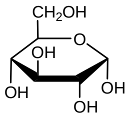
Chemistry Support for Biological Molecules

The associated videos together with some self assessment questions can be found at
http://science.uwe.ac.uk/LS/chem

1. Introduction

- The aim of this series of clips is to enable you to understand the structures and concepts which are introduced in the module, Biological Molecules
- Some of these structures might be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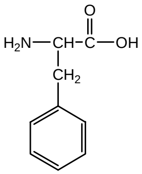
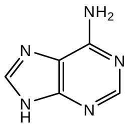
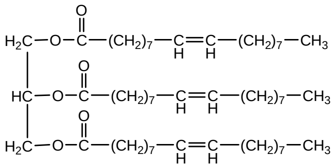

phenylalanine


adenine


a triglyceride - triolein

- These structures, at the moment, probably look horribly complicated! In time though, once you have been introduced initially, to some more simple organic molecules they should become less frightening!

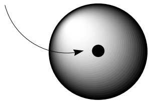
2. The Elements

- You will be familiar with the names of many of the elements, e.g. hydrogen, helium, lithium, berylium, boron, carbon etc., etc..
- They all have symbols

Hydrogen	**H**
Helium	**He**
Lithium	**Li**
Berylium	**Be**
Boron	**B**
Carbon	**C**
Nitrogen	**N**
Oxygen	**O**
Fluorine	**F**
Neon	**Ne**
etc.	

- You need to remember the symbols of the more common elements.

- The elements are made up of atoms.
- Atoms are made up of a dense nucleus containing protons and neutrons, surrounded by electrons.



- Protons are positively charged, electrons are negatively charged and neutrons have no charge
- Within each neutral atom there will be an equal number of protons and electrons.
- One element is **distinguished** from another by the number of protons (= the number of electrons) its atoms contain.
- The number of protons in an atom of an element is its **ATOMIC NUMBER**.
- The atomic numbers of some of the elements are:

Element	**Symbol**	**Atomic Number**
Hydrogen	**H**	**1**
Helium	**He**	**2**
Lithium	**Li**	**3**
Berylium	**Be**	**4**
Boron	**B**	**5**
Carbon	**C**	**6**
Nitrogen	**N**	**7**
Oxygen	**O**	**8**
Fluorine	**F**	**9**
Neon	**Ne**	**10**
Sodium	**Na**	**11**
Magnesium	**Mg**	**12**
Aluminium	**Al**	**13**
Silicon	**Si**	**14**
Phosphorus	**P**	**15**
Sulphur	**S**	**16**
Chlorine	**Cl**	**17**
Argon	**Ar**	**18**
etc.		

Mass Number and Isotopes

- All atoms of a given element have the same number of protons.
- They can have different numbers of neutrons.
- **Isotopes** are atoms of a given element (∴ same nos. of protons) which have different numbers of neutrons.
- The **Mass Number** of an atom is the sum of the number of its protons and neutrons.
- Isotopes therefore have the same atomic number but different mass numbers.
- Carbon is an element which has isotopes:
- The most abundant isotope (98.89% of naturally occurring carbon) has a mass no. of 12, written ^{12}**C**. As carbon has an atomic no. of 6, this isotope ∴ has 6 neutrons

- There is also ^{13}**C** (1.11% naturally occurring carbon). This isotope ∴ has 7 neutrons.
- Finally ^{14}**C** (occurring in trace amounts). This isotope ∴ has 8 neutrons. This isotope is radioactive and is the isotope used in ‘carbon dating’.

3. Masses of Atoms, Relative Atomic Mass, the Mole

- The majority of the mass of an atom is accounted for by its protons and neutrons.
- The mass of a proton is very similar to that of a neutron.
- The mass of an electron is ~1/2000 that of a proton.

- Atoms are very, very small with very, very low masses.
- e.g. the mass of an atom of gold is ~ 3.3x10^{-22}g
- 1g of gold ∴ consists of ~ 1/ 3.3x10^{-22} atoms = ~3x10^{21} atoms i.e. **a very large number of atoms.**
- To overcome this chemists use a scale of Relative Atomic Masses which is based on ^{12}C.
- The Relative Atomic mass of ^{12}C is set at exactly 12.

- The relative atomic mass of all other elements is the average mass of an atom of that element relative to ^{12}C.
- The relative atomic masses of some of the more common elements are

Element		**Relative Atomic Mass**
Hydrogen	**H**	**1.01**
Carbon	**C**	**12.0**
Nitrogen	**N**	**14.0**
Oxygen	**O**	**16.0**
Sodium	**Na**	**23.0**
Chlorine	**Cl**	**35.5**
Bromine	**Br**	**79.9**

- Notice that some of the values are not whole numbers. This is because of the existence of isotopes, e.g. for chlorine, there are two isotopes, ^{35}Cl and ^{37}Cl which occur in a ratio of ~75:25. The result is a relative atomic mass of 35.5.
- Bromine is another example – 2 isotopes, ^{79}Br and ^{81}Br.

The Mole

- The mass of one atom of ^{12}C = 1.9926 x10^{-23} g
- 12g of ^{12}C ∴ contains 12/1.9926x10^{-23} = 6.022x10^{23} atoms
- This is defined as ONE MOLE of ^{12}C.
- 6.022x10^{23} is called the AVOGADRO CONSTANT.
- One mole of He is 6.022x10^{23} atoms
- One mole of Zn is 6.022x10^{23} atoms
- And in simple terms, the relative atomic mass in g of an element represents 1 mole of that element.

4. Atoms, Electrons and the Periodic Table

- In the simplest model electrons in atoms occupy shells which contain fixed numbers of electrons. These shells are numbered 1, 2, 3….
- Shell 1 is closest to the nucleus, shell 2 lies further from the nucleus than shell 1 and so on.

- Within each shell the electrons are grouped into one or more subshells known as atomic orbitals – labelled s, p, d, f.

- There is a maximum number of electrons in the subshells:

  2 in s

  6 in p

  10 in d etc.

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	labelled
• Shell 1 – only one s subshell	1s
• Shell 2 – s and p subshells	2s 2p
• Shell 3 – s, p and d subshells	3s 3p 3d
• Shell 4 – s, p, d and f subshells	4s 4p 4d 4f

- **The subshells or orbitals have different energies**. They are filled one shell at a time, with the lowest energy shell filled first.

- The order of increasing energy of the subshells or orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p etc. and this is the order in which they are filled.

- So for H, 1 electron – in the 1s subshell
- The electron configuration for H is ∴ labelled $1s^1$.

- for He, 2 electrons - both in the 1s subshell which is now full .
- The electron configuration for He is ∴ $1s^2$.

- for Li, 3 electrons - 2 in the 1s subshell and the 3rd in the subshell of next highest energy, the 2s subshell. Electron configuration ∴ $1s^2 2s^1$.

- for Be, 4 electrons - 2 in the 1s subshell and the 3rd and 4th in the 2s subshell. Electron configuration ∴ $1s^2 2s^2$.

- The 2s subshell is now **full,** so for the next element, the additional electron must 'go' into the 2p subshell.

- So for B, 5 electrons – 4 of these fill the 1s and 2s subshells, with the 5th in the 2p subshell. Electron configuration ∴ $1s^2 2s^2 2p^1$.

- Using the list we had earlier of increasing energy of the subshells or orbitals, **1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p** etc. the electron configuration of each of the elements can be deduced.

- So for elements, atomic numbers 1 - 20

H $1s^1$							**He** $1s^2$
Li $1s^2 2s^1$	**Be** $1s^2 2s^2$	**B** $1s^2 2s^2 2p^1$	**C** $1s^2 2s^2 2p^2$	**N** $1s^2 2s^2 2p^3$	**O** $1s^2 2s^2 2p^4$	**F** $1s^2 2s^2 2p^5$	**Ne** $1s^2 2s^2 2p^6$
Na $1s^2 2s^2 2p^6 3s^1$	**Mg** $1s^2 2s^2 2p^6 3s^2$	**Al** $1s^2 2s^2 2p^6 3s^2 3p^1$	**Si** $1s^2 2s^2 2p^6 3s^2 3p^2$	**P** $1s^2 2s^2 2p^6 3s^2 3p^3$	**S** $1s^2 2s^2 2p^6 3s^2 3p^4$	**Cl** $1s^2 2s^2 2p^6 3s^2 3p^5$	**Ar** $1s^2 2s^2 2p^6 3s^2 3p^6$
K $1s^2 2s^2 2p^6 3s^1 3p^6 4s^1$	**Ca** $1s^2 2s^2 2p^6 3s^1 3p^6 4s^2$						

- Again using the list of the order of increasing energy of the subshells which we had earlier i.e. 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p etc.) the next subshell to be filled is 3d (filled when it contains 10 electrons) and then 4p and so on…..

- A useful point to note here is that He, Ne, Ar (and others whose electron configuration we have not considered in detail) are called the Noble gases They are very inert and tend to exist as atoms. **This is because their electron configuration is very stable.**

- The electron configurations of the elements considered so far can be re-written to show how their electron configurations relate to those of the noble gases:

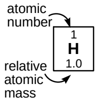
H $1s^1$							**He** $1s^2$
Li $1s^22s^1$ or [He] $2s^1$	**Be** $1s^22s^2$ or [He] $2s^2$	**B** $1s^22s^22p^1$ or [He] $2s^22p^1$	**C** $1s^22s^22p^2$ or [He] $2s^22p^2$	**N** $1s^22s^22p^3$ or [He] $2s^22p^3$	**O** $1s^22s^22p^4$ or [He] $2s^22p^4$	**F** $1s^22s^22p^5$ or [He] $2s^22p^5$	**Ne** $1s^22s^22p^6$ or [He] $2s^22p^6$
Na $1s^22s^22p^6$ $3s^1$ or [Ne] $3s^1$	**Mg** $1s^22s^22p^6$ $3s^2$ or [Ne] $3s^2$	**Al** $1s^22s^22p^6$ $3s^23p^1$ or [Ne] $3s^23p^1$	**Si** $1s^22s^22p^6$ $3s^23p^2$ or [Ne] $3s^23p^2$	**P** $1s^22s^22p^6$ $3s^23p^3$ or [Ne] $3s^23p^3$	**S** $1s^22s^22p^6$ $3s^23p^4$ or [Ne] $3s^23p^4$	**Cl** $1s^22s^22p^6$ $3s^23p^5$ or [Ne] $3s^23p^5$	**Ar** $1s^22s^22p^6$ $3s^23p^6$ or [Ne] $3s^23p^6$
K $1s^22s^22p^6$ $3s^13p^6\ 4s^1$ or [Ar] $4s^1$	**Ca** $1s^22s^22p^6$ $3s^13p^6\ 4s^2$ or [Ar] $4s^2$						

- The Periodic table arranges all of the elements in a way which reflects the way in which electrons are arranged within the atoms.

The Periodic Table

Group	1	2											3	4	5	6	7	8
	1 **H** 1.0																	2 **He** 4.00
	3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
	11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 39.9
	19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.8	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
	37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** 98.9	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 131
	55 **Cs** 133	56 **Ba** 137	71 **Lu** 175	72 **Hf** 178	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Tl** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** 209	85 **At** 210	86 **Rn** 222
	87 **Fr** 223	88 **Ra** 226	103 **Lr** 262															

57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 145	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173
89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 254	100 **Fm** 257	101 **Md** 258	102 **No** 259



- The elements are arranged in rows called periods, and in columns called groups.
- **Elements in the same group have a similar electron configuration over and above that of a noble gas.**
- For group 1 elements this ‘outer’ electron configuration is s^1
- For group 2 elements this ‘outer’ electron configuration is s^2
- For group 3 elements this ‘outer’ electron configuration is s^2p^1 and so on.

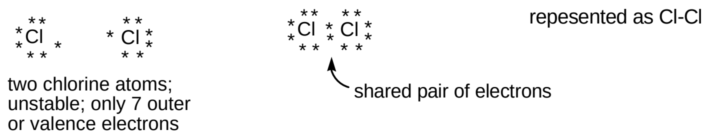
5. Families of Elements

- As previously noted **He, Ne, Ar, Kr** etc. are called the **Noble gases**. They are very inert, exist as atoms and show very, very little tendency to share electrons and form molecules. This is because their electron configuration is very stable.
- Atoms of all other elements do not have such stable electron configurations and endeavour to achieve them by loosing or gaining electrons, or by sharing electrons and in doing so form compounds.
- **Li, Na, K** all have 1 electron over and above that of a noble gas, e.g. Li can be represented as [He] $2s^1$, Na as [Ne]$3s^1$. To attain a **stable** noble gas electron configuration they ∴ loose 1 electron and form single positive ions e.g. Li^+, Na^+, K^+.
- **Be, Mg, Ca** etc. all have 2 electrons over and above that of a noble gas (s^2). To attain a noble gas electron configuration they ∴ loose 2 electrons and form double positive ions e.g. Be^{2+}, Mg^{2+}, Ca^{2+}.

- **F, Cl, Br** etc. all have a valence shell s^2p^5. They are ∴ all 1 electron short of the electron configuration of a noble gas. Sometimes they attain a stable electron configuration by gaining 1 electron to form F^-, Cl^- etc.
- In other instances they achieve stability by sharing one electron with another atom by forming a **covalent bond.**
- Similarly **O, S** etc. have a valence shell containing 6 electrons and need to gain 2 electrons to attain a noble gas electron configuration and so on.
- This arrangement of families of elements is included in the format of the Periodic Table

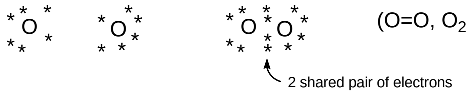
6. Bonding

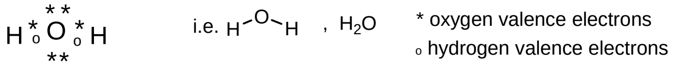
- In **ionic substances**, e.g. NaCl, the structure is made up of a collection of equal number of Na^+ and Cl^- ions. There is strong attraction between the positive and negatively charged ions – **ionic bonding**.
- **Covalent bonding** occurs when atoms attain a noble gas electron configuration by sharing electrons.
- Consider chlorine. The electron configuration of Cl is 1 electron short of that of argon. Chlorine atoms form chlorine molecules, Cl_2, in which each of the 2 Cl atoms share one electron with each other:

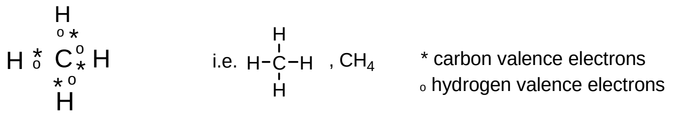


- The result is that each Cl atom now has the stable electron configuration of argon.

- There are millions of examples of covalent molecules in which atoms share electrons and in doing so attain noble gas electron configurations, e.g.







- Structures such as those above which illustrate the valence electrons in each atom and how they are shared to form covalent bonds are called Lewis structures
- Note that in the examples we have so far, that H always forms one covalent bond, oxygen two, carbon four. This is because they need 1, 2 or 4 electrons respectively to attain a noble gas electron configuration. 1, 2 and 4 are called the **valencies** of H, O and C respectively.

7. Carbon Compounds – Organic Chemistry - an introduction

- **Organic compounds** are compounds based on carbon.
- They often have very complicated structures, BUT this need not be a problem when you start looking at them in terms of the **functional groups** they contain.
- **Carbon** : 4 valence electrons; in Group 4 of the Periodic table. Carbon acquires 4 electrons (and hence the electron configuration of neon) by forming 4 covalent bonds. **Thus in the structures of organic compounds, carbon atoms always have a valency of 4.**
- Carbon can form covalent bonds with hydrogen, oxygen, nitrogen, the halogens such as chlorine, bromine etc. and other elements, as well as with other carbon atoms.

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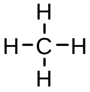
8. Some Organic Compounds – Organic Functional Groups

1. Compounds containing just H and C (hydrocarbons)

Alkanes (C_nH_{2n+2})

- Contain only C-C single bonds and C-H bonds.

  The simplest molecule formed from carbon and hydrogen is methane,



, CH_4

- It is the first member of a series of compounds which have a general formula C_nH_{2n+2}.
- The first few members of this series of alkanes are

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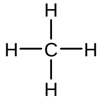
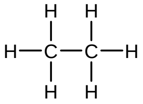
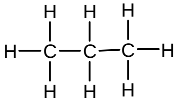
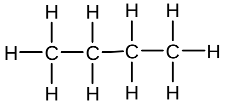
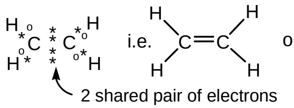
name	structural formula	
methane		i.e. CH_4
ethane		i.e. CH_3-CH_3
propane		i.e CH_3-CH_2-CH_3
butane		i.e. CH_3-CH_2-CH_2-CH_3

- Then pentane, $CH_3CH_2CH_2CH_2CH_3$, hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$, etc..

- Used as fuels. Burn in air to give CO_2 and H_2O. Otherwise not very reactive.
- Compounds with only C-C single bonds are said to be **saturated**.

Alkenes (C_nH_{2n})

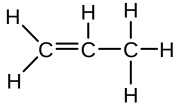
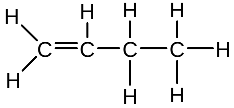
- Alkenes contain carbon-carbon double bonds in their structures in which adjacent pairs of carbon atoms share two pairs of electrons. The simplest structure is that of ethene:



or $H_2C{=}CH_2$

2 shared pair of electrons

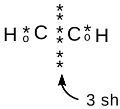
- As with alkanes there is a series of related structures. The straight chain structures are named on the basis of the number of carbon atoms they contain, using the letters 'ene' to complete the name rather than 'ane':

name	structural formula	
ethene	as above	
propene		i.e. $CH_2=CHCH_3$
but-1-ene		i.e. $CH_2=CHCH_2CH_3$

- Then pentene, hexene etc..
- The double bond makes alkenes more reactive than alkanes.
- **The double bond is a functional group.** When compounds contain double bonds they are said to be **unsaturated.**

Alkynes (C_nH_{2n-2})

- Contain carbon-carbon triple bonds in which adjacent pairs of carbon atoms share 3 pairs of electrons. The simplest structure is that of ethyne:



i.e. H—C≡C—H

3 shared pairs of electrons

- As with the alkenes there is a series of related structures. The straight chain structures are again named on the basis of the number of carbon atoms they contain, using the letters 'yne' to complete the name :

name	structural formula
propyne	$H-C\equiv C-CH_3$
but-1-yne	$H-C\equiv C-CH_2CH_3$

- Then pentyne, hexyne etc..
- The alkynes are also more reactive than the alkanes, this time because of the presence of the triple bond. Like the double bond in the alkenes, **the triple bond is also a functional group**.
- **In organic molecules functional groups account for the properties of the molecules, not the saturated hydrocarbon chains which are also present.**

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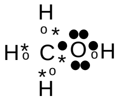
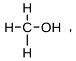
9. Some Organic Compounds
– Organic Functional Groups 2

Other Organic Functional Groups

- There are many other types of organic molecules. Their structures can all be thought of as being derived from hydrocarbon structures by replacing one or more hydrogen atoms by other atoms or groups. These new functional groups give rise to more families of compounds whose properties are, as with the alkenes and the alkynes dependent on the type of functional group. Some examples include:

- **Alcohols :** contain an **OH** group e.g.



i.e.  ,

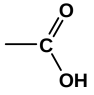
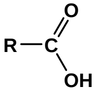
CH_3-OH	CH_3-CH_2-OH	CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH
methanol	ethanol	hexanol (hexan-1-ol)

General formula is **R-OH**

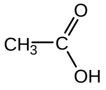
R = CH_3- in methanol
R = CH_3CH_2- in ethanol
R = $CH_3CH_2CH_2CH_2CH_2CH_2$- in hexanol

- The simple alcohols are named by replacing the 'e' at the end of the straight chain alkane from which they are derived with 'ol'.

- **Carboxylic acids**

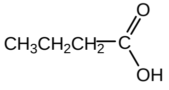
Contain a  $-C(=O)OH$ group; general formula is therefore  $R-C(=O)OH$

Examples :



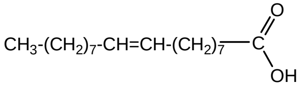
$CH_3-C(=O)OH$

ethanoic acid
(acetic acid)



$CH_3CH_2CH_2-C(=O)OH$

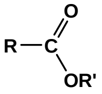
butanoic acid



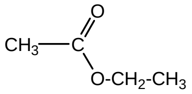
$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-C(=O)OH$

oleic acid

- **Esters**

General formula is  $R-C(=O)OR'$

e.g. ethyl ethanoate
(ethyl acetate)



$CH_3-C(=O)O-CH_2-CH_3$

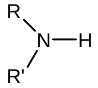
- Esters are formed from a carboxylic acid and an alcohol via a condensation reaction.

- **Amines** : contain an **NH_2** group e.g.

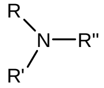
CH_3-CH_2-NH_2	CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2
ethylamine	hexylamine

General formula is **therefore R-NH_2 - for a primary amine**

Secondary amines have the general formula

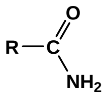


Tertiary amines have the general formula

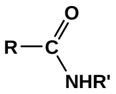


- **Amides**

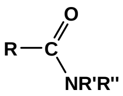
General formula is



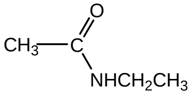
or



or

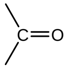


e.g.

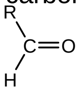


- Amides are also formed via a condensation reaction – from a carboxylic acid and an amine

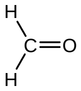
- **Aldehydes**
- Both aldehydes and ketones contain the carbonyl group,



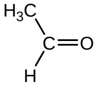
- The general formula for an aldehyde is



and examples are



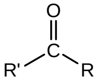
methanal



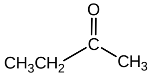
ethanal

- **Ketones**

- In ketones two carbons are bonded to the carbonyl group. They therefore have the general formula

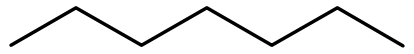


e.g. butanone

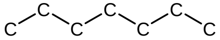


10. Representation of Organic structures

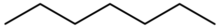
- You will often see structures drawn which appear to be nothing more than squiggles! e.g.



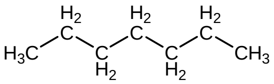
- These are skeletal structures and they tell you exactly what the structure is. Each line represents a covalent bond between 2 carbon atoms – so for the above we have:



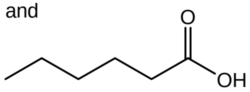
- Carbon atoms have a valency of 4; **all of the unaccounted for bonds to each carbon in the structure are occupied by hydrogen**, so



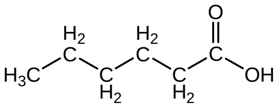
is



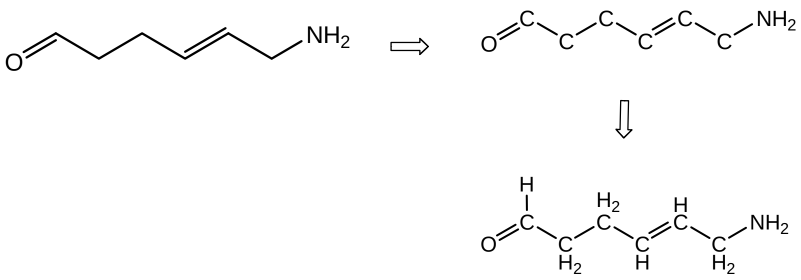
and



is

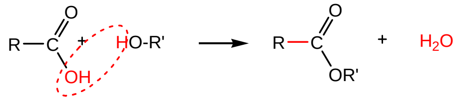


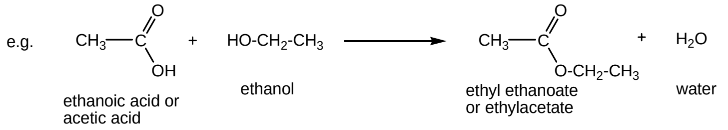
and



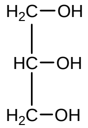
11. Some Simple Reactions of Organic Molecules

- **Condensation Reactions**
- Reactions in which two molecules combine with the elimination of a small molecule, often water.
- A simple example is the reaction of a carboxylic acid with an alcohol to form an ester and water:

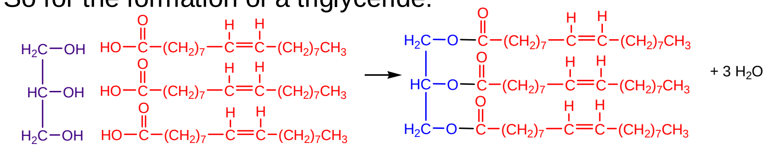




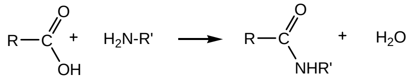
- The structures of lipids are formed as a result of condensation reactions between alcohol and carboxylic acid groups – a triglyceride is formed from glycerol, , and 3 carboxylic acids called fatty acids.

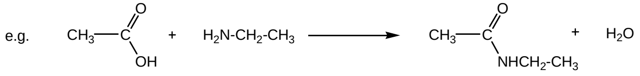


- So for the formation of a triglyceride:

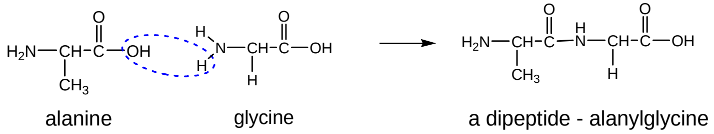


- The reaction between a carboxylic acid and an amine to form an amide is also a condensation reaction:



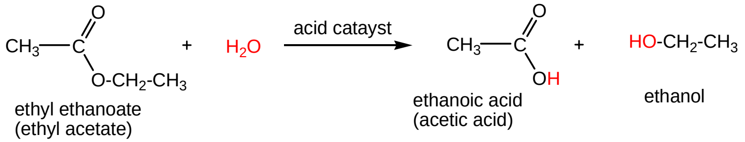


- or the reaction between the COOH of one amino acid and the NH_2 of another amino acid.

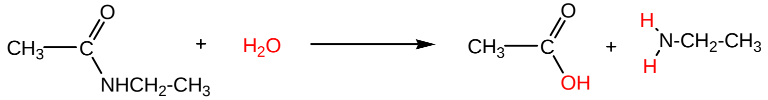


- **Hydrolysis**

Essentially the reverse of condensation reactions. A hydrolysis reaction is the breaking of a compound into smaller parts using water as a reactant, e.g. an ester is hydrolysed to give a carboxylic acid and an alcohol in the presence of an acid catalyst, e.g.

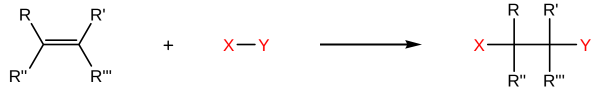


- Similarly amides are hydrolysed to give a carboxylic acid and an amine, e.g.

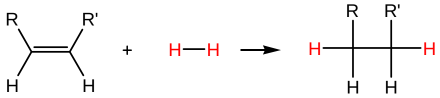


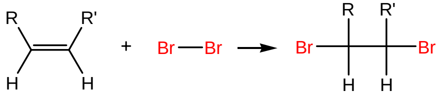
- **Addition Reactions**

Reactions in which two atoms or groups of atoms are added across a double bond:



- Typical examples include the addition of H_2, Br_2 HCl, e.g.

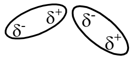




12. Intermolecular Forces – Attractive Forces between Covalent Molecules

- **London forces (type of Van der Waals forces)**

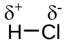
The electrons in a molecule are in constant motion. As a result the centres of positive charge and negative charge are constantly changing relative to each other and transient dipoles arise. Attraction occurs between these transient dipoles:



- In general the greater the number of atoms in the molecule, the greater the number of electrons and the greater the strength of the London forces.

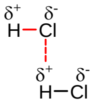
- **Dipole-dipole forces**

Some atoms are more strongly electron attracting than others, e.g. Cl, Br, N, O. When a covalent bond is between two different atoms, where one is more electron attracting than the other, the electron cloud is attracted towards that atom. The result is a **permanent dipole**, e.g.



$\overset{\delta^+}{H}-\overset{\delta^-}{Cl}$

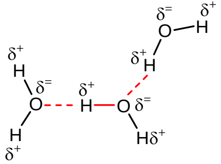
- which results in attraction between the molecules:



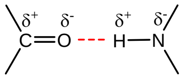
- Stronger than London forces.

- **Hydrogen bonds**

Special dipole-dipole forces. Occur in molecules with H bonded to the strongly electron attracting atoms N, O, F. The resulting bonds are very polar – the H atom is left almost devoid of its electron. The resulting dipole-dipole forces are called hydrogen bonds, e.g.



- Important in stabilising the α-helix and β-pleated sheet secondary structures in proteins, where the H-bonds are between the CO and NH groups of peptide bonds:

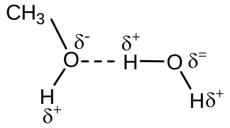


- **Melting points and boiling points and intermolecular forces**

- The stronger the attractive forces between covalent molecules, the more energy is required to break them, and the higher the melting point and boiling point.
- Thus methane, CH_4, a small molecule whose covalent bonds are not polar, and which therefore has only relatively weak London forces between the molecules has a low boiling point and is a gas at room temperature.
- Water however which is also a small molecule but which also has hydrogen bonds between its molecules has a much higher boiling point (100°C).
- Ionic compounds in which there are very strong forces of attraction between the oppositely charged ions all are solids at room temperature and have very high melting points.

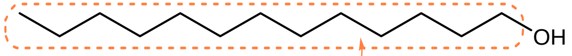
13. Solubility

- Usually like dissolves like.
- Non polar structures tend to be soluble in non polar solvents like hexane.
- Polar structures tend to be soluble in polar solvents like water.
- Reason – water is polar and there are many H-bonds between the water molecules. When other molecules dissolve in water H-bonds between the water molecules must be broken. Molecules which can replace these broken H-bonds by H-bonds between themselves and the water molecules are the ones which will dissolve.
- So small alcohol molecules like CH_3OH, CH_3CH_2OH, whose OH group can form these H-bonds



dissolve in water.

- As the size of the R group in the alcohol increases the solubility decreases; the solubility of $CH_3(CH_2)_{12}OH$ in water is very low.



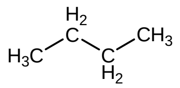
- Although this molecule carries an OH group which can form H-bonds, the size of the non polar alkyl group is large. To accommodate this in the water solvent many, many more H-bonds would have to be broken than could be formed, which is energetically very unfavourable.
- The words **hydrophilic** and **hydrophobic** are often used by biologists.
- **Hydrophilic** molecules or groups are described as being 'water loving' – these are structures which are polar like the 'small' alcohols above – which are capable of H-bonding with the water molecules.
- **Hydrophobic** molecules or groups are described as being 'water hating' – the large non polar alkyl group in $CH_3(CH_2)_{12}OH$ is hydrophobic. It cannot H-bond with the water and the only type of attractive forces which can occur between such groups are London forces.

14. Isomerism

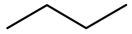
- **Isomers** are compounds which have the same molecular formulae but which do not have identical structures.
- Two types of isomers are **structural** isomers and **stereoisomers.**

- **Structural Isomers**

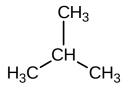
  - have the same molecular formula, but their atoms are bonded together in a different order.
- Consider molecules with molecular formula C_4H_{10}:
- This is the molecular formula for the alkane, butane:



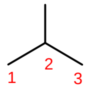
i.e.



- However, the carbon atoms need not be bonded together in a straight chain and another isomer exists:



i.e.

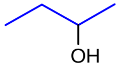


called 2-methylpropane

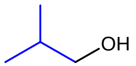
- Note that in both structures each carbon atom still has a valency of 4, and that the molecular formula of C_4H_{10} has been satisfied.
- Now consider $C_4H_{10}O$.
  The carbon atoms can bond together either as a straight chain or in a branched fashion as before and if the single oxygen is part of an OH group then possible isomers include

(i)

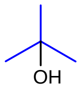
(ii)



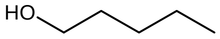
(iii)

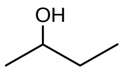


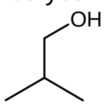
(iv)



- You may need to write out the full structural formulae to convince yourself that each of the above do have the molecular formula $C_4H_{10}O$.
- You may need to use molecular models to convince your self that

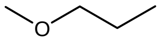






are the same as isomers (i), (ii) and (iii) respectively, above.

- Note – there are other structural isomers for $C_4H_{10}O$. They are



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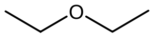


These structures are called ethers. They contain C-O-C in their structures and have a general formula R-O-R'.

- Structural isomers have different physical properties such as melting points, boiling points, solubilities.

15. Stereoisomerism 1

- **Stereoisomers** have the same molecular formulae and their atoms are bonded in the same order. They differ in the way in which their atoms are orientated in space.
- There are two types of stereoisomers – **geometric isomers** and **optical isomers**.

Geometric isomers

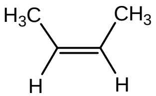
In organic molecules there is generally free rotation about carbon-carbon single bonds.

However this is **not** so about a carbon-carbon double bond.

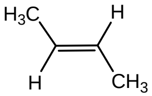
- Consider but-2-ene, $CH_3CH{=}CHCH_3$
  1 2 3 4

There are two ways in which the H and CH_3 groups at each end of the double bond can be arranged:

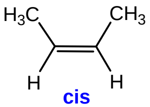
(i)



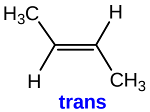
(ii)



- In (i) the two CH_3 groups are lying on the same side of the C=C.
- In (ii) the two CH_3 groups are lying on opposite sides of the C=C.
- Because there is no free rotation about the C=C (i) and (ii) are **not interconvertible**. They are therefore isomers of but-2-ene.
- The atoms are bonded in the same order but are orientated differently in space. They are therefore stereoisomers.
- Isomers which arise because of this restricted rotation are called **geometric isomers**.
- The two isomers are labelled:



cis

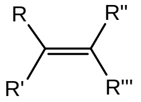


trans

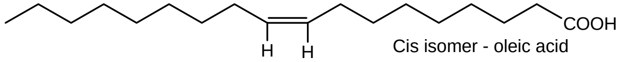
- In the cis isomer the like groups are on the same side of the C=C.
- In the trans isomer the like groups are on opposite sides of the C=C.

- In alkenes, geometrical isomerism only occurs when

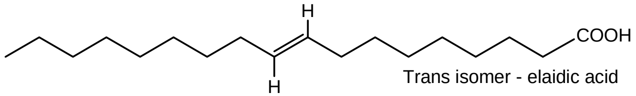
$R \neq R'$ and $R'' \neq R'''$ in



- So in molecules such as $CH_3CH{=}CH_2$ (R = CH_3, R', R'', R''' = H) there are no geometric isomers.
- In the fatty acids which are important in the structure of lipids, when there is unsaturation, geometric isomers can occur, such as in the fatty acid $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$:



Cis isomer - oleic acid



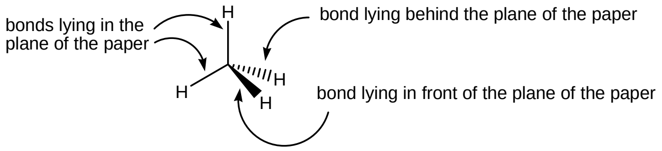
Trans isomer - elaidic acid

- Some cyclic compounds also exhibit geometrical isomerism because of restricted rotation due to the ring structure.

16. Stereoisomerism 2

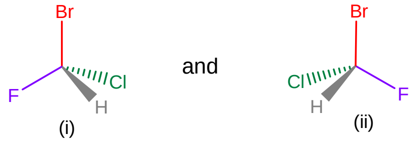
Optical Isomerism

- A carbon atom which has four single bonds is said to be saturated. The four single bonds point to the four corners of a regular tetrahedron as in methane:

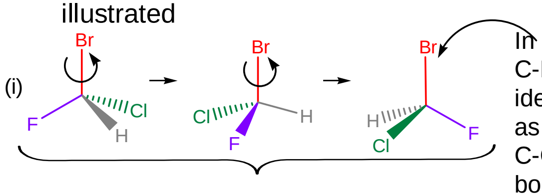


- As a result of this, when a carbon atom in a molecular structure has **four different atoms or groups attached** it can exist as a pair of stereoisomers.
- The two stereoisomers are **non-superimposable mirror images of each other.**
- These are the **optical isomers** and are called **enantiomers**.

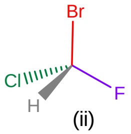
- A simple example is bromochlorofluoromethane, CHBrClF. The two enantiomers can be represented



- Molecular models are useful if you need convincing that the above two enantiomers are not superimposable and are therefore two distinct structures. Perhaps the following might also help. Starting with the above representation of (i), and with the Br atom maintained in the same position, rotation of the C and its other 3 bonds is illustrated

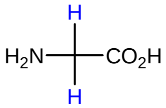


In the C-Br and C-F bonds are in identical positions as in (ii), but the C-Cl and C-H bonds are not



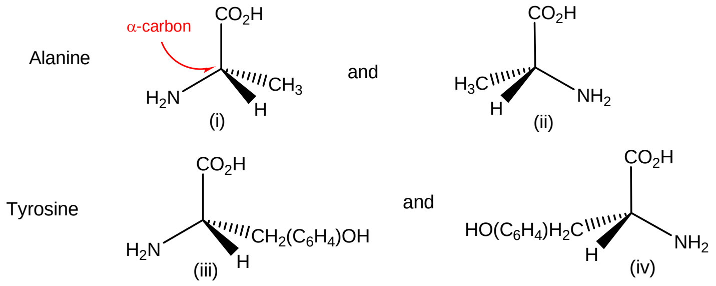
- (i) and (ii) can never superimposed upon each other. They are non-superimposable mirror images.

- A carbon atom with 4 different atoms or groups attached is called a **chiral** centre.
- A molecule therefore with a chiral centre can exist as a pair of enantiomers
- The term optical isomerism comes from the fact that optical isomers rotate the plane of plane polarised light. One enantiomer rotates it in a clockwise direction (denoted (+)) and the other in an anticlockwise direction (denoted (-)), and to an equal extent.
- Carbon atoms with three or less different groups attached do not exist as optical isomers. An example here is the amino acid glycine, in which the α-carbon, *, has 2 H's bonded to it.



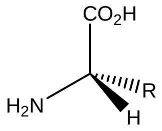
glycine

- **All** of the other amino acids which occur in protein structure are chiral. In them the α-carbon is a chiral centre and they therefore do exist as pairs of optical isomers. Examples include



- In protein structure amino acids always have the same configuration. The configuration of a molecule describes how the atoms/groups are orientated in space. Different configurations of a molecule can only be interconverted by breaking bonds.
- A pair of enantiomers therefore have different configurations.

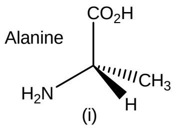
- The configuration of amino acids in protein structure is



where R is the side chain

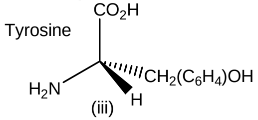
- So for alanine and tyrosine configurations (i) and (iii) respectively are therefore the ones which occur in protein structure.

Alanine



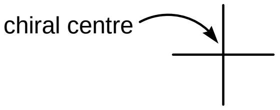
(i)

Tyrosine

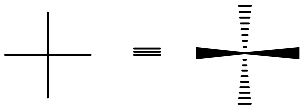


(iii)

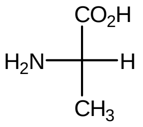
- This is called the L- configuration.
- Biological molecules are often represented by ‘Fischer Projection’ formulae. In these a chiral centre is represented at the point where two lines cross



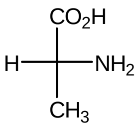
- The east-west bonds represent bonds coming out of the page and the north-south bonds represent bonds extending behind the page:



- The two enantiomers for alanine are therefore



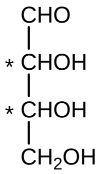
and



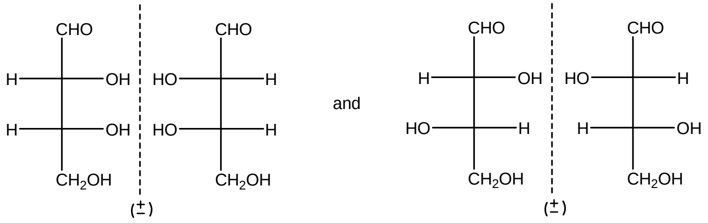
- of which the one on the left represents the L-configuration and is therefore the configuration of alanine which occurs in protein structure.

17. Stereoisomerism 3
Molecules with more than one chiral centre

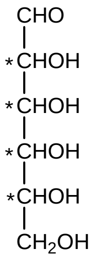
- A number of biological molecules, in particular the carbohydrates contain within their structures a number of chiral centres.
- Consider the general formula for an aldotetrose :



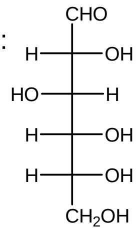
- It possesses two chiral centres, * and *.
- As a result there are 4 optical isomers, two pairs of enantiomers:



- In the aldopentoses there are 3 chiral centres and as a result 8 optical isomers (4 pairs of enatiomers)
- With ‘n’ different chiral centres in a molecule there are 2^n stereoisomers.
- So for the aldohexoses for which there are 4 chiral centres, *:



- There are 2^4 i.e.16 optical isomers.
- Which consist of 8 pairs of enantiomers.
- D(+)glucose is just one of the 16 optical isomers:



D(+)glucose