Topic 11: Measurement and data processing SL

|  |  |
| --- | --- |
| **11.1** | **Uncertainties and errors in measurements and results** |
| 10.1.1 | Qualitative data includes all non-numerical information obtained from observations not from measurements |
| 10.1.2 | Qualitative data are obtained from measurements, and are always associated with random errors/uncertainties, determined by the apparatus, and by human limitations such as reaction times |
| 10.1.3 | Propagation of random errors in data processing shows the impact of the uncertainties on the final result |
| 10.1.4 | Experimental design and procedure usually lead to systematic errors in measurement, which cause a deviation in a particular direction |
| 10.1.5 | Repeat trials and measurements will reduce random errors but not systematic errors |
| 10.1.6 | Distinction between random errors and systematic errors |
| 10.1.7 | Record uncertainties in all measurements as a range (±) to an appropriate precision |
| 10.1.8 | Discussion of ways to reduce uncertainties in an experiment |
| 10.1.9 | Propagation of uncertainties in processed data, including the use of percentage uncertainties |
| 10.1.10 | Discussion of systematic errors in all experimental work, their impact on the results and how they can be reduced |
| 10.1.11 | Estimation of whether a particular source of error is likely to have a major or minor effect on the final result |
| 10.1.12 | Calculations of percentage error when the experimental result can be compared with a theoretical or accepted results |
| 10.1.13 | Distinction between accuracy and precision in evaluating results |

# Quantitative and Qualitative Data

* Quantitative data is data **taken from measurements** made in the laboratory and is associated with random errors
* Qualitative data includes non-numerical data **obtained from observations**, not from measurements
* A results table should include quantitative data with units and uncertainties
* Quantitative data should be recorded to the appropriate precision
* Qualitative data should also be recorded

# Absolute and Percentage uncertainties

* The absolute uncertainty of digital apparatus is ± the smallest scale division
* Absolute uncertainty of mass balance is ±0.01g
* Absolute uncertainty of analog apparatus is ± half the smallest scale division

Absolute uncertainty of measuring cylinder is ±0.5cm3

* Absolute uncertainty of burette is ±0.05cm3

# Random Errors

* **Random errors are caused by unpredictable changes in the experiment (in the conditions or apparatus)**
* With random errors, there is an equal probability of the measured value being too high or too low
* Examples of random error:
  + Changes in the environment during the experiment (such as a change in the room temperature)
  + Observer misinterpreting the reading
  + Insufficient data (not conducting repeat trials)
* **Random errors cannot be eliminated but can be reduced by conducting repeat trials**
* They can also be reduced by using precise apparatus (such as a volumetric pipette rather than a beaker to measure volume)

# Systematic Errors

* Systematic errors occur as a result of a flaw in the experimental design of apparatus
* Systematic errors cause the measured value to be consistently higher or lower than the actual value
* They cannot be reduced by conducting repeat trials
* Examples of systematic error:
  + Heat loss in an experiment to measure enthalpy change
  + Losing a product (such as a gas) in a reaction
  + Overshooting the endpoint in a titration
  + Reading from the top of the meniscus when measuring volume
  + Forgetting to zero a mass balance

# Percentage error

* Percentage error is a measure of how close the experimental value is to the theoretical or accepted value
* If the experimental value is less than the theoretical value, the percentage error will be negative

|  |  |
| --- | --- |
| **11.3** | **Spectroscopic identification of organic compounds** |
| 10.1.1 | The degree of unsaturation or index hydrogen deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule |
| 10.1.2 | Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy (1H NMR) and infrared spectroscopy (IR) are techniques that can be used to help identify compounds and to determine their structure |
| 10.1.3 | Determination of the IHD from a molecular formula |
| 10.1.4 | Deduction of information about the structural features of a compound from percentage composition data, MS, 1H NMR or IR |

# Index of Hydrogen Deficiency (IHD)

**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***)**

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

* The index of hydrogen deficiency (IHD) is a count of how many molecules of H2 need to be added to convert the molecule to the corresponding, saturated, non-cyclic molecule. In other words a degree of unsaturation
* The IHD for a hydrocarbon with carbon atoms and hydrogen atoms:
* Note:
  + Sulfur and oxygen do not affect IHD
  + Halogens (F, Cl, Br and I) are treated like H atoms
  + For each nitrogen atom, subtract one from the number of hydrogen atoms.

By calculating the IHD, we can tell from the molecular formula how many multiple bonds and rings are present in the molecule. For compounds that contain other atoms other than hydrogen:

**To work out the number of double bond equivalents in molecule containing nitrogen, we must subtract one hydrogen for every nitrogen atom and then calculate as above. Why?**

1. Work out the index of hydrogen deficiency for C3H5N and suggest a possible structure for the molecule.
2. What is the IHD for benzene (C6H6)?

|  |  |
| --- | --- |
| IHD | Multiple bonds/rings present in molecule |
| 0 | Single bonds |
| 1 | Double bond/Ring structure |
| 2 | Triple bond |

# Infrared Spectroscopy

* When molecules absorb energy in the IR region of the electromagnetic spectrum, it causes the bonds between the atoms to vibrate (the bonds stretch and bend)
* The frequency of IR radiation that is absorbed is measured as the number of waves per centimeter
* 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.
* The fingerprint region can be used to identity an unknown compound by comparing with the IR spectra of known compounds
* For example, butanone and propanone both show very similar bands in the region above 1500 cm–1, because they have the same functional group (C=O), but can be distinguished using their fingerprint regions, which are very different



* However a bond will **only interact with IR radiation if it is a polar covalent bond** (non-polar bonds do not absorb IR radiation)
* The intensity depends on the dipole moment of the bond:
  + Strongly polar bonds produce strong bands
  + Bonds with medium polarity produce medium bands
* Note IR is not generally used to determine the whole structure of an unknown molecule

**Exam tip**

A table of infrared absorption frequencies is given in the IB Chemistry data booklet. You will use the values in the data booklet for the examination.

**We can use infrared spectra to identify the bonds present in molecules but we cannot always distinguish between functional groups.**

To identify the bonds present in the molecule, we first of all look at the region above 1500 cm−1.

* In order to analyze IR graph we need to look for:
  + Tongue: A broad, rounded peak in the region
  + Swords: These peaks are almost always the strongest peaks in the entire spectrum and are relatively narrow, giving them a somewhat “sword-like” appearance
* Once we have identified our “tongue” and our “swords” compare the wavelength value to the value in Table 26
* Note that the graph can be divided up into a functional group region, and the fingerprint region. The fingerprint region is located on the right while the functional group region is located on the left and involves the tongue





butanoic acid – CH3CH2CH2COOH. propan-1-ol, CH3CH2CH2OH.

T**he** broadness of the O–H band is due to hydro**gen bonding between molecules.** A very broad band in this region is characteristic of carboxylic acids.

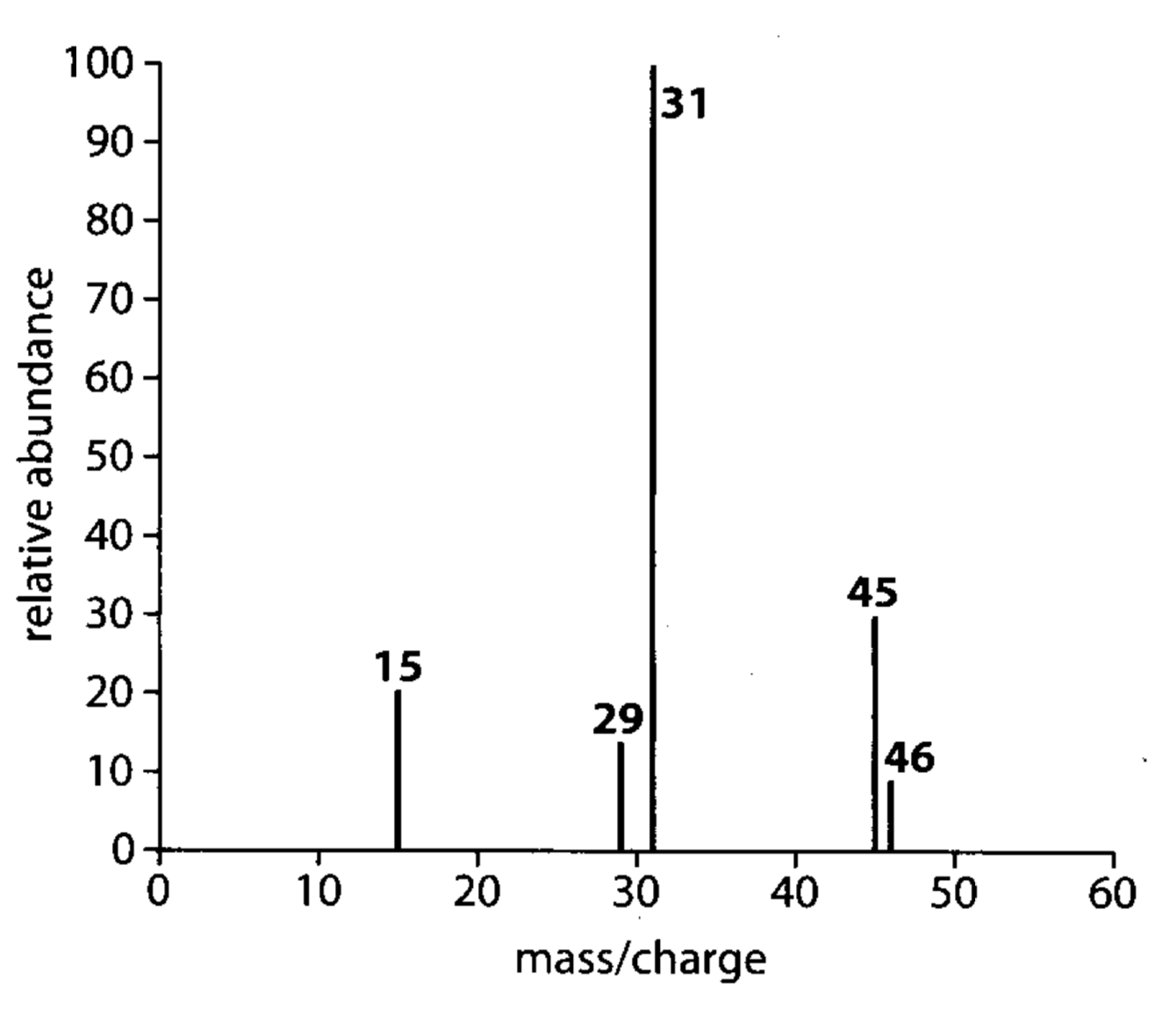
The region below 1500 cm−1 contains many absorptions due to C–C bonds and C–H bonds and is difficult to interpret. We usually look only at the fingerprint region to confirm the presence of a particular vibration once we have a good idea of the structure of the molecule.





# 

# Mass Spectrometry

* While mass spectrometry is used to determine the relative atomic mass (Ar) of an element **it can also be used to determine the structure of a compound**
* Inside the mass spectrometer, some of the molecular ions break down to produce fragments
* A fragmentation pattern is produced which gives useful information about the structure of the compound
* When determining the structure of a compound don’t use the mass/charge (m/z) value
* Instead take the largest value and subtract every other value from it

**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**

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

When a sample of propane (C3H8) is introduced into a mass spectrometer, C3H8+ positive ions are produced:



# 

**The** molecular ion peak is not necessarily the biggest peak in terms of abundance, but it has the highest *m/z* value. A molecule can break apart into smaller fragments when high-energy electrons bombard it to give **fragmentation pattern.**

All the positive ions resulting from fragmentation will produce a peak in the mass spectrum.

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 13C in some molecules. 13C is an isotope of carbon – its natural abundance is low at 1.1%.



*Mass spectrum for propanoic acid*

Exam tip

Groups lost from a molecular ion do not need a positive charge, but any species that forms a peak in the mass spectrum *must* have a positive charge.

**

*The mass spectrum of chloroethane – CH3CH2Cl.*

Structure determination using nuclear magnetic resonance spectroscopy 1H NMR:

1H NMR means NMR absorption due to protons or 1H.

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.

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



**Peaks in an NMR spectrum correspond to groups of protons (hydrogen atoms) in different chemical environments.**

The three peaks in the spectrum correspond to three different chemical environments for the protons (hydrogen atoms) in one molecule of the aldehyde.

Hydrogen atoms joined to the same carbon atom are said to be chemically equivalent (or just ‘equivalent’*)*.

The peaks have different sizes. The area underneath a peak is proportional to the number of hydrogen atoms in that environment.

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**

There are only two different chemical environments for the hydrogen atoms in pentan-3-one (below) 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 ratio 2 : 3 is because there are four hydrogen atoms in one environment and six hydrogen atoms in the other.

Butanone has three different environments for its protons and the ratio of number of hydrogens in each environment is 3: 2: 3.



**What is the total number of chemical environments in the following molecules and the ratio of hydrogens in each environment? (propan-2-ol and 2-methylpropan-2-ol.)**

****

* NMR or nuclear magnetic resonance spectroscopy is a technique used to determine a compound’s unique structure
* The position of the NMR signal is measured relative to the signal produced by TMS tetramethylsilane
* The chemical shift is measured relative to the point 0
* If there are two of the same group (two CH3 groups), look at the groups of atoms that those groups are bonded to, if they are the same then the protons are in the same chemical environment, if not they are in different chemical environments
* First look at:
  + Number of hydrogen types
  + Peaks
  + Neighbors
  + Cause of shift

