

10.1 Fundamentals of organic chemistry

Modern organic chemistry

- While viruses aren't living, they can reproduce themselves quite quickly when in a host.
 - They manipulate the genetic "machinery" of the host for their own gain.
- Viruses can be crystallized and their structures analyzed.
 - The structures are made up of carbon-containing molecules such as DNA or RNA, and proteins.
- We long being in the viruses, form macro-organisms such as bacteria, fungi, and plants using systems based on nucleic acids and proteins.
 - These are macromolecules.
 - Proteins are made by assembling amino acids into long chains.
 - The chains then fold and organize themselves into complex structures.

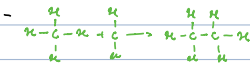
The distinctive features of carbon

- Six common compounds of carbon are known.
- Carbon has 5 special features of covalent bonding that allow it to have so many compounds.
 - Carbon atoms can bond with one another to form a very long chain.
 - Atoms of other elements can attach themselves onto the chain.
 - The carbon atoms in a chain can be linked by single, double, or triple covalent bonds.
 - Carbon atoms can also arrange themselves in rings, involving both single & multiple bonds.
- Atoms of other elements can copy some of the versatility of carbon.
 - Silicon can form short chains.
 - Sulphur atoms can arrange themselves into rings.
 - Only carbon is able to achieve all the bonding arrangements, to its extent.
- The ability of carbon to form chains and rings is known as catenation.
- Carbon is unique because it can also form double and triple bonds with other elements.
 - E.g. Oxygen (carbonyl group, $C=O$) an important feature of aldehydes, ketones, and carboxylic acids.
 - Nitrogen (in nitriles, $C\equiv N$).
- The C-C bond is particularly strong compared with the strength of other similar bonds between other groups of elements.
 - This leads to thermal stability of organic compounds.
 - The C-H bond is also more stable than other comparable bonds, such as Si-H bond.
 - $C-H \rightarrow 412.85 \text{ kJ mol}^{-1}$, $Si-H \rightarrow 318.25 \text{ kJ mol}^{-1}$.
- When a carbon atom is bonded to 4 other elements it's particularly stable as the outer shell ($n=2$) is filled.
 - Thus, CCl_4 (tetrachloromethane) can't be hydrolysed by water, but $SiCl_4$ (silicon tetrachloride) can.
 - Water molecules are thought to bond with the silicon by attacking the $SiCl_4$ molecule through lone pairs on their oxygen atoms.
 - This will expand the octet of electrons.

The nature of a homologous series

- The most basic structures in one when a chain of carbon atoms is bonded to only hydrogen atoms.
 - A series of compounds of this structure would be when another carbon is added to the end.
- When a substance is bonded to different elements with a single bond (no double or triple bonds), it's said to be "saturated".
- The simplest compound of the series in the hydrocarbon, C_1H_4 (methane).
- Therefore, a series where molecules are progressively extended by a carbon atom (precisely a $-CH_2$ group).

E.g. methane \rightarrow Ethane



- This series is known as the homologous series, and the single bonded carbon atoms are known as alkanes.

Alkanes (homologous series):

Alkane	Molecular formula C_nH_{2n+2}	Melting point / K	Boiling point / K	Physical state at room temp & pressure
Methane	CH_4	91	109	gas
Ethane	C_2H_6	90	186	gas
Propane	C_3H_8	93	231	gas
Butane	C_4H_{10}	155	273	gas
Pentane	C_5H_{12}	144	309	liquid
Hexane	C_6H_{14}	178	342	liquid
Heptane	C_7H_{16}			
Octane	C_8H_{18}			
Nonane	C_9H_{20}			

- the homologous series of compounds illustrates certain key features of all such series:

- the names of the compounds all contain a consistent feature that denotes the series.

- for the series above this ending is -ane.

- the formulae show the increasing chain lengths.

- for the series above (alkanes) C_nH_{2n+2} is added to the molecules.

- the molecules all have the same general formula.

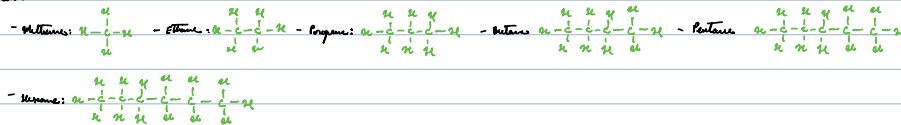
- for alkanes it is C_nH_{2n+2}

- where n is the number of carbon atoms

- there is a gradual physical change in the properties of the carbon chain as the carbon chain is increased.

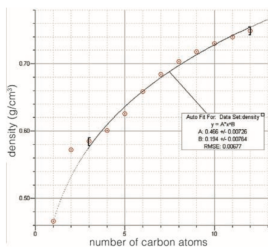
- increase in boiling point of the compound in the series.

- Propan-1-ol:



- there is a gradual increase in the boiling point, although it's not linear.

Figure 10.8 Graph of the densities of the early members of the alkane series. This graph is drawn, and the line fitted, by feeding data into the computer program Graphical Analysis (Vernier).



- the alkanes are the simplest homologous series as it only contains Carbon and hydrogen.

- All of the bonds between the Carbon and Carbon are single bonds

- there are two more homologous series which contain a straight chain carbon hydrogen:

- the alkenes, which contain a single carbon-carbon double bond.

- formula: C_nH_{2n}

- the alkynes, which contain a single carbon-carbon triple bond.

- formula: C_nH_{2n-2}

- Multiple carbon-carbon bonds are a determining factor called the "functional group" for each series.

- When a hydrogen atom is replaced with $-OH$, then the series is known as the alcohols.

- Alcohols

Alcohol	Molecular formula ($C_nH_{2n+2}O$)	Melting point / °C	Boiling point / °C	Physical state at room temp & pressure
Methanol	CH_4O (C_1H_4O)	-	58	gas
Ethanol	C_2H_6O (C_2H_6O)	-	78	gas
Propanol	C_3H_8O (C_3H_8O)	-	97	gas
Butanol	$C_4H_{10}O$ ($C_4H_{10}O$)	-	117	gas
Pentanol	$C_5H_{12}O$ ($C_5H_{12}O$)	-	138	liquid
Hexanol	$C_6H_{14}O$ ($C_6H_{14}O$)	-	157	liquid
Heptanol	$C_7H_{16}O$ ($C_7H_{16}O$)	-	171	liquid
Octanol	$C_8H_{18}O$ ($C_8H_{18}O$)	-	177	liquid
Nonanol	$C_9H_{20}O$ ($C_9H_{20}O$)	-	194	liquid

- Since the $-OH$ group is what gives the alcohol its distinctive properties, then it's considered the functional group for all alcohols.

- In summary, a homologous series is a group of compounds that:

- contain the same functional group.

- share the same general formula, with successive members of the series having an additional $-CH_2-$ group.

- share similar chemical properties.

- show a steady gradation in certain basic physical properties.

- the following table shows the distinctive properties of the particular homologous series:

- Homologous series are just the groups that functional groups pertain to.

- for species where the functional group is in the middle, its location won't have to be specified.

- If the functional group is in the middle of the compound, then the other carbons bonded on the chain will be numbered

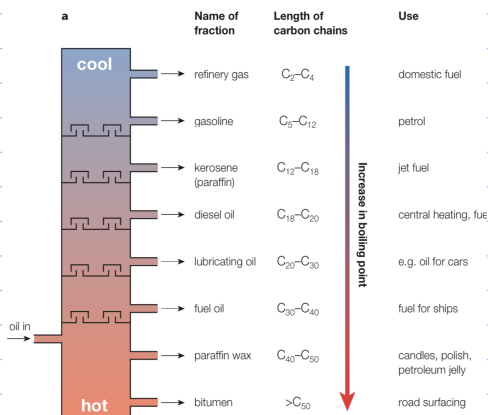
Homologous series	Functional group and condensed structural formula	Suffix in name of compound	General formula	Structure of the functional group
Alkanes	-CH ₂ -CH ₂ -	-ane	C _n H _{2n+2}	*
Alkenes	-CH=CH- alkenyl	-ene	C _n H _{2n}	
Alkynes	-C≡C- alkynyl	-yne	C _n H _{2n-2}	
Halogenoalkanes	-X (where X = F, Cl, Br, I)	name uses a prefix (chloro-, bromo-, etc)	C _n H _{2n+1} X	-X (where X = F, Cl, Br, I)
Alcohols	-OH hydroxyl	-ol	C _n H _{2n+1} OH or ROH	-O-H
Aldehydes	-CHO aldehyde (carbonyl)	-al	C _n H _{2n+1} CHO or RCHO	
Ketones**	-CO- carbonyl	-one	C _n H _{2n+1} COC _m H _{2m+1} or RCOR'	
Carboxylic acids	-COOH or -CO ₂ H carboxyl	-oic acid	C _n H _{2n+1} COOH or RCOOH	

*The alkane structure is the basic backbone into which the functional groups are introduced.

**R and R' represent hydrocarbon chains (alkyl groups) attached to the group. These chains can be identical or different (as represented here).

- trends in the physical properties in a series

- As the carbon chain becomes longer, the boiling point will increase.
- As they increase in molecular mass, they become less volatile.
- Alkanes are an example of an increasing boiling point with an increasing chain length.
 - Due to their non-polar nature, the only forces are London dispersion forces.
 - London dispersion forces occur due to the temporary dipoles (due to temporary electron distribution shifts) being generated in the covalent.
 - The strength of the force is related to the number of electrons in the structure, and the surface area of the molecule (surface interactions occur).
 - the more electrons, the stronger the force.
 - the longer the chain, the stronger the force.
- As more CH₂'s are added, the increase in boiling temps will be less significant.
- A number trend is observed with aldehydes.
 - Aldehydes, their initial boiling temperatures are much higher than the alkanes.
 - This shows that they have a stronger intermolecular forces acting between them.
- The idea of chain lengths, and the increase in temps is used in fractional distillation.
 - Fractional distillation is where crude oil is separated into useful fractions.
 - Crude oil (petroleum) is the major commercial source of hydrocarbons.



- the compounds with the shortest carbon chain are at the top, and vice versa.
- In the crude oil is heated at the bottom the different homologous series with a lower boiling point will move up (in gas form), and become liquids as the temp. increases.

- families of organic compounds

Types of formulae

There are three types of formulae for organic compounds:

- Structural

- Molecular

- The molecular formula is the actual amount of atoms in the molecule

- Empirical

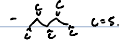
- Empirical formulae are the simplest whole number ratio of the atoms in the formula.

- The formula can be derived from the percentage composition data combined from combustion analysis.

There is a difference between a $C_2H_4O_2$ (ethanol) and CH_3COOH (ethanoic acid (vinegar)), one of them has an alcohol group (-OH) and the other has a carboxylic acid group (-COOH).

- A skeleton formula in a formula shows only the carbon-carbon bonds are shown.

- It each corner there is a carbon.



- The condensed structural formula is a formula which doesn't show the bonds that can be assumed.

- It also groups atoms together.

- E.g. propane can be written as $CH_3CH_2CH_3$ and butane as $CH_3CH_2CH_2CH_3$ or C_4H_{10} .

- The full structural formula shows every bond.

- There are other abbreviations:

- When exact details don't have to be shown, part of the molecule can be abbreviated to R.

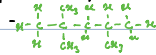
- Molecules which contain a benzene ring, aromatic compounds, or wood.

Main and rings

- The alkane series of hydrocarbons are often described as straight-chain hydrocarbons, since there are no branches from the main chain.

- There are molecules with branches.

- One of the most important is: 2,2,4-trimethylpentane.



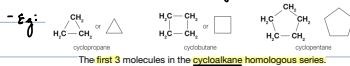
- The isomer properties of 2,2,4-trimethylpentane are the basis of the octane rating of gasoline.

- The alkanes are saturated when all the C-C bonds are single bonds.

- Unsaturated bonds are C=C bonds which aren't single bonds.

- Therefore all alkenes and alkynes are unsaturated.

- Carbon atoms can also be bonded in a ring, this is known as a cyclic molecule.



- Despite the formula, the cycloalkanes are saturated molecules.

- Unsaturated cycloalkenes exist though.

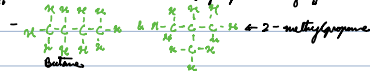
Structural isomerism

- Different compounds with the same molecular formula can differ, they're known as isomers.

- For the alkanes the first 3 are unchangeable.

- After the first 3, butane can be changed from $CH_3CH_2CH_2CH_3$ to $CH_3CH(CH_3)CH_3$.

- The difference is that there is a $-CH_3$ group branching off the middle carbon atom.



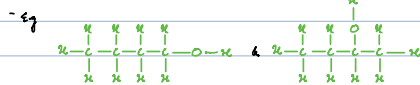
- The molecule on the left is known as 2-methylpropane.

- Due to the structural differences, the two compounds are known as structural isomers.

- In the alcohol series the first possible isomer occur with propanol and butanol.

- The name in the alcohol group is attached to a terminal carbon atom, or one in the middle.

- Isomers: isomers are compounds with the same molecular formula but with different arrangements of atoms in the molecule.



Butan-1-ol

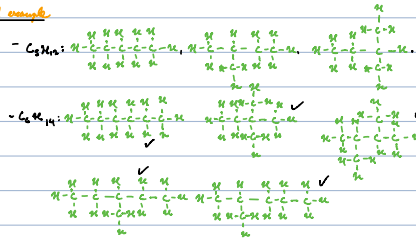
Butan-2-ol

- Remembering the compound isn't our answer (NO DONT FUCK IT UP).

Predicting structural formulae of alkanes

- the longer the carbon chain the more structural isomers are possible for a given molecular formula.
- When trying to find isomers, it is important to remember that C-C bonds can rotate freely.

Worked example



Naming alkanes

Prefix name	Number of carbon atoms in chain	Name of alkane	Condensed structure
Meth-	1	Methane	CH ₄
Eth-	2	Ethane	CH ₃ CH ₃
Prop-	3	Propane	CH ₃ CH ₂ CH ₃
But-	4	Butane	CH ₃ CH ₂ CH ₂ CH ₃
Pent-	5	Pentane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃
Hex-	6	Hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃

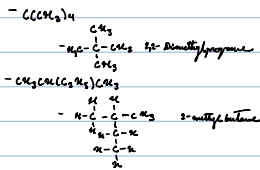
Name of side-chain (R group)	Condensed structure
Methyl	-CH ₃
Ethyl	-CH ₂ CH ₃
Propyl	-CH ₂ CH ₂ CH ₃
Butyl	-CH ₂ CH ₂ CH ₂ CH ₃

Table 10.7 Names of some alkyl groups

- Steps to determine name:

- Identify longest chain
- Not necessarily middle one.
- Branches
- Position & Carbon #s

Worked example



Predicting structural formulae of alkenes

- Alkenes have a C=C double bond.
- General formula is: C_nH_{2n}
- Simplest alkene is ethene (C_2H_4).
- With alkenes the double bond can be located anywhere, therefore, more isomers are possible.

Naming isomers of some cyclic alkenes and alkyenes

- Position of the double bond is what establishes the location of the other branches.
- E.g. $CH_3CH=CHCH_3$ 2-butene
- Simplest alkene is C_2H_4

Priority of organic compounds

Alcohols - $R-OH$ or $C_nH_{2n+1}OH$

- Characterised by the -OH group.
- Name of the alcohol end in -ol.
- The position of the alcohol group determines the name:
 - E.g. $CH_3CH_2CH_2OH$ - propan-1-ol.
 - $CH_3CH(OH)CH_3$ - propan-2-ol.
- The alcohol group can be placed in the chain or on a branch.
- The name of the compound will use the same name as above, but with a different suffix.

Aldehyde - general formula $R-CHO$ or $C_nH_{2n-2}O$

- the $-CHO$ group always occurs at the end of the carbon chain.
 - the $C=O$ bond is a double bond.
 - the $-CHO$ group is the functional group.
- for naming purposes, the first carbon is the one from the aldehyde group.
 - this means its position isn't required to be mentioned.
- the only α -ol.
 - E.g. Ethanol CH_3-CH_2-OH , Ethanal CH_3-CHO , Propanal CH_3-CH_2-CHO , ...

Ketone - general formula $R-CO-R'$ (R' = same alkyl group as R , or different)

- ending in $-one$.
- has to be a branch (can't go on the end).
 - therefore, it has to be counted.
 - Propanone and Butanone don't have numbers because they have no isomers.

Carboxylic acid - $R-COOH$ or $R-CO_2H$

- $-COOH$ / $-CO_2H$ ($C=O$ is a double bond).
- ending in $-oic acid$.
- always on the end (terminal).
 - it being the functional group will always be counted as the first carbon.

Haloalkanes - general formula $R-X$, $X = F, Cl, Br, I$

- the haloalkanes (from the halogen) is simply where a halogen atom replaces the hydrogen atoms.
- for the naming, it depends on the halogen in the compound e.g.
 - 1-halobutane, 2-chloropropane, 1-bromo-2-chloropropane.
 - the common ones: fluoro-, chloro-, bromo-, and iodo-.

naming structural isomers

- there are three types of isomers:
 - chain isomers:
 - these involve branching of the hydrocarbon backbone of the molecule.
 - E.g. $CH_3CH_2CH_2CH_2CH_2CH_3$ hexane, $CH_3-CH(CH_3)CH_2CH_2CH_3$ 2-methylpentane, $CH_3-C(CH_3)_2-CH_2CH_3$ 2,2-dimethylbutane.
 - position isomers:
 - these are isomers where the functional group occupies a different point of attachment to the chain.
 - E.g. $CH_3-CH_2-CH_2-CH_2-OH$ 1-butanol, $CH_3-CH_2-CH(OH)-CH_3$ 2-butanol.
 - functional group isomers:
 - these are isomers with the same molecular formula, but different properties, and a different formula.
 - E.g. $C_4H_8O_2$ and $C_4H_8O_2$.

Further functional groups

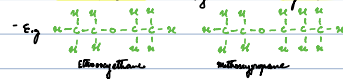
- the additional homologous are:

Homologous series	Functional group and condensed structural formula	Suffix in name of compound	General formula	Structure of the functional group
ethers	$R-O-R'$ ether	alkoxy- (prefix)	$C_nH_{2n+2}OC_nH_{2n+1}$	
esters	$R-COO-R'$ ester	-oate	$C_nH_{2n+1}COOC_nH_{2n+1}$	
amines	$R-NH_2$ amino	-amine (or prefix amino)	$C_nH_{2n+3}NH_2$	
amides	$R-C(=O)NH_2$ carboxamide	-amide	$C_nH_{2n+1}CONH_2$	
nitriles	$R-CN$ nitrile	-nitrile	$C_nH_{2n-1}CN$	$C \equiv N$
arenes	phenyl-	-benzene (or prefix phenyl-)	C_6H_5-	

Ethers - general formula $R-O-R'$ (R' is an alkyl group)

- there are molecules with an oxygen atom inserted in the hydrocarbon chain.
- they're volatile liquids.

- They all have two carbon chains bonded together with a single bond with oxygen (in the middle).



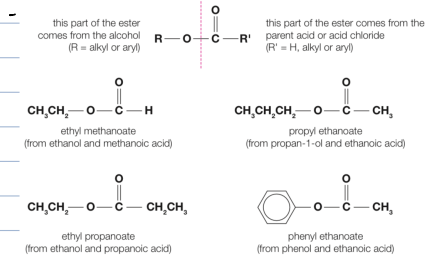
- Ether are isomers of alcohols.
- They don't mix with water because they can't hydrogen bond.

Esters - general formula $R-COO-R'$, (R' is an alkyl group)

- Esters are derived from carboxylic acids by reaction with an alcohol.



- E.g.:



Amides - $R-CO-NH_2$

- Amides are compounds derived from carboxylic acids by replacing the $-OH$ group by an $-NH_2$.
- They retain the $C=O$ group as part of $-CONH_2$.
- Muffin is -amide

Nitriles ($R-CN$)

- Derived from carboxylic acids.
- group = $-CN$
- $-CON$
- Muffin - nitrile
- E.g. C_2H_5CN becomes propanenitrile
- Another the nitrile group gives precedence to the name of a carboxylic acid group ($-COOH$ - oic acid).
- E.g. $CH_2(COO)CH_2CN$ - carboxylic acid group, nitrile group.

Amino - $R-NH_2$

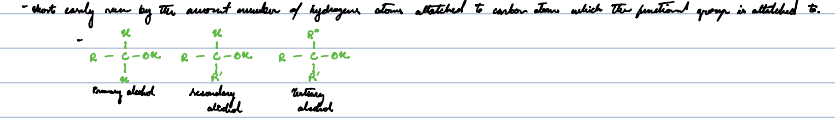
- Amino group is $-NH_2$
- Muffin = amino-, suffix = -amine
- Attached to the chain

Classifying molecular structures

- Functional groups define the chemistry of a homologous series.
- The reactivity is influenced by its position in the carbon chain.
- Primary, secondary, and tertiary structures are used to show different position isomers.
- They're used to identify the location of the carbon atoms which the functional group is attached to.

Primary, secondary, and tertiary

- For alcohols and halogenoalkanes, the primary, secondary, and tertiary refer to the degree of chain branching at the carbon atom to which the functional group is attached to.



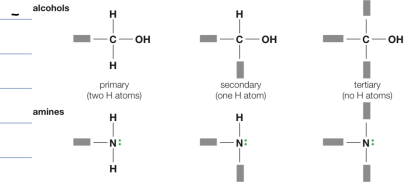
- Muffin:

- The primary carbon atom is attached to the functional group ($-OH$ in example above) with at least 2 hydrogen atoms.
- The secondary carbon atom is attached to the functional group with one hydrogen atom.

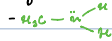
- A tertiary carbon atom is attached to the functional group with no hydrogen atoms

Amines

- there are compounds derived from ammonia.
- the number of nitrogens is key, but hydrogen atoms are the best way to tell
- the amount of hydrogen attached to nitrogen.



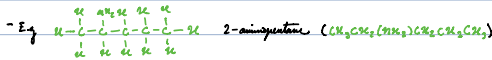
- If only one hydrogen atom has been replaced, then a primary amine is formed.
- E.g. methanamine or methylamine.



- If two hydrogen atoms are replaced, then a secondary amine is formed.
- the alkyl groups aren't necessarily the same type.

- If alkyl groups replace all three hydrogen atoms then a tertiary amine is formed.

- Prefix -amino



- when two hydrogens are removed from the series, then the name change to -diamines, and 3° Triamines.

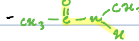
- Aromatic amines are compounds where the -NH₂ group is directly bonded to the benzene ring.

- Most commonly phenylamine, C₆H₅NH₂.



- A peptide bond is a chemical bond formed between two molecules.

- this occurs when the carbonyl group of one molecule reacts with the amino group of the other molecule releasing H₂O.



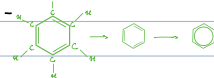
Aromatic compounds (arenes)

- Hydrocarbons with linear chain of carbon atoms or the backbone of the compound are described as aliphatic hydrocarbons.

- the other class of hydrocarbons are called aromatic hydrocarbons, or arenes.

- Arenes are compounds which contain a benzene ring.

- Benzene is C₆H₆ arranged in a ring structure.



- Methyl groups are bonded on a benzene ring with the simplest being -C₆H₅.

- Inside the ring are delocalised electrons.

- Methyl groups are functional groups derived from an aromatic ring compound where a hydrogen was removed.



Establishing the structure of benzene

- Benzene is a colourless liquid that is immiscible with water.

- The carbon-carbon bond lengths are all the same in the benzene molecule.

- They have a value of 0.139 nm (between a single and double bond).

- Only one isomer exists for 1,2-disubstituted benzene compounds

- Benzene is a resonance structure.

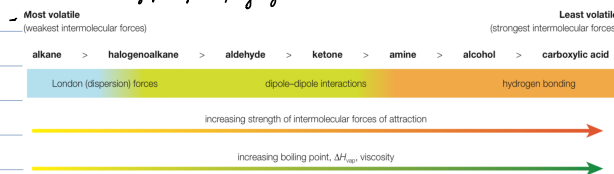
- The resonance structures is a structures which blend the characteristics of both resonance forms.

Further trends in homologous series

Volatility

- Members in the same homologous series have similar chemical properties.

- Volatility is a measure of how easily a substance evaporates.
 - If highly volatile substance evaporates easily and has a low boiling point.
 - This depends on the intermolecular forces of a molecule.
- Volatility such as:
 - An increase in boiling point means that the volatility will decrease.
 - As the chain increases in size, the volatility will decrease.
 - Can mean stronger London dispersion forces between the molecules.
 - If branched isomers will most likely have a lower boiling point than its straight chain isomer.
 - The branching will result in the molecule being a more spherical shape.
 - This will result in less surface area for attraction between molecules, resulting in lower intermolecular forces.
 - This results in a lower boiling point.
 - The nature of the functional group determines volatility.
 - Polar groups will form dipole-dipole intermolecular bonds, making them less volatile.
 - Groups capable of hydrogen bonds will be less volatile.



- Solubility of water

- The solubility of an organic compound in water is determined by two factors, the functional groups & the hydrocarbon.
 - If the functional groups in the compound is able to interact with water, e.g. forming hydrogen bonds, then this will favor the compound being soluble.
 - The hydrocarbon chain of the molecule not being polar worsens the solubility of the carbon chain.
 - In general, the longer the carbon chain, the lower the solubility of the molecule.
- Halogenoalkanes and alcohols aren't soluble because their functional groups can't form hydrogen bonds with water.

- 10.2 Functional group chemistry

- Alkanes

- Following key points to follow:

- All alkanes are hydrocarbons, and therefore contain carbon hydrogen only.
- General formula C_nH_{2n+2} .
- Alkanes are saturated hydrocarbons.
 - saturated means that carbon-carbon bonds are single bonds.
- Although, they are relatively unreactive compounds, some of their reactions are highly significant and important.

- Explaining the low reactivity of the alkanes

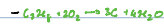
- Alkanes are chemically unreactive.
 - The relatively strong covalent bonding in the molecules means that the alkanes are kinetically stable until sufficient energy has been provided.
 - $C-C = 356 \text{ kJ mol}^{-1}$, and $C-H = 412 \text{ kJ mol}^{-1}$.
 - The molecules will only combust when enough energy to break all the bonds has been supplied.
 - Due to the non-polar character of alkanes, they aren't susceptible to attack by nucleophiles (electron pair donors), and electrophiles (electron pair acceptors).

- The combustion of alkanes

- The reason that alkanes are good fuels is because its combustion reactions of these molecules are highly exothermic.
 - This is due to the relatively high strength of the $C=O$ bond in carbon and the $H-O$ bond in water.
 - These are better products of the combustion.
- Alkanes burn in the presence of excess oxygen to form CO_2 & H_2O :
 - E.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H_c^\ominus = 890 \text{ kJ mol}^{-1}$
 - $C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$ $\Delta H_c^\ominus = -1560 \text{ kJ mol}^{-1}$
 - propane
- When the alkanes are burnt in limited oxygen, then carbon monoxide is formed rather than CO_2 .
 - $2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$



- when oxygen is extremely limited, carbon can be produced:



- the incomplete combustion of oil allows can take place in the flames where the soot was burnt to give the characteristic yellow flame.

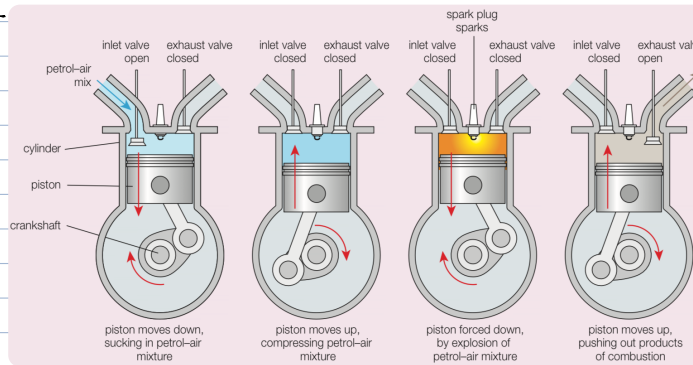
- the glow of the hot solid carbon particles give the flame the yellow color.

- soot is produced from organic waste when it decays in the absence of air.

- soot is actually used to produce energy.

- the role of the fuel in a petrol engine

- the gasoline (petrol) engine



- the first downward stroke of the piston

- the fuel must be drawn from the carburetor through the inlet valve.

- for this to happen the fuel has to be able enough to form a homogeneous (same phase) fuel-air mixture in the carburetor.

- in a fuel-injection car, the piston moving down will suck in the fuel-air mixture into the cylinder.

- heat stroke

- when the piston is moving back up, the fuel-air mixture is compressed.

- goes to $\frac{1}{16}$ th of its original volume.

- the compression will result in the ΔT being measured by a few hundred degrees.

- this is due to more London dispersion forces between the gas molecules as they're pushed closer together.

- the fuel shouldn't have an ignition temperature.

- this is so that the self-heating doesn't cause pre-ignition of the fuel.

- pre-ignition is defined as: the air/fuel mixture igniting before the spark plug fires.

- known as "engine knocking".

- second downward stroke

- following the sparking of the spark plug, the fuel-air mixture ignites and expands.

- this will push the piston down.

- the burning of the fuel must be smooth, and must be completed at the same time which the piston takes to travel down the cylinder.

- second upward stroke

- in an ideal situation, the fuel will have completely burnt to form gaseous CO_2 & H_2O .

- if insufficient O_2 has been drawn in the fuel/poor mixing / insufficient time for complete burning, then other reactions will be produced.

- quality of petrol

- long-chain hydrocarbons tend to burn unevenly in car engines.

- this will mean that they'll ignite too soon.

- branched-chain alkanes burn in a more controlled fashion.

- therefore, they're added to the gasoline fraction when petrol is blended.

- the octane number of petrol is a measure of its quality.

- it's based on the ignition properties of an isomer of octane, C_8H_{18} .

- the branched alkane 2,2,4-trimethyl pentane, has a good anti-knock properties.

- reaction of alkanes with halogens

- once the alkanes are saturated molecules the main type of reaction this can undergo are substitution reactions.

- % substitution reaction is when one of the carbons is replaced by the atoms of another element.
- Under appropriate conditions, a mixture of methane, and chlorine gases reacts to form chloromethane and hydrogen chloride.
 - $CH_4(g) + Cl_2(g) \rightarrow HCl(g) + CH_3Cl(g)$
- The degree of substitution achieved in these reactions can be easily controlled.
- Ethane and other alkanes will undergo similar substitution reactions with chlorine or bromine.
 - E.g. (Conditions: sunlight / UV radiation)
 - $C_2H_6(g) + Br_2(l) \rightarrow C_2H_5Br(l) + HBr(g)$
Bromomethane
 - $C_2H_6(g) + Br_2(l) \rightarrow C_2H_4Br_2(l) + 2HBr(g)$
Mixture of dibromomethane
- The product of the second reaction will be a mixture of dibromomethane (1,1-dibromomethane & 1,2-dibromomethane).
 - 25% a mixture of the two possible isomers after the substitution.
 - This mixture is due to there being an equal over which hydrogen atom is substituted.
- The halogen molecules are able to act in this way because they're split into fragments with an unpaired valence electron.
 - These are known as free radicals.
 - Once formed, they will initiate a chain reaction where halogenoalkanes are produced.

Bond breaking and bond cleavage

- % covalent bond, is a bond where electrons are shared between two atoms.
 - When the bond breaks there are two possible ways in which the electrons in the bond can distribute themselves.
 - 1) In homolytic fission, the bond breaks so that one electron remains with each fragment.
 - $Cl-Cl \rightarrow \cdot Cl + \cdot Cl$
 - Two chlorine free radicals are produced by UV radiation.
 - When one of the chlorine free radicals meets a methane molecule, they can react together:
 - $\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl + \cdot Cl$
 - The carbon-hydrogen bond is broken homolytically (the atom will retain its original amount of atoms) by the chlorine free radical (Cl·) to produce a methyl free radical (·CH₃).
 - The chlorine free radical (Cl·) will remove hydrogen from H₂O₂ producing HCl.
 - 2) In heterolytic fission, the bond breaks, and one atom retains both electrons, resulting in ions being produced.
 - $Cl-Cl \rightarrow Cl^- + Cl^+$ (9 retains the electron).
 - This never occurs.

- Both of these bond fission play their part in reaction mechanisms.

- Halogen substitution in alkanes are homolytic fission.

Name of species	Carbon atom	Methane molecule	Methyl free radical	Methyl carbocation
Structure	$\cdot C \cdot$	$\begin{array}{c} H \\ \times \\ H \times C \times H \\ \times \\ H \end{array}$	$\begin{array}{c} H \\ \times \\ H \times C \cdot \\ \times \\ H \end{array}$	$\begin{array}{c} H \\ \times \\ H \times C^+ \\ \times \\ H \end{array}$
Carbon valence shell electrons	4	8 ÷ 2 = 4	(6 ÷ 2) + 1 = 4	6 ÷ 2 = 3
Charge	neutral	neutral	neutral	+1

The free-radical reaction mechanism

- The formation of halogenoalkanes by substitution requires the presence of UV.
 - The reaction is a photochemical reaction.
 - The energy of a UV photon is of the order 400 kJ mol⁻¹.
 - Enough to break Cl-Cl into Cl· + Cl· (B.E. = 242 kJ mol⁻¹).
- The homolytic fission of the bond between the Cl atoms is thought to be the initial step of the reaction.
 - The next step would be one of the Cl· radicals will react with a methane molecule.
 - $Cl\cdot + CH_4 \rightarrow \cdot CH_3 + HCl$
 - The methyl free radical then reacts with a chlorine molecule to form a chlorine free radical.
 - $\cdot CH_3 + Cl_2 \rightarrow \cdot Cl + CH_3Cl$
 - Due to the fact the final step produces another Cl· a chain reaction will be initiated.
 - As the reaction proceeds there is a build up of free radicals leading to the termination step.

- the final steps involve the recombination of two free radicals with each other.

- there are three possible termination steps:



- In the termination steps the free radicals are removed from the reaction mixture.

- It has been experimentally found that on average one chlorine radical will form 10,000 chloromethanes.

- 3 steps reaction:

- **Initiation:** A photochemical reaction will occur splitting a chlorine molecule into chlorine free radicals.

- **Propagation:** 1) A chlorine free radical will react with methane forming hydrochloric acid and a methyl free radical.

2) The methyl radical then reacts with a chlorine molecule forming chloromethane and a chlorine free radical.

- **Termination:** the final reaction is decided between 3 different possible reactions:



- Overall reaction: $\text{Cl}_2 + \text{C}_2\text{H}_6 \xrightarrow{\text{UV}}$ $\text{C}_2\text{H}_5\text{Cl} + \text{HCl}$

- Alkenes

- the alkenes are hydrocarbons (contain carbon & hydrogen only).

- general formula: C_nH_{2n}

- the alkenes are unsaturated hydrocarbons containing a carbon-carbon double bond.

- the bond is made of a sigma (σ) and pi bond (π).

- the carbon atoms have a trigonal planar arrangement with 120° .

- alkenes are relatively more reactive than alkanes due to the carbon-carbon bond.

- they undergo a range of addition reactions.

- the reaction of alkenes with hydrogen and halogens

- the carbon double bond in the functional groups of the alkenes

- the pi bond (π) is weaker than the sigma (σ) bond.

- it is therefore easier to break the pi bond, without the molecule falling apart.

- either an addition reaction on atoms of another element will be added on both of the carbon that are part of the double bond.

- this will make all of the carbons in the molecule saturated.

- Hydrogenation

- the simplest reaction is that of adding hydrogen across the carbon-carbon double bond, producing an alkane.

- Hydrogen reacts with alkenes to form alkanes in the presence of a nickel catalyst at 180°C .



- Hydrogenation is defined as the addition of hydrogen to a molecule.

- Halogenation

- Halogenation is the addition of a halogen atom to a molecule.

- Halogens react with alkenes to produce dichlorinated compounds.

- these reactions take place at room temp, and also has a low color of the reacting halogen.

- the halogen atoms will bond onto the carbon atoms with the double bond.

- the halogen is usually dissolved in a non-polar solvent such as benzene.

- E.g:

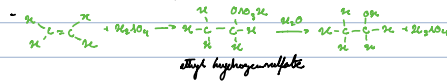


Reaction addition reactions

- Hydrogen halides (HCl, HBr, etc.) react with alkenes to form halogenoalkanes.
 - the reactivity order is $\text{HCl} > \text{HBr} > \text{HI}$.
 - the reason that HCl is the best reagent is because it is the least electronegative, meaning the Cl^- is quite low meaning it will react much easier than the stronger HBr & HI bonds.

Hydration

- the reaction with water is known as hydration and the alkene is converted into an alcohol (C-OH).
 - water can't react with the alkene directly.
 - in the lab this is accomplished with the use of concentrated sulphuric acid to form an addition product.
 - the reaction will have an H^+ ion and an HSO_4^- ion both bond to one of the two carbon atoms.
 - water is then added and hydrolysis takes place with replacement of HSO_4^- by OH^- and the reformation of H_2SO_4 .



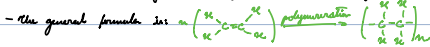
- this process requires 60 min, catalyst of concentrated phosphoric(V) acid at 300°C.

Testing for unsaturation

- whereas unsaturated addition reactions, alkenes can only undergo substitution reactions.
 - Methyl test substance (an alkene and another alkene) in bromine water will result in the alkene retaining its color, and the alkene losing it.
 - Alkenes will have a double, smaller flame due to the higher carbon-hydrogen.

Alkene polymerization of alkenes

- whereas substituted alkenes undergo addition reactions by breaking one of their double bonds (π bond).
 - because of this they can be joined together to produce long chains known as polymers.
 - the alkene used in this reaction is a monomer (a molecule that can be bonded to other identical molecules to form a polymer).
 - many of the most useful and common plastics are polymers of alkenes.
 - E.g. ethene polymerises to form poly(ethene), known as polythene.

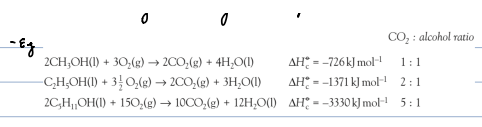


- It is the amount of
 - Even though the monomers are saturated when they form a polymer, they retain the ending -ene.
 - the way to write it is to have the prefix "poly" followed by the name of the monomer.
 - E.g. poly(butene), poly(pentene), poly(hexene), etc.

Polymer (and trade-name(s))	Monomer	Properties	Examples of use
Poly(ethene) (polythene, polythene, PE)	Ethene $\text{CH}_2=\text{CH}_2$	Tough, durable	Plastic bags, bowls, bottles, packaging
Poly(propene) (polypropylene, PP)	Propene $\text{CH}_3\text{CH}=\text{CH}_2$	Tough, durable	Crates and boxes, plastic rope
Poly(chloroethene) (polyvinyl chloride, PVC)	Chloroethene $\text{CH}_2=\text{CHCl}$	Strong, hard (not as flexible as polythene)	Insulation, pipes and guttering
Poly(tetrafluoroethene) (polytetrafluoroethylene, Teflon, PTFE)	Tetrafluoroethene $\text{CF}_2=\text{CF}_2$	Non-stick surface, withstands high temperatures	Non-stick frying pans, non-stick taps and joints
Poly(phenylethene) (polystyrene, PS)	Phenylethene (styrene) $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Light, poor conductor of heat	Insulation, packaging (foam)

Alcohols

- Alcohols contain hydroxyl (-OH) functional group.
 - General formula $\text{C}_n\text{H}_{2n+2}\text{O}$.
- the hydroxyl group is a polar group containing a hydrogen atom, it increases the solubility in water of the molecule relative to the corresponding alkane.
 - the most common alcohol, ethanol $\text{C}_2\text{H}_5\text{OH}$, is readily soluble in water.
- the alcohol molecules can form hydrogen bond with water with the hydroxyl group.
- the complete combustion of alcohols
 - Alcohols burn in air/oxygen to form CO_2 and H_2O .
 - these reactions are highly exothermic.
 - the further up in the homologous series, the more energy is released per mole.
 - due to more CO_2 being created as more carbon is.



- C₂H₅OH = C₂H₅O
 = 46 g mol⁻¹

5 C₂H₅OH = 5 × 46 = 230 g
 15 O₂ = 15 × 32 = 480 g
 → 10 CO₂ + 12 H₂O ΔH_c^o = -3330 kJ mol⁻¹

$\frac{5 \times 46}{114} = 47.98$ $\frac{15 \times 32}{480} = 98.72$ $\frac{47.98 - 98.72}{29.72} = 67.94\%$

Methanol may be less efficient than hydrocarbons, but they can be produced by renewable resources.

the oxidation reaction of alcohols

- the functional group of alcohols can be considered to often represent organic molecules
- these reactions alter the functional groups
- the carbon chain will be unaffected
- the products depend on whether the alcohol concerned is primary, secondary, or tertiary
- various oxidising agents can be used. E.g. acidified potassium dichromate (VI).

Primary alcohols

- Primary alcohols, e.g. ethanol, are oxidised in a two-stage process.
 - first to an aldehyde. (A-C=O)
 - therefore, ethanol goes to ethanal. (Removal of Hydrogen (oxidation)).
 - CH₃CH₂OH + O → CH₃CHO + H₂O
 - then to a carboxylic acid.
 - the second stage in the conversion of ethanol is ethanoic acid.
 - this is essentially a ring being left in the
 - CH₃COH + [O] → CH₃COOH
- General reaction:

$$\text{Primary alcohol} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{Aldehyde} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{Carboxylic acid}$$

Secondary alcohol

- secondary alcohols have a single hydrogen attached to the carbon that carries the functional group (-OH).
- this means that the only oxidation that can occur is a ketone.
- the oxidation of propan-2-ol produces propanone as the organic product.
- CH₃CH(OH)CH₃ + [O] → CH₃COCH₃ + H₂O
- $\text{H}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H} \xrightarrow[\text{[O]}]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{H}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$ (Propanone (ketone)).
- CH₃CH(OH)CH₃ + 2[O] → CH₃COCH₃ + 2H₂O (Half-equation).

Tertiary alcohols

- tertiary alcohols have no hydrogen on the carbon with the functional group.
- therefore, they can't be oxidised under the same conditions.
- any oxidation of a tertiary alcohol requires more drastic conditions or it necessary to break the skeleton
- therefore, no color change in dichromate (VI).

oxidation products of primary and secondary alcohols

- the initial products of the oxidation of alcohols, whether from primary or secondary alcohols, all contain >C=O groups.
- present in both aldehydes and ketones.
- the standard test for an aldehyde or ketone is that they both form orange crystalline precipitates with 2,4-dinitrophenylhydrazine solution.
- the precipitates can be recrystallised and its melting point determined.
- knowing the melting point of the crystals enables us to identify the particular aldehyde or ketone tested.
- to determine what is a ketone and an aldehyde, oxidise the substances.
- ketones won't oxidise (no hydrogen), and aldehydes will oxidise (one hydrogen).

esterification reactions

- Esters are derived from carboxylic acids (A-C(=O)OH) by reaction with alcohols.
- glycerol is an Ester.
- hydrolysis also exists.
- Esterification is a reversible reaction which occurs between an alcohol and a carboxylic acid when their initial water release in the presence of a catalyst, usually concentrated

carboxylic acid.

- alcohol + carboxylic acid \rightleftharpoons ester + water

- the reaction is regarded as a condensation reaction.

- Because as the solution of the two molecules takes place there is the elimination of water.

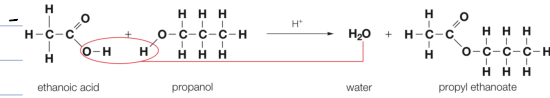
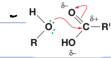


Figure 10.81 The esterification reaction involves the elimination of water

- the initial stage of the reaction can be viewed as the nucleophilic attack of the alcohol molecule.

- this occurs to the electron deficient carbon atom in the carboxylic acid group.

- the carbon is electron deficient due to the two oxygen atoms with a higher electronegativity value.



- the ester has the lowest boiling point of the components of the reaction mixture and so can be separated by distillation.

- Halogenoalkanes

- Halogenoalkanes contain an atom of fluorine, chlorine, bromine, or iodine bonded to the carbon skeleton of the molecule.

- General formula $C_nH_{2n+1}X$, X = halogen.

- Generally don't mix with water.

- the substitution reaction of halogenoalkanes with sodium hydroxide

- Halogenoalkanes are saturated molecules, but the halogen atom can be replaced in a substitution reaction.

- Halogenoalkanes are the group of compounds known as CFCs (chlorofluorocarbons).

- the greater the electronegativity of the halogen atom means that the Carbon-Halogen bond will become more polarised.



- the carbon can be said to be electron deficient.

- this means that the carbon is an electrophile, meaning it's susceptible to attack by nucleophiles.

- Nucleophiles have a lone pair of electrons and may be negatively charged.

- Electrophilic substitution - reaction of benzene

- Aromatic ring system such as benzene can participate in reactions with electrophiles.

- the electrophiles are attracted by the pi cloud above and below the benzene ring.

- these reactions are usually called electrophilic substitution.

- chlorination and nitration of benzene.