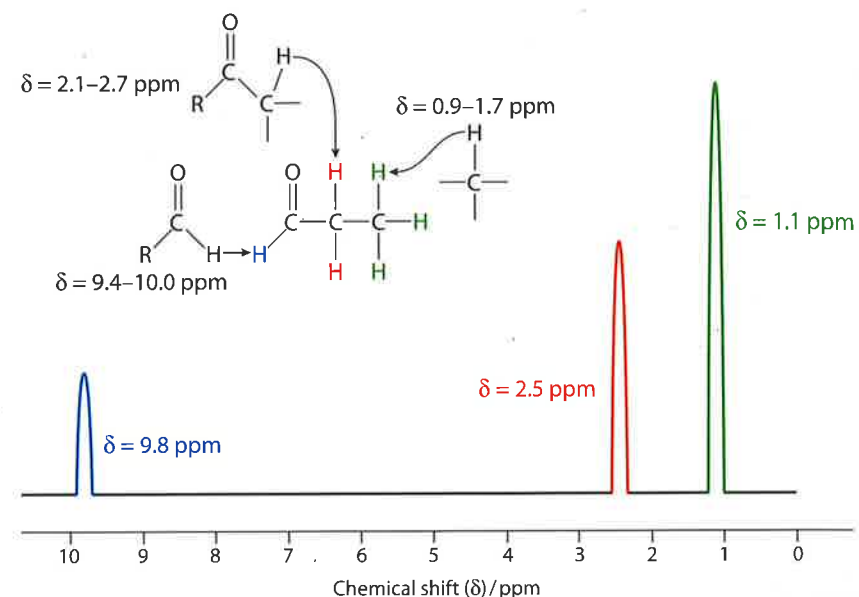

Figure 11.27 The NMR spectrum of propanal – CH_3CH_2CHO.

The ranges in which the chemical shifts of the other protons would be expected to occur are also shown in Figure 11.27 and it can be seen that all the chemical shifts occur within the expected ranges.

High-resolution NMR spectra

The low- and high-resolution NMR spectra of 1,1,2-trichloroethane are shown in Figure 11.28.
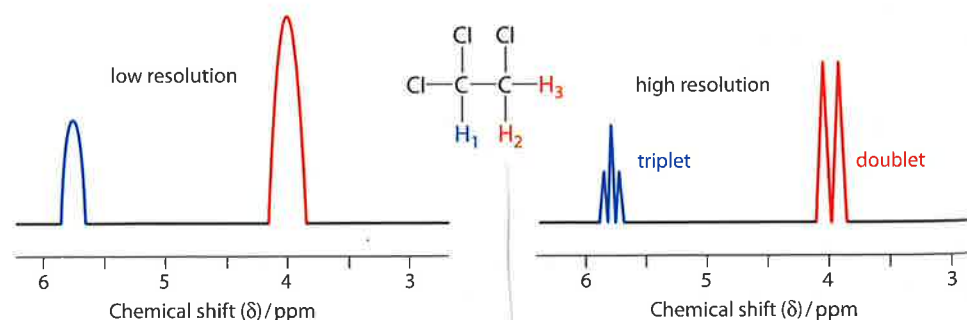

Figure 11.28 The low- and high-resolution NMR spectra of 1,1,2-trichloroethane.

There are two peaks in the low-resolution spectrum because there are two different chemical environments for protons (hydrogen atoms). However, in the high-resolution spectrum each of these peaks is split. The splitting is due to the hydrogen atoms on adjacent carbon atom(s). This results in the signal due to H_1 being split into three (a triplet), because there are two Hs on the adjacent carbon atom. The signal due to H_2 and H_3 is split into two (a doublet), because there is one H on the adjacent carbon atom. This **splitting** is called spin–spin splitting or spin–spin coupling.

We sometimes talk about the **multiplicity** of a peak – the number of smaller peaks it is split into. The multiplicity of a triplet is 3 and that of a doublet is 2.

In general, if there are n protons (hydrogen atoms) on an adjacent atom, the signal for a particular proton will be split into $(n+1)$ peaks. Another way of saying this is that if the multiplicity of a peak is x then the number of hydrogen atoms on the adjacent atom is $x - 1$.

The NMR spectrum of chloroethane is shown in Figure 11.29.

There are two sets of peaks in the NMR spectrum of chloroethane because there are two different chemical environments for protons (hydrogen atoms). The total area under the peaks at δ 1.5 ppm is larger than that under the peaks at δ 3.5 ppm, because there are more protons in this environment.

The signal at δ 3.5 ppm is split into a quartet – a quartet consists of four peaks and, therefore, has a multiplicity of 4. Now, $4 - 1 = 3$ and so we can deduce from the presence of the quartet that there are three hydrogen atoms on the adjacent carbon atom.

The signal at δ 1.5 ppm is split into a triplet – this has a multiplicity of 3. Now, $3 - 1 = 2$ so there must be two hydrogen atoms on the adjacent carbon atom.

Splitting of the signal of a particular group of protons is due to the protons on *adjacent* (carbon) atoms.

Exam tip
When a signal due to two hydrogen atoms is split into a quartet and the signal due to three hydrogen atoms is split into a triplet, this indicates the presence of an ethyl group (CH_3CH_2) in a molecule – well worth remembering!
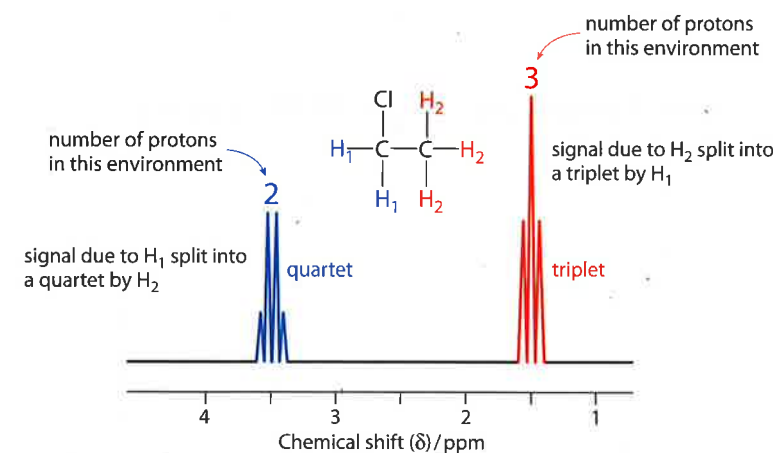
Figure 11.29 The NMR spectrum of chloroethane.

1				singlet
1		1		doublet
1	2		1	triplet
1	3	3		1	quartet

Figure 11.30 Pascal's triangle.

	singlet	1:1 doublet	1:2:1 triplet	1:3:3:1 quartet
Multiplicity	1	2	3	4
No. of equivalent protons on adjacent C atoms	0	1	2	3

Table 11.15 Different types of splitting patterns.

The intensities of the lines in a splitting pattern are given by Pascal's triangle (Figure **11.30**). So we talk about a 1:1 doublet (the areas under the peaks are equal) or a 1:2:1 triplet etc.

A summary of the different types of splitting patterns is given in Table **11.15**.

'Rules' for spin–spin coupling

- Protons on the same atom (e.g. CH_3, CH_2) do not split each other – they are **chemically equivalent** and behave as a group.
- Splitting generally only occurs with protons on adjacent atoms – see Figure **11.31**.
- Protons attached to oxygen atoms do not usually show or cause splitting – this is because the protons exchange with each other and with the solvent and experience an 'average' environment.

Figure 11.31 H_a protons couple only with H_b protons – H_c and H_d are too far away.

Working out structures from NMR spectra

Worked examples

11.6 The NMR spectrum for a compound with molecular formula C_4H_8O is shown below. Deduce the structure of the compound.

First, we must measure the vertical heights of the steps in the integration trace – these are 1 cm, 1.5 cm and 1.5 cm. Multiplying by 2 to get whole numbers we get 2, 3, 3 – this gives us the ratio of the number of protons (hydrogen atoms) in the different environments. Because there is a total of eight hydrogen atoms in the molecule, we also know the actual number of hydrogen atoms in each environment.

Chemical shift / ppm	2.4	2.1	1.1
No. of protons in environment	2	3	3

The signal at δ 2.4 ppm is split into a quartet (multiplicity 4). Now $4 - 1 = 3$, so we know that there must be three hydrogen atoms on the adjacent C atom. Analysing all the peaks in the spectrum gives the following data:
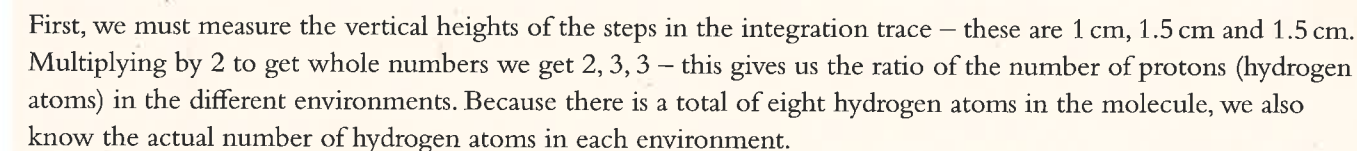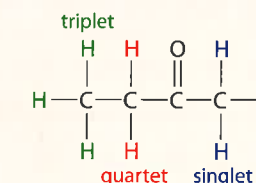
Chemical shift / ppm	2.4	2.1	1.1
No. of protons in environment	2	3	3
Splitting	quartet	singlet	triplet
Multiplicity	4	1	3
No. of protons on adjacent C atom	3	0	2

Remember: multiplicity $- 1 =$ number of hydrogen atoms on adjacent carbon atom.

The peaks at δ 2.4 ppm and δ 1.1 ppm are caused by an ethyl group – the signal due to 2Hs is split by 3Hs on the adjacent C and the signal due to 3Hs is split by 2Hs on the adjacent C.

We know that there are four C atoms in the molecule but only three sets of peaks. There are also three Hs that have no Hs on the adjacent C. These two pieces of information together suggest that there is a carbon atom with no hydrogen atoms attached.

Also the molecular formula C_4H_8O has two fewer hydrogen atoms than the alkane with four carbon atoms, so there must be a double bond (or a ring) in the molecule (IHD $= 1$).

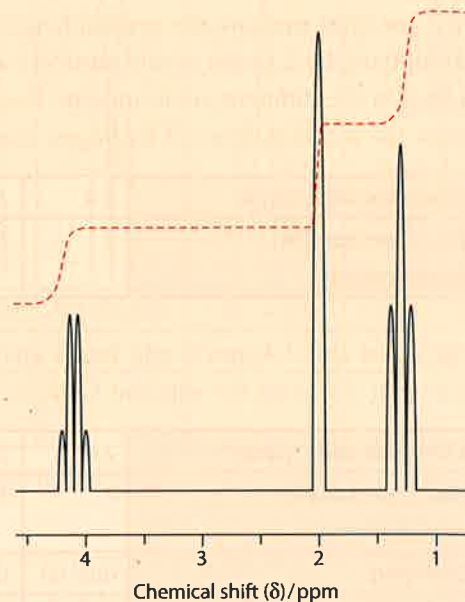The only structure that fits with all this information is:

As a final check, we should try to match up the chemical shifts of the protons with the values given in Table **11.14**.
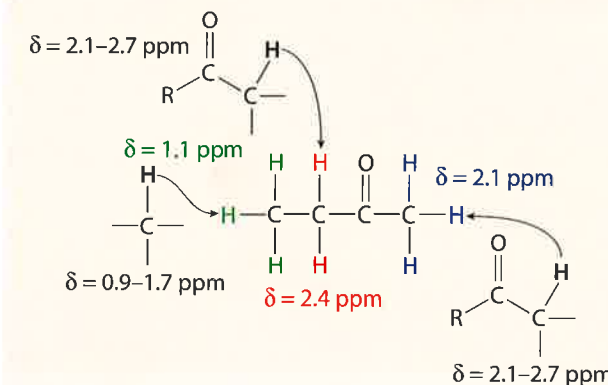

All protons have chemical shifts in the expected ranges.

**11.7** The NMR spectrum for an ester with molecular formula $C_4H_8O_2$ is shown. Deduce the structure of the compound.

Chemical shift (δ)/ppm

Following the procedure from the previous example we get:

| Chemical shift / ppm	4.1	2.0	1.3
No. of protons in environment	2	3	3
Splitting	quartet	singlet	triplet
Multiplicity	4	1	3
No. of protons on adjacent C atom	3	0	2

As in the previous example, there is an ethyl group present and a group of three hydrogen atoms with no hydrogens on the adjacent carbon. The only two possible esters that would have this splitting pattern are:
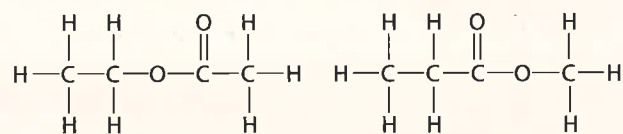
We can distinguish between these two possibilities using the chemical shift values. If we consider the singlets, we can use the values in Table **11.14** to predict the chemical shifts for these protons:

$\delta = 2.0–2.5$ ppm

$\delta = 3.7–4.8$ ppm
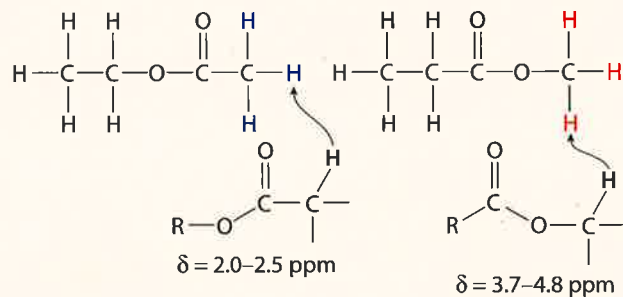
The singlet in the spectrum occurs at δ 2.0 ppm, so this molecule is the one on the left in the diagram above – ethyl ethanoate:
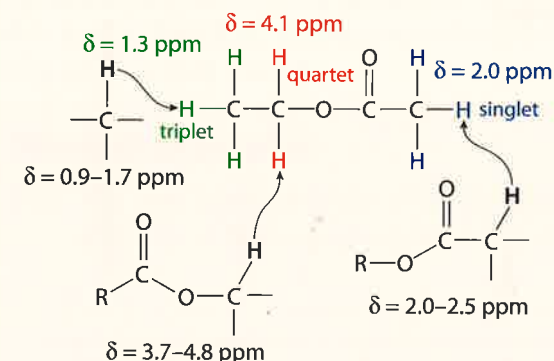
Notes on NMR spectra

When a molecule is non-symmetrical and there are non-equivalent protons on both sides of a particular group, the spectrum becomes complex. Figure **11.32** shows the structural formula of propan-1-ol. In the NMR spectrum of this compound the H_b signal is split by H_a and H_c. Depending on the strength of the coupling to each set of protons, the signal for H_b could either be described as a quartet of triplets or a triplet of quartets. This signal is very complicated, and it is difficult to see the exact nature of the splitting. One way of describing this peak is as a **complex multiplet**.

For a molecule such as methylbenzene (Figure **11.33**), the protons on the ring are not all equivalent, but because they are in very similar environments they could show up as just one peak in the NMR spectrum – unless a very high-resolution spectrum is generated.

The presence of highly electronegative atoms in a molecule (Figure **11.34**) can cause chemical shifts to move to higher values. The closer the protons are to the very electronegative atom, the greater the effect.
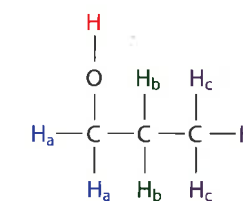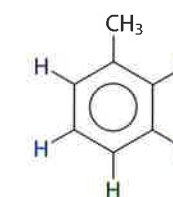

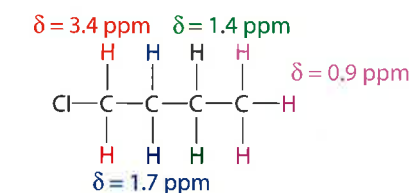**Figure 11.32** Propan-1-ol.

Figure 11.33 Methylbenzene.

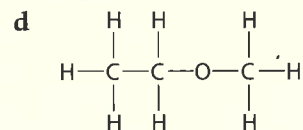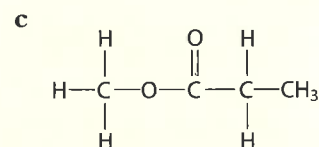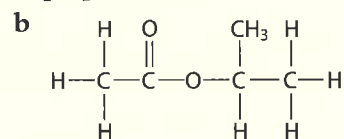**Figure 11.34** Chlorine is more electronegative than hydrogen and carbon.

18 Suggest the splitting pattern for each of the following:
  a 1,1-dibromo-2,2-dichloroethane
  b 1,1,3,3-tetrachloropropane
  c propanoic acid
  d
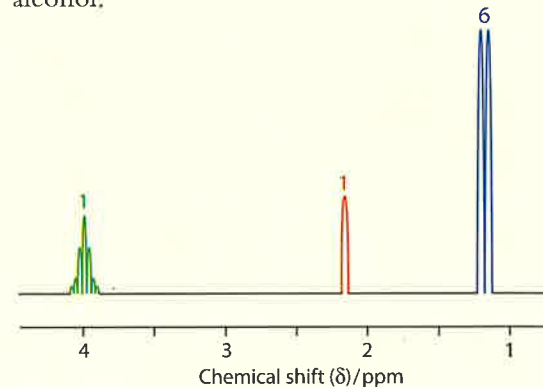
  H   H   H
  | | |
H—C—C—O—C—H
  | | |
  H   H   H

19 The NMR spectrum of each of the following contains a singlet. Suggest the chemical shift range for the singlet.
  a propan-2-ol
  b

      H   O   CH₃ H
      | ‖ | |
  H—C—C—O—C—C—H
      | | |
      H   H   H

  c

      H   O   H
      | ‖ |
  H—C—O—C—C—CH₃
      | |
      H   H

20 The NMR spectrum shown below is of an alcohol.

Work out the structure of the alcohol and state the multiplicity of the peak at $\delta = 4.0\,ppm$

Single crystal X-ray crystallography

Further evidence for the structures of molecules can be obtained from **single crystal X-ray crystallography**. This involves irradiating a crystal with X-rays and looking at the positions and intensities of the diffracted beams. This is an extremely powerful technique and gives a three-dimensional picture of the molecule with bond lengths and bond angles (Figure 11.35). If a single crystal can be grown, X-ray crystallography usually provides the final word on the structure.
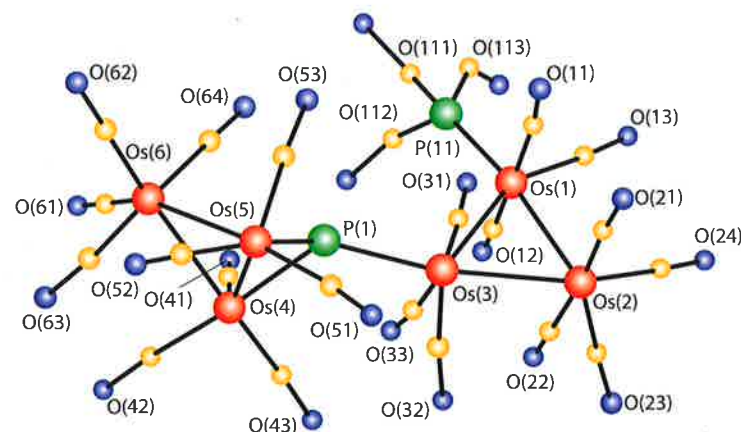

Figure 11.35 The structure of a molecule obtained by X-ray crystallography.

Using combined spectroscopic techniques to determine the structure of a molecule

In practice, information from more than one spectroscopic technique is often used to determine the structure of a molecule. This is best illustrated using some worked examples.

Worked examples

11.8 The mass spectrum below is for a compound, **X**, that contains carbon, hydrogen and oxygen. The infrared spectrum of **X** has an absorption band at $1725\,cm^{-1}$.
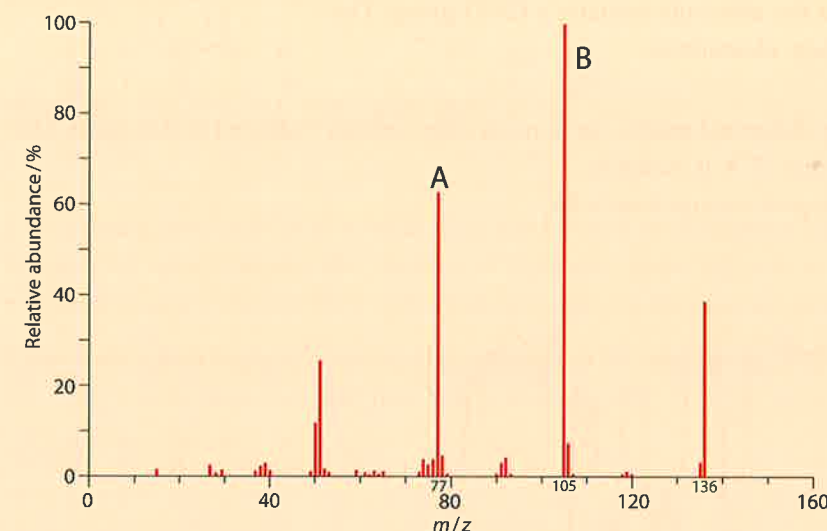

  a What is the relative molecular mass of **X**?
  b Given that **X** contains two oxygen atoms, suggest the molecular formula for **X**.
  c Identify which group is lost to form the peak marked **B**.
  d Suggest the identity of the species responsible for the peak marked **A**.
  e Calculate the IHD for **X**.
  f Deduce the structural formula of **X**.

a Using the mass spectrum, the peak at highest m/z value represents the molecular ion – so the relative molecular mass is 136.
b The only possible molecular formula containing two oxygen atoms that adds up to 136 is $C_8H_8O_2$.
  Two oxygen atoms have a combined mass of 32 and if we subtract this from 136 we get 104. The only other elements in the molecule are carbon and hydrogen, so we must make 104 from a combination of the masses of these. Seven carbon atoms gives a combined mass of $7 \times 12 = 84$, which would require there to be $104 - 84 = 20$ hydrogen atoms in the molecule. However, the alkane with seven carbon atoms has only 16 hydrogen atoms, therefore $C_7H_{20}O_2$ is not possible
c Peak **B** occurs at m/z 105. Now, $136 - 105 = 31$. So we must think of combinations of C, H and O that add up to 31. The only possible combination is CH_3O, so this group is lost from the molecular ion to produce peak **B**. (Note that C_2H_7 also adds up to 31, but the maximum number of hydrogen atoms for two carbon atoms is six.)
d Peak **A** occurs at m/z 77. The fragment responsible for this is $C_6H_5^+$.

e IHD $= \frac{1}{2} \times [2c + 2 - h - x + n]$ for a molecule with formula $C_cH_hN_nO_oX_x$, where X is a halogen atom. The molecular formula is $C_8H_8O_2$, so $c = 8$ and $h = 8$.

$$\text{IHD} = \tfrac{1}{2} \times [(2 \times 8) + 2 - 8] = 5$$

f A benzene ring has an IHD of 4 because it has a ring and three double bonds – so we can conclude that, apart from the benzene ring, there is one other double bond or ring present.

The peak at m/z 77 indicates that the compound contains a benzene ring substituted in one position. The loss of 31 mass units from the group suggests that it contains the $-O-CH_3$ group. The presence of an absorption band at $1725\,cm^{-1}$ in the infrared spectrum suggests (using Table **11.11**) that the molecule contains a C=O group. The only possible molecule that contains all these elements is:
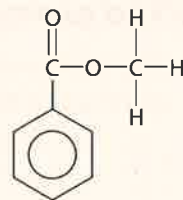
11.9 An organic compound, **Y**, is shown by elemental analysis to contain only carbon, hydrogen and oxygen. The following information about the structure of **Y** is available:

- **mass spectrum:** the molecular ion peak occurs at m/z 86
- **IHD** = 1
- **infrared spectrum:**
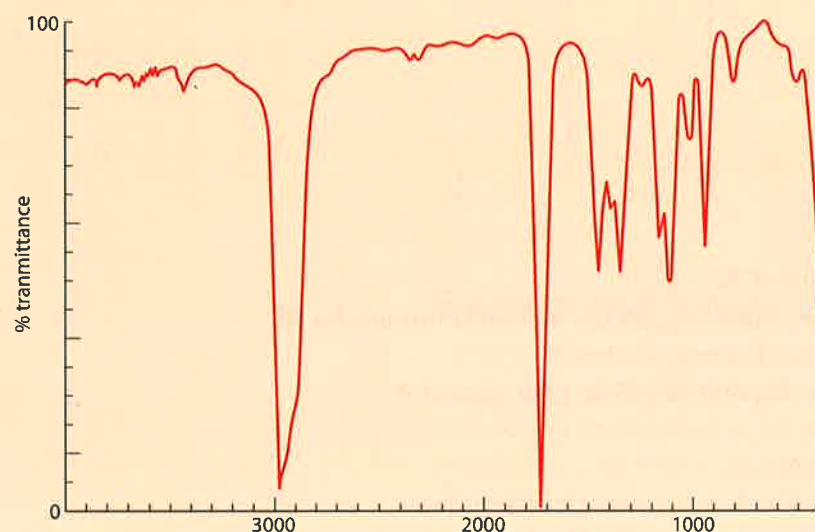
- **nuclear magnetic resonance spectrum:** shows two peaks – one quartet (δ 2.4 ppm) and one triplet (δ 1.1 ppm)

Determine the structure of the molecule from these data.

Adding up possible combinations of C(12), H(1) and O(16) to make the molecular ion peak at m/z 86 produces $C_5H_{10}O$, $C_4H_6O_2$, $C_3H_2O_3$ as possible formulas.

The IHD can be worked out for each of these molecular formulas using IHD $= \frac{1}{2} \times [2c + 2 - h - x + n]$ for a molecule with formula $C_cH_hN_nO_oX_x$, where X is a halogen atom. The IHD corresponding to the possible formulas are:

$C_5H_{10}O$: $\frac{1}{2} \times [(2 \times 5) + 2 - 10] = 1$
$C_4H_6O_2$: $\frac{1}{2} \times [(2 \times 4) + 2 - 6] = 2$
$C_3H_2O_3$: $\frac{1}{2} \times [(2 \times 3) + 2 - 2] = 3$

Because the IHD is given as 1, the molecular formula must be $C_5H_{10}O$.

The infrared spectrum has an absorption band in the range 1700–$1750\,cm^{-1}$ indicating a C=O group in an aldehyde, ketone, carboxylic acid or ester. Because there is only one oxygen atom in the molecule, we can rule out esters and carboxylic acids because they both have two oxygen atoms in the functional group. Therefore the compound must be an aldehyde or a ketone.

The NMR spectrum indicates that there are only two different chemical environments for the hydrogen atoms in the molecule. There are several different isomers that can be drawn for a compound with molecular formula $C_5H_{10}O$ containing a C=O group – but only the two below have just two different chemical environments for protons:
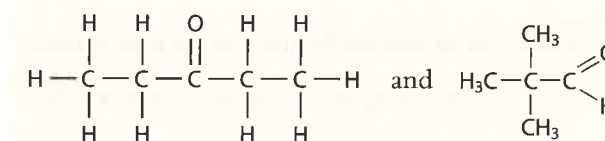
The splitting pattern from the NMR data can be used to distinguish between these two structures:
- a quartet signal indicates the presence of hydrogen atoms adjacent to a C atom with three H atoms attached
- a triplet signal indicates the presence of hydrogen atoms adjacent to a C atom with two H atoms attached.

These two signals together indicate the presence of an ethyl group. This group is present in only the left-hand structure – so we can conclude that **Y** is pentan-3-one:
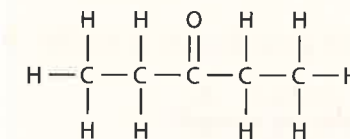
The NMR spectrum of the right-hand molecule would consist of two singlets because all the hydrogen atoms have no hydrogen atoms on the adjacent carbon.

As a final check you should use Table **11.14** to compare the chemical shift values given with what you would expect for pentan-3-one.

Nature of science

Advances in technology have allowed scientists to derive ever more detailed information about the structure of compounds. Theories of structure and bonding have developed further as more information has become available.

Exam-style questions

1 Rosie carried out an experiment in which she measured a temperature change. Her data are shown in the table.

Initial temperature/°C	18.7	±0.5
Maximum temperature/°C	37.6	±0.5

The temperature change should be quoted as:

A 18.9 ± 0.5 **C** $18.9 \pm 1.0\,°C$

B $19 \pm 1\,°C$ **D** $19.0 \pm 1.0\,°C$

2 Aazaish obtained the value $0.002560\,m^3$ from an experiment. The number of significant figures and decimal places is:

	Significant figures	Decimal places
A	4	6
B	6	4
C	6	6
D	3	6

3 Molly carried out an experiment to measure the enthalpy change of solution of a salt. In order to calculate a final value, the following calculation was carried out:

$$\frac{[(50 \pm 1) \times 4.2 \times (20 \pm 1)]}{1000 \times (0.10 \pm 0.01)}$$

Quantities without uncertainties can be assumed to be exact. How should the final value be quoted?

A $-42 \pm 7\,kJ\,mol^{-1}$ **C** $-42.00 \pm 2.01\,kJ\,mol^{-1}$

B $-42 \pm 2\,kJ\,mol^{-1}$ **D** $-42.1 \pm 7.1\,kJ\,mol^{-1}$

4 Which of the following would be a good method for reducing the random uncertainty in an experiment to measure the enthalpy change of neutralisation when $50\,cm^3$ of $0.50\,mol\,dm^{-3}$ sodium hydroxide reacts with $50\,cm^3$ of $0.50\,mol\,dm^{-3}$ hydrochloric acid?

A Insulate the reaction vessel with cotton wool.

B Stir the mixture more rapidly.

C Repeat the experiment.

D Measure out the liquids using a $50\,cm^3$ measuring cylinder instead of a burette.

5 The graph shows the results of a series of experiments to investigate how the rate of the reaction $X \rightarrow Y$ varies with the concentration of X.
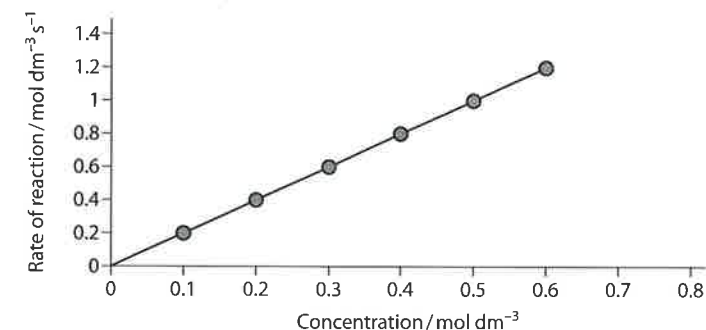
The gradient (slope) of this graph is:

A $2.0\,mol\,dm^{-3}\,s^{-1}$ **C** $2.0\,s^{-1}$

B $0.5\,s$ **D** $0.5\,mol^{-1}\,dm^3$

6 Which of the following would produce only a single peak in the low-resolution ^1H NMR spectrum?

A CH_3CH_2OH **C** CH_3CHO

B $(CH_3)_3CCl$ **D** $CH_2ClCHClCH_2Cl$

7 Which of the following has an index of hydrogen deficiency of 2?

A $C_3H_6O_2$ **C** C_4H_7N

B C_6H_6 **D** $C_5H_8Cl_2$

8 Which of the following is unlikely be a peak in the mass spectrum of propanoic acid?

A m/z 45   **C** m/z 74

B m/z 15   **D** m/z 50

HL 9 The following information is provided about a compound **M**:

- There is only one peak in the NMR spectrum.
- IHD = 1.
- The molecular ion peak occurs at m/z 56.
- There is only one major band above $1500\,cm^{-1}$ in the IR spectrum.

Which of the following could be the structure of compound M?
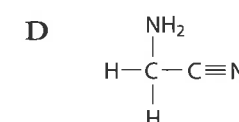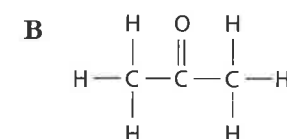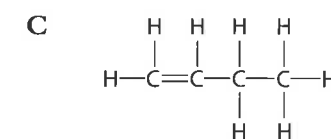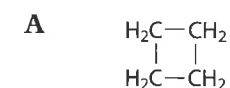
HL **10** Which of the molecules below will **not** have a triplet in its NMR spectrum?

A

$$H-C-C-H$$

(molecule A: CH$_3$CH$_2$Br with H, H on top; H, Br on bottom)

C

(molecule C: H$_3$C-CH$_2$-COOH)

B

$$H-C-C-C-C-H$$

(molecule B with H, Br, Br, H on top; H, H, H, H on bottom)

D

(molecule D: ester structure)

11 Two separate experimental methods were used to determine the value of a particular experimental quantity. Each experiment was repeated five times. The values obtained from these experiments are shown in the table.

Experiment	A	B
Trial	Value	Value
1	49.7	50.6
2	53.2	51.2
3	51.5	51.1
4	52.3	50.8
5	49.2	51.0

The literature value for this quantity is 50.9.

a Explain which set of experimental values is more precise. **[2]**

b Work out a mean value for each experiment and use this to explain which set of data is more accurate. **[3]**

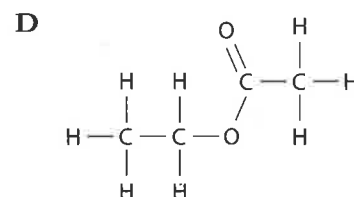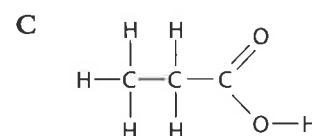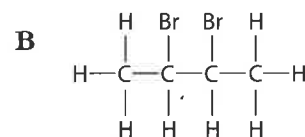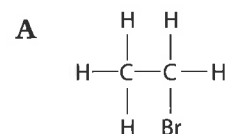**12** Yi Jia carried out an experiment to measure a certain quantity. The value she obtained was 56.1 ± 0.5 kJ. The literature value for this quantity is 55.2 kJ.

a Calculate the percentage error for this experiment. **[1]**

b The student maintained that any errors could be explained solely by random uncertainties.
Is she correct? Explain your answer. **[2]**

13 Jerry carried out an experiment to measure the rate of the reaction between magnesium and hydrochloric acid. He did this by recording the volume of hydrogen gas collected every 15 s. His data are shown in the table.

a Plot a graph of these data. **[3]**

b Use your graph to determine the initial rate of reaction – include units. **[3]**

Time / s	Volume / cm³
0	0
15	19
30	33
45	44
60	50
75	54
90	56
105	57
120	57

14 Certain molecules absorb infrared (IR) radiation.

a IR spectroscopy is one of the techniques that is used to determine the structure of organic molecules. A student recorded the IR spectrum of a compound, **X**:
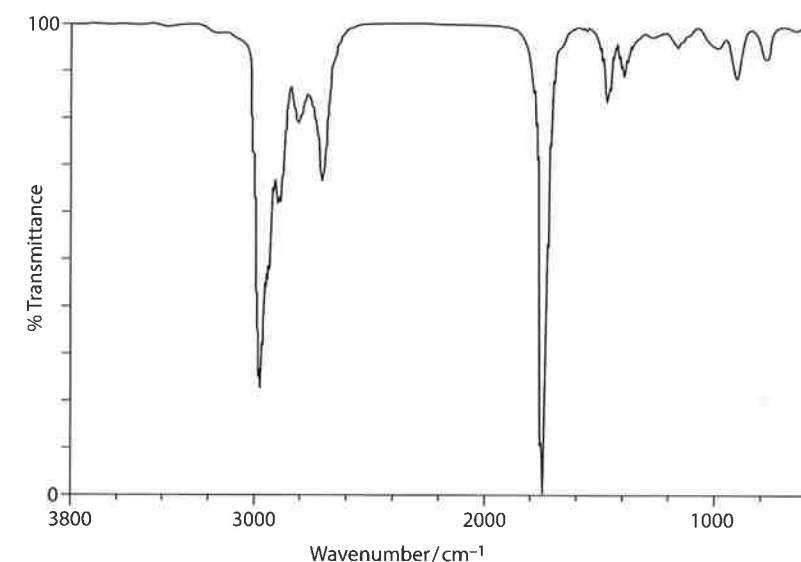
The student knew that **X** was one of the following compounds:

HO—C—C—C—C—H (with H, CH$_3$, H, H)	I
H—C—C—C—C=O (aldehyde, with H, H, CH$_3$, H)	II
H—C—C—C—C=O with O—H (carboxylic acid, with H, H, CH$_3$)	III
H—C—C—C—C—O—C—C—C—C—H (ester, with H, H, CH$_3$, H, O, CH$_3$, H, H)	IV

Deduce which of the molecules is **X** and explain your choice by reference to the spectrum. **[4]**

b Explain why NMR is more useful than IR spectroscopy in distinguishing between propanal and propanone. **[4]**

15 The NMR spectrum of propan-2-ol is shown below.

Chemical shift (δ)/ppm
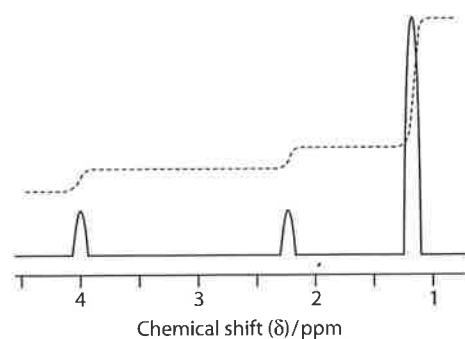
a Draw the full structural formula of propan-2-ol. [1]

b Explain why there are three peaks in the NMR spectrum of propan-2-ol. [2]

c The integration trace is shown on the spectrum. Explain what information can be obtained from the integration trace. [2]

d **i** Draw the full structural formula of butan-2-ol. [1]

   ii State the number of peaks and the relative areas under the peaks in the NMR spectrum of butan-2-ol. [2]

(HL) **16** Compounds may be identified using a combination of spectroscopic techniques. The mass spectrum for a compound, **Z**, is shown below. Elemental analysis showed that **Z** contains C, H and O.
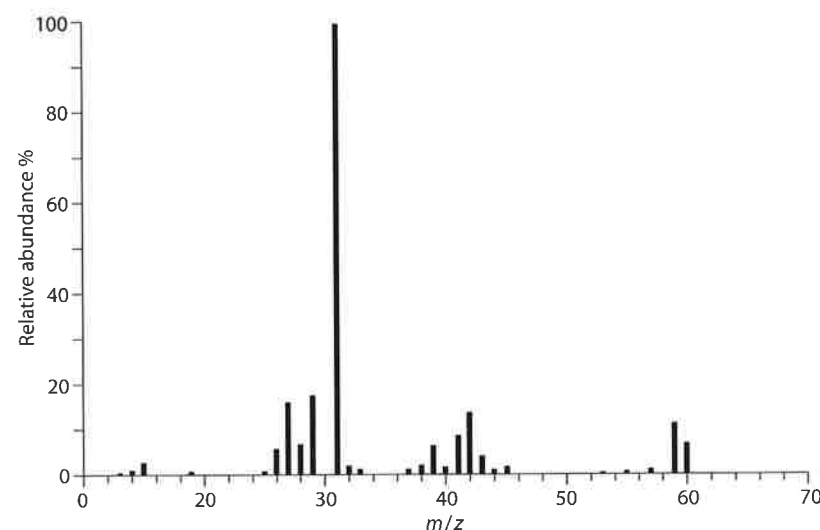
a Determine the relative molecular mass of **Z**. [1]

b Work out two possible molecular formulas for **Z**. [2]

c Deduce the formula of the fragments responsible for the peaks at m/z 31 and m/z 29. [2]

d The IR spectrum of Z shows a strong absorption band at about $3350\,\text{cm}^{-1}$ but no absorptions in the range $1600–1800\,\text{cm}^{-1}$. Explain what conclusions about the structure of **Z** can be drawn from these data. [2]

e On the basis of the information above, suggest two possible structural formulas for **Z**. [2]

f The low-resolution NMR spectrum of **Z** is shown below.

Chemical shift (δ)/ppm
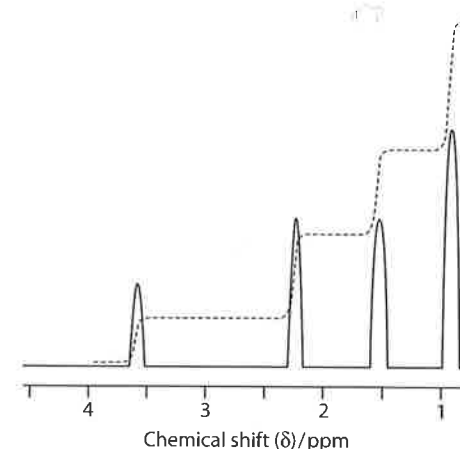
Explain how information from this spectrum can be used to deduce the structural formula of **Z** and draw the structural formula of **Z**. [4]

(HL) **17** NMR spectroscopy is a very powerful tool in the identification of organic compounds.

a Predict and explain the splitting pattern of the hydrogen atom marked **bold** in the molecule below. [2]
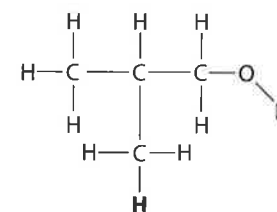
b A compound with the formula $C_4H_{10}O$ has the NMR spectrum shown below. Draw the structural formula of the compound and explain your reasoning. [4]

Chemical shift (δ)/ppm
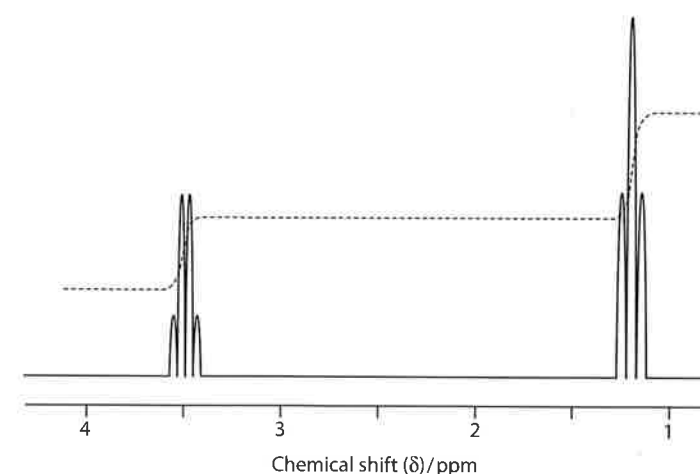
c There are two esters that have the molecular formula $C_3H_6O_2$. Draw the structural formulas of these esters and explain the differences between their NMR spectra. [5]

d There are four esters with the molecular formula $C_4H_8O_2$. Draw the structural formulas of these esters and explain which will give rise to the NMR spectrum shown below. [6]

Chemical shift (δ)/ppm
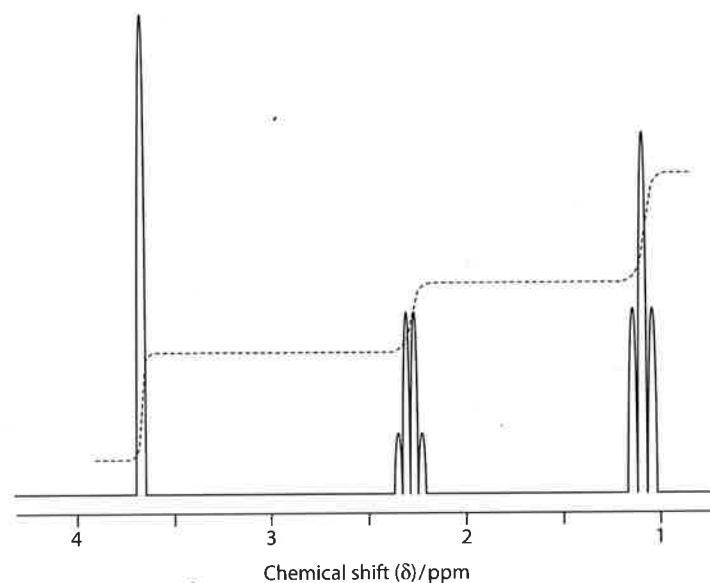
Summary

Measurements are distributed either side of the mean.

Random uncertainties in experimental values are caused by limitations of the measuring apparatus and other uncontrollable factors.

analogue instruments – uncertainty is half the smallest division

can never be completely eliminated but their effect can be reduced by repeating the experiment.

digital instruments – uncertainty is equal to the smallest division

No figures should be quoted after the uncertainty.

add **absolute** uncertainties together

add **percentage** uncertainties together

The uncertainty is in the last significant figure of the measured value.

adding and subtracting

multiplying and dividing

give answer to fewest number of decimal places

give answers to fewest number of significant figures

given to one significant figure

UNCERTAINTIES

calculations

precision – how close repeat readings are to each other

accuracy – how close measured value is to actual value

cannot be reduced by repeat readings

possible to have great precision but low accuracy

systematic error – introduced due to apparatus or procedure

shifts measured value in one direction away from the actual value

existence indicated by percentage error > total random uncertainty

percentage error $= \dfrac{|\text{experimental value} - \text{accepted value}|}{|\text{accepted value}|} \times 100\%$

Summary – continued

IHD gives the number of double bond equivalents in a molecule. For $C_cH_hN_nO_oX_x$

$IHD = \frac{1}{2} \times [2c + 2 - h - x + n]$

HL Single crystal X-ray crystallography provides a 3-D picture of a molecule with bond lengths and bond angles.

IR spectroscopy —— Infrared radiation

allows identification of bonds/functional groups present in a molecule

SPECTROSCOPIC TECHNIQUES

mass spectrometry

radio frequencies used

HL chemical shift gives information about the environment that protons are in

fragmentation pattern provides information about the structure of a molecule

molecular ion peak gives the relative molecular mass

proton NMR

TMS used as a reference standard to set the zero on the chemical shift scale

only positive ions produce a peak in the mass spectrum

only H nuclei produce signals

integration trace gives information about the ratio of the numbers of H in each environment

number of peaks gives the number of different chemical environments for H atoms/protons

HL splitting pattern gives information about the number of H atoms on adjacent atom —— multiplicity – 1 = number of H atoms on adjacent C
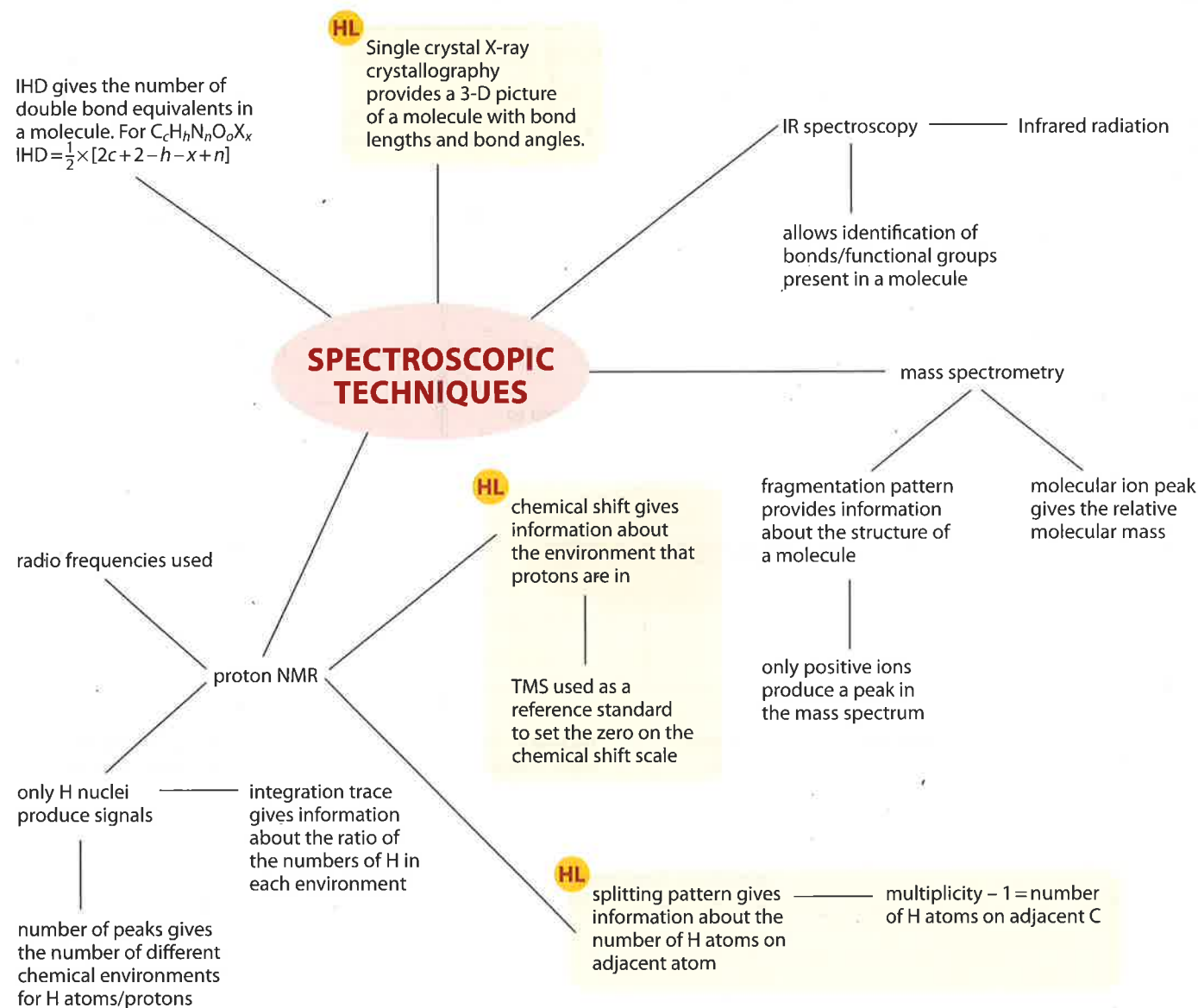

Appendix: the periodic table

Group

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1.01 H hydrogen 1																		4.00 He helium 2
6.94 Li lithium 3	9.01 Be beryllium 4												10.81 B boron 5	12.01 C carbon 6	14.01 N nitrogen 7	16.00 O oxygen 8	19.00 F fluorine 9	20.18 Ne neon 10
22.99 Na sodium 11	24.31 Mg magnesium 12												26.98 Al aluminium 13	28.09 Si silicon 14	30.97 P phosphorus 15	32.07 S sulfur 16	35.45 Cl chlorine 17	39.95 Ar argon 18
39.10 K potassium 19	40.08 Ca calcium 20		44.96 Sc scandium 21	47.87 Ti titanium 22	50.94 V vanadium 23	52.00 Cr chromium 24	54.94 Mn manganese 25	55.85 Fe iron 26	58.93 Co cobalt 27	58.69 Ni nickel 28	63.55 Cu copper 29	65.38 Zn zinc 30	69.72 Ga gallium 31	72.63 Ge germanium 32	74.92 As arsenic 33	78.96 Se selenium 34	79.90 Br bromine 35	83.80 Kr krypton 36
85.47 Rb rubidium 37	87.62 Sr strontium 38		88.91 Y yttrium 39	91.22 Zr zirconium 40	92.91 Nb niobium 41	95.96 Mo molybdenum 42	(98) Tc technetium 43	101.07 Ru ruthenium 44	102.91 Rh rhodium 45	106.42 Pd palladium 46	107.87 Ag silver 47	112.41 Cd cadmium 48	114.82 In indium 49	118.71 Sn tin 50	121.76 Sb antimony 51	127.60 Te tellurium 52	126.90 I iodine 53	131.29 Xe xenon 54
132.91 Cs caesium 55	137.33 Ba barium 56		138.91 La * lanthanum 57	178.49 Hf hafnium 72	180.95 Ta tantalum 73	183.84 W tungsten 74	186.21 Re rhenium 75	190.23 Os osmium 76	192.22 Ir iridium 77	195.08 Pt platinum 78	196.97 Au gold 79	200.59 Hg mercury 80	204.38 Tl thallium 81	207.2 Pb lead 82	208.98 Bi bismuth 83	(209) Po polonium 84	(210) At astatine 85	(222) Rn radon 86
(223) Fr francium 87	(226) Ra radium 88		(227) Ac * actinium 89	(267) Rf rutherfordium 104	(268) Db dubnium 105	(269) Sg seaborgium 106	(270) Bh bohrium 107	(269) Hs hassium 108	(278) Mt meitnerium 109	(281) Ds darmstadtium 110	(281) Rg roentgenium 111	(285) Cn copernicium 112	(286) Uut ununtrium 113	(289) Fl flerovium 114	(288) Uup ununpentium 115	(293) Lv livermorium 116	(294) Uus ununseptium 117	(294) Uuo ununoctium 118

Key

relative atomic mass
atomic symbol
name
atomic number

lanthanoids *

140.12 Ce cerium 58	140.91 Pr praseodymium 59	144.24 Nd neodymium 60	145 Pm promethium 61	150.36 Sm samarium 62	151.96 Eu europium 63	157.25 Gd gadolinium 64	158.93 Tb terbium 65	162.50 Dy dysprosium 66	164.93 Ho holmium 67	167.26 Er erbium 68	168.93 Tm thulium 69	173.05 Yb ytterbium 70	174.97 Lu lutetium 71

actinoids **

232.04 Th thorium 90	231.04 Pa protactinium 91	238.03 U uranium 92	(237) Np neptunium 93	(244) Pu plutonium 94	(243) Am americium 95	(247) Cm curium 96	(247) Bk berkelium 97	(251) Cf californium 98	(252) Es einsteinium 99	(257) Fm fermium 100	(258) Md mendelevium 101	(259) No nobelium 102	(262) Lr lawrencium 103