

12.1 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 synthesized and their structure analyzed
- the structures are made up of carbon-containing molecules such as DNA or RNA, and proteins.
- all living things in the universe, from macro-organisms such as bacteria, reproduce and grow using systems based on nucleic acids and proteins.
- there are **macromolecules**.
- proteins are made by connecting amino acids into long chains.
- the chains then fold and aggregate themselves into complex structures.

- the distinctive features of carbon

- the **fourth column** of carbon are known
- carbon has 3 special features of covalent bonding that allow it to have so many compounds.
 - carbon atoms can bond with one another to form a very large chain.
 - atoms of other elements can attach themselves onto the chains.
 - 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.
- **nitrogen** can form short chains.
- **sulfur** 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 **extensibility**.
- carbon is unique because it can also form double and triple bonds with other elements.
 - e.g. oxygen (carbonyl group, $\text{C}=\text{O}$) is an important feature of aldehydes, ketones, and carboxylic acids.
 - nitrogen (in nitro, $\text{N}=\text{O}_2$).
- the C-C bond is particularly strong compared with the strength of other **multiple bonds** between other groups of elements.
- this leads to thermal stability of organic compounds.
- the C-H bond is also more stable than other **covalent bonds**, such as H-I bond.
- $\text{C-H} \rightarrow 413 \text{ kJ mol}^{-1}$, $\text{H-I} = 319 \text{ kJ mol}^{-1}$.

- when a carbon atom is bonded to 4 other elements it's **bulletinically stable** as the outer shell ($n=2$) is filled
- thus, CCl_4 (tetrachloromethane) can't be hydrolysed by water, but NaCl (anion tetrachloride) can.
- water molecules are **unable** to bond with the chlorine by attacking the Na^+ cation through lone pairs on their oxygen atoms
- this will expand the extent of delocalisation.

- the nature of a homologous series

- the most basic structures in one class: a chain of carbon atoms is bonded to only hydrogen atoms.
- the series of compounds of this structure would be where another carbon is added to the end.
- when a substituent is bonded to different elements with a single bond (no double or triple bond), it's said to be **"substituted"**.
- the simplest component of the series is the hydrocarbon, CH_4 (methane).
- therefore, a series of molecules are progressively extended by a carbon atom (precisely a $-\text{CH}_2$ 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 $\text{C}_n\text{H}_{2n+2}$	Melting Point / K	Boiling Point / K	Physical state at room temp & pressure
Methane	CH_4	91	104	gas
Ethane	C_2H_6	90	106	gas
Propane	C_3H_8	93	131	gas
Butane	C_4H_{10}	155	275	gas
Pentane	C_5H_{12}	124	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 illustrate certain **key features** of all such series:

- the members of the compounds all contain a **constant feature** that denotes the series.

- for the series above the ending is **-ane**.

- the formulae show the **increasing chain length**.

- for the series above (ethane) CH_3 is added to the molecule.

- the molecules all have the same **general formula**.

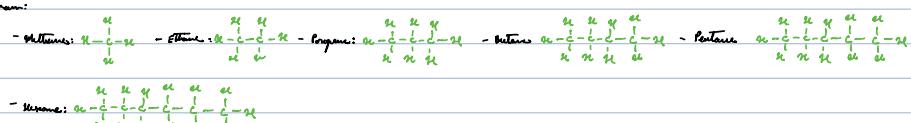
- for ethane it's: $\text{C}_n\text{H}_{2n+2}$

- 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.

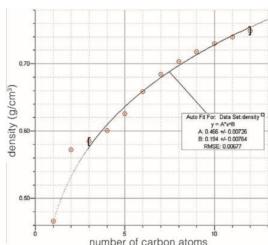
- increase in **boiling point** of the compound in the series.

- **Diagram:**



- 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 line carbon-hydrogen**:

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

- formula: C_nH_{2n}

- the aldehydes, which contain a **single carbon-carbon triple bond**.

- formula: $\text{C}_n\text{H}_{2n-2}$

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

- When a hydrogen atom is replaced with $-\text{CO}_2$, then the series is known as the **alcohols**.

- **Alcohols**

Molecule	Molecular formula ($\text{C}_n\text{H}_{2n+1}\text{OH}$)	Melting Point/°C	Boiling Point/°C	Physical state at room temp & pressure
Methanol	CH_3OH ($\text{C}_1\text{H}_3\text{O}$)	-	39	gas
Ethanol	$\text{C}_2\text{H}_5\text{OH}$ ($\text{C}_2\text{H}_5\text{O}$)	-	57	gas
Propanol	$\text{C}_3\text{H}_7\text{OH}$ ($\text{C}_3\text{H}_7\text{O}$)	-	97	gas
Butanol	$\text{C}_4\text{H}_9\text{OH}$ ($\text{C}_4\text{H}_9\text{O}$)	-	110	gas
pentanol	$\text{C}_5\text{H}_{11}\text{OH}$ ($\text{C}_5\text{H}_{11}\text{O}$)	-	140	gas
hexanol	$\text{C}_6\text{H}_{13}\text{OH}$ ($\text{C}_6\text{H}_{13}\text{O}$)	-	170	liquid
heptanol	$\text{C}_7\text{H}_{15}\text{OH}$ ($\text{C}_7\text{H}_{15}\text{O}$)	-	200	liquid
octanol	$\text{C}_8\text{H}_{17}\text{OH}$ ($\text{C}_8\text{H}_{17}\text{O}$)	-	231	liquid
nonanol	$\text{C}_9\text{H}_{19}\text{OH}$ ($\text{C}_9\text{H}_{19}\text{O}$)	-	-	-

- since the $-\text{OH}$ group is what gives the molecule its **determining property**, then it's considered the **functional group** for all alcohols.

- the **monomers** is a **homologous series** of compound that:

- contain the same **functional group**.

- share the same **general formula**, with successive members of the series having an additional $-\text{C}_n\text{H}_2-$ group.

- have similar **chemical properties**.

- show a **steady gradient** in certain **basic physical properties**.

- the following table shows the **determining property** of the particular homologous series:

- Homologous series are just the groups that functional group belongs 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 carbon bonded on the chain will be branched.

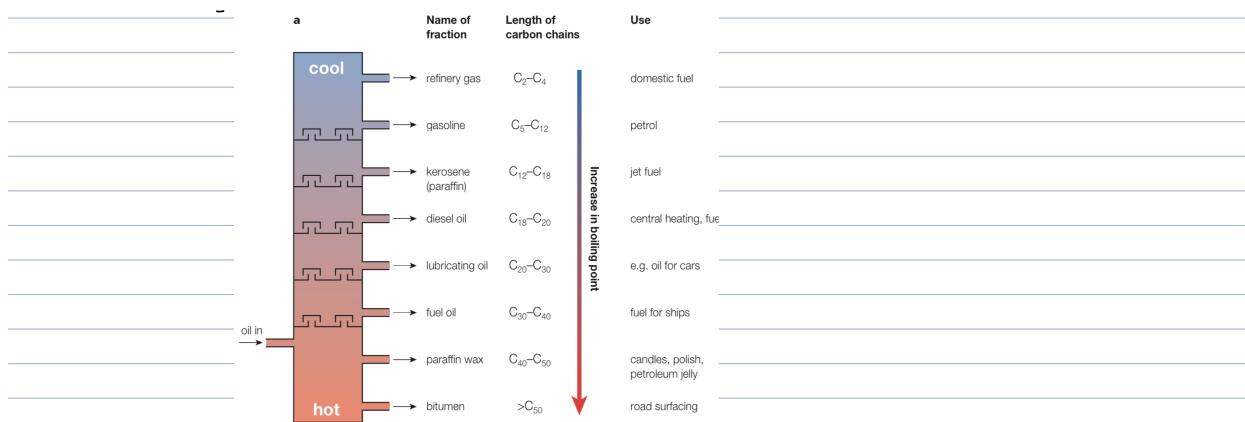
Homologous series	Functional group and condensed structural formula	Suffix in name of compound	General formula	Structure of the functional group
Alkanes	$-\text{CH}_2-\text{CH}_2-$	-ane	$\text{C}_n\text{H}_{2n+2}$	*
Alkenes	$-\text{CH}=\text{CH}-$ alkenyl	-ene	C_nH_{2n}	$\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$
Alkynes	$-\text{C}\equiv\text{C}-$ alkynyl	-yne	$\text{C}_n\text{H}_{2n-2}$	$-\text{C}\equiv\text{C}-$
Halogenoalkanes	$-\text{X}$ (where X = F, Cl, Br, I)	name uses a prefix (chloro-, bromo-, etc)	$\text{C}_n\text{H}_{2n+1}\text{X}$	$-\text{X}$ (where X = F, Cl, Br, I)
Alcohols	$-\text{OH}$ hydroxyl	-ol	$\text{C}_n\text{H}_{2n+1}\text{OH}$ or ROH	$-\text{O}-\text{H}$
Aldehydes	$-\text{CHO}$ aldehyde (carbonyl)	-al	$\text{C}_n\text{H}_{2n+1}\text{CHO}$ or RCHO	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$
Ketones**	$-\text{CO}-$ carbonyl	-one	$\text{C}_n\text{H}_{2n+2}\text{COC}_m\text{H}_{2m+1}$ or RCOR'	$\begin{array}{c} \diagup \\ \text{R} \\ \\ \text{C}=\text{O} \\ \\ \text{R}' \end{array}$
Carboxylic acids	$-\text{COOH}$ or $-\text{CO}_2\text{H}$ carboxyl	-oic acid	$\text{C}_n\text{H}_{2n+1}\text{COOH}$ or RCOOH	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \\ \text{O}-\text{H} \end{array}$

*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).

Motifs 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 more polar nature, the only forces are London dispersion forces.
 - London dispersion forces occur due to the temporary dipole (due to temporary electron distribution shifts) being generated in the compound.
 - The strength of the force is related to the number of electrons in the structure, and the surface area of the molecule (vdw interactions occur).
 - The more electrons, the stronger the force
 - The larger the chain, the stronger the force.
- As more C-H's are added, the increase in boiling temp will be less significant.
- A number bond is formed with alcohols.
- Although, their initial boiling temperatures are much higher than the alkanes.
- This shows that they have a stronger intermolecular force acting between them.
- The idea of chain lengths, and the increase in temp 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.

- As 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.

Formulae of organic compounds

Type of formula

- there are three types of formula 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 obtained from combustion analysis.

- there is a difference between a cyclohexane (cyclohexene) and CH₂CO₂ (acetic acid (vinegar)), one has an aliphatic group (-CH₂) and the other has a carboxylic acid group (-CO₂).

- its skeletal formula is a formula where only the carbon-carbon bonds are shown.

- it looks like 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 CH₃CH₂CH₃ and butane as CH₃CH₂CH₂CH₃ or CH₃(CH₂)₂CH₃.

- the full structural formula shows every bond.

- there are other abbreviations:

- when next atoms don't have to be written, part of the molecule can be abbreviated to R.

- molecules which contain a benzene ring, aromatic compounds, are used.

Chain and rings

- the alkanes 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.



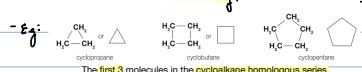
- the ignition properties of 2,2,4-trimethylpentane are the basis of the octane rating of gasoline.

- 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, these cycloalkanes are saturated molecules.

- unsaturated cycloalkanes exist though.

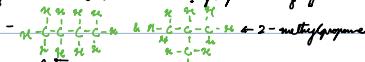
Structural isomers

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

- for the alkanes the first 3 are isomorphous.

- after the first 3, butane can be changed from CH₃CH₂CH₂CH₃ to CH₃CH(CH₃)CH₃.

- the difference is that there is a -CH₃ group branching off the middle carbon atom.



- the molecule on the latter is known as 2-methylpropane.

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

- in the alkene series the first possible isomer occur with propene and butene.

- the isomer in the alkene group is attached to a terminal carbon atom, or one in the middle.

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

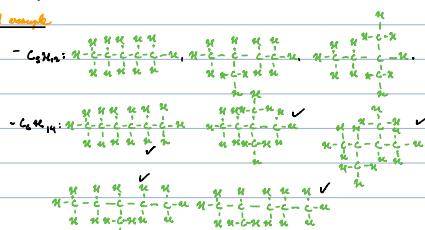


- Rearranging the compound into an isomer (**DO YOU'T FLICK IT UP**).

- Deriving 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 number them C-C bonds can rotate freely.

- Worked example



- Naming alkanes

Prefix of name	Number of carbon atoms in chain	Name of alkane	Condensed structure
Meth-	1	Methane	CH_4
Eth-	2	Ethane	CH_3CH_3
Prop-	3	Propane	$CH_3CH_2CH_3$
But-	4	Butane	$CH_3CH_2CH_2CH_3$
Pent-	5	Pentane	$CH_3CH_2CH_2CH_2CH_3$
Hex-	6	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$

Name of side-chain (R group)	Condensed structure
Methyl	$-CH_3$
Ethyl	$-CH_2CH_3$
Propyl	$-CH_2CH_2CH_3$
Butyl	$-CH_2CH_2CH_2CH_3$

■ Table 10.7 Names of some alkyl groups

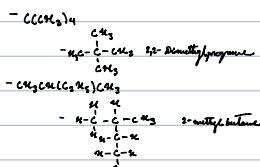
- How to determine name:

- Identify longest chain
- Not necessarily middle one.

- Branches

- Position & carbon #s

- Worked example



- Deriving 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, many isomers are possible.

- Naming isomers of non-cyclic alkenes and alkynes

- Position of the double bond is not establishes the location of the other branches.

- Eg: $CH_3CH_2CH=CH_2$ But-1-ene

- simplest alkene is C_2H_2

- Acidity of organic compounds

- Haloalkanes - $R-Cl$ or C_6H_5-Cl

- characterised by the -Cl group.

- Name of the alcohol ends in -ol

- The position of the alcohol group determines the name:

- Eg: $CH_3CH_2CH_2CH_2OH$ = propan-1-ol.

$CH_3CH_2CH(OH)CH_3$ = propan-2-ol.

- The alcohol group can be placed in the chain or as a branch.

- The name of the compound will use the same name, however, but with a different order.

- aldehydes - general formula R-CHO or C_nH_{2n+1}CHO

- 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 put carbon one from the aldehyde group.
- this means its position isn't required to be mentioned.
- the ending is -al.



- ketones - general formula R-C(=O)-R' (R' is never alkyl group or R, or different).

- ending is -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 acids - R-COOH or R-C₂O₄H

- -COOH / CO₂H (C=O is a double bond).
- ending -oic acid.
- always on the end (terminal).
- It being the functional group will always be counted as the first carbon.

- halogenoalkanes - general formula R-X, X = F, Cl, Br, I

- the halogenoalkane (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-bromethane, 2-chloropropene, 1-bromo-2-chloropropane.
- the names are: fluoro-, chloro-, bromo-, and iodo-.

- naming structural isomers

- there are three types of isomers:

- same carbon branching of the hydrocarbon backbone of the molecule
- E.g.: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ butane, $\text{CH}_3-\text{CH}_2\text{CH}_2\text{CH}_3$ 2-methylbutane, $\text{CH}_3-\overset{\text{CH}_3}{\text{CH}}-\text{CH}_2$ 2,2-dimethylpropane

- Position isomers:

- there are isomers where the functional group occupies a different point of attachment to the chain.
- E.g.: $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}\text{H}$ 1-Propanol, $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}\text{H}$ 2-Butanol

- Functional group isomers

- there are isomers with the same molecular formula, but different properties, and a different formula.
- $\text{C}_2\text{H}_5\text{OSO}_3\text{K}$ and $\text{C}_2\text{H}_5\text{OCO}_2\text{K}$.

- 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'	-alkoxy (prefix)	C _n H _{2n+1} OC _n H _{2n+1}	
esters	R-COO-R'	-oate	C _n H _{2n+1} COOC _n H _{2n+1}	
amines	R-NH ₂	-amine (or prefix amino-)	C _n H _{2n+1} NH ₂	
amides	R-C(=O)N ₂	-amide	C _n H _{2n+1} C(=O)NH ₂	
nitriles	R-CN	-nitrile	C _n H _{2n+1} C≡N	
arenes	phenyl-	-benzene (or prefix phenyl-)	C ₆ H ₅ -	

- ethers - general formula R-O-R', R' is an alkyl group

- ethers are molecules with an oxygen atom inserted in the hydrocarbon chain.
- They are volatile solvents.

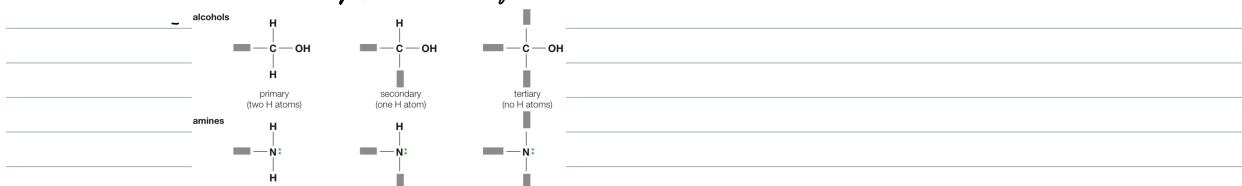
- A tertiary carbon atom is attached to three functional groups with no hydrogen atoms.

Amines

- There are compounds derived from ammonia.

- The number of nitrogens in legs 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.

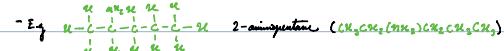


- If two hydrogen atoms are replaced, then a secondary amine is formed.

- The alkyl groups aren't necessarily the same type.

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

- Prefix -amine



- When two hydrogens are removed from the ring, then the name changes to -diamine, and 3° Triamine.

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

- Most commonly phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.



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

- This occurs when the carbonyl group of one molecule reacts with the amine group of the other molecule releasing H_2O .



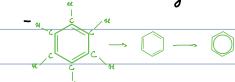
Hydrocarbons (aromatic)

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

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

- These are compounds which contain a benzene ring.

- Benzene is C_6H_6 arranged in a ring structure.



- Benzyl groups are based on a benzene ring with the methyl group $= \text{C}_6\text{H}_5\text{CH}_3$.

- Inside the ring are delocalized electrons.

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



Establishing the structures of benzene

- Benzene is a colorless 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.

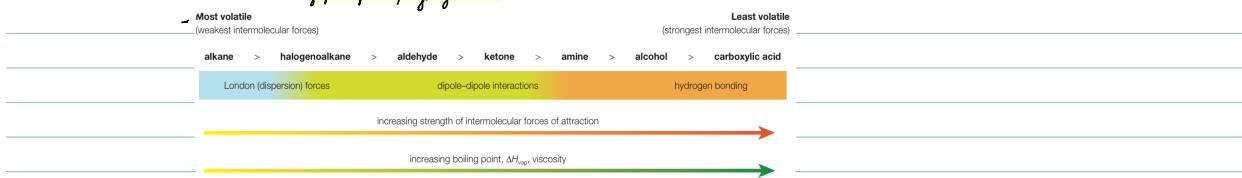
- Resonance structures is a structure which blends the characteristics of both resonance forms.

Fraction trends in homologous series

Methane

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

- Volatility is a measure of how easily a substance evaporates.
- A highly volatile substance evaporates easily and has a low boiling point.
 - This depends on the intermolecular forces of a molecule.
- Volatility rules are:
 - An increase in boiling point means that the volatility will decrease.
 - As the chain increases in size, the volatility will decrease.
 - This means stronger London dispersion forces between the molecules.
 - Branched isomers will work. Why? They have a lower boiling point than its straight chain isomer.
 - The branching will result in the molecule having 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 bonding will be less volatile.



Volatility of water

- The solubility of an organic compound in water is determined by two factors: the functional groups & the hydrocarbon.
- If the functional group in the compound is able to interact with water, e.g. strong hydrogen bonds, then this will favour 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.
- Halogenoethanes and others aren't soluble because their functional groups can't form hydrogen bonds with water.

10.2 Saturated group chemistry

Alefenes

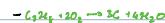
- Following key points to follow:
 - Alkenes are hydrocarbons, and therefore contain carbon-carbon double bonds.
 - General formula C_nH_{2n+2} .
 - Alkenes are saturated hydrocarbons.
 - Retained means that carbon-carbon bonds are single bonds.
 - Although they are relatively unreactive compounds, some of their reactions are highly significant and important.
- Explaining the low reactivity of the alkenes
 - Alkenes are chemically unreactive.
 - The relatively strong covalent bonding in the molecule means that the alkenes are extremely stable until sufficient energy has been provided.
 - $E_C = 326 \text{ kJ/mol}^{-1}$, and $E_C - E = 412 \text{ kJ/mol}^{-1}$.
 - The molecule will only react when enough energy to break all the bonds has been supplied.
- Due to the non-polar characteristic of alkenes, they aren't susceptible to attack by nucleophiles (electron pair donor), and electrophiles (electron pair acceptor).

The combustion of alkenes

- The reason that alkenes are good fuels is because the combustion reactions of these molecules are highly exothermic.
- This is due to the relatively high strength of the C=O bond in carbon monoxide and the C=O bond in water.
- There are better products of the combustion.
- Alkenes burn in the presence of excess oxygen to form CO_2 & H_2O .
 - E.g. $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^\circ = -890 \text{ kJ/mol}^{-1}$
 - $C_2H_4 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad \Delta H^\circ = -2220 \text{ kJ/mol}^{-1}$
- When the alkenes are burnt in limited oxygen, then carbon monoxide is formed rather than CO_2 .
 - $2C_2H_4 + 3O_2 \rightarrow 2CO + 4H_2O$



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



- the incomplete combustion of acetylene can take place in the flame where the cold wire burns to give the characteristic yellow flame.

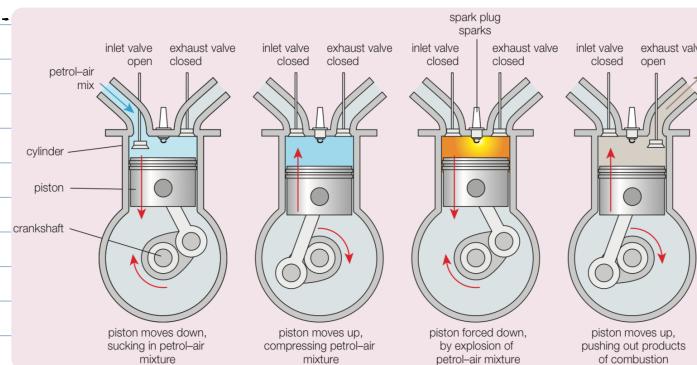
- the glow of the hot solid carbon particles give the flame the yellow color.

- sootene is produced from organic waste when it decomposes in the absence of air.

- sootene is actually used to produce energy.

- the role of the fuel in a petrol engine

- the gasoline (petrol) engine



- the first downward motion of the piston

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

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

- in a fuel-injection car, the piston moves down with each in the fuel-air mixture into the cylinder.

- first cylinder

- 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 OT being increased by a few hundred degrees.

- this is due to inter-molecular dispersion forces between the gas molecules as they're forced 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

- 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 cylinder

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

- if insufficient O_2 has been drawn in the fuel/air mixture / insufficient time for complete burning, then other substances 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.

- the 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 alkenes with halogens

- since the alkenes are unsaturated molecules, the main type of reaction they can undergo is substitution reaction.

- % substitution reaction is where one of the carbons is replaced by the atom of another element.
- Under the appropriate conditions, a mixture of methane and chlorine gases reacts to form chloromethane and hydrogen chloride.



- the degree of substitution observed in these reactions can't be easily controlled.
- Ethane and other alkanes will undergo similar substitution reactions with chlorine or bromine.

- Eg (conditions: sunlight / UV radiation)



- the product of this second reaction will be a mixture of dibromomethane (1,1-dibromethane & 1,2-dibromethane).

- It's a mixture of the two possible isomers after the substitution.

- This mixture is due to there being no control over which hydrogen atom is substituted.

- The halogen molecules are able to act in this way because they're split into unpaired atoms with an unpaired valence electron.
- There are however as free radicals.
- Once formed, they will initiate a chain reaction where halogen molecules are produced.

Bond breaking and bond cleavage

- A 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 bond scission, the bond breaks so that one electron remains with each fragment:
 Structure: $\text{Cl}-\text{Cl} \rightarrow \text{Cl}\cdot + \text{Cl}\cdot$

- Two chlorine free radicals are produced by UV radiation.

- When one of the chlorine free radicals meets a methane molecule, they can react together:



- The carbon-hydrogen bond in broken homolytically (the atom will retain its original amount of electrons) by the chlorine free radical ($\text{Cl}\cdot$) to produce a methyl free radical ($\text{C}_2\text{H}_5\cdot$).

- One chlorine free radical ($\text{Cl}\cdot$) will remove hydrogen from $\text{H}-\text{C}_2\text{H}_5$ producing HCl .

2) In heterolytic fission, the bond breaks, and one atom retains both electrons, resulting in ions being produced.
 Structure: $\text{Cl}-\text{C}_2\text{H}_5 \rightarrow \text{Cl}^- + \text{C}_2\text{H}_5^+$ (9 retains one electron).

- This won't normally occur.

- 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				
Carbon valence shell electrons	4	$8 \div 2 = 4$	$(6 \div 2) + 1 = 4$	$6 \div 2 = 3$
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 photocatalytic reaction.

- The energy of a UV photochemical is of the order 1000 J/mol.

- Enough to break $\text{C}-\text{Cl}$ into $\text{Cl}\cdot + \text{C}\cdot$ (1000-2000 J/mol).

- The homolytic fission of the bond between the Cl atom is thought to be the initial step of the reaction.

- The next step would be one of the $\text{Cl}\cdot$ radicals will react with a methane molecule.



- The methyl free radical then reacts with a chlorine molecule to form a chlorine free radical.



- Due to the fact the final step produces another $\text{Cl}\cdot$ a chain reaction will be induced.

- As the reaction proceeds there is a build up of free radicals thanks to the termination step.

- the final step involves the recombination of two free radicals with each other.

- there are three possible termination steps:



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

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

- 3 step 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 dichloromethane and a chlorine free radical.

- Termination: The final reaction is divided between 3 different possible reactions:



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.

- One 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 reactions of alkenes with hydrogen and halogens

- The carbon double bond is the functional group of the alkene.

- 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.

- With an addition reaction an atom of another element will be added on both of the carbons 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.

- Halogen reacts with alkenes to produce substituted compounds.

- These reactions take place at room temp, and also has a loss of 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 hexane.

- E.g.:



- Electrophilic addition reactions

- Hydrogen halides (HCl , HBr , etc.) react with alkenes to form halogenoalkanes.

- The reactivity order is $\text{HCl} > \text{HBr} > \text{HCl}$.

- The reason that HCl is the best reagent is because it is the least electronegative, meaning its δ^+ is quite low meaning it will react much easier than the stronger HBr & HCl bonds.

- Hydration

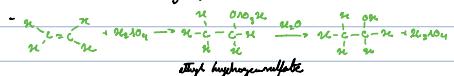
- The reaction with water is known as hydration and the alkene is converted into an alcohol ($-\text{OH}_2$).

- Water can't react with the alkene directly.

- In the lab this is accomplished with the use of concentrated sulfuric acid to form an addition product.

- The reaction will have an H^+ ion and an SO_4^{2-} ion both bond to one of the two carbon atoms.

- Water is then added and hydrolysis takes place with replacement of SO_4^{2-} by OH^- and the regeneration of H_2SO_4 .



- This process requires 60 min, catalyst of concentrated phosphoric(V) acid at 200°C .

- Taking for nitration

- In nucleophilic addition reactions, alkene can only undergo substitution reaction.

- Making two substances (an alkene and another alkene) in bromine water will result in the alkene losing its color, and the alkene losing it.

- Alkene will have a shorter, rougher flame due to the higher carbon-hydrogen

- Allotopic polymerization of alkenes

- Alkene and substituted alkene undergo addition reactions by breaking one of their double bonds (1 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 polymerizes to form poly(ethene), known as polythene.

- The general formula is $n \left(\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{H} \end{array} \right)$ polymer $\left(-\text{C}-\text{C}- \right)_n$

- n 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(heptene), etc.

Polymer (and trade-name(s))	Monomer	Properties	Examples of use
Poly(ethene) (polyethylene, 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

- Molecules contain hydroxyl (-OH) functional group.

- General formula $\text{C}_n\text{H}_{2n+1}\text{OH}$.

- 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 bonds with water with the hydroxyl groups.

- Non-combustion of alcohols

- Alcohol burn in air/oxygen to form CO_2 and H_2O .

- These reactions are highly exothermic.

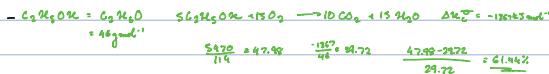
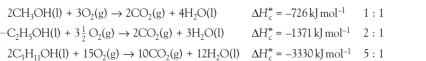
- The further up in the homologous series, the more energy is released per mole.

- Due to more CO_2 being created as you move up.

0 0

CO₂ : alcohol ratio

- Eg:



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

The oxidation reactions of alcohols

- the functional group of alcohols can be oxidised to other important organic molecules
- these reactions alter the functional group
- the reaction 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 alcohol

Will result in one oxidised twice?

- primary alcohols, e.g. ethanol, are oxidised in a two-stage process

- first to an aldehyde ($\text{-CH}_2\text{OH}$)

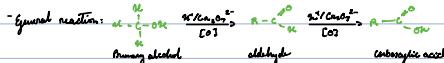
- therefore, ethanol goes to ethanal. (Removal of Hydrogen (Oxidation)).



- then to a carboxylic acid

- the second stage is the conversion of ethanal to ethanoic acid.

- this is essentially adding OH^- to the



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.

- an oxidation of propan-2-ol produces propanone as the organic product.



(propan-2-ol (secondary alcohol))



Tertiary alcohol

- tertiary alcohols have no Hydrogen on the carbon with the functional group.

- therefore, they can't be oxidised under the same conditions.

- their oxidation on a tertiary alcohol requires more drastic conditions or it's necessary to break the skeleton.

- therefore, no colour 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 form orange crystalline precipitates with 2,4-dinitrophenylhydrazine solution.

- the precipitate can be recrystallised and its melting point determined.

- knowing the melting point of the crystals enable us to identify the particular aldehyde or ketone tested.

- to determine what is in a ketone and an aldehyde, oxidise the substance.

- Ketones won't oxidise (no hydrogen), and aldehydes will oxidise (one hydrogen).

Esterification reactions

- Esters are derived from carboxylic acids ($\text{-C}=\text{O}-\text{OH}$) by reaction with alcohols.

- Esterification is an ester.

- Alkyl esters also exist.

- Esterification is a reversible reaction which occurs between an alcohol and a carboxylic acid when they're heated under reflux in the presence of a catalyst, usually concentrated

sulfuric acid.



- the reaction is regarded as a **condensation reaction**.

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

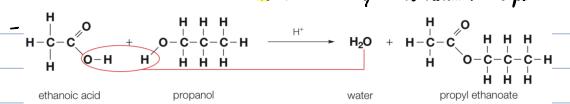
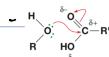


Figure 10.81 The esterification reaction involves the elimination of water

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

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

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



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

Halogenucarbons

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

- general formula $\text{C}_n\text{H}_{m-n}\text{X}_n$, $n > 1$ 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 CX_4 (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 **able to attack by nucleophile**.

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

Electrophilic substitution reactions of benzene

- benzene being delocalised will 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.