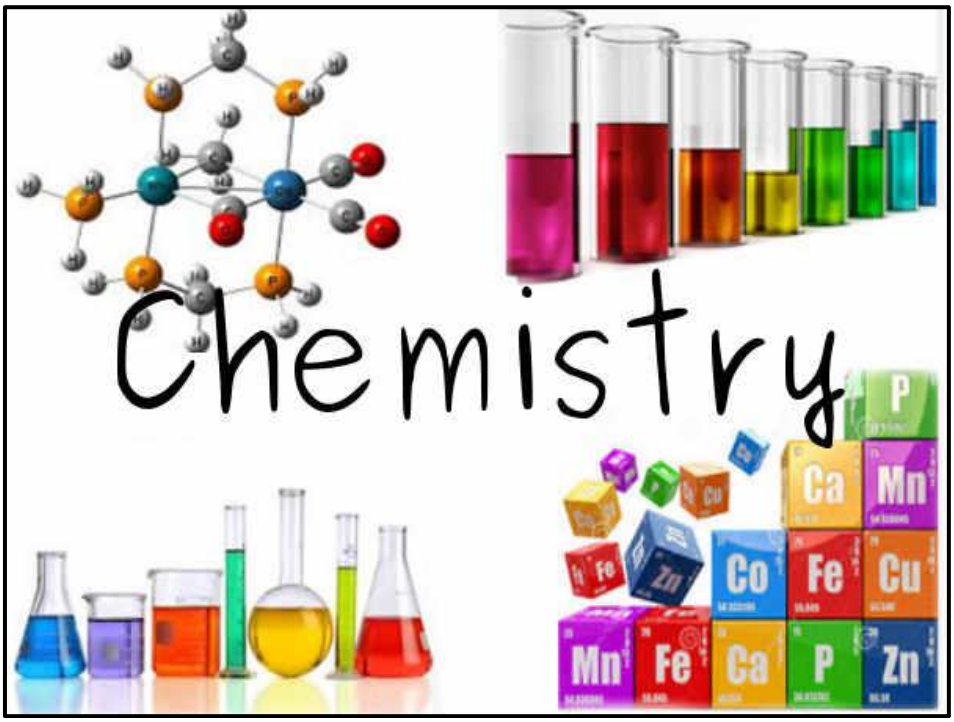

UNIT 4 CHEMISTRY – AREA OF STUDY 1

SUMMARY NOTES FOR THE VCAA EXAMS

WRITTEN BY A STUDENT WHO OBTAINED A NEAR PERFECT STUDY SCORE

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AREA OF STUDY 1: HOW CAN THE DIVERSITY OF CARBON COMPOUNDS BE EXPLAINED AND CATEGORISED?

CARBON COMPOUNDS

Covalent bonds between Carbon and other atoms have a bond energy.

Bond energy – a measure of the energy required to break the covalent bond (indicates bond strength):

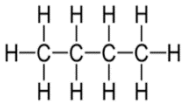
- increases as number of bonds increases (single < double < triple)
- increases with shorter bond length
- increase with smaller atom size
- increases as electronegativity decreases

Covalent bond	Bond energy (kJ mol^{-1})
C≡C	839
C=C	614
C–C	348
C–F	488
C–H	413
C–O	360
C–Cl	330
C–N	308
C–S	272

Why is carbon such an important atom?

- Can form four covalent bonds (leads to long chains)
- A C-C bond has the highest bond energy

Formulas

- molecular formula (C_4H_{10})
- structural formula 
- semi structural formula ($CH_3CH_2CH_2CH_3$).
- empirical formula—simplest whole number ratio of atoms in the compound (e.g Hexane C3H7)

ISOMERS

Isomers are molecules that have to same molecular formula but different structural formulas.

- Behave differently due to different physical and chemical properties.
- Structural isomers (positional and chain isomers)
- Stereoisomers (optical and geometric)

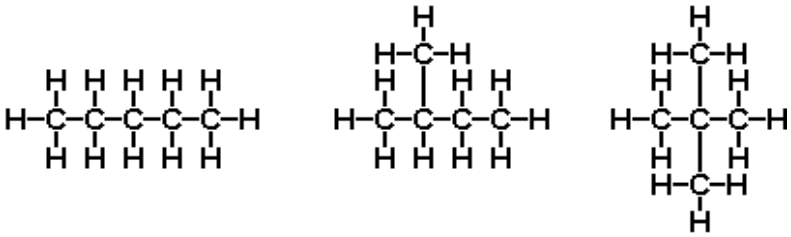
STRUCTURAL ISOMERS

CHAIN ISOMERS

Chain isomers are a result of the branching that is possible in the carbon chains that form the backbone of any large organic molecule. Pentane for example has 2 chain isomers.

i.e. when the longest chain changes from 4 to 3 etc.

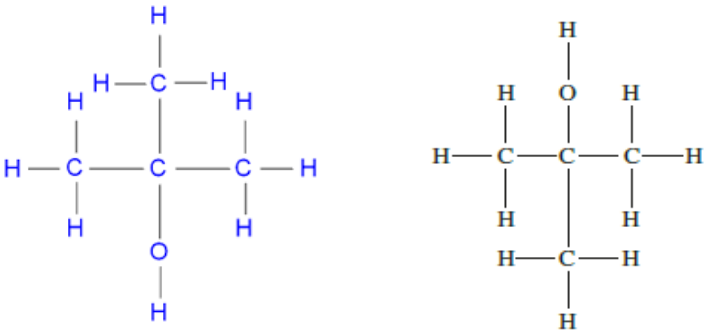
3 isomers of Pentane



POSITIONAL ISOMERS

- Positional isomers occur when organic molecules have the same functional group.
- Functional group is in a different location. Eg butan-1-ol and butan-2-ol.
- It is possible for structural isomers to form both **positional** and **chain** isomers.

2 isomers of butanol—both chain and positional isomers of each other.



STEREOISOMERS

- Stereoisomers are isomers where the atoms in 2 molecules are connected in the same order, but have different spatial arrangements (different 3D shape) .

- have very different chemical properties.

OPTICAL ISOMERS

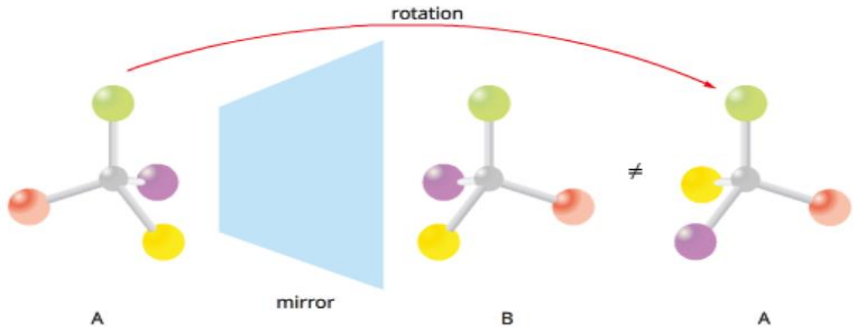
- There is a different placement of groups around one atom in a molecule.
- Their molecular and semi-structural formulas are identical.

CHIRALITY

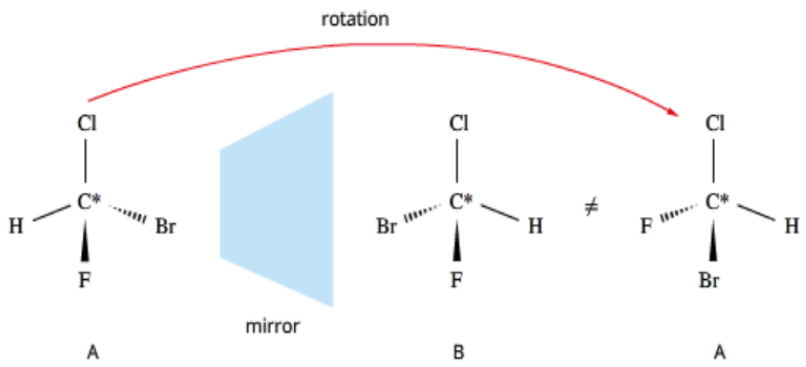
- Molecules that are optical isomers are said to be chiral.

- Molecules are chiral if they have a **chiral centre** (a carbon atom that has formed 4 bonds with 4 unique atoms/groups).

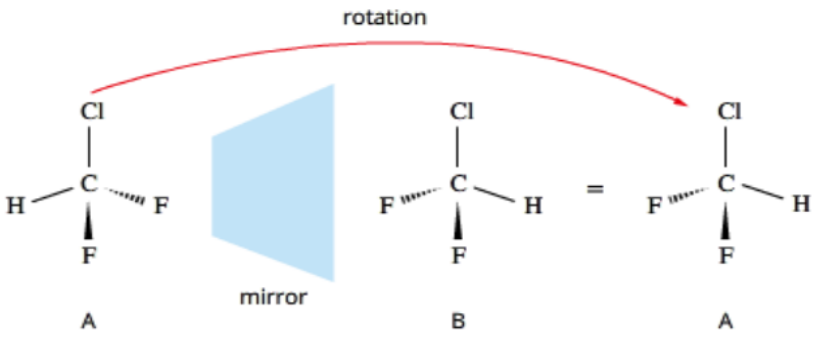
- Chiral molecules are known as **enantiomers**.



Molecules A and B are **enantiomers**.



Bromochlorofluoromethane is a chiral molecule and has 2 **enantiomers**.



Chlorodifluoromethane is achiral because it's mirror image can be superimposed.

IDENTIFYING CHIRAL CENTRES

1. Eliminate all the Carbon atoms that cannot be chiral centres. This includes all CH2, CH3, and any atom that is part of a double or triple bond. These atoms cannot be bonded to 4 different atoms.

2. For the remaining Carbon atoms check the groups bonded to this Carbon. If they are all different then there is a chiral centre.

PROPERTIES OF ENANTIOMERS

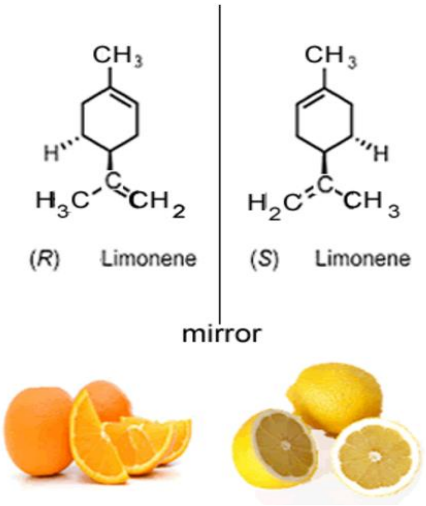
- Enantiomers have identical physical properties except for the way they rotate polarized light.

- They rotate polarised light in opposite directions

- They have the same melting and boiling points and the same levels of solubility.

- Enantiomers react differently with other chiral molecules. In biological systems the spatial arrangement of atoms around a central carbon is critical to the chemical behaviour of the molecule within its biological environment. Such subtle differences amongst isomers provides for a countless number of possibilities when applied to living organisms.

- The two enantiomers (optical isomers) shown below are identical but bind differently to proteins in our noses, known as receptors, to produce smells of lemons or oranges.



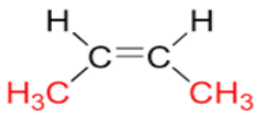
Note: The number of optical isomers is given by the formula:

Number = 2^y

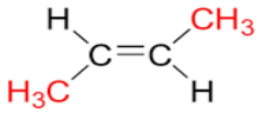
where y is the number of chiral centres in the molecule.

GEOMETRIC ISOMERS

- Geometric isomers are molecules where the atoms are locked into their spatial arrangements via a double bond.
- There is restricted rotation about a C=C double bond or ring structure.
- Different spatial arrangements give the molecules unique properties.
- **Cis**: Longest chain is on the same side of double bond.
- **Trans**: Longest chain on opposite sides of double bond.



cis-2-butene



trans-2-butene

THE EFFECT OF GEOMETRIC ISOMERISM ON PHYSICAL PROPERTIES

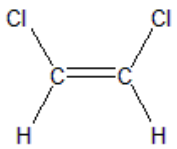
1,2-dichloroethene:

Isomer	**Boiling point (°C)**
cis	60
trans	48

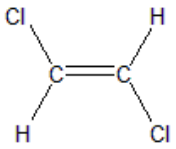
- The cis isomer has the higher boiling point.
- ***Why is the boiling point of the cis isomer higher?***

  There must be stronger intermolecular forces between the molecules of the cis isomers than between trans isomers.

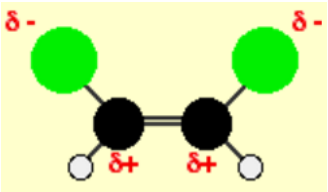
  The cis isomer is a polar molecule whereas the trans isomer is non-polar. Both molecules contain polar chlorine-carbon bonds, but in the cis isomer they are both on the same side of the molecule. That means that one side of the molecule will have a slight negative charge while the other is slightly positive.



cis-1,2-dichloroethene



trans-1,2-dichloroethene



cis-1,2-dichloroethene:

Because of this, there will be dipole-dipole interactions as well as dispersion forces - needing extra energy to break. That will raise the boiling point.

ALKANES AND ALKENES

Hydrocarbons are organic compounds that contain only **hydrogen** and **carbon**.

Hydrocarbons are **non-polar** molecules that attract each other weakly by **instantaneous dipoles/dispersion forces**. Hydrocarbons are non-polar because:

- **Symmetrical molecules**
- **Very little difference in electronegativity between hydrogen and carbon**

Instantaneous dipoles/dispersion forces—temporary dipoles arise between molecules due to the movement of electrons in a bond between atoms.

Dispersion forces increases when:

- **Molecules are closer – straight chain molecules can be more compact**
- **Molecules are larger – more surface area for attraction/more electrons to create dispersion forces**

PROPERTIES

- Do not conduct electricity (non-polar).
- Melting Point/Boiling Point/Viscosity – **low for smaller alkanes, increases as they become larger due to stronger dispersion forces.**
- Solubility – **insoluble in polar solvents as they cannot form H bonds with water**

ALKANES

- Name ends in - ane
- **Homologous** series (a series where a general formula applies i.e. increase by $–CH_2$ each time).
- Saturated molecules (which means **that every carbon has four single bonds around it (maximum)**
- General formula is $\mathbf{C_nH_{2n+2}}$
- First ten are:

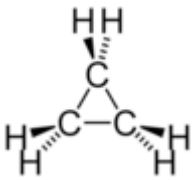
  1) Methane
  2) Ethane
  3) Propane
  4) Butane
  5) Pentane
  6) Hexane
  7) Heptane
  8) Octane
  9) Nonane
  10) Decane

- The structure for each carbon (central atom) is **tetrahedral**.

CYCLIC MONOMERS

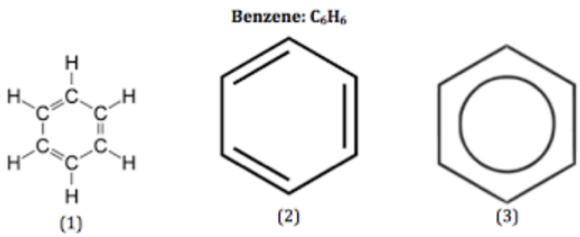
The chain of carbon atoms can also be bent to form a **ring.**

e.g Cyclopropane:



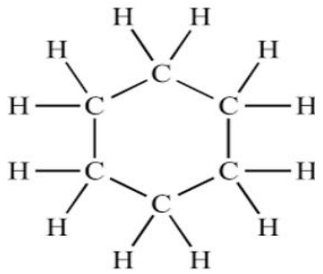
ARENES

Where each carbon member in the ring **doesn't** form **four** covalent bonds. The one left over electron (**delocalised**) from each carbon is shared between all carbons in the ring formation. E.g benzene

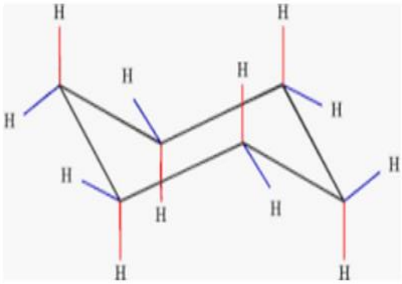


CYCLOHEXANE

Cyclohexane is a cyclic hydrocarbon that is used as a solvent, such as paint stripper. The ability of the carbon atoms to rotate to a limited extent around the single bonds means the ring can take different shapes. The most common form is known as the chair conformation.



Structural formula

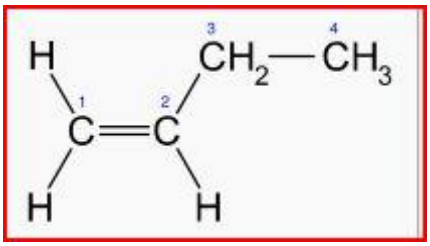


Chair conformation

Cyclohexane is a saturated hydrocarbon despite having 2 less hydrogens than hexane.

ALKENES

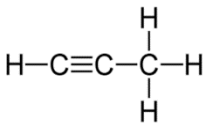
- Name ends in - ene
- **Homologous** series (a series where a general formula applies i.e. increase by $–CH_2$ each time)
- Unsaturated molecules (which means **not all carbon-carbon bonds are single bonds (not maximum atoms around carbon)**
- General formula is $\mathbf{C_nH_{2n}}$



e.g but-1-ene

ALKYNES

Alkynes contain a C to C triple bond and are therefore unsaturated. They have the general formula C_nH_{2n-2}. When there are **four of more** C atoms they have structural isomers.



Eg: Propyne

NAMING (NOMENCLATURE) ALKANES, ALKENES & ALKYNES

1. Count the longest chain of carbon atoms.

2. Locate single, double or triple bonds within molecule.

3. Number carbon atoms so that side chains, functional groups, double bonds and triple bonds have the lowest possible number combination.

4. Identify location of side chain, functional group etc attached to carbon chain.

5. Alphabetical order for side groups/functional groups (e.g. 2-bromo, 3-chloro,2-methyl alkane).

SIDE CHAINS

Alkyl groups

The part in the isomer that comes off main carbon chain needs to be identified.
Same as alkanes but *ane* becomes *yl*

e.g. a one carbon side chain – methyl
a two carbon side chain – ethyl
a three carbon side chain – propyl

Order of importance:

1. Carboxylic Acids
2. Esters
3. Amide
4. Aldehyde
5. Ketones
6. Alcohols
7. Amine
8. Alkene
9. Alkyne
10. Alkane

- The functional group with the highest priority is assigned the lowest possible number and the suffix for this functional group is used in the name.

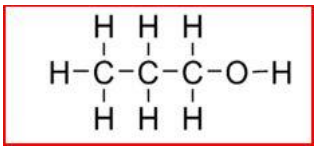
- The lower priority functional group is shown via a prefix or an alternative name.

FUNCTIONAL GROUPS

Functional group: a group of atoms that give characteristic properties to the molecule. It **alters** the chemistry of that group of molecules.

ALKANOLS (-OH) **-** (i.e. alkane + alcohol = alkanol)

Addition of –OH (replaces one H)
Name changes, to –*ol* at the end.
Must show position of –OH group

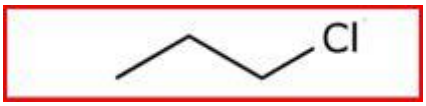


propan-1-ol

Due to addition of –OH group; alcohols are more soluble in water (now polar)

HALOALKANE (-Cl, -I, -F, -Br)

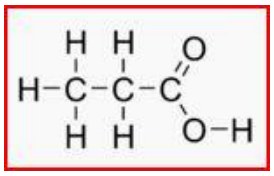
Addition of –Cl (replaces one H)
Name changes, to *chloro, fluoro, bromo or iodo* at beginning
Must show position of halo group



1-chloropropane

CARBOXYLIC ACIDS (-COOH)

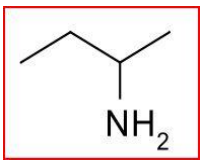
Addition of –OOH (replaces three H)
Name changes, to -*oic acid* at end
Must show position of - COOH



Propanoic acid

AMINES (-NH_2)

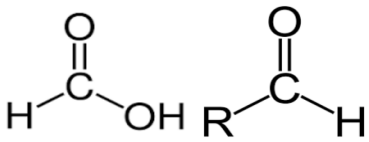
Addition of NH_2 (replaces H)
Name changes by adding *amine* in the name. Eg butan-2-amine or buytl-2-amine.
Must show position of –NH_2

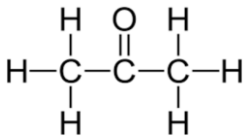


Butan-2-amine

ALDEHYDES and KETONES

Aldehydes and ketones contain the carbonyl functional group C=O. Aldehydes contain a COH group.

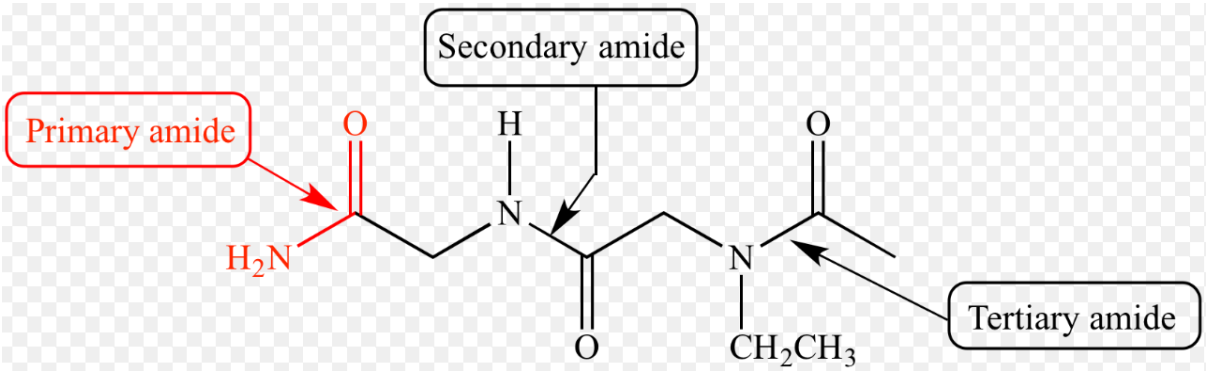




e.g Acetone (ketone)

AMIDES

Amides contain the CONH functional group. This functional group is found in proteins and can be called a peptide link when contained in this compound. Primary amides always have the amide group at the end of the molecule.

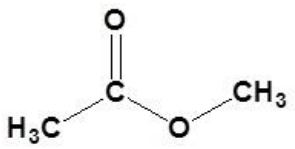


*amides and carboxylic acids have very polar functional groups (more than alcohols or halo alkanes).

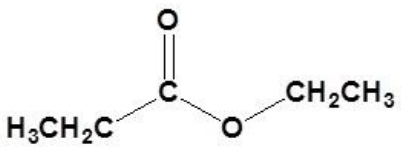
ESTERS

They contain the COO functional group, synthesised by addition of alcohol and carboxylic acid.

Naming: alcohol-thyl acid-oate



Methyl ethanoate



Ethyl propanoate

PROPERTIES OF ORGANIC MOLECULES

Boiling point increases as…

- chain length increases: more bonds, more temporary dipoles hence a greater strength of attraction between molecules
- straight chain isomers are able to pack more closely (branched isomers are further apart), resulting in greater magnitude of dispersion forces **branching reduces the attraction of Van der Waals forces**
- polarity increases: Haloalkanes have a highly polar C-X bond, resulting in stronger dipole-dipole attractions
- carboxylic acids have the highest boiling point due to the presence of two electronegative atoms

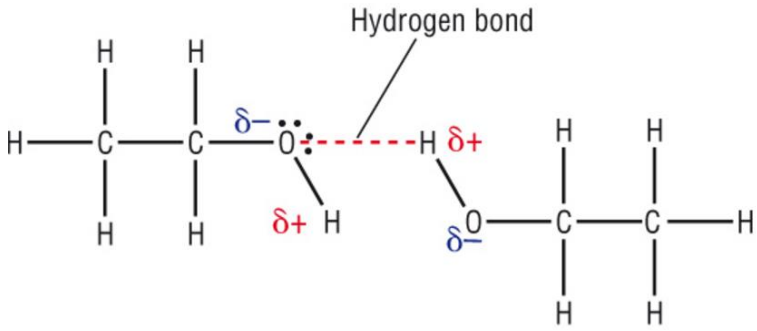
Solubility

- Hydrocarbons and symmetrical haloalkanes are insoluble (immiscible) in water as they are unable to from Hydrogen bonds with water (they're dispersion forces are weaker than hydrogen bonds).
- polar functional groups such as asymmetrical haloalkanes, alcohols, carboxylic acids, amines and amides are polar and therefore more soluble in water than hydrocarbons. However, as the chain increases in size it's solubility in water decreases as the non polar chain becomes more dominant.

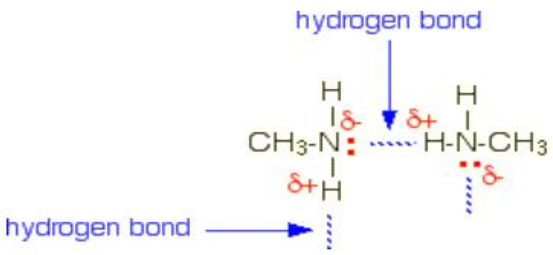
'like dissolves like' —this due to similar strength of attraction

PROPERTIES OF AMIDES, AMINES, ALCOHOLS AND CARBOXYLIC ACIDS

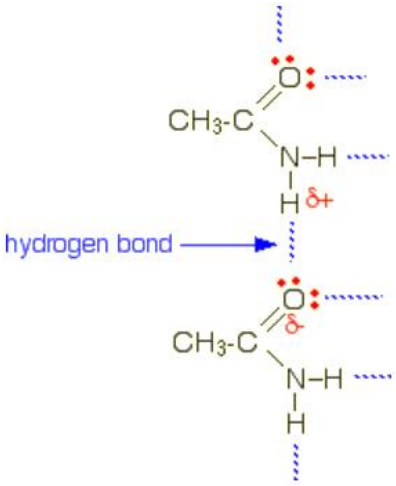
HYDROGEN BONDS IN ALCOHOLS



HYDROGEN BONDS IN AMINES

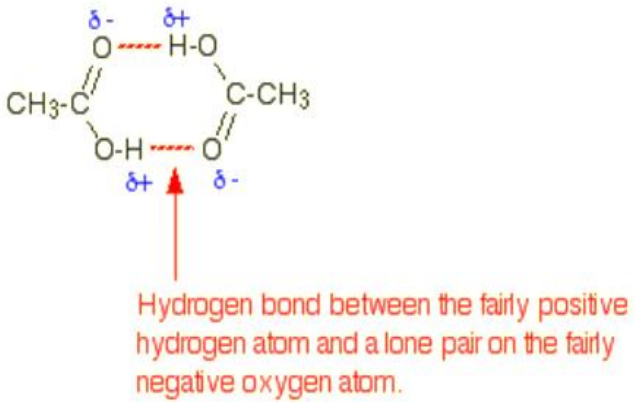


HYDROGEN BONDS IN AMIDES



HYDROGEN BONDS IN CARBOXYLIC ACIDS

The higher boiling points of the carboxylic acids are still caused by hydrogen bonding, but operating in a different way. In a pure carboxylic acid, hydrogen bonding can occur between two molecules of acid to produce a ***dimer***.



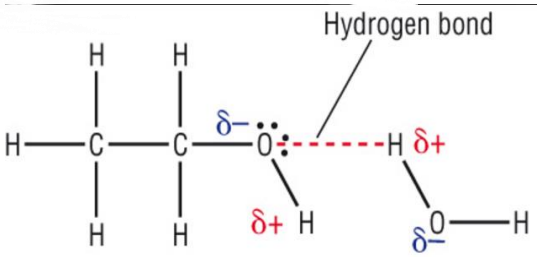
This immediately doubles the size of the molecule and so increases the van der Waals dispersion forces between one of these dimers and its neighbours - resulting in a high boiling point.

- the salt of a carboxylic acid e.g CH3COONa will be more soluble than CH3COOH as it can form stronger ion-dipole bonds with H2O (stronger than H bonds)

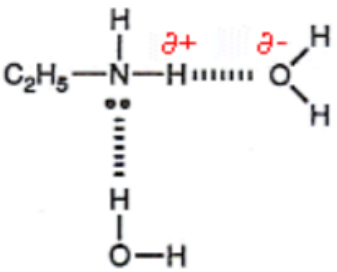
  - ➢ CH3COO- will bond with water
  - ➢ NA+ will bond with water

SOLUBILITY

Small alcohols, amines, amides and carboxylic acids are very soluble in water due to their ability to form hydrogen bonds between their polar functional groups and nearby water molecules.

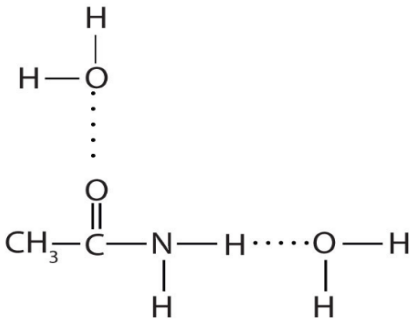


Hydrogen bonds between water and ethanol

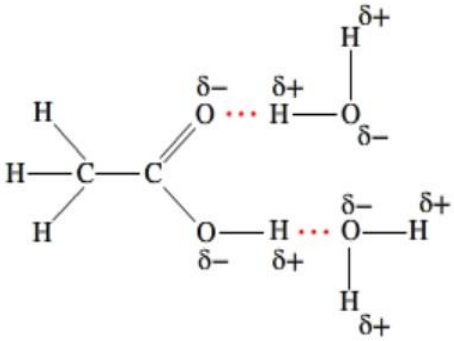


Hydrogen bonds between water and ethylamine

Small amides and carboxylic acids are more soluble than alcohols in water due to them having the C=O group and an -OH group or -NH group.



Hydrogen bonds between water and an amide

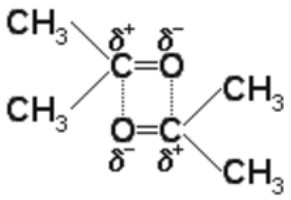


Hydrogen bonds between water and ethanoic acid

Formula	Name	Solubility in Water (g/100g)
CH_3OH	methanol	infinitely soluble
CH_3CH_2OH	ethanol	infinitely soluble
$CH_3(CH_2)_2OH$	propanol	infinitely soluble
$CH_3(CH_2)_3OH$	butanol	9
$CH_3(CH_2)_4OH$	pentanol	2.7
$CH_3(CH_2)_5OH$	hexanol	0.6
$CH_3(CH_2)_6OH$	heptanol	0.18
$CH_3(CH_2)_7OH$	octanol	0.054
$CH_3(CH_2)_9OH$	decanol	insoluble in water

PROPERTIES OF ALDEHYDES, KETONES AND ESTERS

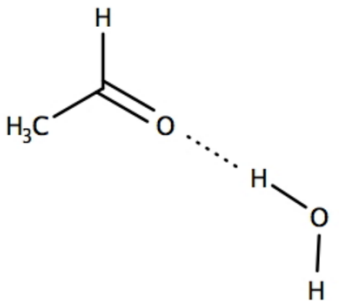
- All held together by dipole-dipole attractions, do not form Hydrogen bonds.
- All contain a C=O group, which results in them having a permanent dipole.
- The strength of dipole-dipole bonds means they have higher boiling points than similar sized alkanes.
- the longer the chain length, the higher the boiling point. This is due to the increased strength of dispersion forces.



Dipole-Dipole attraction between 2 ketone molecules

SOLUBILITY

- The lone pair of electrons on the carbonyl group can form hydrogen bonds with the partially positive Hydrogen atom on water.
- The strength of this interaction is enough to make small molecules of ketones and aldehydes soluble in water.
- Esters are insoluble in water as the alkyl groups are hydrophobic and the COO is polar but cannot form H bonds with H2O.

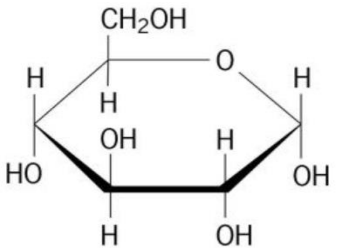


Hydrogen bond between water and an aldehyde

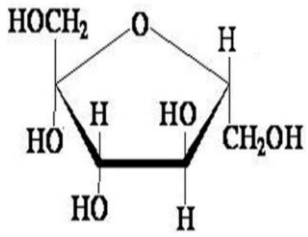
VISCOSITIES AND FLASHPOINTS OF ORGANIC MOLECULES

Viscosity is the ability of a substance to resist flow—determined by the strength of its intermolecular forces. e.g Honey has a high viscosity

Honey which is made up of glucose and fructose means there is a lot of hydrogen bonds between the molecules due to the large number of hydroxyl groups on both molecules.



Glucose



Fructose

Organic molecules with longer chain lengths, have higher viscosities, due to stronger dispersion forces between the molecules.

FLASHPOINT

The flashpoint is defined as the lowest temperature at which a liquid vapourises to ignite when an ignition source is present.

Fuel	Flashpoint (°C)
Ethanol	16
Petrol	–43
Diesel	>52
Jet fuel	>38

Flashpoint values of some common fuels

As the chain length of hydrocarbon fuels increases, both the boiling point and flashpoint increase.

REACTIONS OF ALKANES

As Alkanes are non polar, and bond stability is high, they are quite unreactive.
Usually, three reaction types:

- Combustion
- Substitution
- Addition

COMBUSTION REACTIONS

- Alkane used as **fuel**
- Burnt in **O_2**.
- Release large amounts of **heat** energy
- Common reactions are methane and octane

$$2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$$

SUBSTITUTION REACTIONS

- A reaction when one atom (in alkanes - hydrogen) is **replaced** by another atom/group (functional group).

  e.g. Making chloroethane (a local anaesthetic spray):

- Needs heat and UV to break apart Cl_2

$$CH_3CH_{3(g)} + Cl_{2(g)} \xrightarrow{\text{Heat/light}} CH_3CH_2Cl_{(g)} + HCl_{(g)}$$

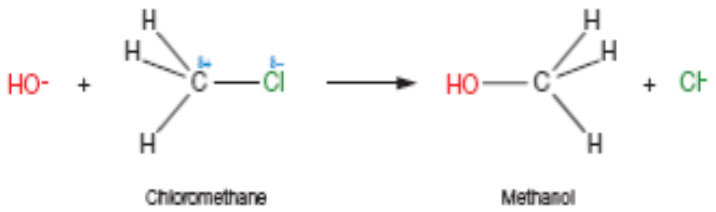
- This reaction will keep going until all of the hydrogens are replaced with Cl

- **Alkanols** can be produced through **substitution** of chloroethane:

  - chloroalkane now **polar**

  - due to +ve nature of Carbon (in C-Cl) bond, it can be attacked by a negative functional group (-OH) and hydroxy group is **SUBSTITUTED** on other side

  - OR C-Cl bond can be attacked and hydroxy substituted on Cl side



- **Amines** can also be formed via substitution of **chloroalkanes**:

  - ammonia reacts with chloroalkanes to produce an amine

$$RCl + \overset{\delta-}{N}H_3 \longrightarrow RNH_2 + HCl$$

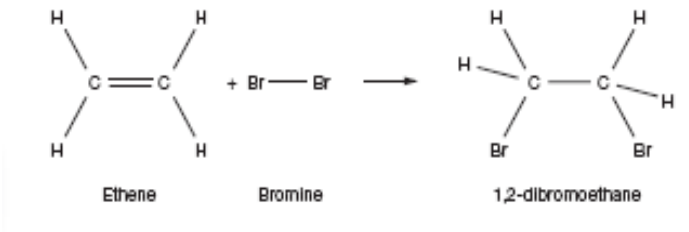
REACTIONS OF ETHENE (C_2H_4)

- Small molecule
- Colourless
- Faint sweet odour
- Unsaturated
- Non-polar (dispersion forces hold molecules together)
- Flammable gas
- Participates in addition reactions
- Polymerises to produce polyethene
- Only used as 'ethene' for ripening fruit

ADDITION REACTIONS

Alkenes can participate in addition reactions do to the presence of a reactive **Double bond.**

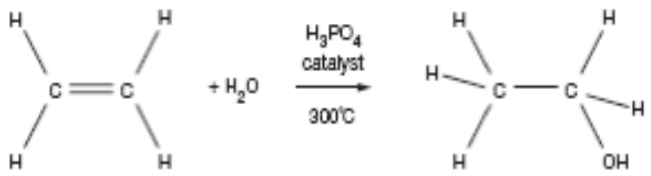
e.g. $C_2H_4 + Br_2 \rightarrow CH_2Br\text{-}CH_2Br$



This reaction could occur with any of the halogens (HCl, Cl_2, HI).

Ethanol is made industrially for **solvents and pharmaceuticals**, for use as a substitute for octane in petrol and for alcoholic drinks (usually by fermentation of sugar).

Ethanol can be made via **addition** reactions between ethene and steam (H_2O), with H_3PO_4 as a catalyst:



Important reactions to know:z

- **Chlorination:** ethene + chlorine —> 1,2-dicholoroethene
- **hydrogenation:** ethene + hydrogen —> ethane (catalyst—nickel)
- **hydration:** ethene + steam —> ethanol (phosphoric acid catalyst)
- HCl + ethene —> chloroethene + H2 (AlCl3 catalyst)

Bromine test:

- Br2 is red-brown and readily undergoes addition reactions with an alkene which causes the solution to turn colourless.
- This colour change is used as a test for unsaturation>

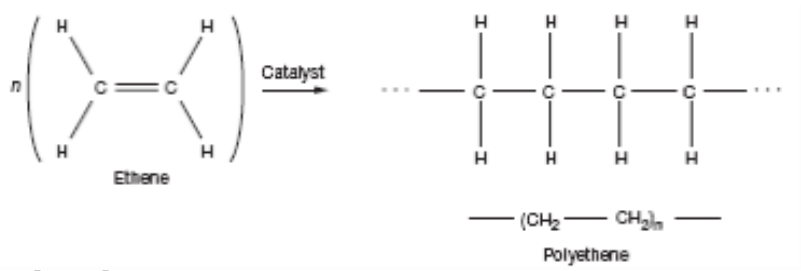
ADDITION POLYMERISATION

MONOMER: one unit

POLYMER: large macromolecules composed of many repeating units called monomers

ADDITION POLYMERISATION:

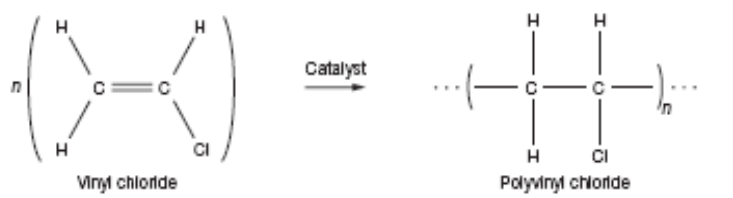
- occurs when unsaturated monomers react under high pressure, temperature and with an appropriate catalyst.



- general formula: [C-C-]n
  e.g polyethene, polypropene, polystyrene

PVC – Polyvinyl chloride (packaging)

made from an **addition polymerisation** reaction between the **monomer** of vinyl chloride (vinyl chloride comes from ethene):



REACTIONS OF ALKANOLS

1. FORM AMINES VIA SUBSTITUTION

$$CH_3CH_2OH(g) + NH_3(g) \xrightarrow[400^oC]{alumina} CH_3CH_2NH_2(g) + H_2O(g)$$

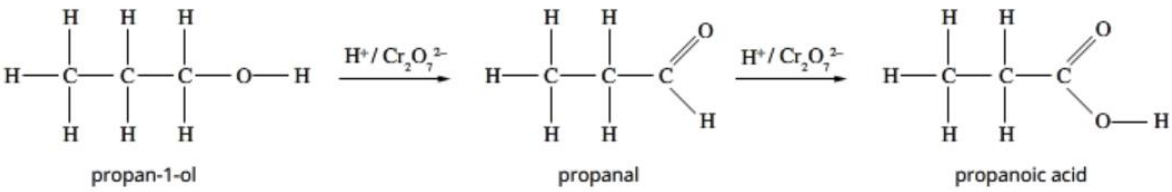
* Note catalyst and 400°C conditions

2. FORM ALDEHYDES AND CARBOXYLIC ACIDS VIA OXIDATION

- oxidation of primary alcohols (OH bonded to one carbon)

$$CH_3CH_2OH(aq) \xrightarrow{O_2(g)} CH_3COOH(aq)$$

- It can also be made rapidly, commercially:

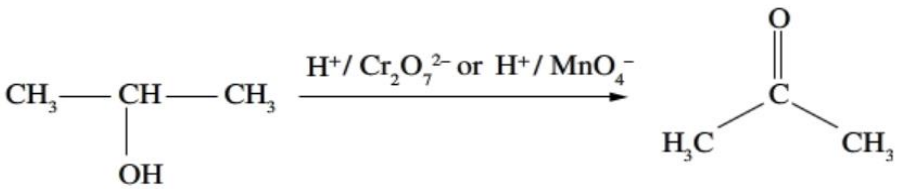


Two steps:

- In the first stage the primary alcohol is oxidised to an aldehyde.
- In the second stage, further heating of the mixture in the presence of the oxidising agent oxidise the aldehyde to a carboxylic acid.
- Requires strong inorganic oxidising agents such as acidified potassium permanganate (KMnO4) or acidified potassium dichromate (K2Cr2O7)

3. FORM KETONES VIA OXIDATION

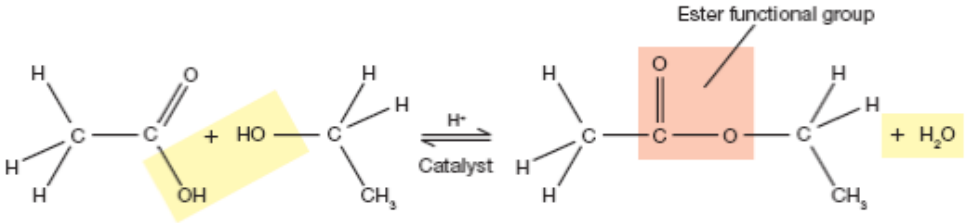
When secondary alcohols are exposed to a strong oxidising agent they form ketones.



Note: Tertiary alcohols do not undergo oxidation when exposed to acidified MnO_4^- or $Cr_2O_7^{2-}$ as there is no C-H bond to break on the carbon attached to the hydroxyl group.

Type of alcohol	Products
Primary (1°)	Mild conditions produce aldehydes. Higher temperatures and longer reaction times produce carboxylic acids.
Secondary (2°)	Ketones
Tertiary (3°)	No products because tertiary alcohols are resistant to oxidation by these oxidising agents.

4. FORM ESTERS BY REACTING WITH CARBOXYLIC ACIDS



REACTIONS OF CARBOXYLIC ACIDS

1. BASES

All carboxylic acids are **weak monobasic acids**, reacting with water (or bases) to form a weakly acidic solution.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

2. REACTIVE METALS (Redox) forming $H_{2(g)}$ + $salt_{(aq)}$

3. Metal CARBONATES → CO_2 + H_2O + Salt

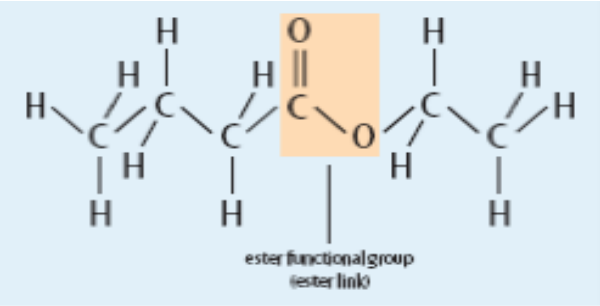
4. ALKANOLS TO FORM ESTERS:

5. Alkalis: RCOOH + NaOH —> RCOONa + H2O

ESTERS

Esters are:

- -COO-
- organic molecules
- varying sizes
- volatile—must be a gas in order to be smelt
- responsible for various smells a flavours in ice-cream, lollies and perfumes
- formed from an organic alcohol and an organic carboxylic acid



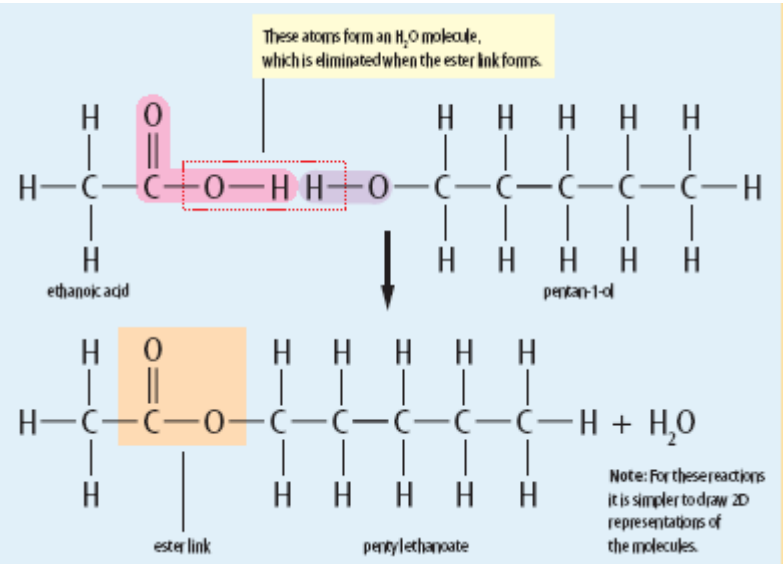
Reactions in which two molecules join as a result of a reaction between their functional groups, and the release of a small molecule (e.g. water, HCl), are **condensation reactions**. (When a condensation reaction produces an ester, it also is classified as an **esterification reaction**).

The general equation for the formation of an ester is:

RCOOH(l) + R'OH(l) → RCOOR'(l) + H2O(l)
carboxylic acid + alkanol = ester + water

where R and R' are hydrocarbon groups.

Requires a catalyst (usually liquid **sulphuric acid**) which is a dehydrating agent that drives the reaction forwards by removing water (Le Chatliers)



Structural
Chemical
eqn

Nomenclature:

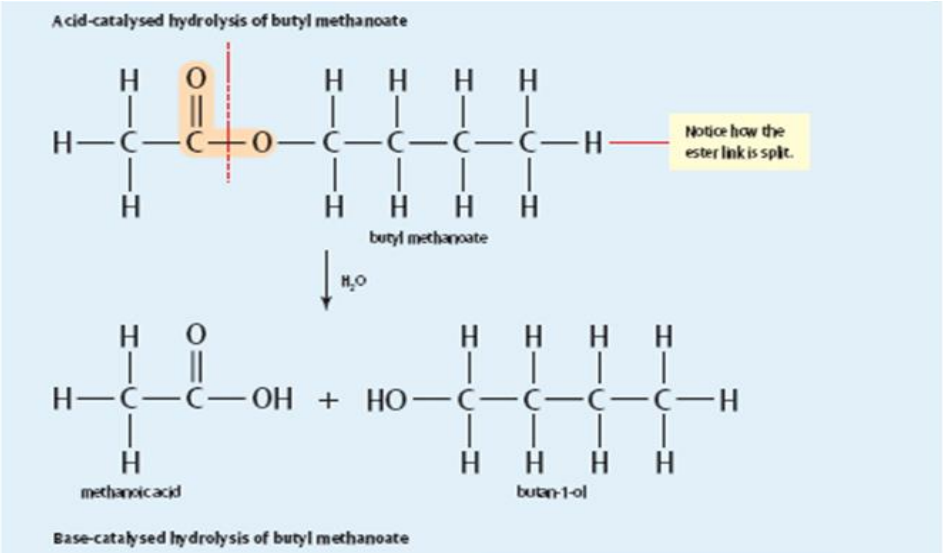
- **alkanol then carboxylic acid**
- alkanol – to **'yl' replaces 'anol'**
- carboxylic acid – **'ate' replaces 'ic acid'**
- **e.g ethyl pentanoate**

Hydrolysis of Esters:

The general overall equations of these **hydrolysis** (**reverse** of condensation reactions) reactions are:

Acid-catalysed hydrolysis:

RCOOR'(l) + H2O(l) → RCOOH(l) + R'OH(l)
ester water = carboxylic acid + alkanol



Base-catalysed hydrolysis:

RCOOR' (l) + OH- —> RCOO- (aq) + R'OH (l)
ester + hydroxide ions —> salt of carboxylic acid + alcohol

POLYESTERS

A polymer of carboxylic acids and alkanols (alternating). A polymer formed by an interaction of functional groups is called **condensation polymerisation** (a small molecule is also eliminated).

For the carboxylic acid and alkanol to react at both ends, they require **double** the functional groups. This can occur in two different ways:

1. **one** type of monomer with both functional groups:

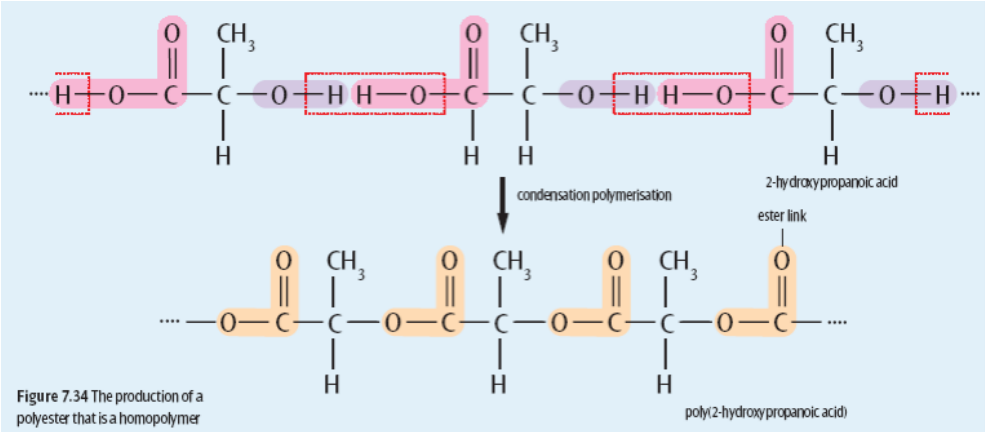


Figure 7.34 The production of a polyester that is a homopolymer

2. **two** types of monomers - each having two of the same functional group (**dicarboxylic** acid and **diol**):

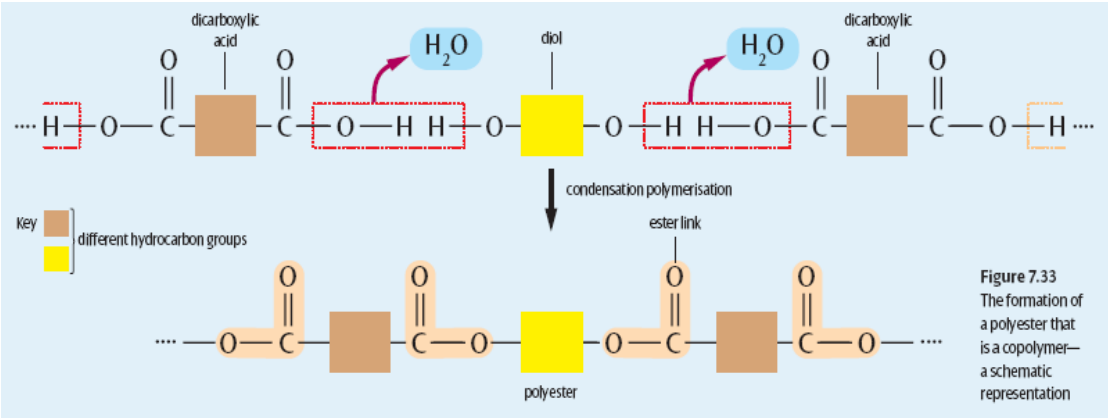
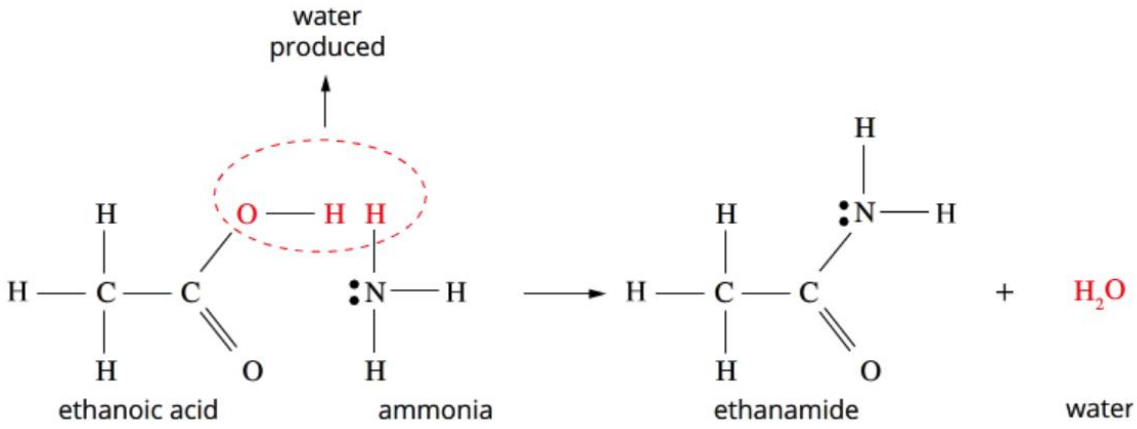


Figure 7.33 The formation of a polyester that is a copolymer—a schematic representation

When all of the monomers in a polymer are identical, it is known as a **homopolymer**. When there are two or more different monomers present in a polymer, it is called a **copolymer**.

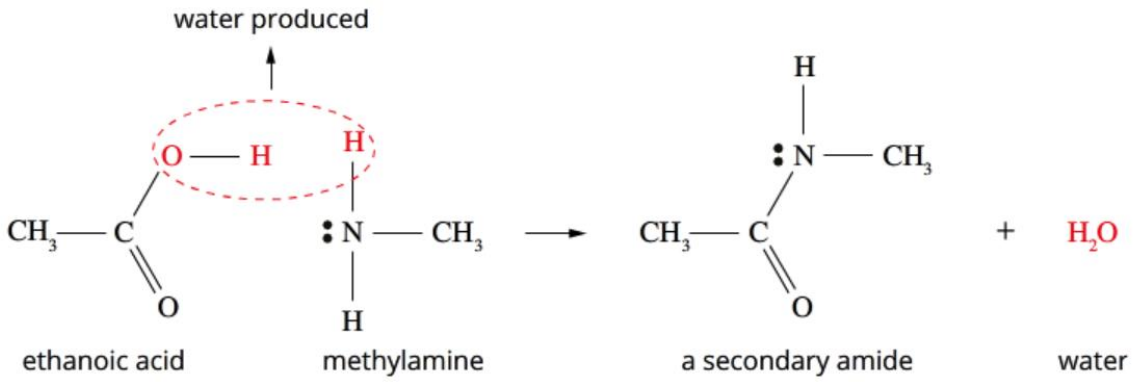
REACTIONS OF CARBOXYLIC ACIDS TO FORM AMIDES

Primary amides are formed when carboxylic acids react with Ammonia. This is also a condensation reaction.



Ethanoic acid and ammonia produces ethanamide (primary amide)

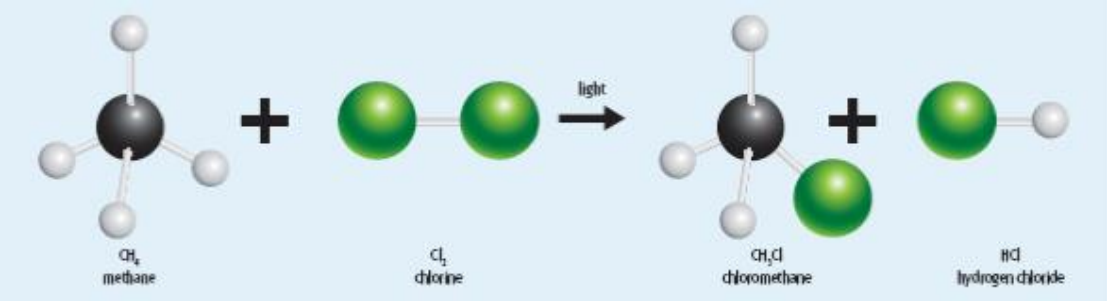
Secondary amides are formed when a carboxylic acid reacts with a primary amine.



ORGANIC PATHWAYS

Halogenation:

Replacement of 1 or more **hydrogen** atoms with a **halogen** (**substitution** reaction)



Hydrogenation:

- Addition of hydrogen
- This is not a useful reaction as you can make many more useful products from ethene than ethane

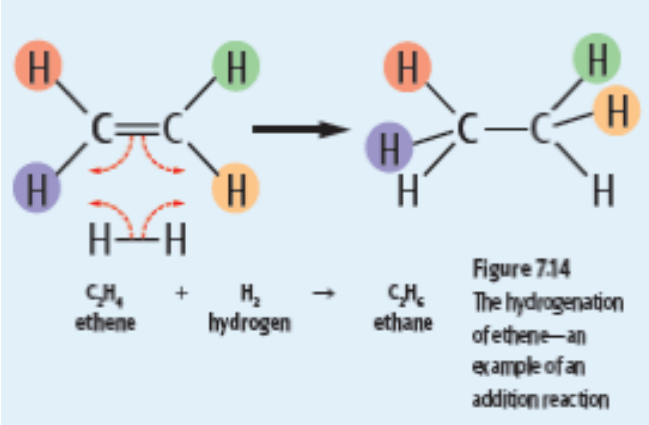


Figure 7.14
The hydrogenation of ethene—an example of an addition reaction

PATHWAYS FOR ALKANES

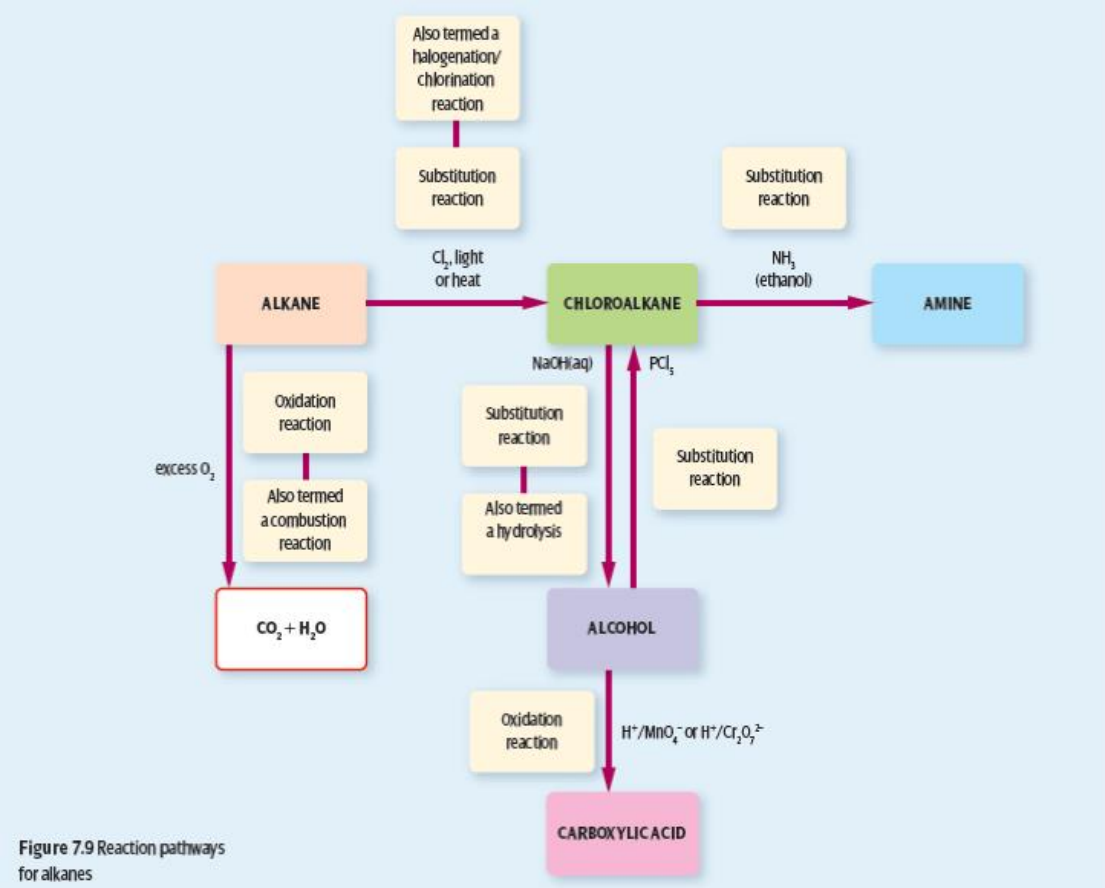
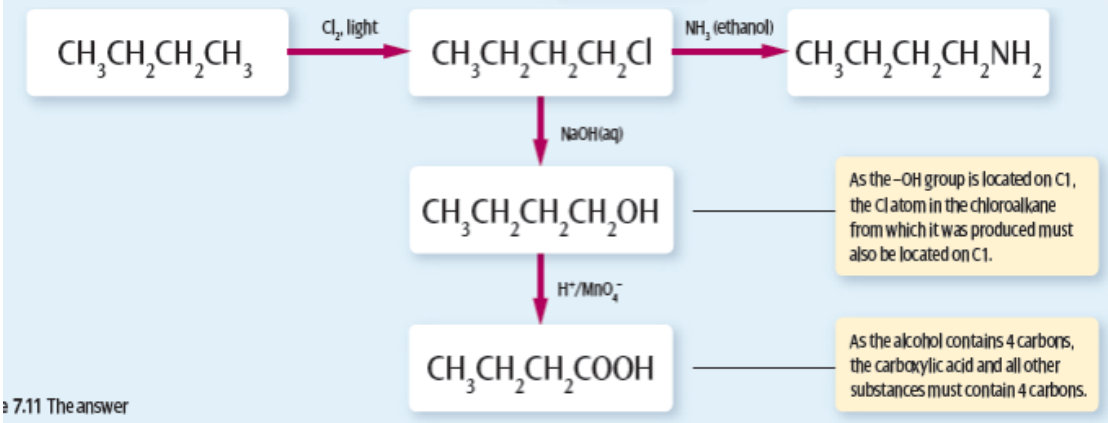


Figure 7.9 Reaction pathways for alkanes

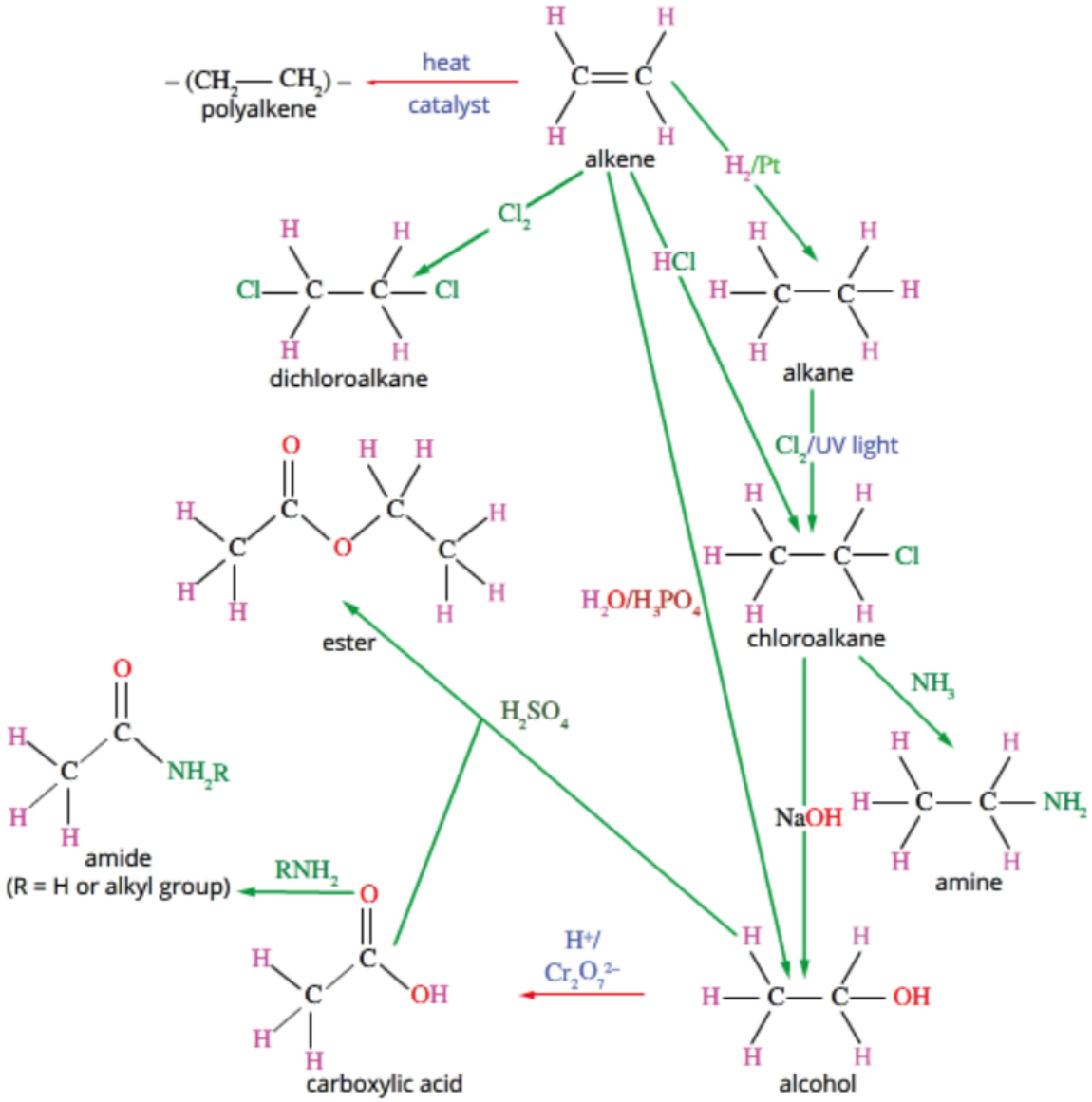


e 7.11 The answer

Alkanes can form…

- haloalkanes (substitution) —> amines (substitution with NH3)
- haloalkanes (substitution) —>alcohols (substitution with NaOH)
- haloalkanes (substitution) —>alcohols (substitution with NaOH)—> ketones (oxidation) or carboxylic acids (oxidation) *product depends on whether the alcohol was primary (acid) or secondary (ketone)

PATHWAYS FOR ALKENES



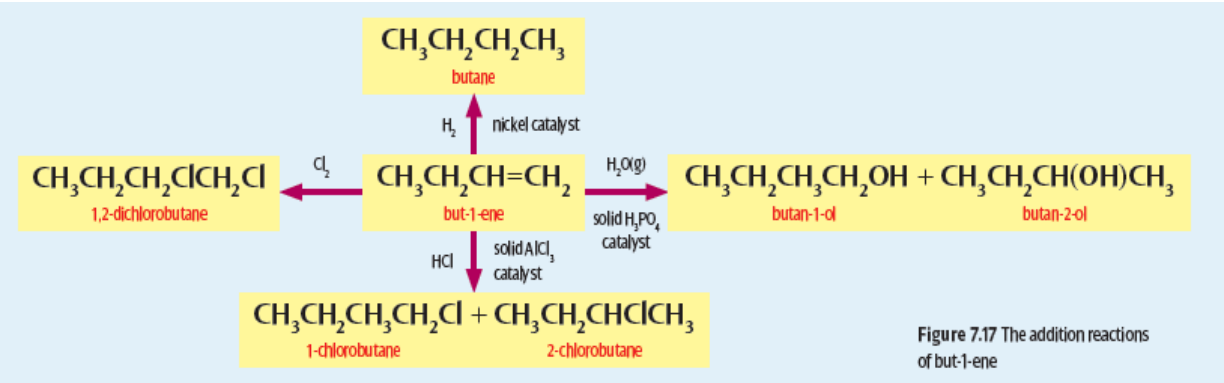


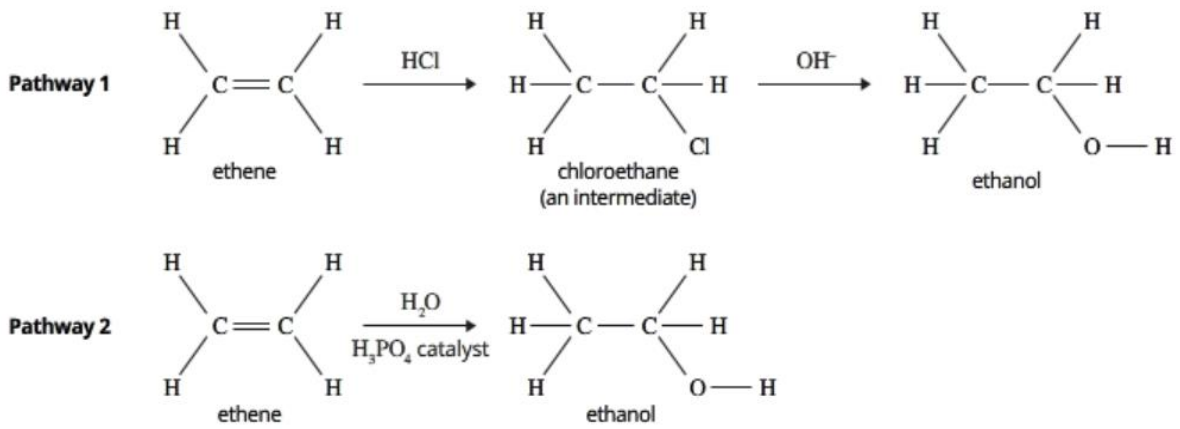
Figure 7.17 The addition reactions of but-1-ene

Alkenes can form…

- polymers (needs high temp and a catalyst)
- alcohols (addition of H2O with H3PO4 catalyst)
- alkanes (addition of H2 with nickel catalyst)
- haloalkanes (addition of HCl)
- alcohols (addition of H2O with H3PO4 catalyst)—> ketones (oxidation) or carboxylic acids (oxidation) *product depends on whether the alcohol was primary (acid) or secondary (ketone)

MAKING ETHANOL

1. ethene —> chloroethane (addition of HCl)—> ethanol (addition of NaOH)
2. ethene—> ethanol (addition of H2O and H3PO4 catalyst)



YIELD AND ATOM ECONOMY

PERCENTAGE YIELD

The percentage yield shows us the efficiency of the production process and can be determined by:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times \frac{100}{1}$$

QUESTION 1
Calculate the overall percentage yield for the preparation of D from A if it proceeds by a 3 step multi-step synthesis:

A → B followed by B → C followed by C → D

The yield of A → B is 90%, the yield of B → C is 80% and the yield of C→ D is 60%.

Answer: 0.9 x 0.8 x 0.6 = 0.432%

ATOM ECONOMY

- *measures the efficiency of a reaction: gives a measure of atoms wasted when making a desired product*
- the higher the atom economy, the more efficient the reaction
- e.g 100%=all reactant particles converted to products particles

$$\text{Atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

QUESTION 1
What is the atom economy of the reaction below in producing water?

$CH_4(g) + 2O_2(g) \Rightarrow 2H_2O(g) + CO_2(g)$

Answer

Step 1 Calculate the total mass of reactants as per equation.
=> 16.0 + 2 X 32.0 = 80.0 g

Step 2 Calculate the mass of water as per equation
=> 2 X 18.0 = 36.0 g

Step 3 Calculate the atom economy
=> (36.0 / 80.0) X 100 = 45.0%

QUESTION 2
Consider the formation of ammonia via the Haber process.

Nitrogen is reacted with hydrogen to produce ammonia, according to the equation below.

$N_2(g) + 3H_2(g) \Rightarrow 2NH_3(g)$

The hydrogen, however, comes from the reaction between methane and water according to the equation below.

$CH_4(g) + H_2O\ (g) \rightarrow CO(g) + 3H_2(g)$

Calculate the atom economy for the formation of ammonia.

Answer

SPECTROSCOPY

Based on the facts that:

- atoms and molecules absorb and emit electromagnetic radiation of specific energies
- atoms and molecules undergo a change when the absorb electromagnetic radiation
- different part of the electromagnetic spectrum (see below) affects atoms or molecules in different ways

	radio waves	microwave	infrared	ultraviolet	X-rays	γ-rays
Frequency (Hz)	10^{6} 10^{7} 10^{8} 10^{9}	10^{10} 10^{11}	10^{12} 10^{13} 10^{14}	10^{15} 10^{16}	10^{17} 10^{18}	10^{19} 10^{20}
Wavelength (m)	10^{3} 1		10^{-3}	10^{-6}	10^{-9}	
Spectroscopic technique	nuclear magnetic resonance (NMR)	microwave	infrared (IR)	ultraviolet (UV)	X-ray	gamma ray

atomic absorption (AAS)

INFRA - RED SPECTROSCOPY

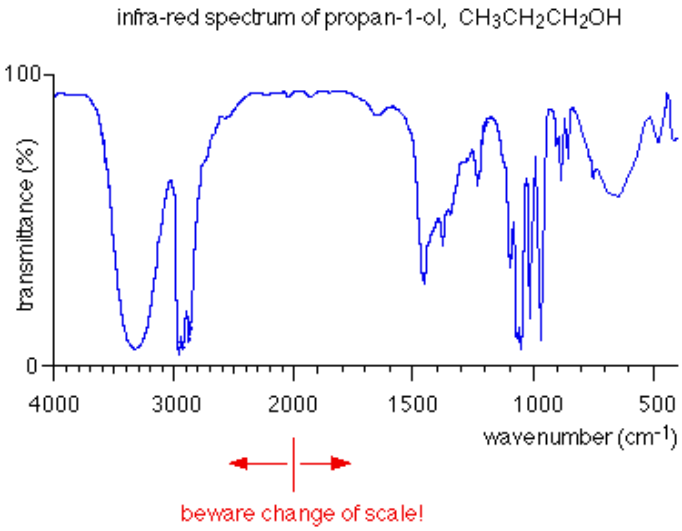
- IR energy has a lower energy (and larger wavelength) than visible or UV light—this makes it too weak to promote electrons to a higher energy level but is sufficient to cause b**ending and stretching** of molecules
- this is due to the **electrostatic forces of attraction** between negative charged shared electrons and a positive nuclei (covalent bond) which can bend and stretch
- just as electrons only have fixed values of energy, **molecules can only have discrete values of vibrational energy** (quantised)—the bonds can only stretch/bend at specific frequencies
- frequency at which it can bend and stretch is dependent on the masses of atoms and strength of bonds

  ➢ **strong** bonds and **light** atoms—absorb at **high** wavenumbers
  ➢ **weak bonds** and **heavy** atoms—absorb at **low** wavenumbers

- ***only polar molecules absorb IR radiation as they have dipoles***

INFRA-RED SPECTRUM

A graph is produced showing how the percentage transmittance varies with the frequency of the infra-red radiation:



- atoms in molecules vibrate all the time as they posses the same energy, when you irradiate (expose to radiation) them with IR radiation, each bond will absorb the precise amount according to its natural vibration—this increases the magnitude of the vibration in the bond
- Y axis—percentage transmission
- X axis—wavenumber
- energy is proportional to the reciprocal of wavelength=wavenumber (*units cm-1*) and proportional to frequency

$$E \propto \frac{1}{\lambda} \qquad E \propto \nu$$

- 'troughs' in the graphs are called ***absorption bands*** occur when IR radiation is absorbed to excite bonds to a higher state of vibration—either stretching or bending

Bond	Functional Group	Absorbance (cm-1)	Shape
O—H	alcohols	3200-3600	strong/broad*
O—H	carboxylic acids	2500-3200	medium/very broad*
C=O	aldehydes/ketones/carboxylic acids/esters	1680-1750	strong and sharp
C—O	alcohols/esters/ethers	1050-1400	medium
C—H	alkanes/alkenes	2850-3100	medium
C—C		1200	
C-Cl		750	
C-Br		600	

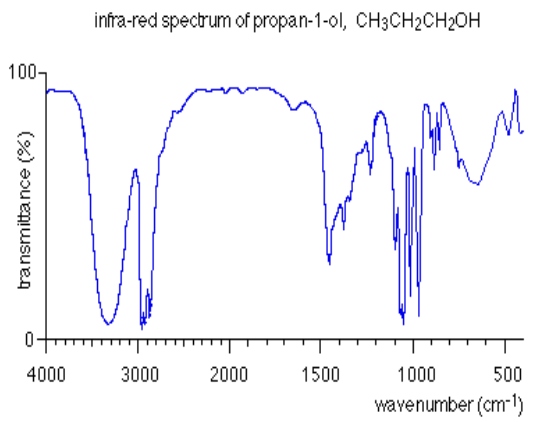
*broadness is due to Hydrogen Bonding

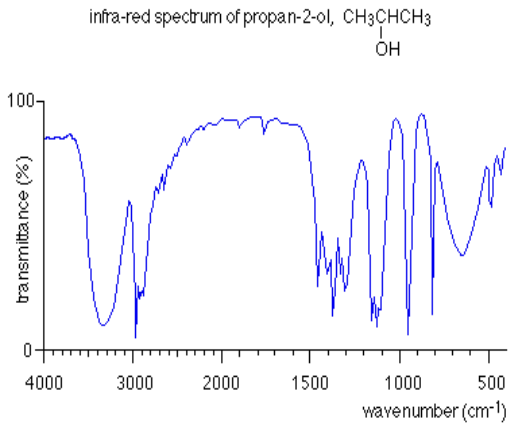
FINGERPRINT REGION

- the right hand side region (1500 to 500 cm-1) is called **the fingerprint region**—usually contains a very complicated series of absorptions
- each compound produces a different pattern of troughs in the fingerprint region

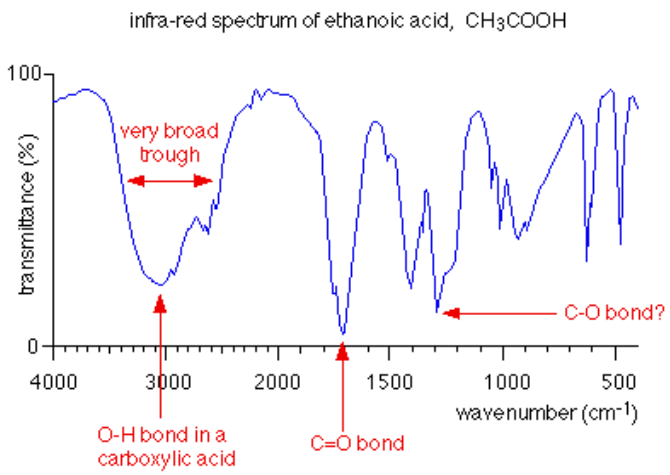
Consider the IR spectra of propan-1-ol and propan-2-ol:

Some of the troughs are easily used to identify particular bonds in a molecule. The big trough at the left-hand side of the spectrum is used to identify the presence of an OH bond. This identifies the compounds as alcohol. The fingerprint region would allow the researcher to identify the particular alcohol present.



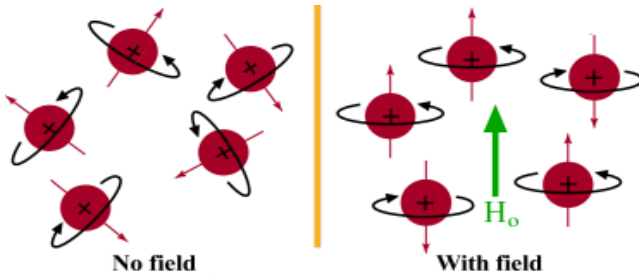


INTERPRETING AN INFRA-RED SPECTRUM

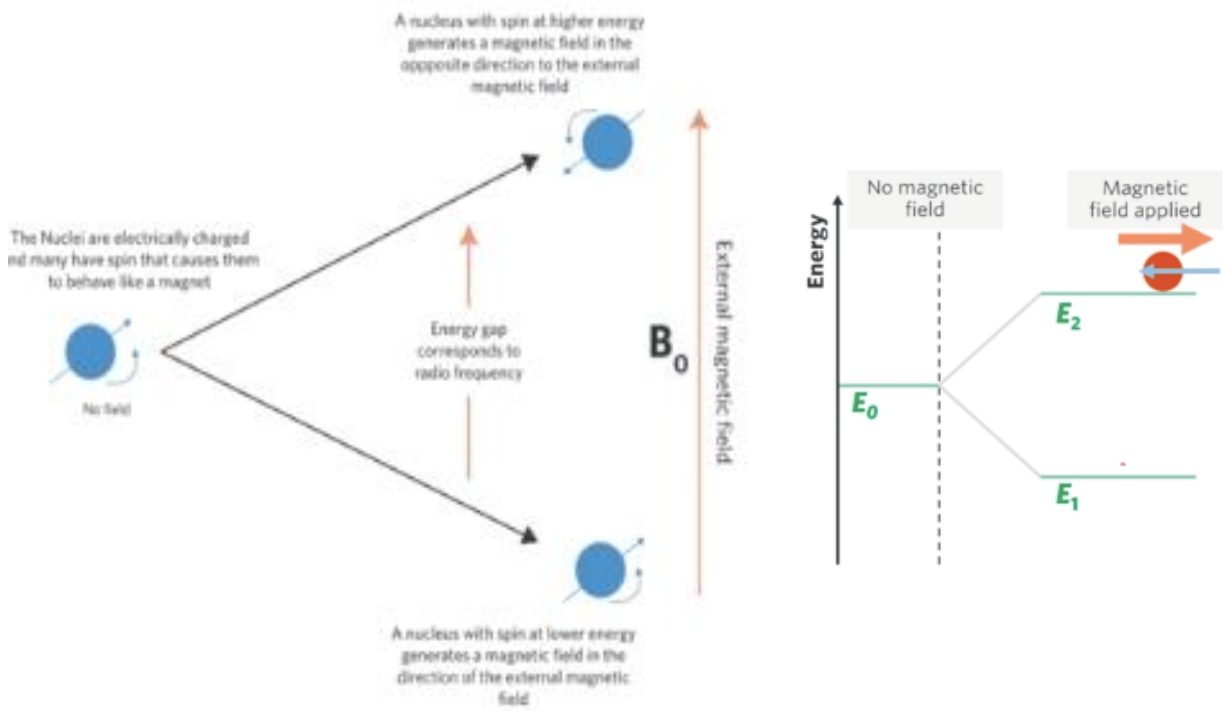


NMR SPECTROSCOPY
PROTON & C -13

- exploits the magnetic properties of a certain metal to determine the structure of an organic compound
- uses the energy in the radio frequency range which is too low to cause emission spectra or vibrational (IR) transitions
- nucleons (protons and neutrons) are spinning on their axis (nuclear spin) in either up or down directions, this allows them to interact with radio waves
- in order to spin, the nucleus needs an odd number of protons and an odd number of neutrons (creates a magnetic field so that the atoms behave like magnets) e.g C13
- nuclear spin oriented with a magnetic field (same direction) results in a lower energy that than random spin, oriented against (opposite direction) the field results in a higher and less stable energy state



- eventually the nuclei flip back to lower energy spin—releasing energy
- energy release depends on the type of nucleus and chemical environment (atoms and electrons surrounding the atom)

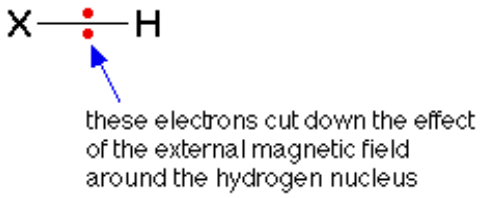


Note:

- the more highly populated state is the lower energy spin aligned
- E1-E2 =hv (radio-frequency energy)
- it is possible to cause nuclei that are in the lower energy state to “spin flip” into the higher energy state by supplying energy—this energy is called ***resonance*** (delta E)
- energy is released when the nucleus relaxes and the same radio frequency is emitted depends on the extent of shielding

H(PROTON) NMR

- provides information about the number and type of hydrogen nuclei by finding the number of distance hydrogen environments present in the molecule
- if atoms are surrounded by the same environment absorb the same environment (equivalent)
- ***nuclear shielding:*** as electrons around the nucleus also have a spin, they also have a magnetic field that shield that nucleus from the applied magnetic field, influencing the amount of energy required to change spin state



- neighbouring atoms also affect the energy required to change spin state

INTERPRETING NMR SPECTRA

HYDROGEN ENVIRONMENTS

- hydrogen atoms with the same surrounding atoms have the same hydrogen environments—these absorb the same frequency (shown as one peak on the spectrum)
- the number of peaks gives the number of different chemical environments that the H1 nuclei are occupying
- area under the peak: tells you the number of hydrogens in that environment (as a ratio)
- all frequencies are giving as a difference with that of TMS as TMS is:
  - ➢ chemically inert
  - ➢ has twelve hydrogens in the same chemical environments
  - ➢ acts as the 'zero' — TMS produces a peak on the spectrum at the extreme right-hand side. Almost everything else produces peaks to the left of it.
  - ➢ this difference in energy is called **chemical shift** (units are ppm)

Each different hydrogen environment will give its **own peak** on the graph (as it requires a different increase in the external magnetic field to bring it back into resonance).

e.g. $CH_3CH_2CH_2OH$ $CH_3CH_2CH_2CH_3$

asymmetrical
4 H environments

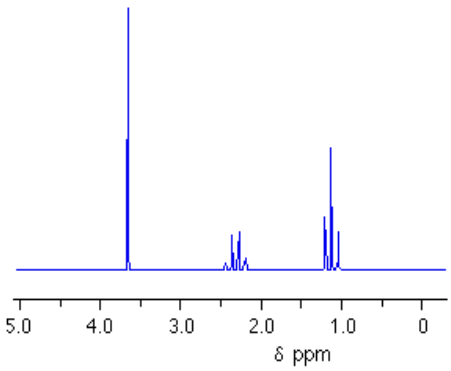
symmetrical
2 Hydrogen environments

^{1}H Proton NMR Spectroscopy – Chemical Shifts					
Functional Group		**Chemical Shift**	**Functional Group**		**Chemical Shift**
Alkane	**C-C**	**0-2.0**	**Acid**	**-COOH**	**10-13.5**
Alkene	**C=C**	**4.3-7.3**	**Ether**	**$-OCH_3$**	**3.9**
Alkyne	**C≡C**	**2.0-3.0**	**Amine**	**$-NH_2$**	**0.5-3.0**
Alcohol	**-OH**	**0.5-4.0**	**Aromatic**	**C_6H_6**	**6.0-9.0**
Aldehyde	**H C=O C**	**9.0-10.0**	**Ketone**	**C C=O C**	**2.0-3.0**

HIGH RESOLUTION NMR-SPECTRA

- involves splits—either singlets, quartets or triplets to give a more detailed representation of the chemical environments
- neighbouring H atoms will affect the strength of the external magnetic field to which another H is subjected to—called spin-spin splitting/coupling
- if a H1 has n protons as its nearest neighbours on C atoms its absorption will be (n+1) peaks

high resolution nmr spectrum for methyl propanoate, $CH_3CH_2COOCH_3$



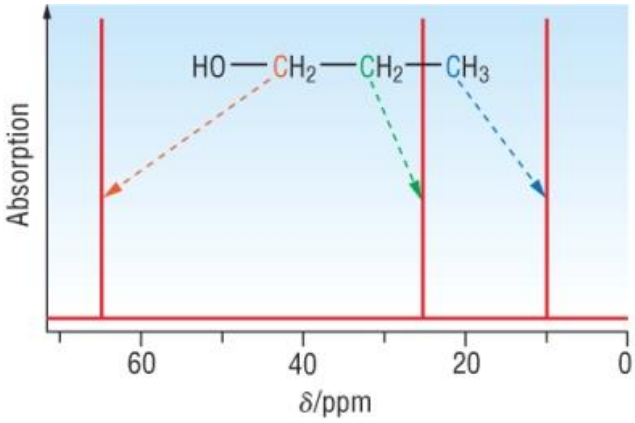
**if neighbours are in an equivalent chemical environments, they wont cause a split and wont count as neighbours.*

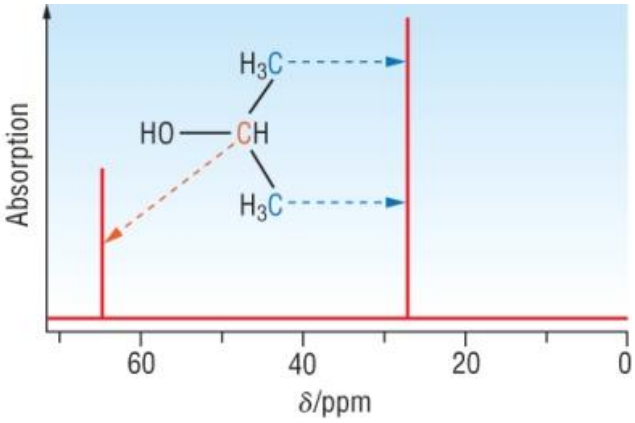
Number of sub-peaks in the cluster	**Number of H's on the C next door**
Singlet	next door to carbon with no hydrogens attached
Doublet	next door to a CH group
Triplet	next door to a CH_2 group
Quartet	next door to a CH_3 group

Information	Observation
# of H environments	# of signals
Type of H environments	position of signal (chemical shift)
# of neighbouring H	splitting pattern (n+1)
# of H in each environment	relative peak area

13C NMR SPECTROSCOPY

- principles are the same as those for H NMR
- Carbon-13 is the second most useful (to hydrogen) atom for providing information
- only the peak number is important as each spectrum gives only single lines for each carbon
- the size in the shifts depends on the proximity of the electronegative atoms e.g in CH3CH2OH, the C in CH2 will have a larger shift because it is closer to oxygen
- **Note:** ^{13}C NMR spectra are run in a way that eliminates any effects from neighbouring H's ('proton decoupled')





MASS SPECTROSCOPY

- measures the effect of exposure to magnetic or electric fields
- used together with IR, GC and NMR to determine the structure of a compound
- uses the gaseous sample of organic compounds

BACKGROUND

Based on the principle that if two masses move horizontally at the same speed, that of a lighter mass will have a greater deflection when a force is applied

- atoms and molecules can be deflected by magnetic fields
- this only occurs if the atom/molecule is first turned into an ion (needs a charge)

PROCESS

The mass spectrometer separates out the different isotopes according to their mass and calculates their relative abundance.

1. ***Vaporisation:*** mass spectrometer vaporises the compounds/elements being investigated

2. ***Ionisation:*** when a high energy electron collides with a molecule it will ionise it by knocking away one or more electrons—this gives a parent molecular ion (m+)

   M + e- —> M+ + 2e-

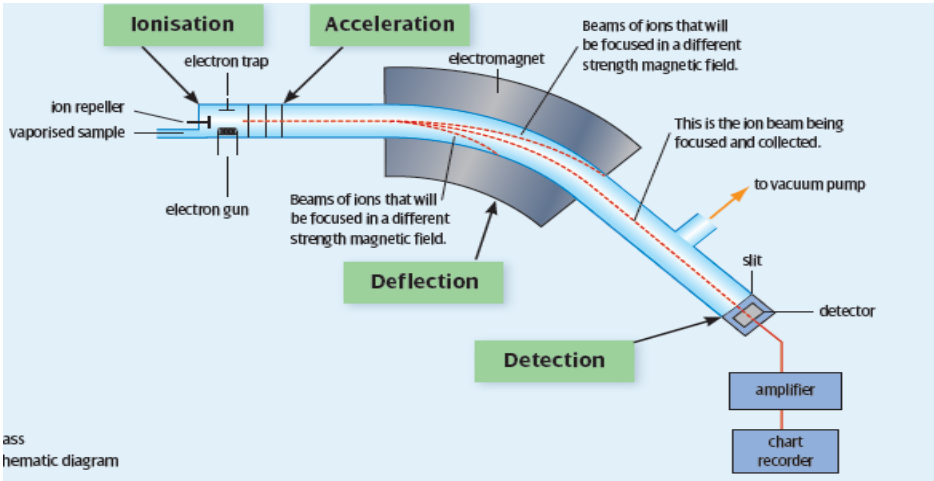
   all peaks by the spectrometer are due to positively charged atoms/molecules

3. ***Acceleration:*** ions accelerated by an electric field so that they all have the same kinetic energy

4. ***Deflection:*** ions deflected by magnetic field according to their mass

- lighter molecules deflect more
- the more positively the ion is charged, the more it is deflected
- these two factors combine to give the **mass/charge ratio (m/z)** e.g an ion of mass 56 and charge of +2 would have a 28m/z

5. ***Detection:*** the beam of ions passing through the detector is measured electrically—the current is due to cations reaching detector



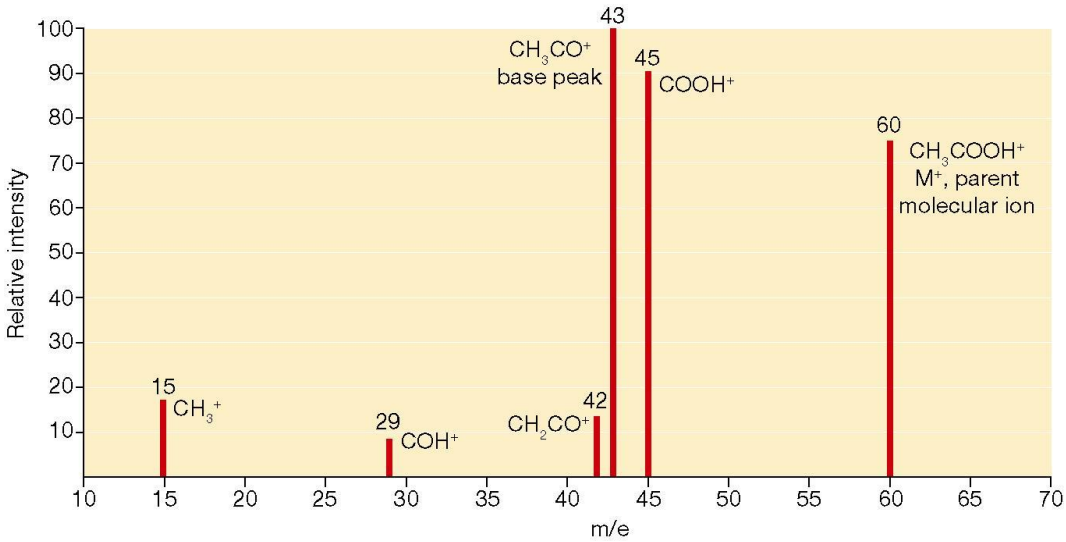
SPECTRA ANALYSIS

The peaks in the spectrum are formed by either:

- ➢ **The occurrence of isotopes of the atoms found in the molecules**
- ➢ **fragmentation of molecules into a large number of positive ions**

The mass spectrum is composed of a set of spikes:

- vertical axis is either relative intensity or relative abundance (same thing)— relates to the current received, the higher the line, the more abundant the isotope
- horizontal axis relate to m/e to show mass of each isotope
- highest m/z value is the **parent ion**
- small peaks may occur at M+1 due to the natural abundance (1%) of C13—the more carbon atoms, the larger this peak



MASS SPECTRA – FRAGMENTATION

- When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind the parent ion:

  $M + e^- \rightarrow M^+ + 2e^-$

- Residual energy from the collision may cause the molecular ion to further fragment into small ions and uncharged

- Free radicals are shown with the dot and are highly reactive (dot is unpaired electrons)

- The fragmentation is random, and will simply be a somewhere in the parent ion

- Fragments of one atom can also occur

- The simplest case is an ion breaks into two parts—a positive ion and an uncharged free radical ***M+ will fragment:***

  M+ → A+ + ·B ***<u>or</u>*** ***M+ → ·A + B+***

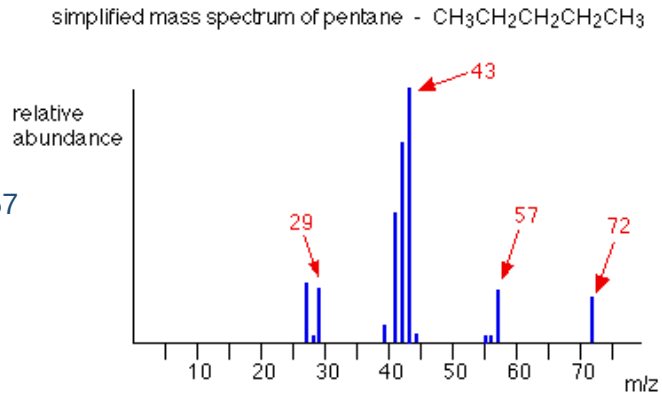
  - *free radicals won't produce a line on the mass spectrum, they are collected via a vacuum pump*

  - *only charged particles are accelerated, deflected and detected (produce a line on the stick diagram)*

- within an element, each line represents a different isotope of the element

- within a compound, each line represents a different fragment produced when the ion breaks up

- the tallest line on a stick diagram is called the **base peak—**most common ion fragment formed either because there are many ways it can be produced or because it is particularly stable



Question Types:

Account for the line at m/z=57

# of Carbon = 4 (4x12 =48) + 9 Hydrogens = 57
= C4H9+

Produced by fragmentation of pentane to produce C3H9+ and CH3 (a free radical)

APPLICATIONS

- Pharmaceutical samples
- Medical screening
- Environmental samples (contaminants in water)
- Geological samples (oil and gas)

CHROMATOGRAPHY

- A technique used to separate substances present in a mixture e.g food, perfumes
- can be performed with very small samples and low concentrations
  - ➢ all techniques include a mobile phase and a stationary phase—the mobile phase flows over the stationary phase
  - ➢ a sample containing mixture is placed in the mobile phase—components absorb onto the stationary phase and desorb onto the mobile phase
  - ➢ the speed at which each component moves depends on **strength of the adsorption** onto the stationary phase and its **solubility** in the mobile phase
  - ➢ the components separate as they undergo these two processes to a different degree

Adsorption:

adhesion of molecules to the surface of a stationary phase—strength depends on polarity and Mr of component

Desorption:

interaction between a component and the mobile phase, the solubility of the component

Stationary phase:

silica gel or Al2O3 (alumina TLC), the role is to retard the movement of components across the surface of the stationary phase

Mobile phase:

dissolves the sample and sweeps it across the stationary phase—it is the solvent in TLC and in HPLC

- must be inert to component

  Retardation Factor: distance moved by component from the origin/distance moved by solvent from the origin

  - will always be less than one
  - the great the Rf, the weaker the strength of adsorption, the greater the strength of desorption

Retention time:

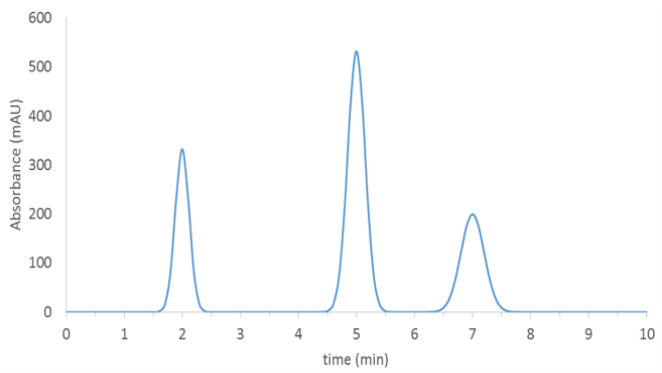
- Time taken for a component to pass through the column
- Dependent on: nature of stationary phase, nature of mobile phase, polarity of component, Mr of component (Rt increases as Mr increases)
- Factors: temperature, pressure, length of column

Eluent:

mobile phase used in HPLC

Chromatogram:

- graphical representation of data of HPLC
- indicates retention time (X axis, this is qualitative), absorbance (Y axis, this is quantitative) and relative concentration (area under the curve)
- highest retention time = most strongly adsorbed to stationary phase
- as Mr increases, Rt increases (takes longer time to pass through to detector)



PAPER CHROMATOGRAPHY: QUALITATIVE

- mobile phase: can be polar (e.g ethanol or water) or non polar (e.g hexane)
- stationary phase: paper—cellulose (polar)
  - ➢ paper with a dot of ink is placed in solvent
  - ➢ solvent travels up the paper through capillary action, taking the dyes with it (constant adsorption onto stationary phase and desorption into mobile phase)
  - ➢ the dye that travels the highest is most attracted to the solvent (mobile phase)—greater desorption
  - ➢ the dye that travels the least highest is most attracted to the stationary phase—greater absorption

THIN LAYER CHROMATOGRAPHY: QUALITATIVE

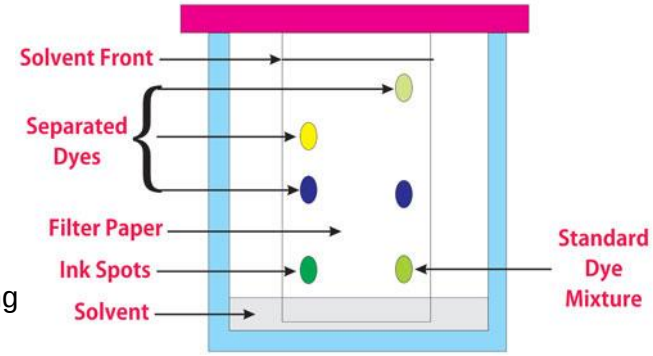
**separates via polarity*

Stationary phase:

alumina Al2O3 coated onto a glass plate

Liquid mobile phase

- colourless compounds are made visible when viewed under UV light or are sprayed by fluorescing compounds



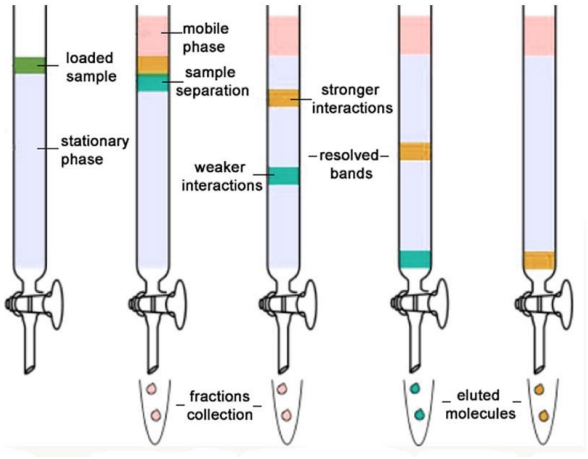
Results:

- retardation factor (Rf) is compared to known samples under same conditions
- *Rob's special question*: the compounds can be tested TWICE by rotating the glass plate 90 degrees and running the compounds using a DIFFERENT solvent—this will give more accurate results when differentiating between compounds of similar Rf values in the first trial

Advantages over paper chromatography:

- faster
- better separation of components
- more sensitive

COLUMN CHROMATOGRAPHY



**separates via polarity*

Stationary phase: alumina Al2O3 coated onto a glass beads

Liquid mobile phase

- sample mixture placed at the top of the column and the mobile phase is also introduced at the top of the column
- separation occurs as the components travel at different rates down the column
- eluent is the solvent released from the column
- compounds determined by retention time—time taken to reach the detector

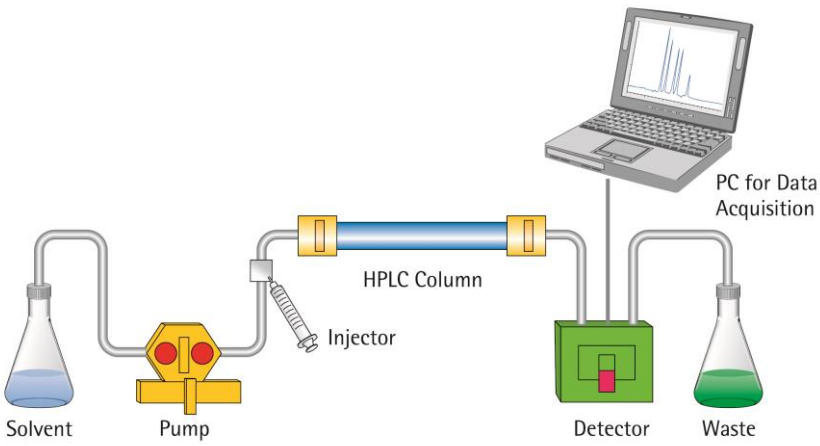
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

- used to analyse organic compounds with high boiling points and those that decompose when heated e.g proteins, sucrose, caffeine (Mr>300)
- based off column chromatography
- can analyse compounds in very small concentrations
- commonly used as reverse HPLC—uses a non polar stationary phase and a polar mobile phase to enhance the separation of components

Column (stationary phase): tightly packed with small solid particles (silica or Al2O3)—increases the surface area and therefore can better separate the mixture

Mobile phase: liquid call the eluent, passed through a beam of UV radiation

Steps:



1. Eluent forced through column at high pressure (to make the process faster)
2. same injected into column
3. mobile phase (eluent) pumped through column and carries the sample through the column
4. sample adsorbs and desorbs to the stationary phase
5. as the samples are eluted (removed) from the column, they are detected by a device—the time taken to be detected by the device is the retention time

INTERPRETING RESULTS

Quantitative:

- absorbance (of UV light) is directly related to the relative concentration of each component
- peak area=concentration of substance
- calibration curve plotted to obtain exact concentration—uses peak areas of standard solutions of a given component
- interpolation from calibration curve gives the concentration

Qualitative:

- obtained from retention time, can be compared with standard Rt values
- mixture can be spiked by adding a sure sample of a given component, this should increase the peak area of the original chromatogram

APPLICATIONS

- analysis of proteins and peptides
- cyanide analysis (used in gold extraction)
- flavonoid analysis in fruit juices
- analysis of toxins in shellfish

VOLUMETRIC ANALYSIS

Volumetric analysis is a technique that finds an **unknown concentration** of a solution. A **known volume** of solution of **known concentration** (called a ***standard solution***) is reacted with a **known volume** of the unknown concentration solution, in a procedure called a **Titration**

UNITS

CONCENTRATION:

The quantity of solute in a given quantity of solution.

- g/L
- %m/v (g/100mL)
- %w/w (g/100g)
- %v/v (mL/100mL)
- ppm (parts per million = g/million g OR mg/L, mg/kg, ug/mL)
- ppb (parts per billion = g/ billion g/L)

Concentration = $\frac{\text{quantity of solute}}{\text{quantity of solution}}$

The UNIT depends on the quantities used for solute and solution.

Molar Concentration = $\frac{n}{V}$

(Molarity)

Unit : mol L^{-1} or M

- **g/L = Mr x mol/L**
- **mg/L=x1000 g/L**
- **ug/L = x1000mg/L**

TITRATIONS

- A **Standard solution** is required for a volumetric analysis to be carried out.
- Results will depend on the accuracy of the standard solution.
- Standard solutions are made from a **Primary Standard**.
- reactions analysed must be spontaneous, fast and go to completion

  - the end point must be clearly defined

  - e.g a weak acid should not be reacted with a weak base as this will not go until completion and does not have a defined end point (instead, a strong base should be used)

PRIMARY STANDARD:

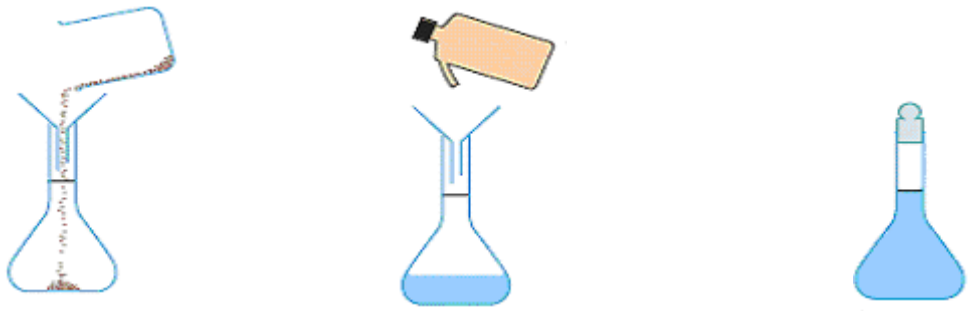
A **substance** so **pure** that the **amount** in a sample can be **accurately calculated** from its **mass**.

must be:

- easily obtained in a pure form
- have a known chemical formula
- be easily stored without reacting with water or gases in the atmosphere
- does not decompose on storage or exposure to the air
- highly soluble at room temperature
- reasonably high molar mass

e.g Na_2CO_3 (base) or $KH(C_8H_4O_4)$
*all solids but can be an acid or a base

STANDARD SOLUTION PREPARATION:



1. Place weighed sample in volumetric flask.

2. Half fill with water Shake to dissolve the sample

3. Add water to the calibration line. Shake again.

1. weigh pure solid on electric balance

2. transfer to volumetric flask using a clean, dry funnel **ensure all solid is transferred by washing the beaker**

3. rinse any remaining solid particles into the flask using deionised water

4. half fill the flask, swirl to suture any solid particles dissolve

5. add deionised water up to the calibration line

concentration can be found by—divide mols of substance by volume of solution

SECONDARY STANDARDS:

- strong acids and bases are purchased in variable concentration form
- strong acids (e.g HCl or HNO3 are very volatile l—>g therefore will lose mass easily)
  - H2SO4 is hydroscopic—absorbs H2O from the air and forms solution (called **deliquescent)**
- strong bases eg NaOH have two problems:
  - they absorb CO2 from air which makes them heavier
  - they are also deliquescent (absorb water from air)

*therefore must be standardised using a primary standard (usually Na2CO3 first)

TITRATION PROCESS:

1. **Dilution:** obtain a convenient concentration by diluting high concentration stock solutions
2. **Titration:**

- a known volume of one of the solutions (the one being tested) is measured using a pipette and transferred into a conical flask (the volume transferred is the aliquot)
- a few drops of an appropriate indicator is added
- the other solution is dispensed slowly into the flask from a burette until the colour change is observed (volume of solution delivered is the titre—initial burette reading-final burette reading)
- titration is reputed several times to found the average titre (usually found by using three concordant results)

KEY TERMS:

- BURETTE – delivers variable volumes of solution accurately (titre)
- PIPETTE – used to measure and deliver a fixed volume of liquid accurately (aliquot)
- ALIQUOT – fixed volume of liquid measured by a pipette
- INDICATOR - substance which changes colour at a certain pH point
- EQUIVALENCE POINT – point during titration when the solutions have been mixed in the mole ratio shown by a balanced chemical equation, one drop after the end point
- END POINT – point during titration when indicator changes colour permanently
- CONCORDANT RESULTS – titres that vary within narrowly specified limits (0.1mL from highest to lowest value)
- TITRE – Volume of liquid delivered/measured by burette (only concordant results within 0.1mL of lowest to highest are used)
- TITRATION FLASK—the reaction vessel
- STANDARDISING—determining the precise concentration of a standard solution

UNCERTAINTIES AND ERRORS

MISTAKES:

Avoidable blunders in method or **incorrect** use of apparatus e.g. incorrectly read burette scale, read top of meniscus, fail to fill burette tip, spill substance, misreading numbers

UNCERTAINTIES **–**

The **quantity of estimation** of **error** within the data (due to limitation of manufacture). e.g. Pipette or burette = 20.00mL **± 0.05mL**. The errors that create uncertainties can be either **random**, or **systematic**:

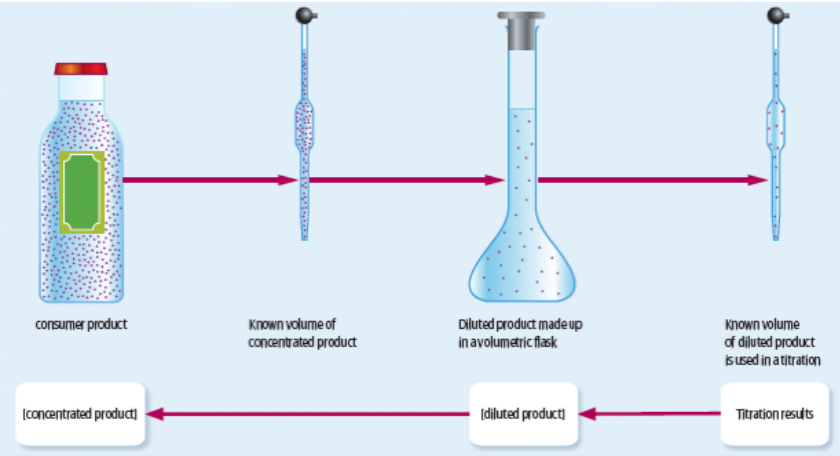
- the end point is often not exact at the equivalence point
- weighing uncertainly **± 0.002**

Accuracy is how well the result agree with the true quantity, precision is associated with a high level of consistency

	Random	Systematic
Type of error	Small errors arising from difficulty in **making judgements**, which will be in an **random** direction, and **different each time**.	**Consistent errors** resulting from **equipment** or **procedural faults**, which will be in the **same** direction, and the **same** each time.
How is it corrected?	**Repeated trials**.	Improving of **equipment**, **procedure**, using a **different technique**, or comparing to other **outside results**
Examples	imprecise definition (reading between two marks on a scale) parallax in reading instruments fluctuations in temperature and pressure during experiment judging indicator endpoint) lack of sensitivity (level of measurement)	apparatus incorrectly calibrated—using a 20mL pipette that delivers 20.5mL using an unsuitable indicator indicator's colour change failure to account for an effect uncertainty in concentration of standard solution

- *Random errors minimised by repeating experiment until we have 3 concordant results (0.1mL between highest and lowest)*

DILUTION OF SOLUTIONS



$$c_1V_1 = c_2V_2$$

Reasons for dilution:

- *safety*
- *waste of solution (environmental) — mainly to ensure not to much standard solution is used*
- *cost*
- *to achieve reasonably sized titres*
- *too much other reactant required to react with it (inaccurate)*

RINSING EQUIPMENT

glassware used	rinse with water	rinse with unknown concentration solution	rinse with standard solution
volumetric flask	✓		
burette			✓
20.00 mL pipette		✓	
conical flask	✓		
titration falsk	✓		

Rinsing Explanations:

- rinsing burette with water will dilute the solution (requires a bigger titre therefore higher concentration)
- rising conical flask with acidic or basic solutions will introduce unmeasured amounts—if unknown concentration solution is in here it will result in a higher concentration calculation
- titration flask always rinsed with water as this won't effect the mols of solution delivered by aliquot
- pipette rinsed with H2O will cause a lower titre volume

ACID-BASE VOLUMETRIC ANALYSIS

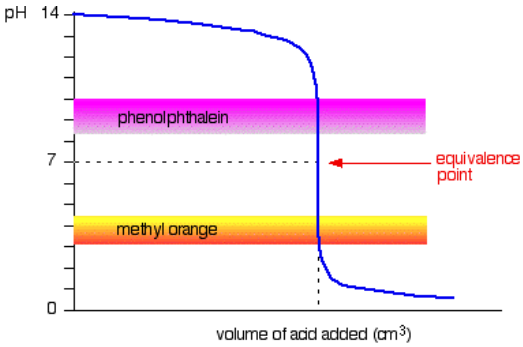
- indictor will change colour at the end point (ideally at the equivalence point therefore must have a colour change pH equal to that of the equivalence point

- to minimise error, the pH of the solution much change dramatically at equivalence point and over a small volume (this gives a sharp end point)

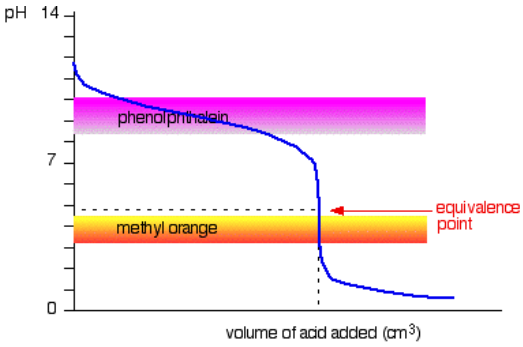
pH Curves: graph of pH against the volume delivered by a burette

➢ the vertical nature at end point is do to logarithmic scale of pH

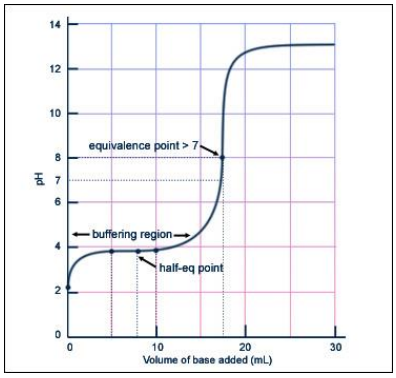
e.g. **strong acid – strong base (7)**



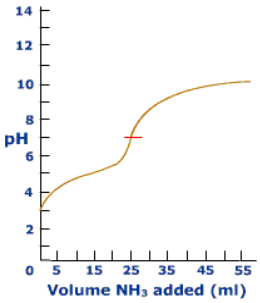
strong acid – weak base (<7)



weak acid – strong base (>7)



weak acid – weak base (7)



Titration curve of weak base (NH_4OH) and weak acid (CH_3COOH)

INDICATORS:

- change colours at a certain pH value—for a more accurate determination of pH, using a pH probe

- must consider how quickly the pH is changed around the point at which it changes colour *this determines whether or not the end point is sharp

Why is pH not always 7 at equivalence point?

strong acid + weak base —> acid has a greater degree of ionisation than the weak base, there will be a higher [H+] at equivalence point

$$pH = -\log_{10}[H_3O^+]$$

$$[H_3O^+] = 10^{-pH}$$

$$10^{-14} = [H_3O^+][OH^-]$$

ACIDS AND BASES

- acids are proton donators
- bases are proton acceptors

Strong Acids	Weak Acids	Strong Bases	Weak Bases
HCl HBr HI HNO3 HClO3 (chloric acid) H2SO4	H2SO3 H3PO4 HNO2 HF CH3COOH	LiOH NaOH KOH	NH3 CH3NH2

- ***Monoprotic:*** acids that can only donate one electron e.g ethanoic acid

- ***Polyprotic:*** acids that donate multiple electrons e.g H3PO4 or oxalic acid (C2H2O4)

pH of polyprotic acids

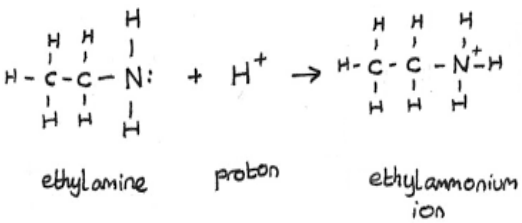
$$H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)} \quad K_{a1} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)} \quad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)} \quad K_{a3} = 4.8 \times 10^{-13}$$

FUNCTIONAL GROUPS:

- carboxylic acids (mostly monoprotic)



- amino—bases, react with acids to produce a salt

REDOX VOLUMETRIC ANALYSIS

Detecting an End Point:

- Use a known reactant that **changes colour** in the reaction

  e.g. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
  purple colourless

- Use excess of a **known reactant** to form a new material that can be titrated to a visible endpoint.

  e.g. $I^- + \text{unknown} \rightarrow I_2$

  $I_2 + S_2O_3^{2-}(aq) \rightarrow I^-(aq)$

  blue/black colourless [using starch indicator]

This process is also considered to be a type of **back titration** since you work "back" from the titration reaction to the original reaction.

Analysing alcohols:

- alcohol undergo oxidation and act as weak reducing agents
- when a primary alcohol is oxidised it forms and aldehyde then a carboxylic acid
- in volumetric analysis, alcohol concentration can be determined by reacting with a strong oxidising agent (H+/K2Cr2O7 or KMnO4) *H+ must be present because they are consumed in the reaction

Selecting Indicators:

- must behave as oxidants or reductants after the equivalence point has been reached
- must be highly coloured in either oxidised or reduced form
- starch is used as an indicator in titrations involving I2 (iodine reacts with starch to form a dark blue complex)
- e.g MnO4- turns from purple to colourless