# Edexcel International AS Chemistry

Your notes

## Organic Chemistry: Techniques & Spectra

### Contents

Your notes

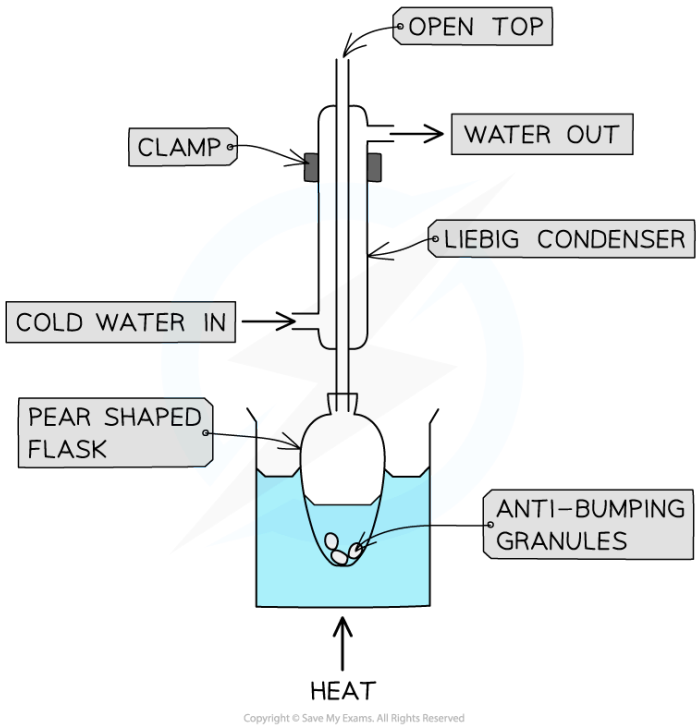
# Reflux, Distillation & Boiling Point Determination

## Heating under reflux

- Organic reactions often occur slowly at room temperature
- Therefore, organic reactions can be completed by heating under reflux to produce an **organic liquid**
- This allows the mixture to react as fully as possible without the loss of any reactants, products or solvent
  - In distillation, you are trying to separate a chemical or product from a mixture
  - When heating under reflux, you aim to keep all the chemicals inside the reaction vessel

## The Heating under Reflux Process:

- Example reactions where heating under reflux could be used include:
  - The production of a carboxylic acid from a primary alcohol using acidified potassium dichromate
  - The production of an ester from an alcohol and acid in the presence of an acid catalyst
- The reaction mixture is placed into a pear-shaped or round bottomed flask
- Anti-bumping granules are, again, added to promote smooth boiling
- The flask is placed in a heating mantle or it can be immersed in a water bath for heating
- Quickfit apparatus is then set up with the condenser clamped vertically in place
  - The joints of the Quickfit apparatus are commonly greased as with distillation
- A steady and constant stream of water passes through the condenser in a 'water jacket' - it enters at the bottom of the condenser and the drainage pipe removes the water from the top of the condenser
- The water is heated and the reaction mixture allowed to boil
- The heated is stopped and the mixture allowed to cool back to room temperature





Your notes

*The preparation of ethyl ethanoate involves heating under reflux for about 15 minutes*

## Distillation

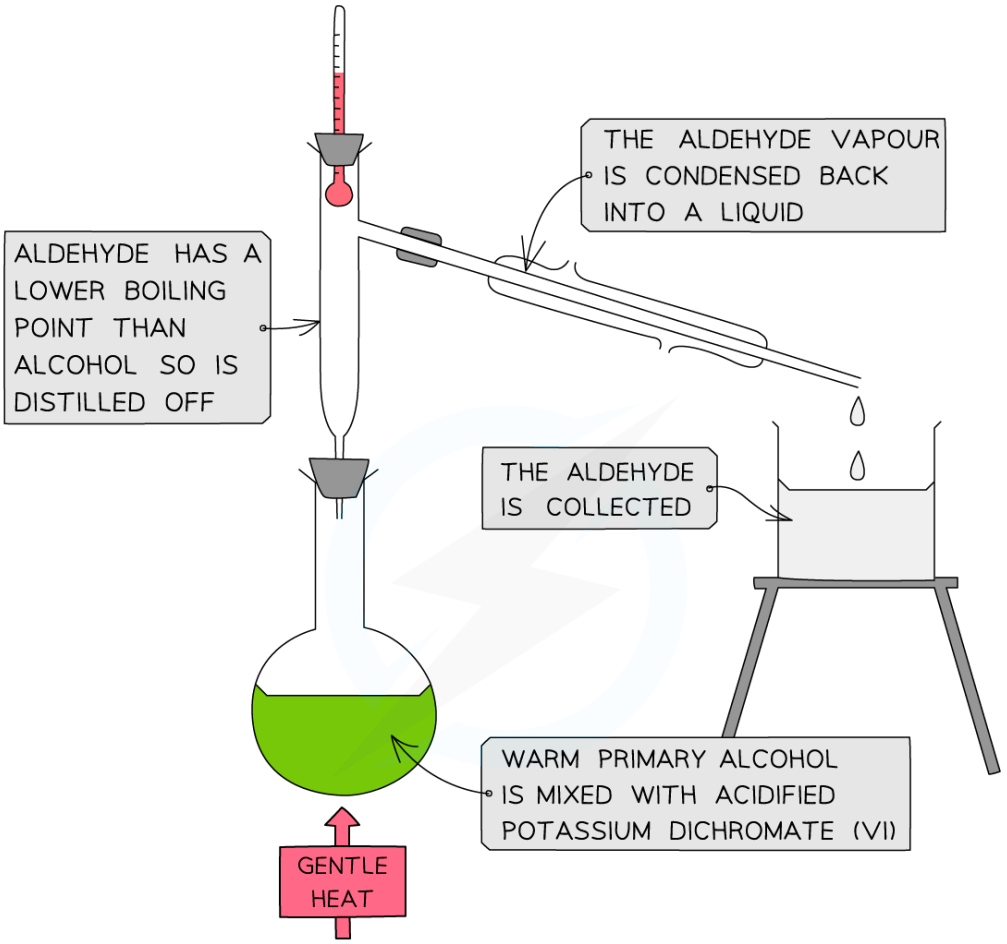
- Distillation is a common practical completed in organic chemistry
- Distillation is used as there are times that a reaction does not go to completion or there are other chemicals produced as well as the desired product
- Distillation allows you to separate compounds by their boiling point
  - Chemicals with the lowest boiling point will distill first
- One of the most common distillation practicals is the oxidation of primary and secondary alcohol to aldehydes and ketones

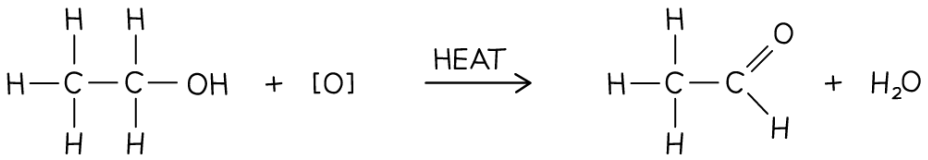
## The Distillation Process:

- To produce an aldehyde from a primary alcohol, a reaction mixture containing the primary alcohol and acidified potassium dichromate solution is placed into a pear-shaped or round bottomed flask
- Anti-bumping granules are added to promote smooth boiling
- Quickfit apparatus is then set up, including a still head and condenser connected to the side
  - The joints of the Quickfit apparatus are often have a thin layer of silicon grease smeared over them to give a better seal as well as to make it easier to disassemble the equipment afterwards

- A Quickfit thermometer can be used, with the thermometer bulb sitting where the vapours will pass into the condenser
- A steady and constant stream of water passes through the condenser in a 'water jacket' - it enters at the bottom of the condenser and the drainage pipe removes the water from the top of the condenser

Your notes






***Heating under Distillation Apparatus***

- The reaction mixture is heated until it boils using a heating mantle
  - Electric heating mantles are used for this because the temperature can be controlled, and because you are using chemicals which are flammable
- The distillate which forms in the condenser drips directly into a receiving vessel

- The distillate which should be collected, is that which is given off at +/- 2 °C of the boiling point of the desired product
- Some distillate may be given off below this temperature - this needs to be discarded and a clean vessel used to collect the desired product
- Stop collecting the distillate if the temperature rises above +/- 2°C of the boiling point of the desired product

- The **aldehyde** product has a lower boiling point than the **alcohol** (since it has lost the **H-bonding**) so it can be **distilled off** as soon as it forms

### Examiner Tips and Tricks

- These practicals give you the opportunity to discuss:
  - The use of an electric heating mantles and water baths rather than a Bunsen burner
  - The choice and setup of laboratory apparatus
  - Health and safety considerations including the careful handling of different liquids, including those which are corrosive, irritant, flammable and toxic

## Boiling point determination

- The boiling point of a liquid is indicative of its purity and identity
- Boiling point is determined by **distillation**
- The sample is gently heated until it boils and this temperature is recorded
  - This boiling point can then be compared against literature / database values
- If the sample contains impurities:
  - The boiling point may appear higher than the literature / database values
  - The sample may boil over a range of temperatures instead of at a single temperature

# Solvent Extraction & Drying

- There are different methods to purify organic compounds, including:
  - Solvent extraction / use of a separating funnel
  - Use of drying agents

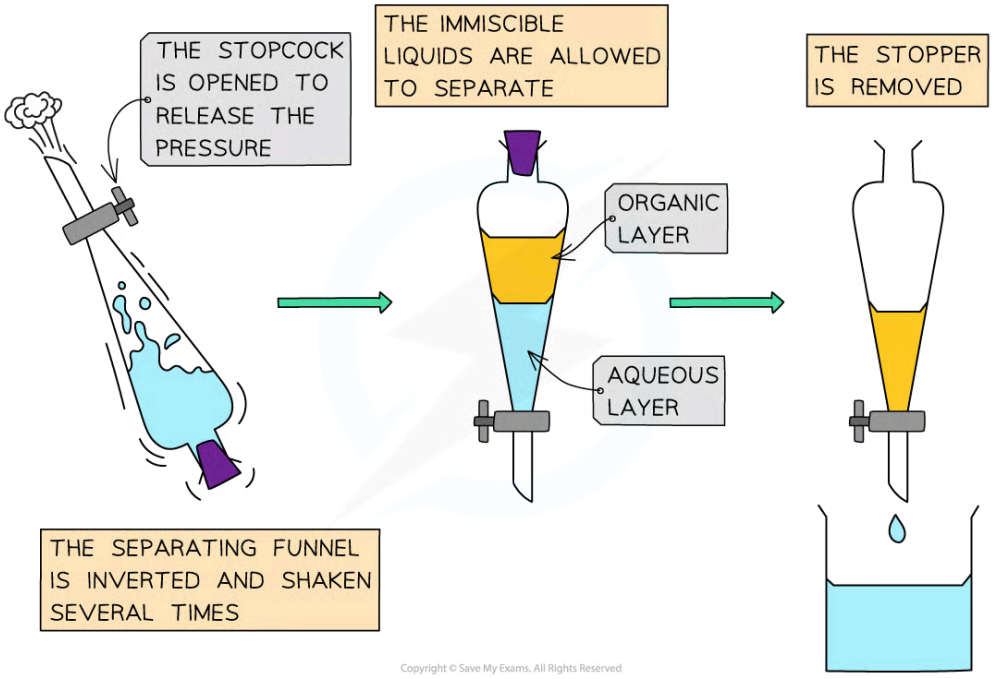
## Solvent extraction / use of a Separating Funnel

- When organic liquids are being prepared, water can often be obtained along with the organic product
- The water will usually form an aqueous layer with the product in the organic layer

Your notes

- It can sometimes be hard to identify which layer is the organic layer - this can be achieved by simply adding water and seeing which layer increases in volume

- Other organic reactions may need to be neutralised before being purified, this can be achieved by adding sodium carbonate solution to the reaction vessel or separating funnel
  - This can also be used to remove other impurities by washing
- The contents of the reaction vessel are transferred to a separating funnel and a stopper added
- The separating funnel is inverted and the stopcock opened to release the pressure - this is repeated 15–20 times
  - If neutralisation has occurred then the stopcock is opened slowly to avoid losing any product
- The two layers are allowed to separate
  - In the following example, the aqueous layer is the bottom layer inside the separating funnel
- The stop cock is opened so that the aqueous layer drains away and the organic layer can be drained into a clean beaker




***A separating funnel allows the product to be cleaned and isolated***

## Use of drying agents

- Drying agents can be used to remove traces of water from an organic product

Your notes

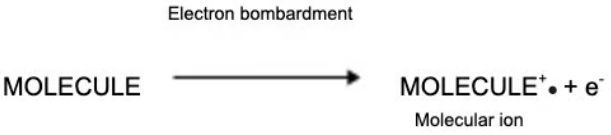
- Drying agents are usually anhydrous inorganic salts that readily hydrate in the presence of water
  - Anhydrous calcium chloride is commonly used to dry hydrocarbons
  - Anhydrous calcium or magnesium sulfate are used as more general purpose drying agents
- A spatula of drying agent is added into the organic product and swirled
  - If the organic product has a low boiling point, a lid / stopped can be added to reduce the potential evaporation of any product
- If the drying agent clumps together, then there is still water in the organic liquid
- More drying agent is added until some remains dispersed in the organic liquid as a fine powder
- The dry organic liquid can then be decanted or filtered
  - If the organic liquid is dry then it should appear clear

Your notes

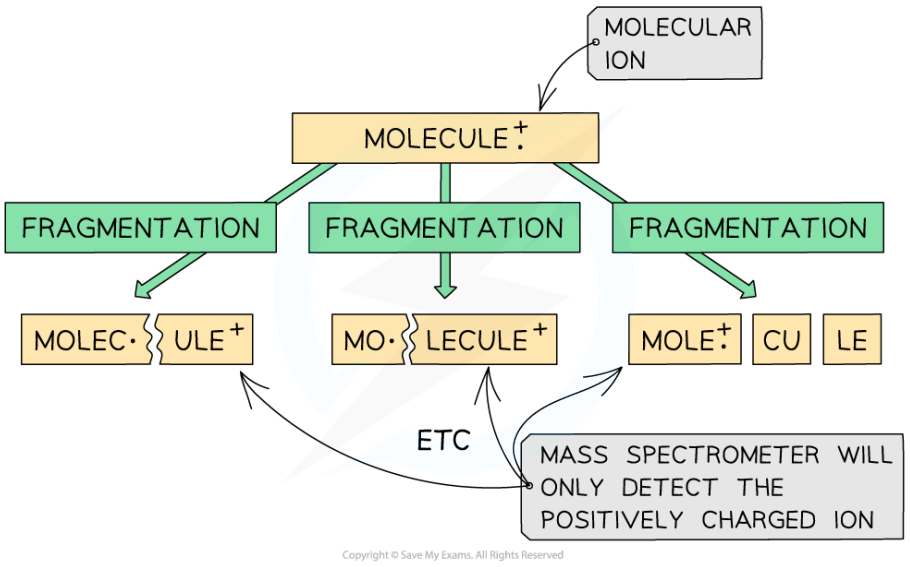
Your notes

# Mass Spectroscopy – Interpretation

- **Mass spectroscopy** is an analytical technique used to identify unknown compounds
- The molecules in the small sample are **bombarded** with high energy electrons which can cause the molecule to lose an electron
- This results in the formation of a positively charged **molecular ion** with one unpaired electron
  - One of the electrons in the pair has been **removed** by the beam of electrons




- The molecular ion can further **fragment** to form new ions, molecules, and radicals




***Fragmentation of a molecule in mass spectroscopy***

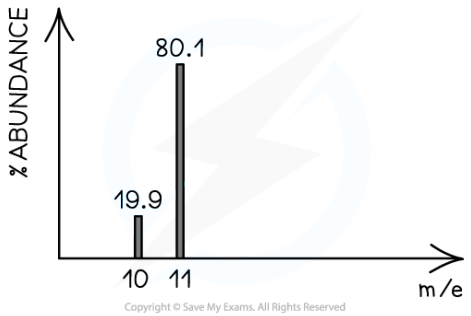
- These **fragmented** ions are **accelerated** by an electric field
- Based on their mass (***m***) to charge (***z***) ratio, the ion fragments are then separated by deflecting them into the **detector**
  - Most ions will only gain a charge of 1+ and therefore a ion with mass 12 and charge 1+ will have an *m/z* value of 12

- It is, however, possible for a greater charge to occur. For example, an ion with mass 16 and charge 2+ will have a *m/z* value of 8

- The smaller and more positively charged fragment ions will be **detected** first as they will get **deflected** the most and are more attracted to the **negative pole** of the magnet
- Each fragment corresponds to a specific **peak** with a particular *m/z* value in the mass spectrum
- The **base peak** is the peak corresponding to the most **abundant** ion
- The *m/z* is sometimes referred to as the *m/e* ratio and it is almost always **1:1**

## Isotopes

- Isotopes are different atoms of the **same element** that contain the same number of **protons** and **electrons** but a different number of **neutrons**.
  - These are atoms of the same **elements** but with different mass number
  - For example, Cl-35 and Cl-37 are isotopes as they are both atoms of the same element (chlorine, Cl) but have a different mass number (35 and 37 respectively)
- Mass spectroscopy can be used to find the **relative abundance** of the isotopes experimentally
- The **relative abundance** of an isotope is the proportion of one particular isotope in a mixture of isotopes found in nature
  - For example, the relative abundance of Cl-35 and Cl-37 is 75% and 25% respectively
  - This means that in nature, 75% of the chlorine atoms is the Cl-35 isotope and 25% is the Cl-37 isotope
- The **heights** of the peaks in mass spectroscopy show the proportion of each isotope present





***The peak heights show the relative abundance of the boron isotopes: boron-10 has a relative abundance of 19.9% and boron-11 has a relative abundance of 80.1%***

Your notes

## Worked Example

### Calculating m/z ratio

In a sample of iron, the ions $^{54}Fe^{2+}$ and $^{56}Fe^{3+}$ are detected. Calculate their m/z ratio and determine which ion is deflected more inside the spectrometer.

**Answer**

$$m/e\ (^{54}Fe^{2+}) = \frac{54}{2}$$

$$= 27$$

$$m/e\ (^{56}Fe^{3+}) = \frac{56}{3}$$

$$= 18.7$$

$$= 19$$

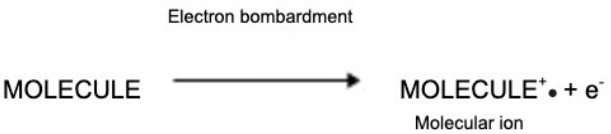
- $^{56}Fe^{3+}$ has a smaller *m/z* ratio and will therefore be deflected more.
    - It also has the largest positive charge and will be more attracted to the negative pole of the magnet within the mass spectrometer.

## Examiner Tips and Tricks

A small *m/z* value corresponds to fragments that are either **small** or have a **high positive charge** or a combination of **both**.

# Deducing molecular formulae

- Each **peak** in the mass spectrum corresponds to a certain **fragment** with a particular ***m/z*** value
- The peak with the highest ***m/z*** value is the molecular ion (**$M^+$**) peak which gives information about the **molecular mass** of the compound
- The molecular ion is the entire molecule that has lost one electron when bombarded with a beam of electrons




- The **[M+1]** peak is a smaller peak which is due to the natural abundance of the isotope carbon-13
- The amount of naturally occurring C-13 is a little over 1%, so the [M+1] peak is very small

Your notes

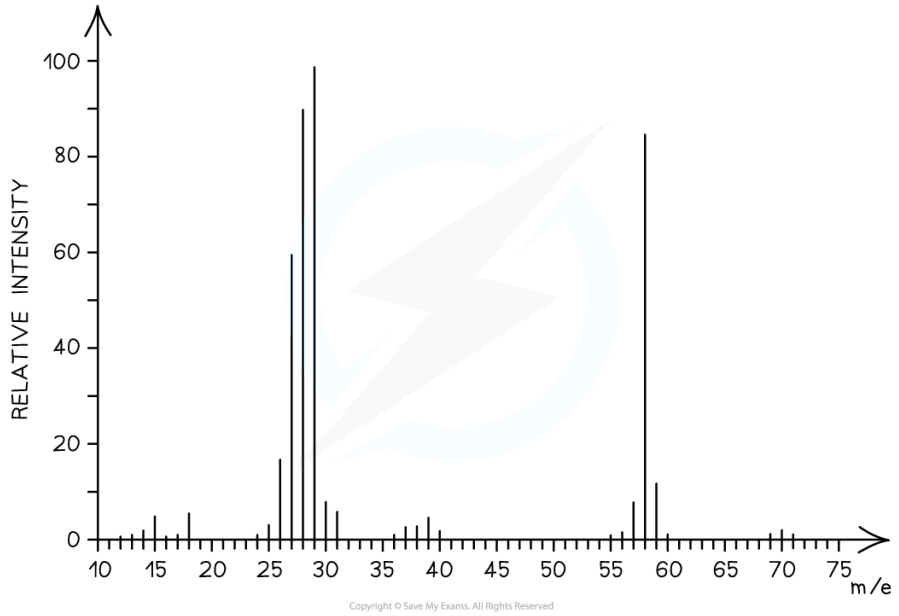
- The height of the [M+1] peak for a particular ion depends on how many carbon atoms are present in that molecule; the more carbon atoms, the larger the [M+1] peak is
  - For example, the height of the [M+1] peak for an hexane (containing six carbon atoms) ion will be greater than the height of the [M+1] peak of an ethane (containing two carbon atoms) ion

Your notes

### Worked Example

**Analysing mass spectra**

Determine whether the following mass spectrum corresponds to but-1-ene or pent-1-ene:





**Answer**

- The mass spectrum corresponds to pent-1-ene as the molecular ion peak is at $m/z = 70$
  - The small peak at m/z = 71 is a C-13 peak, which does not count as the molecular ion peak
  - But-1-ene arises from the $C_4H_8^+$ ion which has a molecular mass of 56
  - Pent-1-ene arises from the $C_5H_{10}^+$ ion which has a molecular mass of 70

# Mass Spectrum – Fragmentation

- The molecular ion peak can be used to identify the **molecular mass** of a compound
- However, different compounds may have the same molecular mass
- To further determine the structure of the unknown compound, **fragmentation** is used

- Fragments may appear due to the formation of **characteristic fragments** or the **loss of small molecules**
  - For example, a peak at 29 is due to the characteristic fragment $C_2H_5^+$
  - Loss of small molecules give rise to peaks at 18 ($H_2O$), 28 (CO), and 44 ($CO_2$)

Your notes

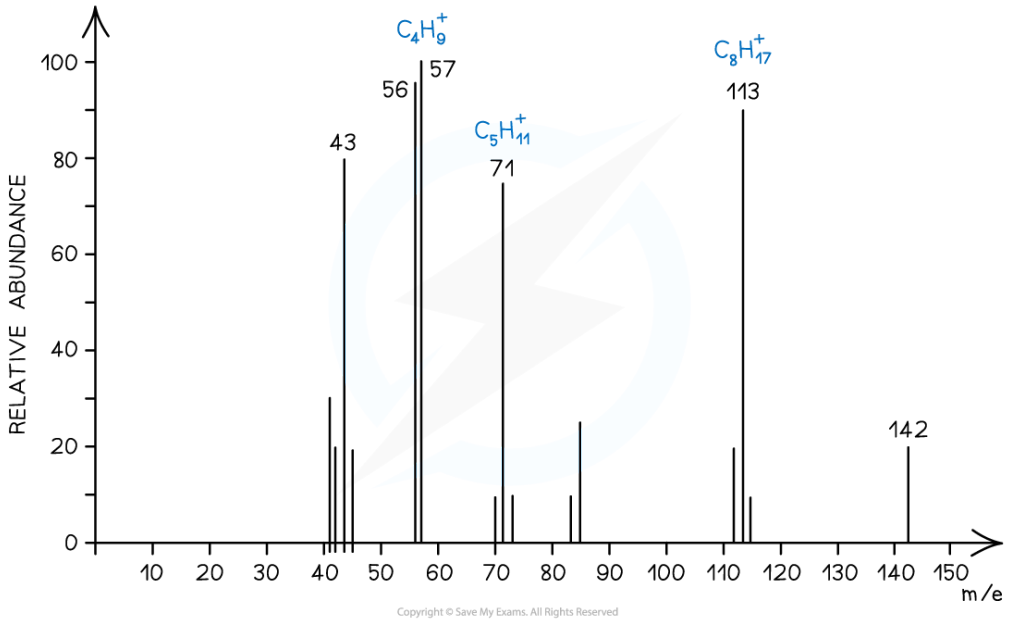
## Alkanes

- Simple alkanes are fragmented in mass spectroscopy by breaking the C-C bonds
- ***M/e*** values of some of the common alkane fragments are given in the table below

## m/e Values of Fragments Table

| Fragment | m/e |
|---|---|
| $CH_3^+$ | 15 |
| $C_2H_5^+$ | 29 |
| $C_3H_7^+$ | 43 |
| $C_4H_9^+$ | 57 |
| $C_5H_{11}^+$ | 71 |
| $C_6H_{13}^+$ | 85 |







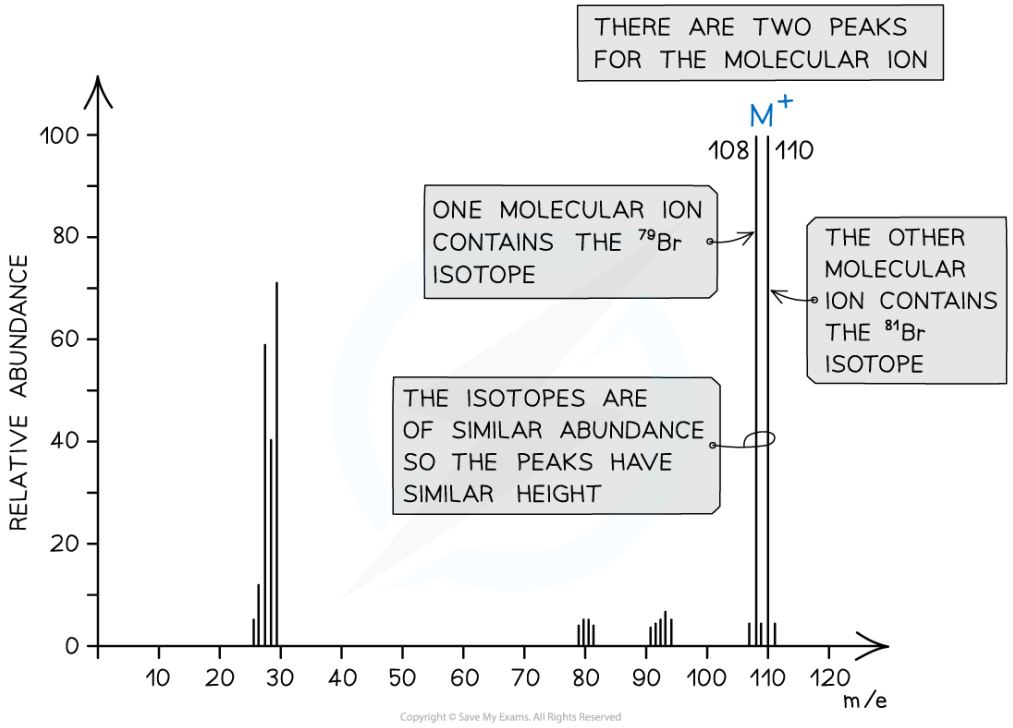

*Mass spectrum showing the fragmentation of $C_{10}H_{22}$*

## Halogenoalkanes



Your notes

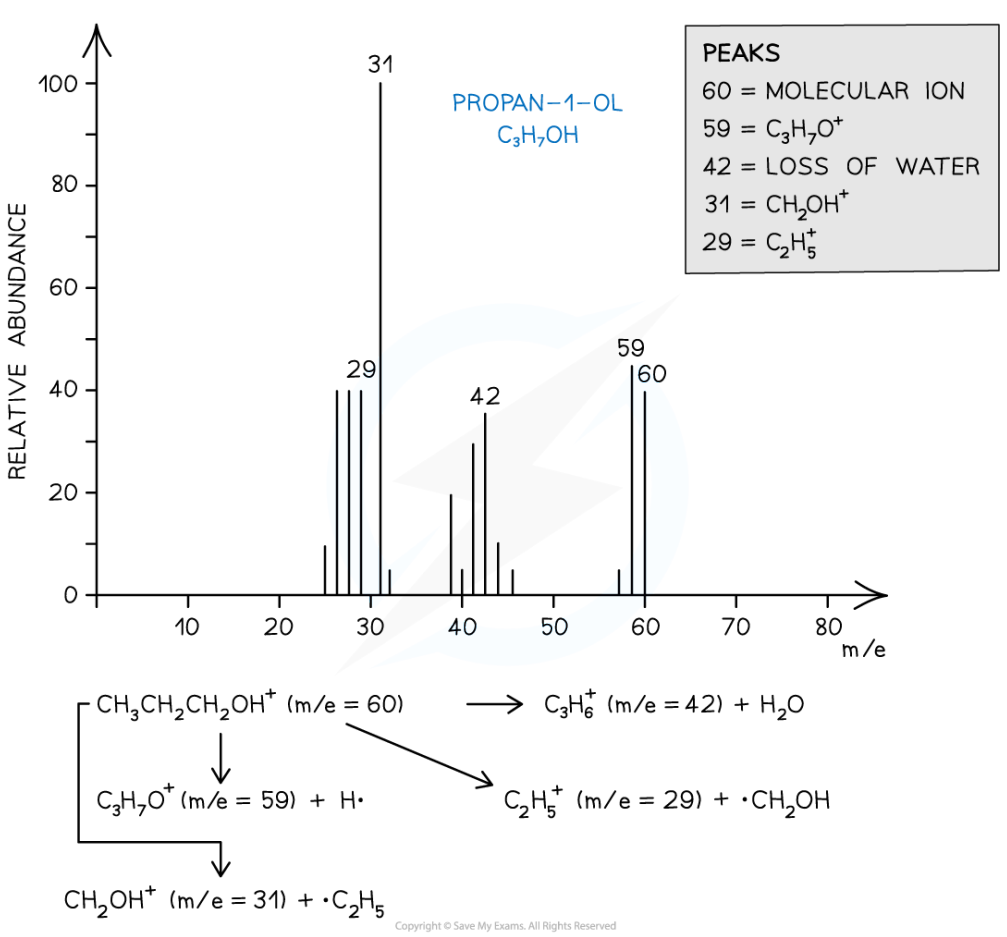
- Halogenoalkanes often have multiple peaks around the molecular ion peak
- This is caused by the fact that there are different isotopes of the halogens




*Mass spectrum showing different isotopes of bromine in the molecular ion*

## Alcohols

- Alcohols often tend to lose a **water molecule** giving rise to a peak at **18 below the molecular ion**
- Another common peak is found at *m/e* value 31 which corresponds to the $CH_2OH^+$-fragment
- For example, the mass spectrum of propan-1-ol shows that the compound has fragmented in four different ways:
  - Loss of $H^\bullet$ to form a $C_3H_7O^+$ fragment with *m/e* = 59
  - Loss of a water molecule to form a $C_3H_6^+$ fragment with *m/e* = 42
  - Loss of a $^\bullet C_2H_5$ to form a $CH_2OH^+$ fragment with *m/e* = 31
  - And the loss of $^\bullet CH_2OH$ to form a $C_2H_5^+$ fragment with *m/e* = 29





*Mass spectrum showing the fragmentation patterns in propan-1-ol (alcohol)*

## Worked Example

**Ion fragmentation**

Which of the following statements about the mass spectrum of $CH_3Br$ is correct?

**A**. There is one peak for the molecular ion with an m/e value of 44

**B**. There is one peak for the molecular ion with an m/e value of 95

**C**. The last two peaks have abundances in the ratio 3:1 and occur at m/e values of 94 and 96

**D**. The last two peaks are of equal size and occur at m/e values of 94 and 96

**Answer**

The correct answer is option **D**

- Bromomethane ($CH_3Br$) can produce 3 peaks

Your notes

- $CH_3{}^{81}Br \rightarrow [CH_3{}^{81}Br]^+ + e^-$ at m/e 96
- $CH_3{}^{79}Br \rightarrow [CH_3{}^{79}Br]^+ + e^-$ at m/e 94
- $CH_3Br \rightarrow [CH_3]^+ + {}^\bullet Br$ at m/e 15
- The last two peaks (which correspond to the molecular ion peak) therefore are equal in size and occur at *m/e* values of 94 and 96

Your notes

## Worked Example

**Alcohol fragmentation**

Which alcohol is not likely to have a fragment ion at m/e at 43 in its mass spectrum?

**A**. $(CH_3)_2CHCH_2OH$

**B**. $CH_3CH(OH)CH_2CH_2CH_3$

**C**. $CH_3CH_2CH_2CH_2OH$

**D**. $CH_3CH_2CH(OH)CH_3$

**Answer**

The correct answer is option **D**

- Because a line at m/e = 43 corresponds to an ion with a mass of 43 for example:
  - $[CH_3CH_2CH_2]^+$
  - $[(CH_3)_2CH]^+$
  - 2–butanol is not likely to have a fragment at m/e = 43 as it does not have either of these fragments in its structure.

Your notes

# Infrared Spectrometry – Interpretation

- **Infrared (IR) spectroscopy** is a technique used to identify compounds based on changes in **vibrations** of atoms when they **absorb** IR of certain **frequencies**
- A **spectrophotometer** irradiates the sample with electromagnetic waves in the infrared region and then detects the **intensity** of the wavelength of IR radiation which goes through the sample
- All organic molecules absorb IR radiation and depending on which energies of radiation are absorbed, bonds between atoms will vibrate by **stretching**, **bending** and **twisting**
- The molecules will only vibrate at a specific frequency
- The **resonance frequency** is the specific frequency at which the molecules will vibrate to stimulate larger vibrations
- Depending on the rest of the molecule, each vibration will absorb specific wavelengths of IR radiation which are also shown as the **reciprocal** of the wavelength
  - This unit is called the **wavenumber** ($cm^{-1}$)
- Particular absorbance have characteristic **widths** (broad or sharp) and **intensities** (strong or weak)
  - For example, hydrogen bonds cause the O-H bonds in alcohols and carboxylic acids to be **broad** whereas the C-O bond in carbonyl (C=O) groups have a strong, sharp absorbance peak
- The energies absorbed by different functional groups are given as a range and an unknown compound can be identified by comparing its IR spectrum to the IR spectrum of a known compound

## Absorption Range of Bonds Table

| Bond | Functional groups containing the bond | Characteristic infrared absorption range (in wavenumbers) ($cm^{-1}$) |
|---|---|---|
| C–O | Hydroxy, ester | 1040–1300 |
| C=C | Aromatic compound, alkene | 1500–1680 |
| C=O | Amide carbonyl, carboxyl ester | 1640–1690<br>1670–1740<br>1710–1750 |
| C≡N | Nitrile | 2200–2250 |
| C–H | Alkane | 2850–2950 |
| N–H | Amine, amide | 3300–3500 |
| O–H | Carboxyl, hydroxyl | 2500–3000<br>3200–3600 |



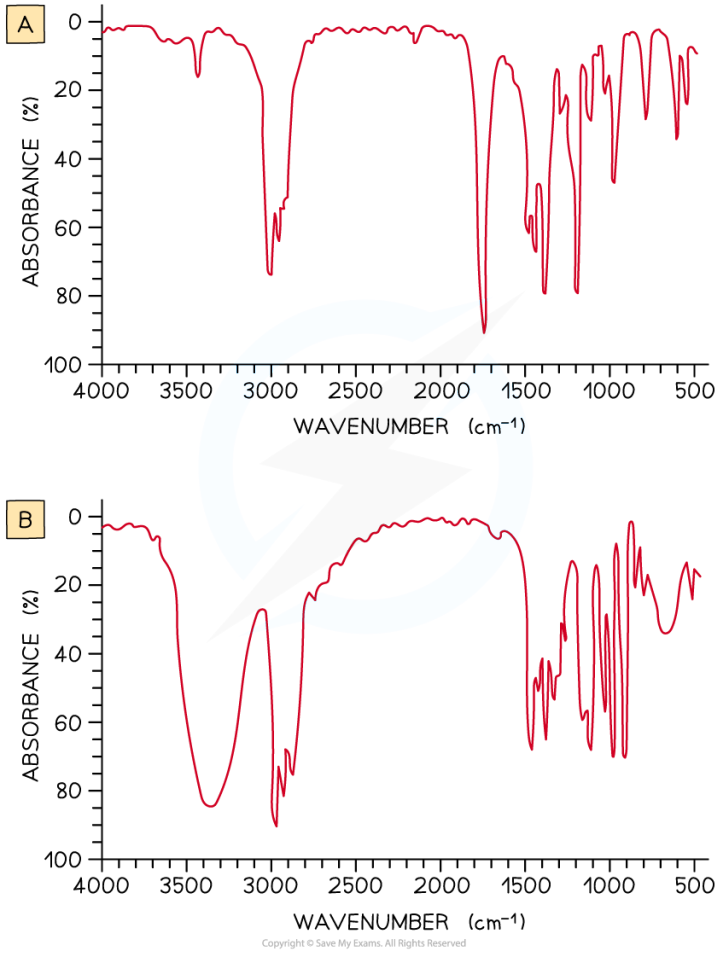
Your notes

- Due to some absorption bands overlapping each other, other analytical techniques such as mass spectroscopy should be used alongside IR spectroscopy to identify an unknown compound

## Worked Example

### Analysing IR Spectra

Look at the two infrared spectra below and determine which one corresponds to propanone and which one to propan-2-ol





Your notes

**Answer**

- IR spectrum **A** is **propanone** and spectrum **B** is **propan-2-ol**.
  - In IR spectrum **A** the presence of a strong, sharp absorption around 1710 $cm^{-1}$ corresponds to the characteristic C=O, carbonyl, group in a ketone.
  - In spectrum **B** the presence of a strong, broad absorption around 3200–3500 $cm^{-1}$ suggests that there is an alcohol group present, which corresponds to the -OH group in propan-2-ol.