WJEC
CBAC

AS/A LEVEL
GCE in Chemistry

REVISION AID

CH2

Unit CH2 Properties, Structure and Bonding

TOPIC 4 BONDING

4.1 - **Chemical Bonding**

4.2 - **Forces between molecules**

4.3 - **Shapes of molecules**

4.4 - **Solubility of compounds in water**

TOPIC 5 SOLID STRUCTURES

TOPIC 6

6.1 - **The Periodic Table**

6.2 - **Trends in properties of the elements of the s-block and Group 7 (17)**

TOPIC 7

7.1 - **Organic Compounds and their reactions**

7.2 - **Hydrocarbons**

7.3 - **Halogenoalkanes**

7.4 - **Alcohols**

TOPIC 8 ANALYTICAL TECHNIQUES

4.1 Chemical Bonding

Visit http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/bondcon.html#c1

and http://members.aol.com/profchm/bonding.html

Candidates should be able to:

(a) *describe ionic and covalent bonding (including coordinate bonding) and represent this in terms of appropriate 'dot and cross' diagrams;*

(b) *describe qualitatively the nature of the attractive and repulsive forces between ions in an ionic crystal;*

(c) *show an understanding of the covalent bond in terms of the sharing (and spin pairing) of electrons and show awareness of the forces of attraction and repulsion within the in molecule;*

(d) *understand the concepts of electronegativity and of bond polarity, recall that bond polarity is largely determined b differences in electronegativity and use given values to predict such polarities:*

(e) *appreciate that main bonds are intermediate in character between purely ionic and purely covalent and understand the way in which the electron density, distribution varies with the ionic character of the bond.*

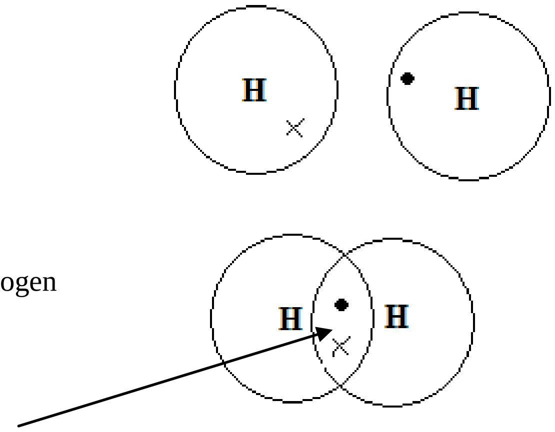
Covalent bonding.

A covalent bond exists between two atoms when they share a pair of electrons. The electrons usually come one from each atom and pair up in an orbital. See UNIT 1.Alternatively we can say that by sharing a pair of electrons each atom has the electronic structure of a noble gas, usually an octet of electrons.

Two simple cases are molecules of hydrogen and chlorine.

The hydrogen molecule.

Each hydrogen atom has one electron.



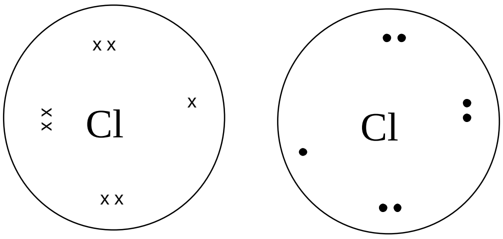
The single electrons in the two hydrogen atoms are represented by a dot and a cross. In the hydrogen molecule, H_2, each atom has a share of two electrons, like the noble gas helium. We could also say the electrons occupy the same orbital in the molecule but have opposite spins.

We can also represent the hydrogen molecule as H-H

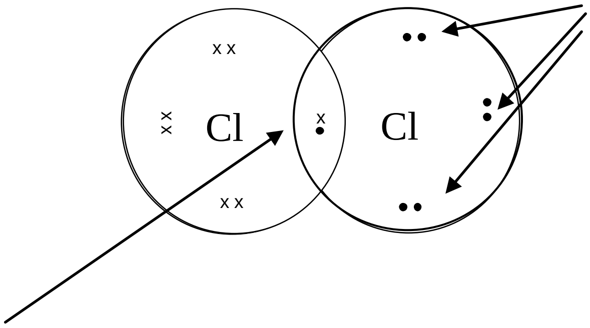
a shared or bonding pair of electrons

The chlorine molecule

Two chlorine atoms, outer electrons only shown.



Chlorine molecule, Cl_2, each atom has electronic structure of argon.
Can be written Cl-Cl.

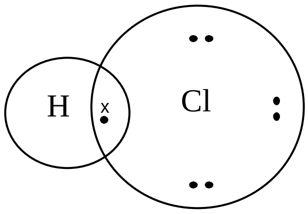


non-bonding or lone Pairs of electrons

a shared or bonding pair of electrons

The hydrogen chloride molecule

The outer electrons of the chlorine atom are shown.



The hydrogen chloride molecule is interesting because although the hydrogen atom and the chlorine atom share a pair of electrons, the pair is not evenly shared.

Some atoms are able to attract the electrons in a shared pair more than others.

This is measured by a quantity called **electronegativity**. **Topic 4.1(d)**

The **electronegativity index** is a measure of how strongly an atom in a compound attracts the pair of electrons in a bond.

Pauling gave values for the electronegativity index and some values are shown below.

					H	He											
					2.1												
Li	Be											B	C	N	O	F	Ne
1.0	1.5											2.0	2.5	3.0	3.5	4.0	
Na	Mg											Al	Si	P	S	Cl	Ar
0.9	1.2											1.5	1.8	2.1	2.5	3.0	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	CU	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.3	1.5	1.	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8	

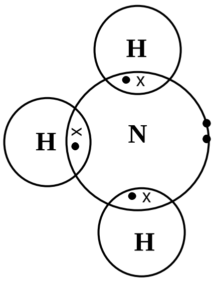
This means that chlorine (3.0) will attract the pair of electrons more than hydrogen (2.1).

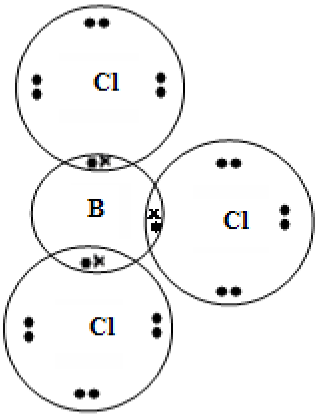
We can write the hydrogen chloride molecule as $^{\delta+}\text{H} – \text{Cl}^{\delta-}$ and describe it as a **polar molecule**.

Sometimes a covalent bond is formed by one atom, or group of atoms, donating both electrons to another atom. This is called a coordinate or dative covalent bond.

Consider a molecule of ammonia, NH_3, there are three bonding pairs of electrons and one non-bonding or lone pair of electrons. There is a total of eight outer electrons.

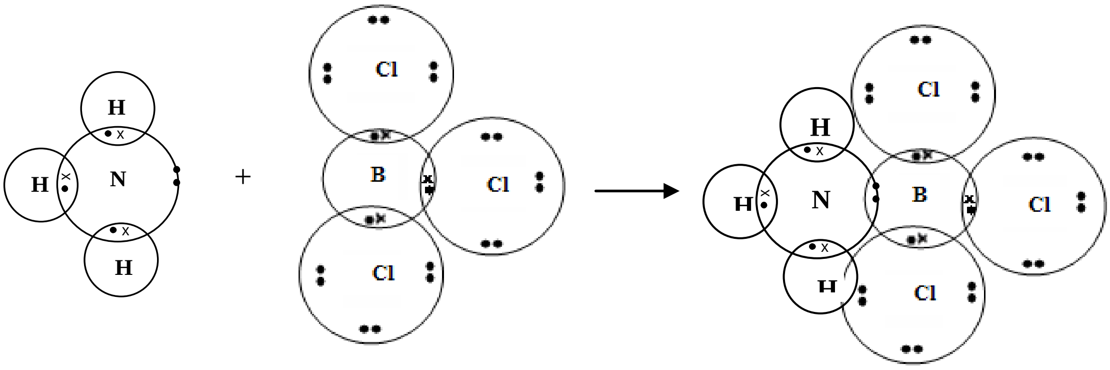
Consider a molecule of boron trichloride, BCl_3, there are three bonding pairs of electrons but only six outer electrons. There is room for two more electrons to make up the octet of a noble gas.



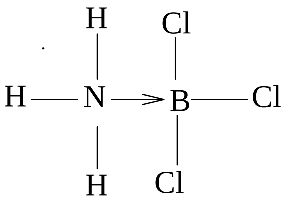


Ammonia and boron trichloride form a compound by ammonia donating its lone pair of electrons to the BCl_3 molecule to complete its octet of electrons.

The bond formed is a coordinate or dative covalent bond as shown below.



The new compound is drawn as



$$\begin{array}{ccccc} & H & & Cl & \\ & | & & | & \\ H - & N & \rightarrow & B & - Cl \\ & | & & | & \\ & H & & Cl & \end{array}$$

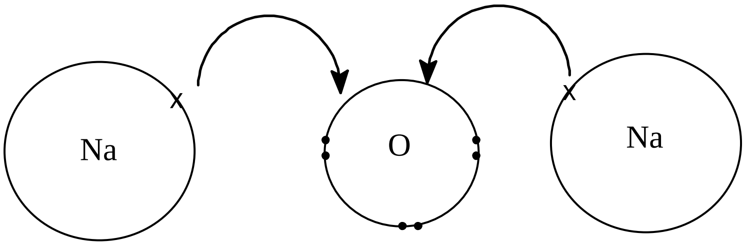
The arrow is the coordinate bond and shows the direction in which the pair of electrons is donated.

Simple ionic bonding Topic 4.1 (a) and (b)

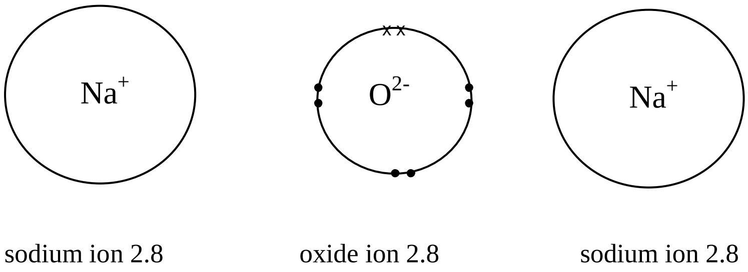
Ionic bonding is the result of electrons being transferred completely from one atom to another and the resulting ions packing together into a **crystal lattice**

Example: The formation of sodium oxide

The atomic number of sodium is 11 and of oxygen is 8. Their ground state electronic configurations are Na 2.8.1 and O 2.6

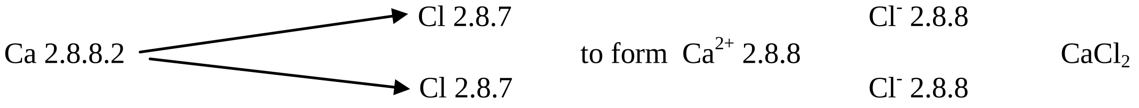


Each sodium atom donates an electron to the oxygen atom



Result is sodium oxide, Na_2O, an ionic compound

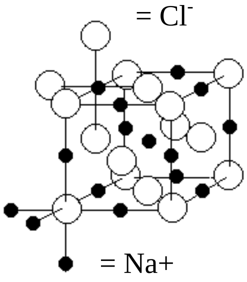
In the same way, calcium chloride is formed from one calcium atom and two chlorine atoms.



Simple ionic compounds form when the difference in electronegativity of the two elements is large. When ionic compounds are formed there is electrostatic attraction between ions of opposite charge and electrostatic repulsion between ions of the same charge.

These electrostatic forces are strong and the ions arrange themselves in a regular arrangement called an ionic crystal lattice. The arrangement depends on the charges on the ions and upon the sizes of the ions.

Sodium chloride forms a cubic lattice.

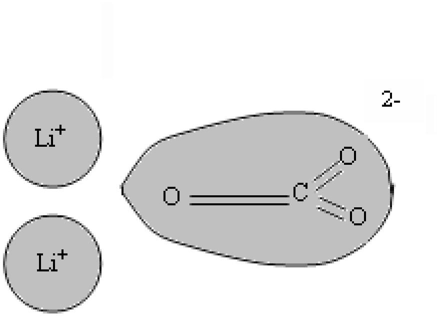


The bonding in binary metal-non-metal compounds is ionic but cations may polarize anions to produce some covalent character.

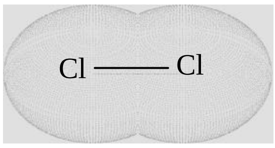
Polarization of an anion is distortion of the shape of a polarisable anion.

The electric field at the surface of a small cation is higher than the field at the surface of a larger cation with the same charge. This electric field will tend to pull the electrons in the anion towards it and alter the electron distribution and shape.

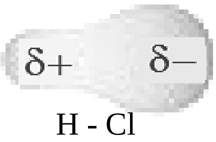
The carbonate ion, CO_3^{2-}, is spherical in shape but in lithium carbonate the highly polarising lithium ion distorts the carbonate ion.
As a result of this distortion, lithium carbonate decomposes into the oxide and carbon dioxide
on heating in a test tube whereas the carbonates of the other Group 1 metals do not.



The electron density of a non-polar covalent molecule is symmetrical.
e.g. Chlorine, Cl_2



A polar molecule such as hydrogen chloride has an asymmetric electron density.



Although many common compounds such as sodium chloride and calcium oxide are almost entirely ionic, there are a large number of compounds in which the bonding is partially ionic and partially covalent.
The percentage ionic character can be estimated in a single bond by the difference in the electronegativities between the two atoms. The following table gives some approximations.

Electronegativity difference	**Percentage ionic character**	**Electronegativity difference**	**Percentage ionic character**
0.1	0.5	1.9	59
0.3	2	2.1	67
0.5	6	2.3	74
0.7	12	2.5	79
0.9	19	2.7	84
1.1	26	2.9	89
1.3	34	3.1	91
1.5	43	3.2	92
1.7	51		

4.2 Forces between molecules.

Candidates should be able to:

(a) *explain the concept of a dipole and give a simple account of van der Waals forces dipole-dipole,(induced dipole-induced dipole):*

(b) *explain the nature of hydrogen bonding and recall the types of elements with which it occurs e.g. with hydrogen attached to highly electronegative atoms;*

(c) *describe and explain the influence of hydrogen bonding on boiling points and solubility;*

(d) *appreciate that forces within molecules generally influence their chemical properties. whilst forces between molecules usually affect their physical properties;*

(e) *appreciate the relative orders of magnitude of the strength of: covalent bonds: hydrogen bonds and van der Waals forces.*

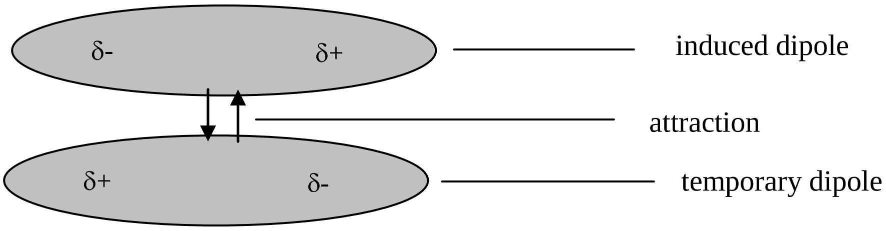
Topic 4.2(a)

Van der Waals forces are the weak intermolecular forces that exist between all atoms and molecules and include induced-dipole - induced-dipole interactions and dipole-dipole interactions. .

The electrons within an atom or molecule are in motion and at a given instant they may be so displaced that the effect is to produce an instantaneous dipole.

[A dipole in a molecule is a separation of charge so that one end of the particle is positive with respect to the other. Such a particle in an electric field would undergo a twisting force (or couple) in the field. The particle is said to have a dipole moment. Some molecules like HCl have a permanent dipole moment which is measured in the unit called a Debye.]

Instantaneous dipoles described above may induce an equal and opposite dipole in a neighbouring molecule causing momentary attraction.



The next instant the dipole will have changed and more induced dipole-induced dipole interactions will occur. The more electrons in the atom or molecule the greater the number of these induced dipole interactions. For neutral and non-polar molecules or atoms these instantaneous dipoles average out over time to give zero permanent dipole moment.

In the case where the molecule has a permanent dipole then there will be permanent attractive forces between molecules.

These van der Waals forces are weak compared with the covalent bonds within a molecule. This accounts for the low melting and boiling points of many covalent compounds.

The effect of van der Waals forces arising from induced dipole-induced dipole interactions is seen in the boiling temperatures of the noble gases.

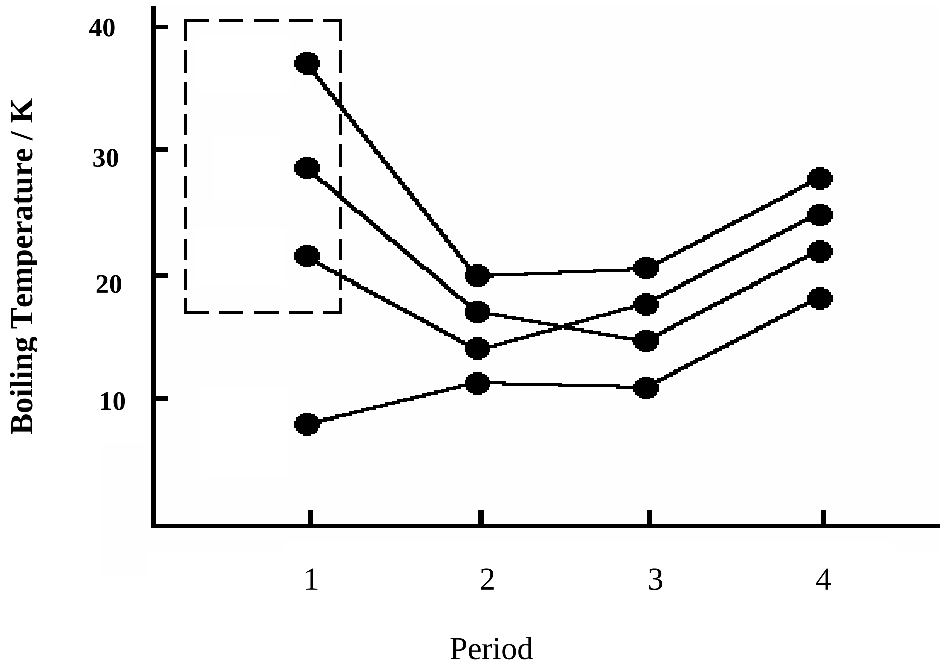
Element	He	Ne	Ar	Kr	Xe
T_b / °C	-269	-249	-186	-152	-108

boiling temperature increases →

Hydrogen bonding Topic 4.2(b)

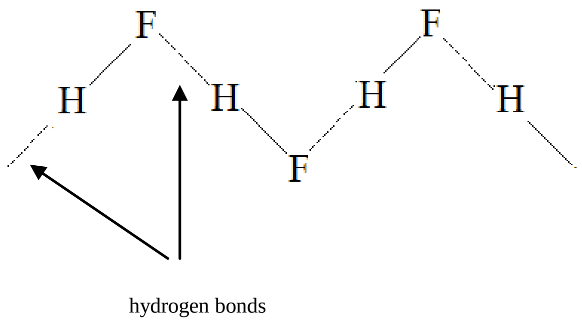
When hydrogen is covalently bonded to a very electronegative atom such as fluorine, nitrogen, oxygen, the covalent bond is very polar and the bonding pair of electrons drawn closely to the electronegative atom leaving an almost bare proton as the δ+ end of the bond. This is attracted to any negative region of an adjacent molecule, in particular the lone pairs of electrons of adjacent electronegative atoms. As the proton is small it can approach closely and form an electrostatic bond called a **hydrogen bond**. If we considered van der Waals forces for the hydrides of Groups 5, 6 and 7 of the Periodic Table than the boiling temperatures of the first hydrides of the Groups would be expected to be lower than they are.

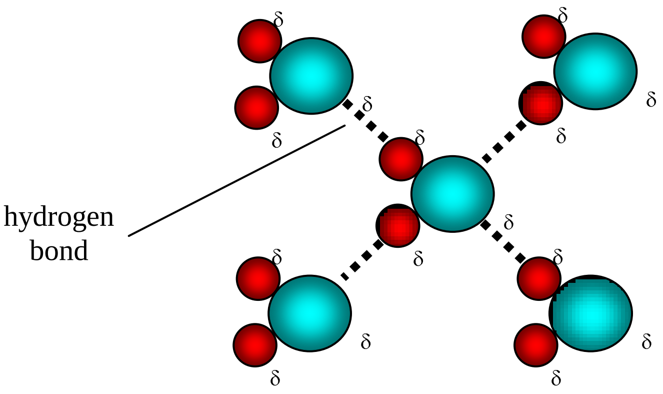
Compare with Group 4 and methane, CH_4.



The effect of hydrogen bonding in water is very pronounced. The hydrogen bond in HF is stronger than the hydrogen bond in water but on average there are about twice as many hydrogen bonds per molecule in water as there are between HF molecules in liquid hydrogen fluoride so that the boiling temperature of water is significantly higher than that of liquid hydrogen fluoride.

In hydrogen fluoride in aqueous solution, chains of HF molecules are hydrogen bonded but there is evidence that hydrogen fluoride can behave as the dibasic acid H_2F_2. The salt KHF_2 is known and the HF_2^- ion is symmetrical and the H-F bond lengths are equal.





The hydrogen bonding extends through the liquid with a tetrahedral arrangement.

Hydrogen bonding between water molecules

We have already seen the abnormally high boiling points of water, ammonia and hydrogen fluoride. Hydrogen bonding also affects solubility in water. The presence of an –OH group in a molecule makes it more likely to be soluble in water.

Methoxymethane, CH_3OCH_3, is a gas at room temperature which is insoluble in water but ethanol, CH_3CH_2OH, is a liquid which is miscible with water. The hydrogen atom of the –OH group of ethanol can hydrogen bond with water molecules.

Visit http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/H/HydrogenBonds.html
http://www.chemguide.co.uk/atoms/bonding/hbond.html

Hydrogen bonding is very important in biochemistry. It plays an important role in the formation of the double helix in DNA.

Visit http://www.chemguide.co.uk/atoms/bonding/hbond.html for an animation showing the hydrogen bonds in DNA. The hydrogen bonds form between pairs of bases on the two strands.

Visit http://www.accessexcellence.org/RC/VL/GG/dna_molecule.html

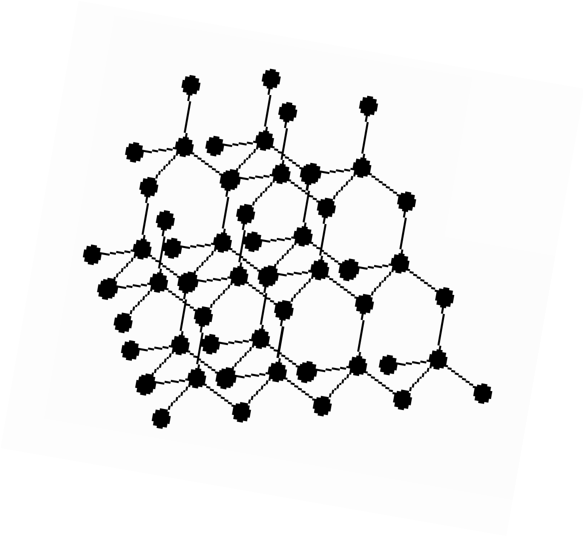
Topic 4.2(d)

We should remember that hydrogen bonding is stronger than van der Waals forces and permanent dipole–dipole attractions but weaker than covalent bonding.

The strong covalent bonds within molecules are largely responsible for their chemical properties whereas the weaker intermolecular forces are important in determining physical properties.

The low melting and boiling points of covalent compounds such as methane, ammonia and hydrogen chloride (all gases at room temperature) are due to weak intermolecular forces. The slightly higher boiling point of ethanol (78 ^{o}C) is due to hydrogen bonding between molecules.

The strength of covalent bonds between atoms is illustrated by diamond which is a giant molecule of carbon and is a very hard substance.



Part of a diamond crystal. Each carbon atom is joined to four others by covalent bonds pointing towards the corners of a regular tetrahedron.

4.3 Shapes of molecules

Candidates should be able to:

(a) *explain what is meant by the terms lone pairs and bonding pairs of electrons and recall and explain the sequence of repulsions between: two bonding pairs; a bonding pair and a lone pair; two lone pairs;*

(b) *explain the VSEPR principle in terms of minimising the total repulsions between electrons in the valence shell of a given molecule or ion, giving examples where appropriate;*

(c) *recall and explain the shapes of the species listed (recall of exact bond angles is required for* BF_3*,* CH_4*,* SF_6*, and* NH_4^+ *) and apply the VSEPR principle to predict or explain the shapes of other specified simple species involving up to six electron pairs in the valence shell of the central atom.*

We have already seen that covalent molecules contain pairs of electrons which are involved in bonding two atoms together (bonding pairs) and pairs of electrons which are not involved in bonding (non-bonding or lone pairs of electrons).

These pairs of electrons will repel one another.

The Valence Shell Electron Pair Repulsion **(VSEPR)** theory states that the pairs of electrons repel one another so that there is minimum repulsion between them.

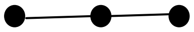
This will cause the centres of the atoms in the molecule to define a particular shape.

Since a lone pair of electrons occupies a slightly larger volume than a bonding pair of electrons, the relative magnitudes of electron pair repulsions are

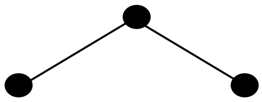
Lone pair: Lone pair > Lone pair: Bonding pair > Bonding pair: Bonding pair

Names of Shapes

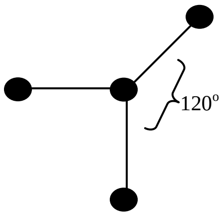
Linear



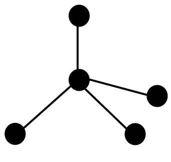
Bent



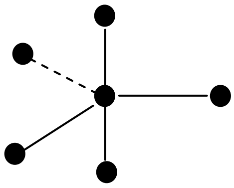
Trigonal planar



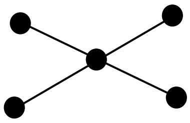
Tetrahedral



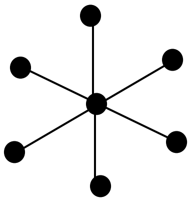
Trigonal bipyramidal



Square planar



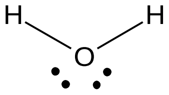
Octahedral

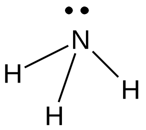


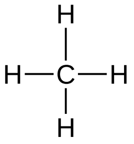
Predicting shapes of molecules and ions

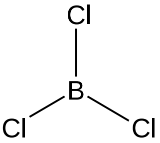
First write formulae to show all electron pairs both bonding and non-bonding in the valence shell.

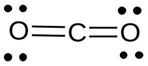
e.g.











Assume the electron pairs move equally as far apart as possible from each other but treat double bonds as a single bond.

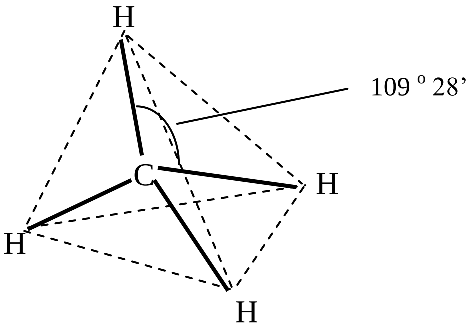
Remember bond angles are affected by the following rule for repulsion between bonded and non-bonded electron pairs:

Lone pair: Lone pair > Lone pair: Bonding pair > Bonding pair: Bonding pair

Examples

Methane

This is an easy case as there are four identical bonding pairs of electrons. These repel each other to point to the corners of a regular tetrahedron. The bond angle is 109 ° 28'. The shape is **tetrahedral**.

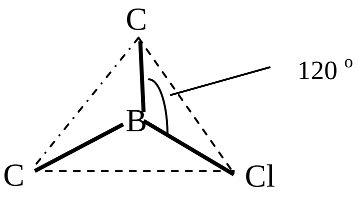


Boron trichloride

The valence shell of boron in BCl_3 contains only six electrons as three bonding pairs.

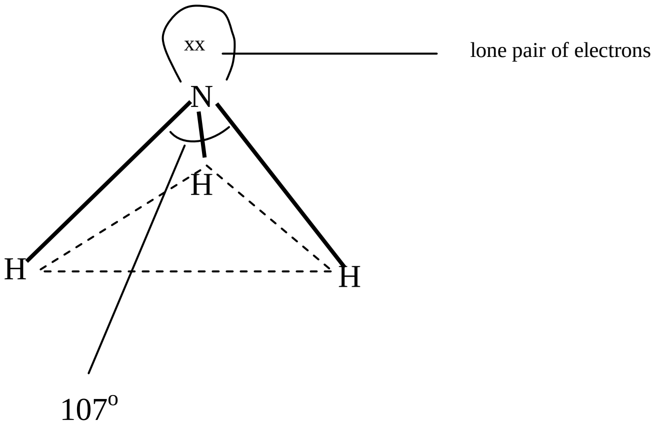
These repel each other to point to the corners of an equilateral triangle and the bond angle is 120 °.

The shape is **trigonal planar.**

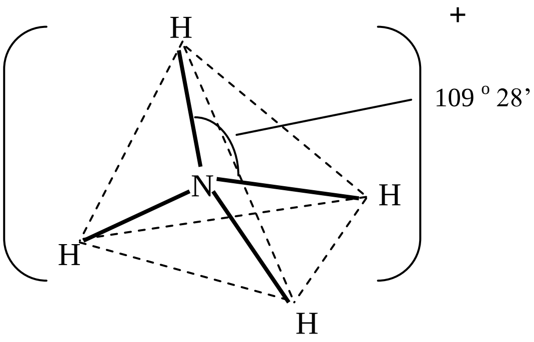


Ammonia

The valence shell of the nitrogen atom contains three bonding pairs of electrons and one non-bonding pair. The non-bonding pair – bonding pair repulsions are greater than the bonding pair- bonding pair repulsions. This results in the centres of the four atoms forming a **trigonal pyramidal** structure with bond angle 107°.

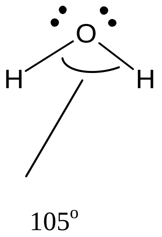


The ammonium ion, NH_4^+, has four bonding pairs of electrons and so the shape is **tetrahedral**.



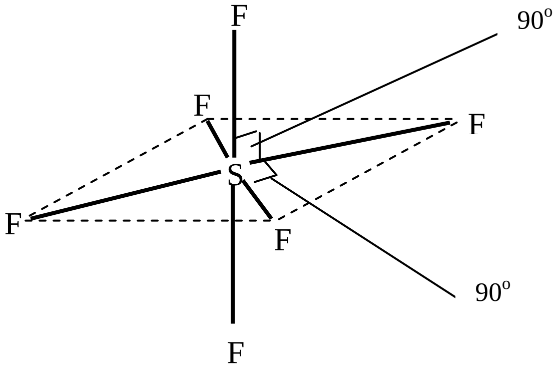
Water

In this molecule we have two bonding pairs of electrons and two non-bonding pairs of electrons.
The result is a **bent** molecule with a bond angle of 105o. Note that the second lone pair of electrons gives a smaller bond angle than in ammonia where there is only one lone pair of electrons.



Sulphur hexafluoride SF_6

This molecule has six bonding pairs of electrons which repel towards the corners of a regular octahedron and the shape is **octahedral**. The bond angles are 90°.



4.4 Solubility of compounds in water

Candidates should be able to:

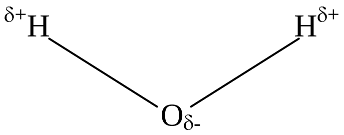
(a) *use a simple model to explain the ability of certain solutes to dissolve in water either by virtue of hydrogen bonding or dipolar forces and apply this to explain the solubility of ethanol and sodium chloride, and the insolubility (immiscibility) of hydrocarbons, in water;*

(b) *understand and use solubility both qualitatively and quantitatively (i.e. in terms of mass or moles per unit volume) and understand the recovery of soluble salts from aqueous solution by crystallisation.*

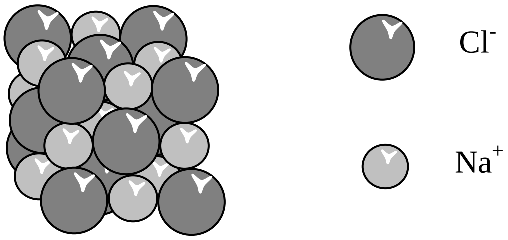
Topic 4.4 Solubility of compounds in water.

Aqueous chemistry is the basis of life on Earth. Water is sometimes called the universal solvent as it dissolves a wide range of compounds.

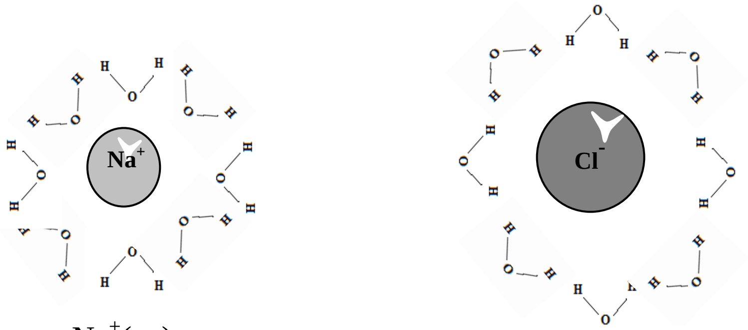
Water is a polar solvent



Anions and cations attract polar water molecules and in doing so release energy. A simple approximation is that if the energy released by water molecules being attracted to the anions and cations is greater than the energy needed to separated the anions and cations in the crystal lattice, then an ionic compound will dissolve in water. Sodium chloride exists in the solid state as sodium ions and chloride ions in a crystal a lattice.



When sodium chloride dissolves in water the ions are surrounded by the polar water molecules and are said to have become ***hydrated***.



$Na^+(aq)$ Cl^- (aq)

Diagrammatic representation of the hydration of sodium ions and chloride ions.
The δ+ hydrogen atoms of water molecules are attracted to the chloride ion and the δ- oxygen atom is attracted to the positive sodium ion.

$$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$$

The ions which are fixed in the sodium chloride lattice become hydrated and free to move.

Many covalent compounds are insoluble in water except where there is polarity which can interact with polar water molecules.

The gas hydrogen chloride is made up of molecules, $^{\delta+}$H-Cl$^{\delta-}$, with a permanent dipole moment.

When hydrogen chloride is passed into water, the gas dissolves accompanied by almost complete ionisation.

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

The covalent gas ammonia is very soluble in water.

Ammonia molecules themselves dissolve as NH_3 associated with water molecules by hydrogen bonding and some molecules actually accept a proton from a water molecule

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Aqueous ammonia is a weak base.

Ethanol, C_2H_5OH, is soluble in water since the polar –O-H group in the molecule can hydrogen bond with water molecules.

Hydrocarbons such as methane, CH_4, butane, C_4H_{10}, and hexane, C_6H_{14}, are insoluble (or immiscible) with water.

A non-polar hydrocarbon chain is said to be *hydrophobic* (water-hating) and does not interact with water molecules.

The lower members of the alcohols methanol, ethanol, propan-1-ol etc. are all soluble in water as the hydrogen bonding with water is the most important interaction between solvent and solute.

As the hydrocarbon chain of the alcohol increases, its hydrophobic nature reduces the solubility significantly. So that hexan-1-ol, $CH_3CH_2CH_2CH_2CH_2CH_2OH$, is almost completely insoluble in water.

Solutions are comprised of the solvent and the solute.

At a given temperature a solution may be capable of dissolving more solute and is said to be ***unsaturated***.

At a given temperature a solution may be incapable of dissolving more solute and is said to be ***saturated***.

At a given temperature some solutions contain more solute than a saturated solution at the same temperature and are said to be ***supersaturated***. Supersaturated solutions are unstable.

The solubility of a substance at a given temperature is the mass of the substance that will dissolve in a given mass of solvent to form a saturated solution at that temperature.

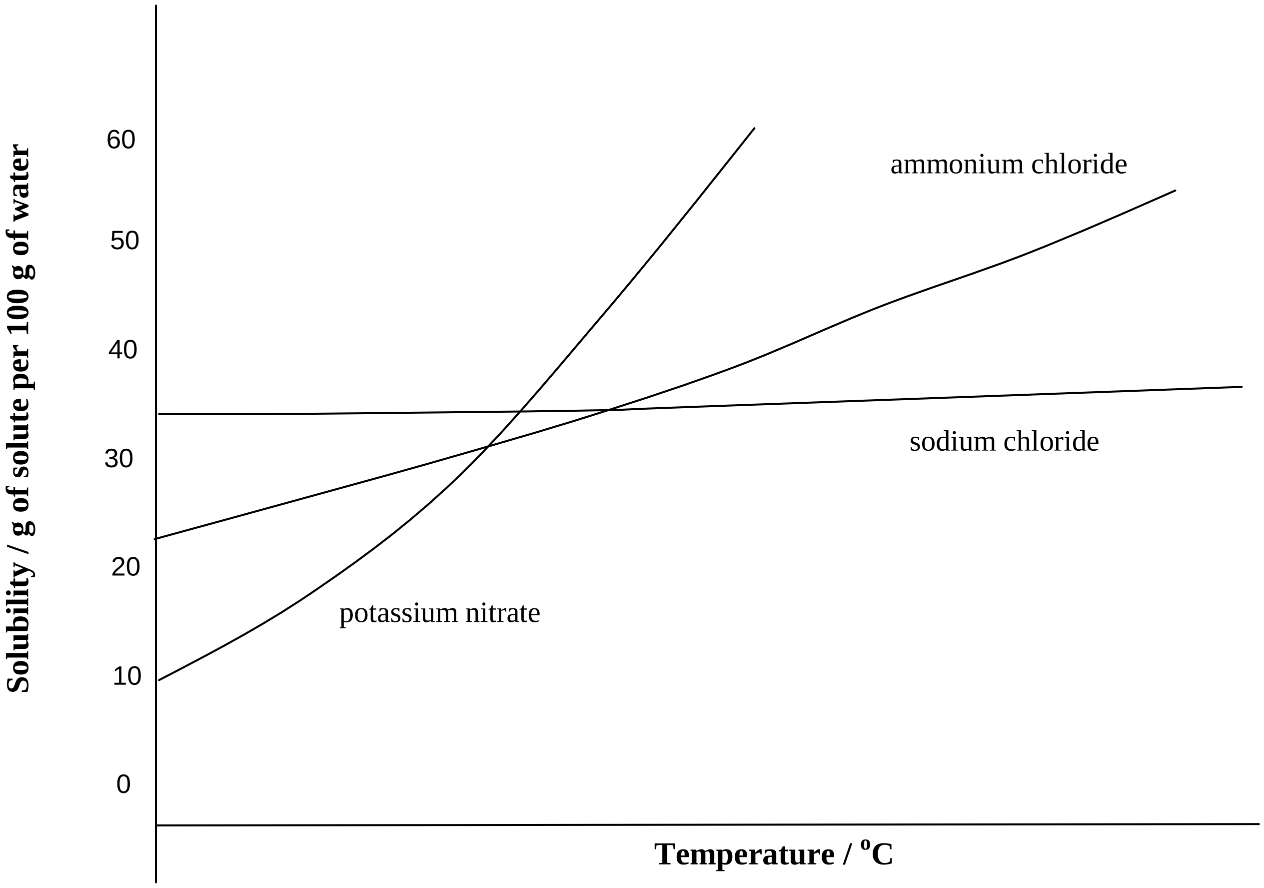
The units of solubility are grams of solute per given mass of solvent. e.g. g per 100 g of solvent.

Solubility may also be expressed as moles of solute per given mass of solvent. e.g. mol kg^{-1}.

Solubility varies with temperature.

A plot of solubility against temperature is called **a solubility curve**.

The solubility curves for sodium chloride, ammonium chloride and potassium nitrate are shown below.



As can be seen from the samples above compounds are usually more soluble at higher temperatures. However, the solubility of common salt, sodium chloride, only increases slightly with a rise in temperature.

Purification by recrystallisation

If an impure compound contains impurities which are soluble in the same solvent as the compound then the mixture can often be purified by recrystallisation.

The simplest procedure is as follows.

Dissolve the impure compound in the minimum volume of hot solvent, forming a solution of the compound and the impurities. Insoluble impurities may be removed by hot filtration of this solution of the impure compound.

Since the main component is the compound, on cooling, a point will be reached when the solution of the compound and impurities becomes saturated with respect to the compound and further cooling will cause crystals of the compound to form. On the other hand, the solution of the impurities will never become saturated and the impurities will remain in the liquid phase even when the solution is cold.

On filtration, the crystals of the compound will remain on the filter paper and the impurities will pass through in the liquid phase.

The crystals on the filter paper may be washed with a little cold solvent, dried and stored.

Note that some of the compound is always lost in the cold saturated solution which passes through the filter paper.

TOPIC 5 Solid Structure

Candidates should be able to:

(a) *recall and describe the crystal structures of sodium chloride and caesium chloride, including the crystal coordination numbers and a simple explanation of the differences in terms of the relative sizes of the cations;*

(b) *recall and describe the structures of diamond and graphite and know that iodine forms a molecular crystal;*

(c) *recall and describe the structure of carbon nanotubes and appreciate the analogy with the graphite structure;*

(d) *understand and explain the simple 'electron sea' model for bonding in metals and use it to explain their physical properties;*

(e) *explain the relationship between physical properties (e.g. hardness, volatility and electrical conductance) and structure and bonding for the examples above;*

(f) *understand that a so-called `smart' material is able to exhibit a change in properties with a change in conditions (temperature, pH, etc) and this is often caused by a change in structure;*

(g) *understand that nano-sized materials often exhibit different properties which can lead to new uses*

Topic 5 (a) The crystal structures of sodium chloride and caesium chloride.

Both these compounds are ionic and exist in the solid state in a giant ionic crystal lattice.

The difference between the two compounds lies in the different sizes of the sodium ion and the caesium ion.

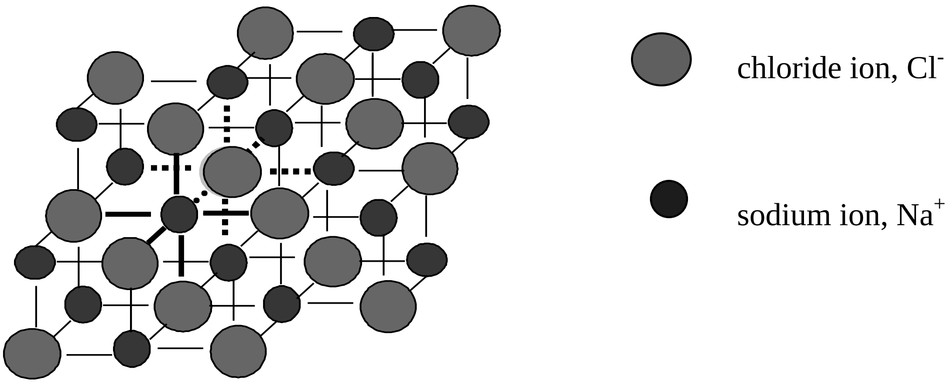
Na^+ ionic radius 0.095 nm Cs^+ ionic radius 0.169 nm

Cl^- ionic radius 0.181 nm

Just looking at these values might suggest that a caesium ion could accommodate more chloride ions around it than a sodium ion. This is the case. The coordination number of an ion in a crystal lattice is the number of nearest neighbours of opposite charge.

Visit http://wwwchem.uwimona.edu.jm:1104/courses/csclJ.htmlisit

The structure of sodium chloride



Note that each chloride ion is surrounded by six sodium ions as nearest neighbours.

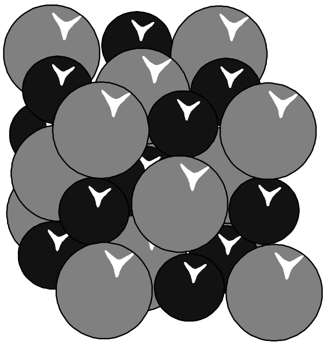
The chloride ion is said to have a coordination number of **six**.

Note that each sodium ion is surrounded by six chloride ions as nearest neighbours.

The chloride ion is said to have a coordination number of **six**.

Sodium chloride is said to have 6:6 coordination.

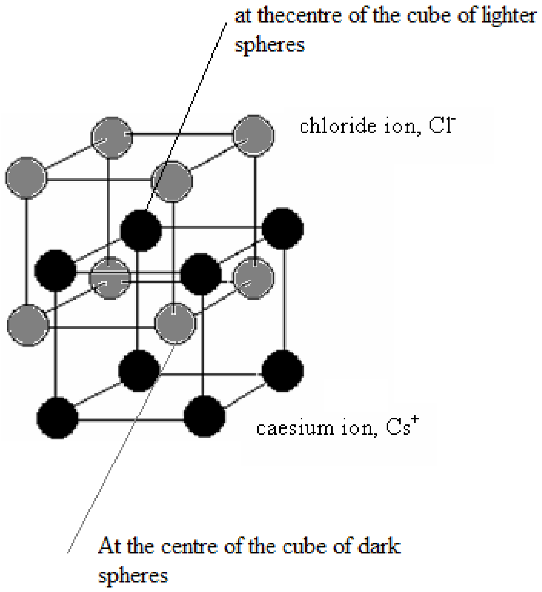
The lattice is cubic and is often described as face-centred-cubic as can be seen from the space-filling representation below.

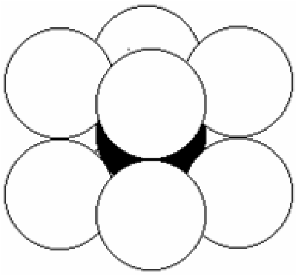


In this diagram there is a chloride ion in the centre of the face of the cube and extension would show a sodium ion in the centre of a face.

The structure of caesium chloride

Caesium chloride has a lattice made up of two interpenetrating simple cubic structures.





Note that each chloride ion is surrounded by eight caesium ions as nearest neighbours and has a coordination number of 8.

Note that each caesium ion is surrounded by eight chloride ions as nearest neighbours and has a coordination number of 8.

Caesium chloride has 8:8 coordination.

Note that each chloride ion is surrounded by eight caesium ions as nearest neighbours.
The chloride ion is said to have a coordination number of **eight**.
Note that each caesium ion is surrounded by eight chloride ions as nearest neighbours.
The chloride ion is said to have a coordination number of **eight**.
Caesium chloride is said to have 8:8 coordination.

Sometimes this is incorrectly referred to as body-centred cubic. This is not so, in true body-centred cubic structures the particles at the edges of the cube are the same as that in the centre.
The electrostatic forces between ions in an ionic lattice are strong. This accounts for the hardness of ionic crystals, their low volatility and high melting points.

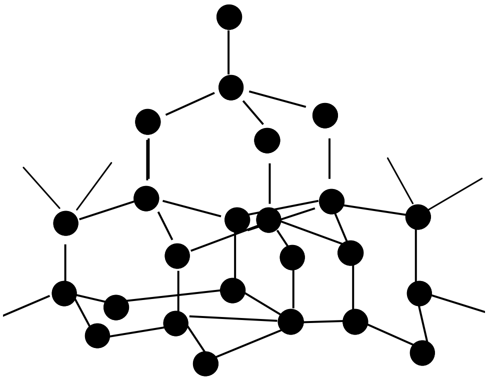
Topic 5 (b)

Diamond and Graphite as giant atomic lattices

Diamond

Visit http://cst-www.nrl.navy.mil/lattice/struk.jmol/a4.html

In diamond the carbon atoms are bonded tetrahedrally in the lattice. Each carbon atom is bonded covalently to four other carbon atoms.

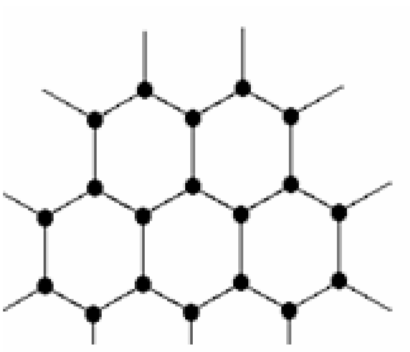


Part of the diamond structure

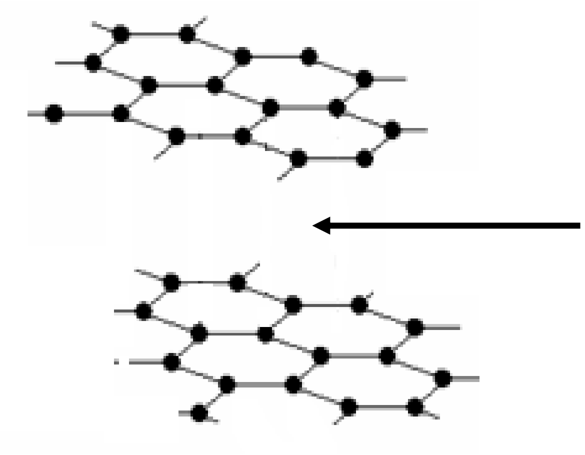
The fact that this tetrahedral bonding forms a rigid structure accounts for the hardness of diamond and the fact that it does not conduct electricity (all four of the atoms outer electrons are involved in covalent bonding).

Graphite

In graphite each carbon atom is bonded to three other carbon atoms in a planar structure.



The planes of carbon atoms can slide over each other.



The planes are held together by van der Waals forces and the fourth electron not used in covalent bonding leads to an electron cloud between the planes, making graphite a good conductor of electricity.

Layers of planes of carbon atoms

The delocalised electrons make graphite a good conductor of electricity, not many non-metals are good conductors. The fact that the layers of carbon atoms can slide over one another makes graphite a lubricant. Both graphite and diamond being giant atomic crystals have high melting points.

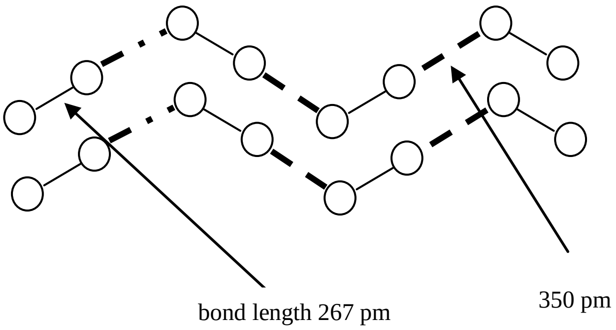
Solid Iodine

The iodine molecule is I_2.

In its crystal lattice, I_2 molecules are held in position by weak van der Waals forces. Evidence for this is the highly volatile nature of solid iodine, purple iodine vapour being evident above the solid at very moderate temperatures. The transition from solid to vapour without passing through the liquid phase is called sublimation.

The sublimation of iodine can be demonstrated by holding a cold surface over some solid iodine which is gently warmed in an evaporating basin. Crystals of iodine form on the cold surface.

The iodine molecules form layers in which the molecules zig-zag in layers.



pm ≡ one pecometre
= 1 × 10^{-12} m

The distance between the layers in the crystal is 427 pm.

Visit

http://web1.caryacademy.org/chemistry/rushin/StudentProjects/ElementWebSites/iodine/structure.html

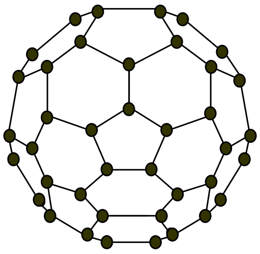
or

http://www.webelements.com/webelements/elements/text/I/xtal-pdb.html

Topic 5 (c)

Carbon exists in forms other than diamond and graphite.

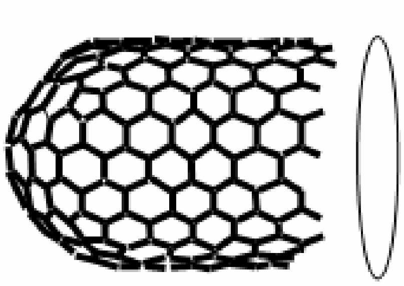
Buckminsterfullerene (usually fullerene) is C_{60}



As a result into research into carbon forms such as fullerene, researchers discovered in 1991 carbon nanotubes (CNT) which are structures made up of a seamless roll of a single graphite plane.

It is extremely hard to sketch a carbon nanotube with average artistic skills and for good pictorial put "carbon nanotubes" into a search engine on the web and go to some of the many websites available..

The diagram below attempts to show part of a nanotube.



It is essentially a rolled up graphite plane with a fullerene type end. Some tubes may be closed at each end.

These tubes are extremely thin; 10,000 times thinner than a human hair. They can conduct electricity and have very high mechanical strength. New uses for carbon nanotubes are being suggested all the time. Their electrical conductivity may make them suitable as connectors in micro electronic circuits. Another interesting fact is that some tubes are good conductors like metals whereas others can behave like silicon as a semiconductor. The tube shown is a single wall carbon nanotube (SWCNT) but it is now possible to synthesise multi-walled tubes (MWCNT).

Some forward looking ideas as to their futures in the computer industry may be found at

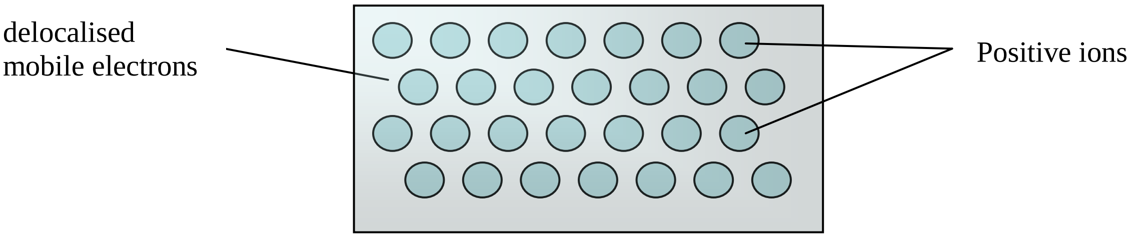
http://searchdatacenter.techtarget.com/originalContent/0,289142,sid80_gci1119403,00.html

and many other web sites.

Topic 5 (d) The Metallic State

The majority of the elements are metals. Mixtures of metallic elements are called alloys.

A simple picture of the metallic state is a lattice of positive ions held together by their attraction to a ‘sea’ of mobile or delocalized electrons in between the ions.



Most metals are close-packed structures. This means that the ions occupy minimal volume.

The ions have a coordination number of 12 and are hexagonal close packed or cubic close packed.

These structures are not required for this unit. The close-packing explains the hardness of many metals.

The alkali metals are body-centred structures with coordination number 8. This is not close packing and the alkali metals are relatively soft.

The general properties of metals can be explained in terms of this model.

- Good electrical conductivity. The mobile electrons are free to move under an electrical potential difference.
- Good thermal conductivity. The mobile electrons can transfer thermal energy through the metal lattice.
- Malleability. (Many metals can be beaten into sheets). The mobile electrons behave as a lubricant allowing the positive ions to move over one another and preventing fracture. The presence of impurities often reduces malleability. Cast iron which contains a significant amount of carbon is very brittle whereas pure iron is malleable.
- Ductility. This means that metals can be drawn out into wires. The reasons are similar to those for malleability.
- Photo-electric effect. When freshly cut surfaces of some metals are exposed to light of a certain frequency, a photon of light may cause one of the mobile electrons to be removed from the metal.

Topic 5 (f) Smart Materials

Smart materials are new materials whose properties change reversibly with a change in conditions such as mechanical deformation, change in temperature, light, pH etc.

Surgical wires that replace tendons Visit

http://www.cs.ualberta.ca/~database/MEMS/sma_mems/smrt.htmlisit

Some examples

Shape memory polymers (SMP).

Visit http://www.crgrp.net/tutorials/smp2.htmisit

These polymers are somewhere between thermoplastics and thermosets first discovered in Japan in 1984.. Polymers can be made with shape memory characteristics. SMPs change between rigid and elastic states by way of thermal changes. The change takes place at what is called the glass transition temperature. Shape memory polymers can be formulated with a transition temperature that matches a particular application. On heating the polymer softens and can be stretched or deformed and on cooling remains in the deformed state. On reheating, it "remembers" its original shape to which it returns. This property is called ***shape retention***. Applications may be plastic car bodies from which a dent could be removed by heating. Medical sutures which will automatically adjust to the correct tension.

Shape memory alloys.

Some alloys, in particular some nickel/titanium alloys and copper/aluminium/nickel alloys show two remarkable properties.

(i) pseudo-elasticity (they appear to be elastic)
(ii) shape retention memory (when deformed they return to their original shape after heating)

Visit
http://www.cs.ualberta.ca/~database/MEMS/sma_mems/sma.html
Suggested applications are

- Deformable spectacle frames
- Surgical plates for joining bone fractures, as the body warms the plates they put tension on the bone fracture.
- Thermostats for electrical devices such as coffee pots
- The aeronautical industry: Shape memory alloy wires can be heated by an electric current and made to operate wing flaps.

Thermochromic paints and colorants.

Complicated organic molecules have been made which can change colour over a specified temperature range. Uses include are T-shirts which change colour at body temperature, coffee mugs which can indicate the temperature of the drink they contain.

Photochromic paints and colorants.

These contain organic molecules that when exposed to light, particularly ultraviolet light, change colour. The light breaks a bond in the molecule which then rearranges into a molecule with a different colour. When the light source is removed, the molecule returns to its original form.

Hydrogels

These are cross linked polymers which have the ability to absorb or expel water when subjected to certain stimuli such as temperature, exposure to infrared radiation or change in pH.
Possible applications could be
Artificial muscles
Underground water cut off in the oil industry, the volume of gel can be pH controlled.

Topic 5(g) Nanomaterials

These are often defined as particulate materials with at least one dimension of less than 100 nanometres (nm). 1 nanometre is 10^{-9} m.
A human hair has a diameter of approximately 70,000 nm.
It has been found that nanomaterials may have properties which are significantly different from the material in bulk.

Nano-scale silver particles are found to have antibacterial, antifungal and antiviral properties.
It is thought that their effect is through the production of silver ions.
It is hoped that they may be effective against MRSA (*Methicillin Resistant Staphylococcus Aureus*). This is the infection which is antibiotic resistant and is a commonly acquired infection in hospital and can be fatal.
Nano-sized silver particles are presently being used in the linings of refrigerators to make them self-sterilising.
Metallic silver in bulk does not have these properties.
Nano-science is a new science and there are concerns about its applications.
Since a substance in the nano form has different properties from the same substance in the bulk form, care must be exercised.

Nano particles may pass through the skin and have adverse biological effects. Since nano particles are so small they may be easily dispersed into the environment. Much that is written is speculation and research is continuing to determine what dangers there are.

In June 2003 the UK Government commissioned the Royal Society, the UK National Academy Of Science, and the Royal Academy of Engineering, the UK National Academy of Engineering, to carry out an independent study on developments in nanotechnology and the potential issues in ethical, health and safety and social issues which are not covered by current regulation.
Visit http://www.nanotec.org.uk/finalReport.htm

6.1 The Periodic Table

Candidates should be able to:

(a) *describe the Periodic Table in terms of the arrangement of elements in groups and periods on the basis of their electronic structure and the classification of elements into s, p and d blocks,*

(b) *understand the general trends in ionisation energy, melting temperature, and electronegativity, across periods and down groups;*

(c) *recall the occurrence of elements as metals or non-metals in different parts of the Periodic Table,realise that metallic oxides are generally basic and non-metallic oxides acidic;*

(d) *assign oxidation states (numbers) to the atoms in a compound or ion and use these to decide which species have been oxidised and which reduced in a redox reaction;*

(e) *understand and explain the nature of oxidation and reduction in terms of electron transfer.*

A version of the Periodic Table is provided by WJEC in Examinations

Please familiarise yourself with this version.

THE PERIODIC TABLE

Key

A_r — relative atomic mass
Symbol
Name
Z — atomic number

Group

s Block | d Block | p Block

Period	1	2											3	4	5	6	7	0
1	1.01 H Hydrogen 1																	4.00 He Helium 2
2	6.94 Li Lithium 3	9.01 Be Beryllium 4											10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12											27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	40.0 Ar Argon 18
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	98.9 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54
6	133 Cs Caesium 55	137 Ba Barium 56	139 La ▶ Lanthanum 57	179 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	(210) Po Polonium 84	(210) At Astatine 85	(222) Rn Radon 86
7	(223) Fr Francium 87	(226) Ra Radium 88	(227) Ac ▶▶ Actinium 89															

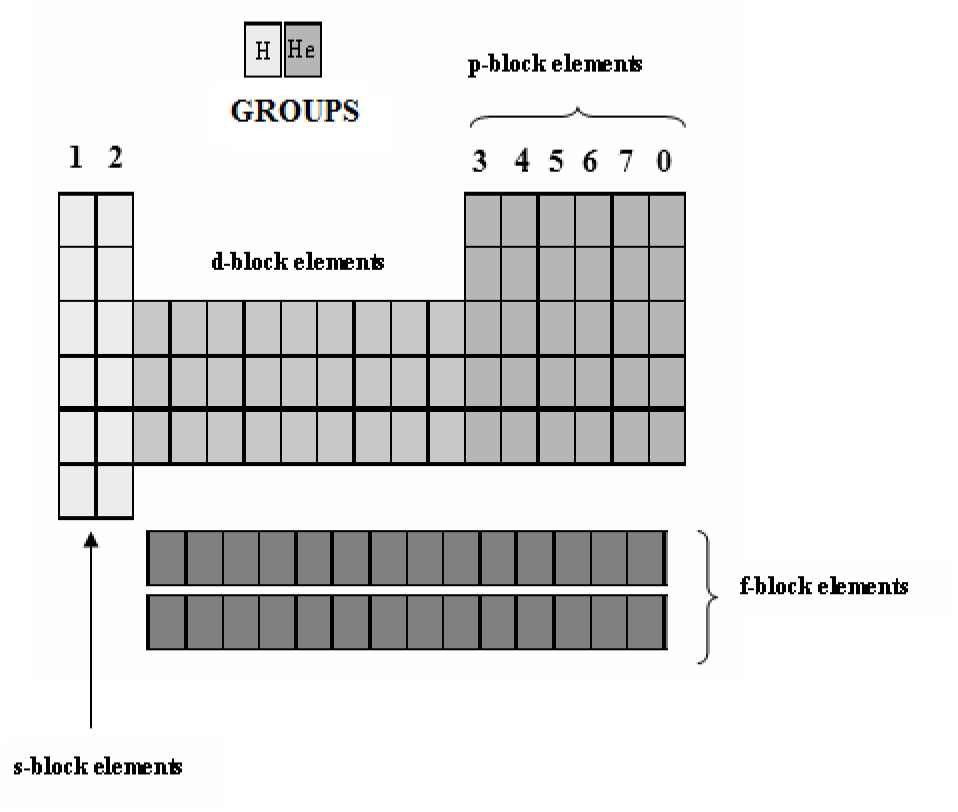
f Block

▶ Lanthanoid elements	140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	(147) Pm Promethium 61	150 Sm Samarium 62	(153) Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	163 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71
▶▶ Actinoid elements	232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(245) Bk Berkelium 97	(251) Cf Californium 98	(254) Es Einsteinium 99	(253) Fm Fermium 100	(256) Md Mendelevium 101	(254) No Nobelium 102	(257) Lr Lawrencium 103

The modern Periodic Table of the elements consists of the chemical elements arranged in order of their atomic numbers.

Hydrogen and helium form the first period of the table as they complete the first principal quantum shell. When the other elements are arranged in order of their atomic numbers they fall into groups (vertical columns) and periods (horizontal rows). The number of the groups shows the number of valency electrons except for Group 0, the noble gases, which have eight outer electrons.

From the electronic structures in terms of s, p, d and f electrons, the elements form blocks which can be labelled as s-block, p-block, d-block and f-block.



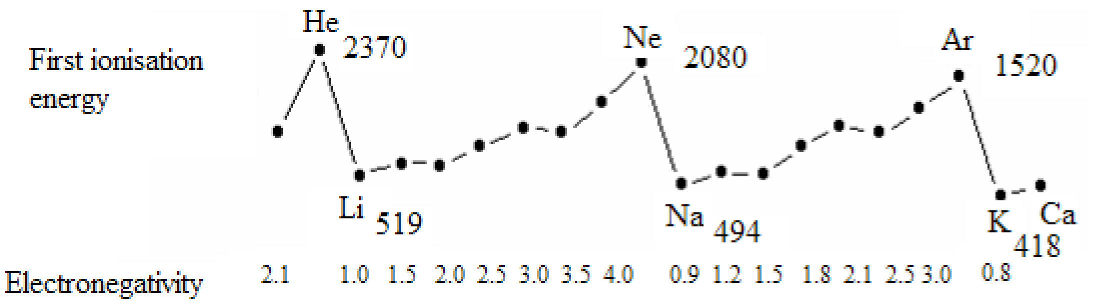
Some periodic trends down groups and across periods.

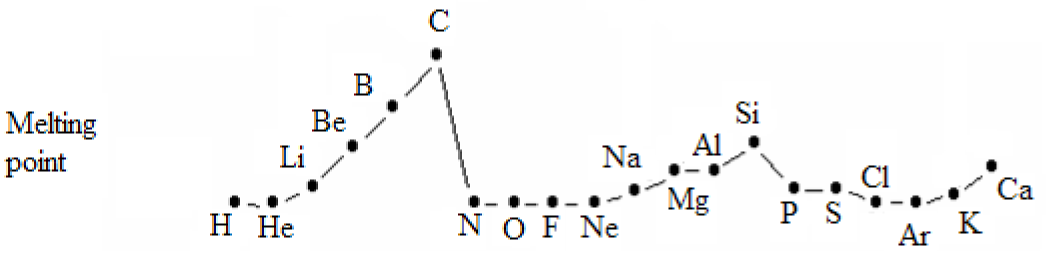
The specification asks for an understanding of trends in first ionisation energies, electronegativities and melting temperatures.

Factors affecting first ionisation energies are discussed in the Revision Aid for Unit 1.

As can be seen from the diagram below, there is general increase in first ionisation energies across a period and a decrease down a group.

Electronegativities increase across a period and decrease down a group.

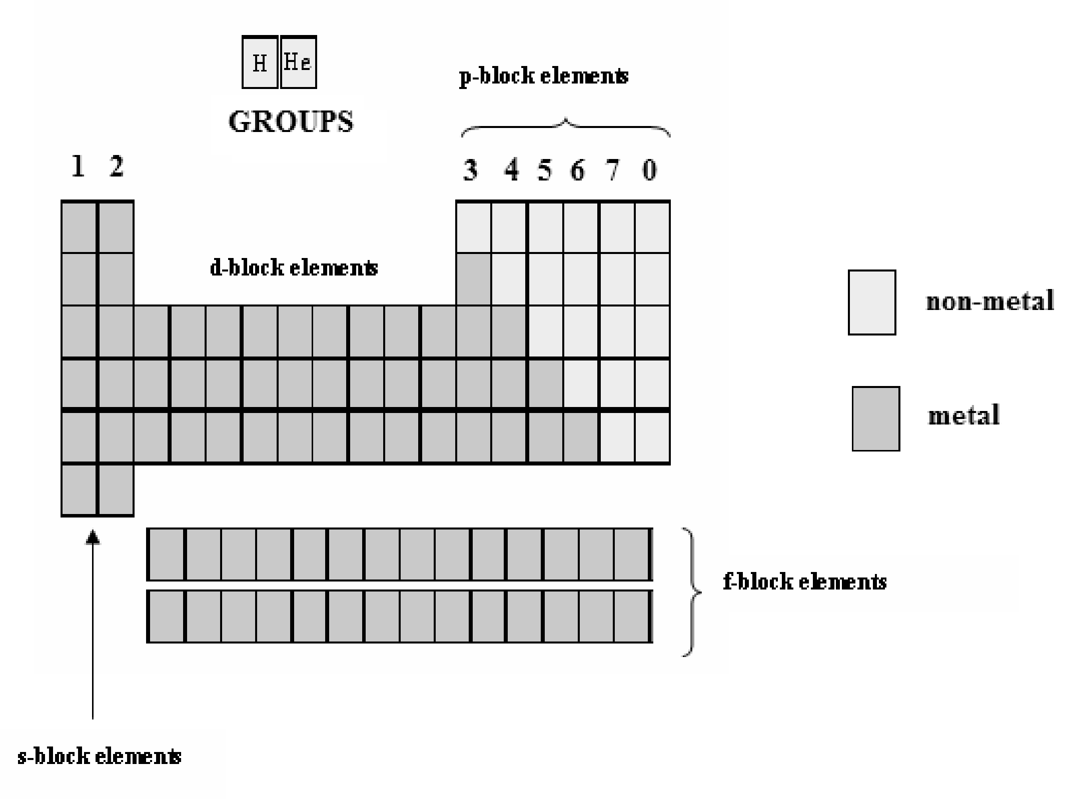




Melting temperatures rise across a period until Group 4 and then fall.

For metals such as those of Group 1, melting temperatures decrease down the Group but for the elements of Group 7 they increase down the group.

Most elements are metals.



The oxides of metals have basic properties.

This means that they react with an acid to form a salt and water

e.g.

$$CaO(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l)$$

$$PbO(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2(aq) + H_2O(l)$$

The oxides of non-metals have acidic properties.

This means that they react with water to form an acid.

e.g.

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

Sometimes a mixture of acids is formed.

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

Topic 6.1 (d) Oxidation states (numbers)

The rules to assign an oxidation state or number to an element are as follows.

	Oxidation number
oxidation number of an uncombined element	0
sum of oxidation numbers of elements in uncharged species	0
sum of oxidation numbers of elements in an ion	the charge of the ion
oxidation number of fluorine	is always -1
oxidation number of an alkali metal	is always +1
oxidation number of an alkaline earth metal	is always +2
oxidation number of oxygen	is always -2
(except oxygen in peroxides)	is -1
oxidation number of halogen in metal halides	is always -1
oxidation number of hydrogen	is always +1
(except hydrogen in metal hydrides)	is -1

Examples of application of the above rules.

(i) The oxidation state of iron in $FeCl_3$.

The oxidation state of chlorine is -1 and so iron must be +3.

The compound is **iron(III) chloride.**

(ii) The oxidation state of manganese in MnO_4^-

The oxidation state of oxygen is -2 and there are four oxygen atom. The overall charge of the ion is -1; therefore the oxidation number of manganese is +7.

The ion is the **manganate(VII) ion.**

(iii) The oxidation state of boron in $NaBH_4$.

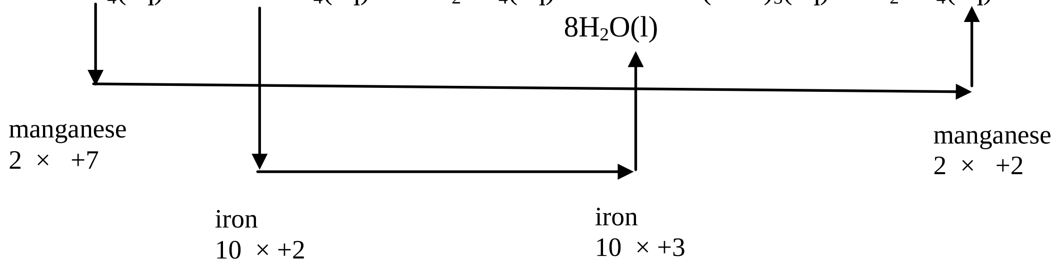
The oxidation state of sodium is +1; the oxidation state of hydrogen as an hydride is -1 and there are four hydrogen atoms. Therefore the oxidation number of boron must be +3.

The compound is **sodium tetrahydridoborate(III)**

An element is oxidized in a chemical reaction if its oxidation state increase and is reduced if its oxidation state decreases.

Consider the reaction

$2KMnO_4(aq) + 10FeSO_4(aq) + 8H_2SO_4(aq) \rightarrow 5Fe2(SO4)_3(aq) + K_2SO_4(aq) + 2MnSO_4(aq) + 8H_2O(l)$



Changes in oxidation number

manganese goes from +14 to +4 Manganese has been reduced

iron goes from +20 to +30 Iron has been oxidised

In the above reaction, oxidation and reduction occur simultaneously. Such reactions are called **redox** reactions.

Redox may also be explained in terms of electron transfer.

Loss of electrons is oxidation and gain of electrons is reduction.

Consider

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

This reaction may be considered redox since

- a magnesium atom has lost two electrons $\mathbf{Mg \rightarrow Mg^{2+} + 2e^-}$ and has been oxidised
- two hydrogen ions from the hydrochloric acid have gained two electrons

$\mathbf{2H^+ + 2e^- \rightarrow H_2}$ and hydrogen ions have been reduced.

The equations in bold above are called ion/electron half equations and are a very useful way of tackling redox reactions.

Notice that chlorine in the reaction has not been changed and can be omitted from an overall ionic equation i.e.

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

In some reactions an element may undergo simultaneous oxidation and reduction. This is called **disproportionation**.

$$\underset{\underset{0}{\uparrow}}{Cl_2(g)} + 2NaOH(aq) \rightarrow \underset{\underset{-1}{\uparrow}}{NaCl(aq)} + \underset{\underset{+1}{\uparrow}}{NaClO} + H_2O(l)$$

oxidation
state of chlorine

6.2 Trends in properties of the elements of the s-block and Group 7(17)

Candidates should be able to:

(a) *recall the typical behaviour of the elements of Groups 1 and 2 with 0_2, H_2O and Group 2 elements with dilute acids (excluding nitric acid) and the trends in their general reactivity ;*

(b) *describe the reactions of the aqueous cations, Mg^{2+}, Ca^{2+} and Ba^{2+} with OH^-, CO_3^{2-} and SO_4^{2-};*

(c) *recall the formulae of the oxides and hydroxides of Groups 1 and 2 and appreciate their basic character;*

(d) *recall the flame colours shown by compounds of Li, Na, K, Ca, Sr and Ba (and that Mg compounds show no colour) and describe their use in qualitative analysis;*

(e) *show an awareness of the importance of calcium carbonate and phosphate minerals as skeletons for living systems and the consequent formation of carbonate rocks and the importance of calcium and magnesium in biochemistry;*

(f) *recall the trend in volatility shown by the elements Cl, Br and I and relate to chemical bonding;*

(g) *recall and explain the tendency of the halogens (F - I) to react by forming anions (F^-, Cl^-, Br^-, F), and recollect that this reactivity decreases on descent of the group ;*

(h) *recall the reactions of the halogens with metals, their displacement reactions with halides, and explain the group trends and displacements in terms of the relative oxidising power;*

(i) *understand the displacement reactions of $C1_2$ and Br_2 in terms of redox;*

(j) *recall the nature of the reaction between aqueous Ag+ and halide (Cl^-, Br^-, I^-) ions followed by dilute aqueous NH_3 , and understand the analytical importance of these reactions in qualitative analysis (ionic equations required for precipitation reactions only).*

Topic 6.2 (a) and (b)

The specification asks for the typical behaviour of the s-block elements. The first member of a group often shows atypical behaviour and so the reactions of lithium and beryllium will be excluded here.

All alkali metals(Group 1) react with water with increasing violence down the group,

e.g. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

The Group 2 metals all react with water

Magnesium will burn in steam

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$

the other members react with water to form the hydroxide

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Calcium hydroxide is only sparingly soluble and may be seen as a white solid.

All the s-block elements burn in air or oxygen to form oxides.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$

Elements such as potassium can form K_2O_2 and KO_2 , potassium peroxide and potassium superoxide.

If magnesium is burnt in air a little magnesium nitride is formed

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

All the s-block elements react with dilute acids to give hydrogen.

The reactions of the Group 1 elements are too violent to be undertaken in a school laboratory.

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

Remember the ionic equation

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

Topic 6(c)

Oxides and hydroxides of the s-block elements

GROUP 1			
sodium oxide	Na_2O	sodium hydroxide	NaOH
potassium oxide	K_2O	potassium hydroxide	KOH
rubidium oxide	Rb_2O	rubidium hydroxide	RbOH
caesium oxide	Cs_2O	caesium hydroxide	CsOH

GROUP 2			
magnesium oxide	MgO	magnesium hydroxide	$Mg(OH)_2$
calcium oxide	CaO	calcium hydroxide	$Ca(OH)_2$
strontium oxide	SrO	strontium hydroxide	$Sr(OH)_2$
barium oxide	BaO	barium hydroxide	$Ba(OH)_2$

All these oxides are basic and react with acids to form salt and water.

$$CaO(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l)$$

The Group 1 oxides dissolve readily in water to form the corresponding alkali.

$$K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$$

The solubility of the Group 2 oxides increases down the group. Barium hydroxide is sufficiently soluble for barium hydroxide solution to be used in volumetric analysis.

Topic 6.2 (d) Flame tests

When many of the s-block elements are introduced into a hot Bunsen burner flame they emit a colour as an emission spectrum. This colour can be used in analysis to identify the element.

Element	colour of flame
lithium	red
sodium	golden yellow
potassium	lilac
calcium	brick-red
strontium	crimson
barium	apple-green
magnesium	no colour

Topic 6.2 (e)

The elements calcium and phosphorus are extremely important in the skeletons of vertebrates. Calcium is the most abundant mineral in the body about 99% of the total calcium in the body is found in teeth and bones. The other element necessary in bone formation is phosphorus. The calcium/phosphorus ratio in bone is about 2:1. Deficiencies in calcium intake in children may lead to the condition known as rickets. Amongst the minerals found in bone are calcium carbonate, $CaCO_3$, and calcium hydroxyapaptite, $Ca_5(OH)(PO_4)_3$.

Sedimentary rocks such as limestone are often formed by accumulation of animal skeletal remains and animal shells and are essentially calcium carbonate. Such deposits are of industrial importance.
Calcium has a role to play in cell function and magnesium is important as part of the chlorophyll molecule.

Topics 6.2 (f) – (j) Group 7 The Halogens

The volatility of the halogens decreases as the Group is descended.

Halogen	Physical state at room temperature	Colour	*M.p.* /°C	*B.p.* /°C
Fluorine	gas	pale yellow	-220	-188
Chlorine	gas	greenish-yellow	-101	-35
Bromine	liquid	red-brown vapour red brown	-8	59
Iodine	solid	lustrous grey-black vapour purple	114	184

The halogen molecules are X-X. As the group is descended the increasing number of electrons causes the van der Waals forces to increase and volatility to decrease.

The halogen elements are oxidising agents usually gaining electrons to form the corresponding halide ion.

$$F_2 + 2e^- \rightarrow 2F^-$$
$$Cl_2 + 2e^- \rightarrow 2Cl^- \text{ etc.}$$

Fluorine is dangerous and its reactions very exothermic, turning other elements into their highest oxidation state.
Most metals catch fire in fluorine and water reacts to form a mixture of products including O_2, O_3 and H_2O_2.

Since the reactivity of the halogens decreases down the group, a more reactive halogen will oxidise the halide ion of a less reactive halogen.

Fluorine is not available in a school laboratory but the following reactions and equations should be known.

When chlorine gas or chlorine water is added to aqueous potassium bromide, a red brown colouration of bromine is observed.

Ion/electron half-equations are

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$
$$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$$

Overall $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(l) + 2Cl^-(aq)$
or $Cl_2(g) + 2KBr(aq) \rightarrow Br_2(l) + 2KCl(aq)$

In the same way chlorine will oxidise aqueous potassium iodide to form a brown colouration of iodine or even a black precipitate of elemental iodine.

Ion/electron half-equations are

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$$
$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$

Overall $Cl_2(g) + 2I^-(aq) \rightarrow I_2(s) + 2Cl^-(aq)$
or $Cl_2(g) + 2KI(aq) \rightarrow I_2(s) + 2KCl(aq)$

also bromine will oxidise aqueous potassium iodide

Ion/electron half-equations are

$$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$$
$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$

Overall $Br_2(l) + 2I^-(aq) \rightarrow I_2(s) + 2Br^-(aq)$
or $Br_2(l) + 2KI(aq) \rightarrow I_2(s) + 2KBr(aq)$

These reactions are often called **displacement reactions.**

They are examples of redox reactions.

In each case the halogen has gained electrons to become the halide ion and has been **red**uced.

In each case the aqueous halide ion has lost an electron and been **ox**idised. Hence it is a **redox** reaction.

Testing for aqueous halide ions

Aqueous chloride, bromide and iodide ions may be tested for and identified by the following procedures.

The test solution is first acidified by aqueous nitric acid to remove any ions such as hydroxide and carbonate which would interfere.

This is followed by aqueous silver nitrate.

Chloride ions produce a white curdy precipitate of silver chloride which darkens on standing.

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$
$$Cl^-(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NO_3^-(aq)$$

The precipitate of silver chloride readily dissolves in dilute aqueous ammonia to form a colourless solution.

When the same procedure is applied to **bromide ions** a cream precipitate of silver bromide is formed which will dissolve in concentrated aqueous ammonia.

$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$$
$$Br^-(aq) + AgNO_3(aq) \rightarrow AgBr(s) + NO_3^-(aq)$$

In the case of iodide ions, a primrose yellow precipitate of silver iodide is formed which is insoluble in aqueous ammonia.

$$I^-(aq) \ + \ Ag^+(aq) \ \rightarrow \ AgI(s)$$
$$I^-(aq) \ + \ AgNO_3(aq) \ \rightarrow \ AgI(s) \ + \ NO_3^-(aq)$$

These reactions are important in analytical chemistry, both in inorganic and organic situations.

7.1 Organic compounds and their reactions

Candidates should be able to:

(a) *write displayed, shortened and skeletal structural formulae of simple alkanes, alkenes, halogenoalkanes, primary alcohols and carboxylic acids given their systematic names, and vice versa;*

(b) *describe the effect of increasing hydrocarbon chain length and of the above functional groups on physical properties, melting and boiling temperature and solubility;*

(c) *describe structural isomerism and be able to write down the structural isomers of non-cyclic organic compounds (up to and including* C_6 *homologues) including those of different chemical class;*

(d) *describe E-Z isomerism in alkenes, give an example, and discuss such isomerism in terms of restricted rotation about the C = C bond, and appreciate that E-Z isomers may have different physical and chemical properties;*

(e) *derive empirical formulae from elemental composition data and use such results, together with additional data, to deduce molecular formulae;*

(f) *identify reactants as electrophilic, nucleophilic or radical in type, explain the basis of this classification, and give examples of each;*

(g) *classify the following types of functional group reactions and describe their nature: electrophilic addition, elimination, oxidation, hydrolysis;*

(h) *describe the total oxidation of primary alcohols,* RCH_20H*, to carboxylic acids, RCOOH. (Knowledge of the properties of aldehydes is not, at this stage, required);*

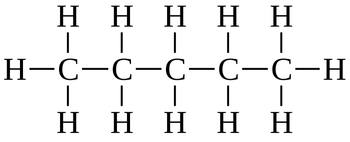
(i) *recognise the following functional group tests by the indicated reactions:*

C = C addition of $Br_2(aq)$*:*

-X (Cl, Br, I) hydrolysis by aqueous base, followed by reaction with $AgNO_3(aq) / HNO_3(aq)$*.*

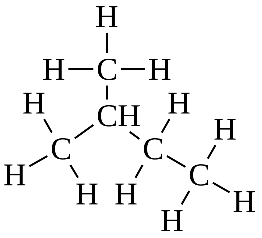
In organic chemistry one molecular formula may represent more than one organic compound.

The formula C_5H_{12} may represent more than one hydrocarbon.

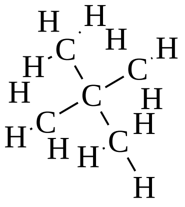


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

pentane



2-methylbutane



2,2-dimethylpropane

Topic 7.1 (a) Requires some knowledge of the systematic names of organic compounds. A brief introduction to nomenclature is necessary.

Nomenclature

Because of the large number of organic compounds it is necessary to devise a way of naming them that leaves no ambiguity. Many organic compounds have been known for a long time and have trivial names that pre-date systematic nomenclature.

Acetic acid, CH_3COOH, which is found in vinegar, has the systematic name **ethanoic acid**.

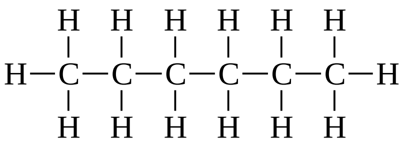
Acetone, C_3H_6O, sometimes used as nail varnish remover, has the systematic name **propanone**.

Naming hydrocarbons.

Organic compounds have a carbon skeleton. Compounds are named in terms of this carbon skeleton and the individual carbon atoms are assigned a number to identify them.

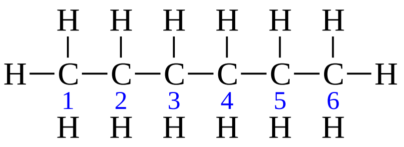
Alkanes.

An alkane in which the carbon atoms form a continuous chain is called a straight chain molecule.



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

hexane



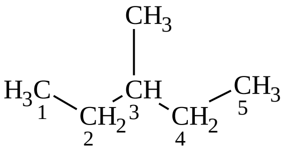
$$H-\overset{H}{\underset{\underset{H}{1}}{C}}-\overset{H}{\underset{\underset{H}{2}}{C}}-\overset{H}{\underset{\underset{H}{3}}{C}}-\overset{H}{\underset{\underset{H}{4}}{C}}-\overset{H}{\underset{\underset{H}{5}}{C}}-\overset{H}{\underset{\underset{H}{6}}{C}}-H$$

The six carbon atoms numbered

One isomer of hexane is 2-methylpentane

The $-CH_3$ group is called the methyl group as it is derived from methane, CH_4. In the molecule above, the methyl group is substituted for a hydrogen atom on the second carbon atom.

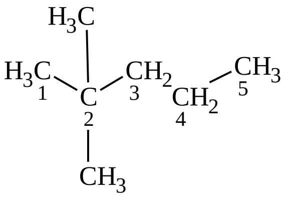
Another isomer is 3-methylhexane



4-methyl hexane does not exist because if we number the hexane chain from the other end it would be the same as 3-methylhexane above. See rules below.

When there is more than one methyl group attached to the chain we use the prefixes *di-* , *tri-* etc.

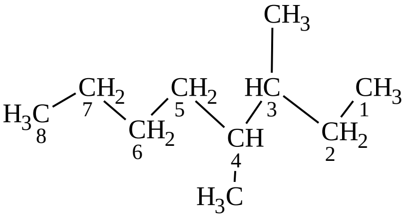
2,2-dimethylpentane



Rules

- Look for the longest continuous carbon chain.
- Base the name on the straight-chain alkane with the same number of carbons.
- Look for the shorter carbon branches and the names of those straight-chain alkanes.
- State the number of identical branches by adding *di-* (two), *tri-* (three), *tetra-* (four), etc.
- Number the positions of the branches on the longest chain so that the arithmetic total of the numbers used is the lowest.
- Keep alphabetical order of branch name.

Example 3,4-dimethyloctane



The longest chain of carbon atoms is eight and so the name is based on the straight-chain alkane with eight carbon atoms which is octane.

To keep the numbers as low as possible we number the octane chain from the right, as shown, and find that there is a methyl attached to carbon atom 3 and one attached to carbon atom 4.

Two methyl groups hence “dimethyl”. So the name is 3,4-dimethyloctane.

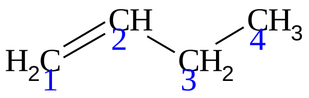
Naming alkenes

Like alkanes the structure is examined for the longest straight-chain carbon chain.

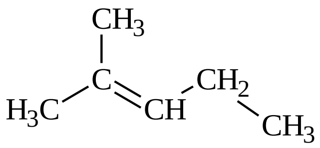
The name is based on the hydrocarbon with the same number of C-atoms as the longest continuous carbon chain that contains the double bond.

The lowest number is used to show the position of the double bond.

The ending "ene" replaces the ending "ane" in the alkanes.



but-1-ene



2-methylbut-2-ene

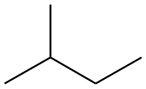
The formulae drawn are called displayed or structural formulae and show how the atoms are arranged in the molecule.

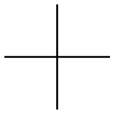
They can also be written as shortened formulae

i.e.

$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2(CH_3)CH_2CH_3$ $C(CH_3)_4$

or as skeletal formulae where each end of a bond there is a carbon atom bonded to the appropriate number of hydrogen atoms





Before beginning the following topics in Unit 2 – it may be wise to look at nomenclature (naming) in organic chemistry.

Visit

http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htmisit

or

http://www.chem.ucalgary.ca/courses/351/orgnom/main/IUPAC.html

Homologous series.

Organic compounds may often be classified s a series of compounds called a homologous series.
The members of such a series are called **homologues**.
The properties of such a series are:

- The members of such a series are capable of being represented by a general formula
- Each member differs from its neighbours by CH_2
- There is a gradual trend in physical properties such as melting or boiling points along the series

The alkanes

This is the simplest homologous series (general formula C_nH_{2n+2}) n is an integer 1,2,3,4,5 etc.

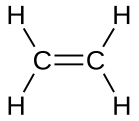
CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12} . . .
methane	ethane	propane	butane	pentane

Note that from butane onwards, isomers exist.

The alkenes

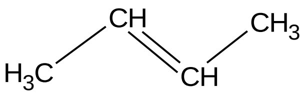
This is the homologous series with general formula C_nH_{2n} n is an integer 1,2,3,4,5 etc.

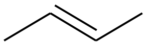
e.g. ethene



= $CH_2{=}CH_2$

but-2-ene





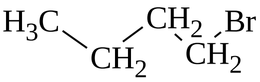
$CH_3CH{=}CHCH_3$

Hydrocarbons are the simplest organic compounds. When a hydrogen atom is replaced by another atom or group of atoms a member of a new homologous series is formed. The atom or group of atoms is called a **functional group**.

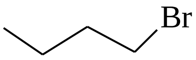
Halogen in the halogenoalkanes.

General formula $C_nH_{2n+1}X$ where X is halogen examples

bromobutane



$H_3C\,CH_2\,CH_2\,CH_2Br$



$CH_3CH_2CH_2CH_2Br$

The aliphatic primary monohydric alcohols

(general formula $C_nH_{2n+1}OH$)

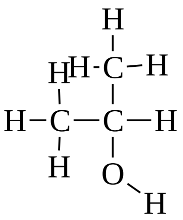
Funtional group –OH

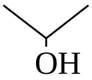
	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$ . . .
	methanol	ethanol	propan-1-ol	butan-1-ol	pentan-1-ol
bp./ °C	64.7	78.3	97.2	117.7	138

The –OH group behaves in a similar way chemically in all the alcohols in the above series.

In all the above the functional group is attached to the first carbon atom.

Propan-2-ol is

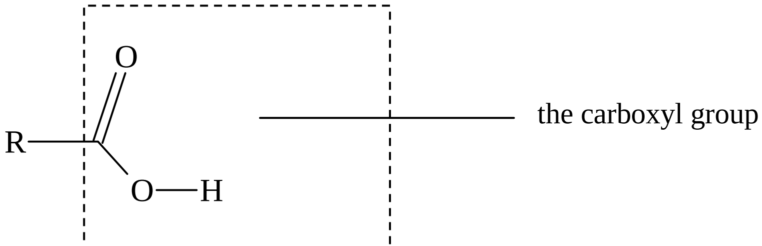




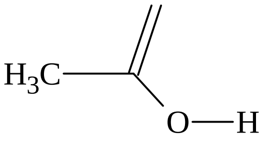
$CH_3CH(OH)CH_3$

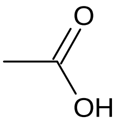
Carboxylic acids

The functional group is the carboxyl group



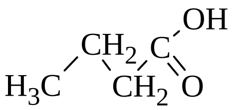
ethanoic acid



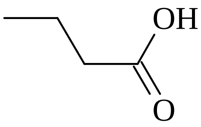


CH_3COOH

butanoic acid



$H_3C\,CH_2\,CH_2\,C(=O)OH$



$CH_3CH_2CH_2COOH$

Topic 7.1 (b)

As the hydrocarbon chain gets larger it has a noticeable effect on the members of a homologous series. This shown for the alcohols above.

Generally boiling points and melting points in all series with a straight hydrocarbon chain increase and solubility in water decreases since hydrocarbon chains do not interact with water molecules. The hydrocarbon chain is hydrophobic.

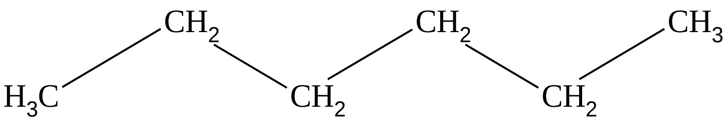
Isomerism

Isomers are different compounds with the same molecular formula.

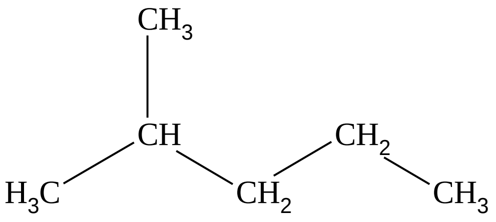
Structural isomerism arises from different arrangements of the atoms in the molecules so that they have different structural formulae.

Chain isomerism.

Here we have different arrangements of the carbon chain.



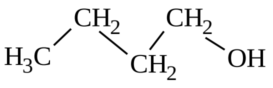
Hexane



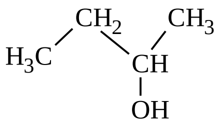
2-Methylpentane

Position isomerism

Here the compounds have the same carbon skeleton but functional groups occupy different positions.



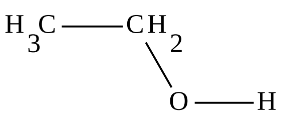
butan-1-ol



butan-2-ol

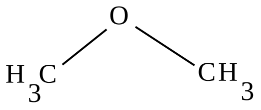
Functional group isomerism

Here the isomers have the same molecular formulae but have different functional groups and so belong to different homologous series.

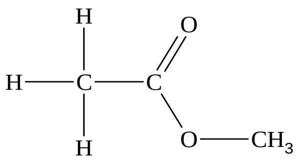


ethanol
(a primary alcohol)

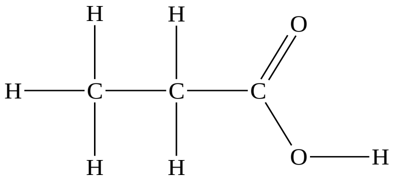
or



dimethyl ether
methoxymethane (an ether)



methylethanoate
an ester



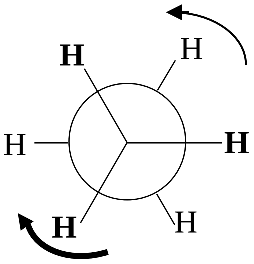
propanoic acid
a carboxylic (or alkanoic) acid

The specification demands the ability to draw isomers for compounds containing up to six carbon atoms.

Topic 7.1 (d) Isomerism in alkenes

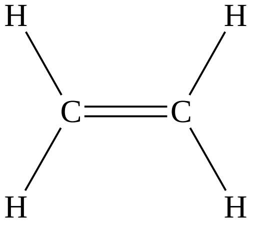
Geometrical isomerism

With an **alkane** such as ethane, C_2H_6, there is free rotation about the carbon-carbon single bond.

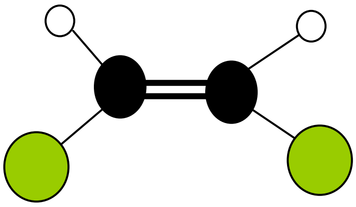


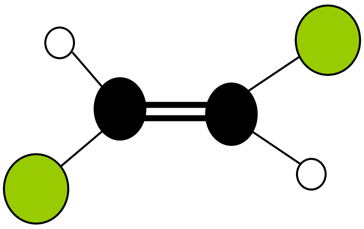
Viewed along the carbon – carbon bond, the three hydrogen atoms of each methyl group can rotate with respect to each other.

In an **alkene** such as ethene, C_2H_4, the double bond prevents this rotation.

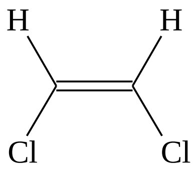


There is no rotation around the carbon-carbon double bond and the molecule is confined to a planar shape. This means that in compounds such as 1,2-dichloroethene, represented by the ball and stick diagrams below, two forms are possible.

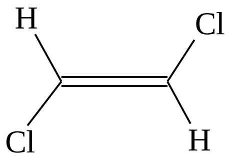




One way of naming them is to call the form which has the hydrogen atoms on opposite sides of the double bond the *trans*-isomer. The other is the *cis*- isomer.



cis-dichloroethene



trans-dichloroethene

These are described as geometrical isomers.

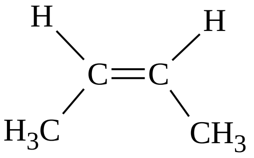
More recently a different method of describing this type of isomerism has been used distinguishing them as E-Z isomers and using quite different criteria.

The rules for assigning E-Z nomenclature are known as CIP rules after the chemists who developed the system, Cahn, Ingold and Prelog.

The first step is to look at the two groups at the end of the double bond and rank the two groups in terms of the atomic number of the atoms concerned. The atom with the higher atomic number takes precedence. This is done for both ends of the double bond. If the higher priority groups are on the same side of the double bond, then it is the Z isomer (from the German ***zusammen*** which is together). If they are on opposite sides then it is the E isomer(from the German ***entgegen*** which is opposite).

Examples

but-2-ene

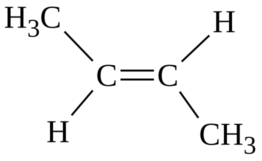


Look at the left hand end of the double bond. C has a higher priority than H.

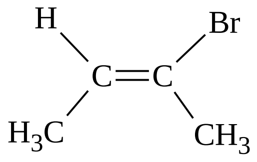
Look at the right hand end of the double bond. C has a higher priority than H.

The carbons are on the same side of the double bond and so this is **(Z) - but-2-ene** and

is (E) – but-2-ene.



Consider the molecule of 2-bromo-but-2-ene.



Look at the left hand end of the double bond. C has a high priority than H.

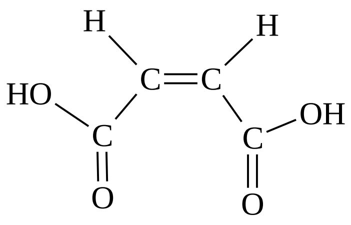
Look at the right hand end of the double bond. Br has a high priority than C.

The higher priority atoms are on opposite sides of the bond and this is **(E) - 2-bromo-but-2-ene.**

Note in *cis/trans* isomerism this would be the *cis* isomer.

The E and Z isomers may have different and physical properties

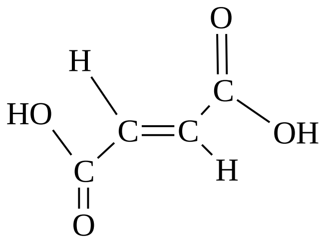
Consider the two butenedioic acids.



(Z) – butenedioic acid

b.p. 130 ^{o}C

forms an anhydride on heating



(E) – butenedioic acid

b.p. 200 ^{o}C sublimes

does not form an anhydride

Topic 7.1 (e)

Analysis of organic compounds often gives its elemental composition, by mass.

From this data the empirical formula of the compound can be determined. The molar mass of the compound can be found by a variety of methods including detecting the value of z/m for the molecular ion peak in its mass spectrum.

Example.

A natural product was extracted from a plant source, purified and subjected to analysis. Its elemental composition by mass was Carbon 74.04%; Hydrogen 8.70%; Nitrogen 17.26%.

The molecular ion peak in the mass spectrum was 162.

Determine the molecular formula of the natural product.

Element	% composition by mass	Relative atomic mass	% ÷ A_r	Divide by lowest
C	74.04	12.01	6.16	5
H	8.70	1.008	8.63	7
N	17.26	14.00	1.232	1

Empirical formula is C_5H_7N

The empirical formula mass is approximately 81

Thus molecular formula is $C_{10}H_{14}N_2$

Topic 7.1 (f) Classification of Reagents

Free radicals or radicals are species with an unpaired electron.

They are usually written $X^{\cdot}$

Nucleophiles and electrophiles

Species which contain a lone pair (non-bonding pair) of electrons are called **nucleophiles**.

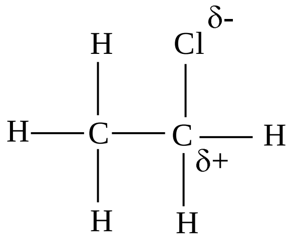
These are negative ions such as OH^-, Cl^-, Br^-, I^-, CN^- etc. and molecules such as H_2O and NH_3.

These species attack regions of low electron density (usually positive centres) in an organic molecule.

Electron deficient species such as NO_2^+, the nitryl cation, are called **electrophiles**. These are susceptible to attack by nucleophiles.

Nucleophiles and electrophiles are important in explaining reaction mechanisms.

Positive centres, subject to nucleophilic attack, also arise through polarity arising in molecules due to the presence of electronegative elements.



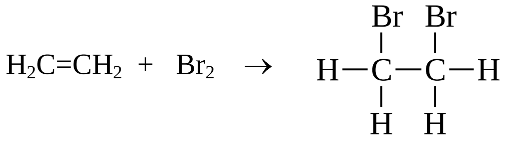
The C-Cl bond is polar so that the carbon atom is positive with respect to the chlorine and is a centre which is susceptible to attack by a nucleophile.

Free radicals also take part in some organic reactions. Free radicals are species with an unpaired electron.

Chlorine radicals can be formed by the action of uv light on chlorine molecules.

$$Cl_2 \; + \; hf \; \rightarrow \; 2Cl^{\cdot}$$

Topic 7.1 (g) Types of reaction



$$H_2C{=}CH_2 + Br_2 \rightarrow H{-}\overset{\overset{\textstyle Br}{|}}{\underset{\underset{\textstyle H}{|}}{C}}{-}\overset{\overset{\textstyle Br}{|}}{\underset{\underset{\textstyle H}{|}}{C}}{-}H$$

is an **electrophilic addition** see **Topic 7.2** The whole reaction involves the addition of a molecule of bromine and no other product is formed so it is an addition reaction. The initial attack is by Br^+ which is an electrophile.

$NaOH + CH_3\text{-}CHBr\text{–}CH_3 \rightarrow NaBr + CH_2{=}CH\text{-}CH_3 + H_2O$

is an **elimination reaction** in which HBr has been removed from the halogenoalkane to form an alkene.

$CH_3CH_2OH \xrightarrow[\textbf{heat}]{\mathbf{Cr_2O_7^{2-}\ /\ H^+}} CH_3COOH + H_2O$ is an **oxidation reaction**

$CH_3CH_2CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2CH_2OH + NaBr$

is an example of **hydrolysis**

Hydrolysis is literally reaction with water but often requires an acid or basic catalyst.

e.g.

$$CH_3COOCH_2CH_3 + H_2O \xrightarrow{HCl(aq)} CH_3COOH + CH_3CH_2OH$$

Topic 7.1 (h) Oxidation of primary alcohols to carboxylic acids.

The general method is to prepare a solution of sodium dichromate(VI) in sulfuric acid. The process is exothermic and is carried out carefully in a flask fitted with a reflux condenser and containing anti-bumping granules.. When all the sodium dichromate(VI) has dissolved, the alcohol mixed with water is poured down the condenser in small portions and an exothermic reaction takes place so that no external heat needs to be applied to keep the mixture refluxing.

When all the alcohol has been added, the mixture is refluxed over gentle heat for a short time. The mixture is then distilled to obtain the crude acid.

The reaction may be written as

$$RCH_2OH + 2[O] \rightarrow RCOOH + H_2O$$

R is often used to represent an alkyl group e.g $–CH_3$, $-C_3H_7$

or

$$\mathrm{RCH_2OH} \xrightarrow[\textbf{heat}]{\mathbf{Cr_2O_7^{2-}\ /\ H^+}} \mathrm{RCOOH} + \mathrm{H_2O}$$

In terms of ion-electron half-equations

$$\mathrm{Cr_2O_7^{2-}} + 14\mathrm{H^+} + 6\mathrm{e^-} \rightarrow 2\mathrm{Cr^{3+}} + 7\mathrm{H_2O} \quad \text{reduction}$$

$$\mathrm{RCH_2OH} \rightarrow \mathrm{RCOOH} + 2\mathrm{H^+} + 2\mathrm{e^-} \quad \text{oxidation}$$

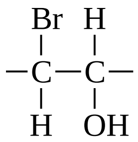
overall $\mathrm{Cr_2O_7^{2-}} + 3\mathrm{RCH_2OH} + 8\mathrm{H^+} \rightarrow 3\mathrm{RCOOH} + 7\mathrm{H_2O}$

Topic 7.1 (i)

Test for carbon-carbon double bond, >C=C<

Compounds containing this bond when shaken with aqueous bromine remove the red brown colour of bromine.

$>\mathrm{C=C}< + \mathrm{H_2O} + \mathrm{Br_2} \rightarrow$



$$-\overset{\overset{\mathrm{Br}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}}-$$

This is an easy test tube reaction for the carbon-carbon double bond.

Test for halogen in organic compounds.

In most organic compounds, the halogen atom is covalently bonded to the rest of the molecule.

The first stage is to remove the halogen to form the aqueous halide ion by hydrolysis.

To do this the compound is heated gently with dilute aqueous sodium hydroxide.

$$\mathrm{R\text{-}X} + \mathrm{NaOH(aq)} \rightarrow \mathrm{R\text{-}OH} + \mathrm{Na^+(aq)} + \mathrm{X^-(aq)}$$

The mixture is then acidified by dilute nitric acid. **This is essential to neutralise excess base which interferes with silver nitrate test.**

Aqueous silver nitrate is the added.

Halogen	***colour of precipitate with $AgNO_3(aq)$***	***Reaction of precipitate with aqueous ammonia***
chlorine	curdy white precipitate	dissolves in dilute aqueous ammonia
bromine	cream precipitate	dissolves in concentrated aqueous ammonia
iodine	primrose yellow precipitate	no reaction with aqueous ammonia

7.2 Hydrocarbons

Candidates should be able to:

(a) *understand and explain the meaning of the terms homolytic and heterolytic bond fission;*

(b) *describe in outline the general nature of petroleum, its separation into useful fractions by fractional distillation, and the cracking process;*

(c) (i) *describe the photochlorination of methane †;*

(ii) *recall the mechanism of the reaction as far as* CH_2Cl_2 *and be aware that the reaction may proceed to* $CC1_4$*;*

(d) *describe the structure of and bonding in ethene (hybridisation is not appropriate here);*

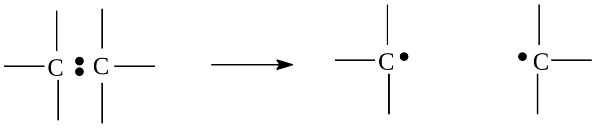
(e) *classify the addition reactions of* Br_2 *and HBr (involving heterolytic fission), with ethene and propene, and relate the orientation of the normal addition of HBr to propene to the recalled mechanism of the reaction and the relative stabilities of the possible carbocations (carbonium ions) involved;*

(f) *recall the catalytic hydrogenation (reduction) of alkenes and the preparation of ethene by elimination of HBr from bromoethane †;*

(g) *understand the nature of alkene polymerisation and show an awareness of the wide range of important polymers of alkenes and substituted alkenes.*

Homolysis or homolytic fission.

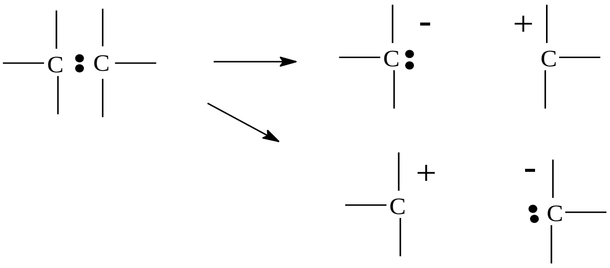
In this case a covalent bond breaks and each atom retains one of the shared pair of electrons in the covalent bond.



Each of the fragments is known as a **free radical** (or just radical). Free radicals are very reactive species.

Heterolytic fission or heterolysis

Here one of the atoms retains both of the pair of shared electrons in the covalent bond.



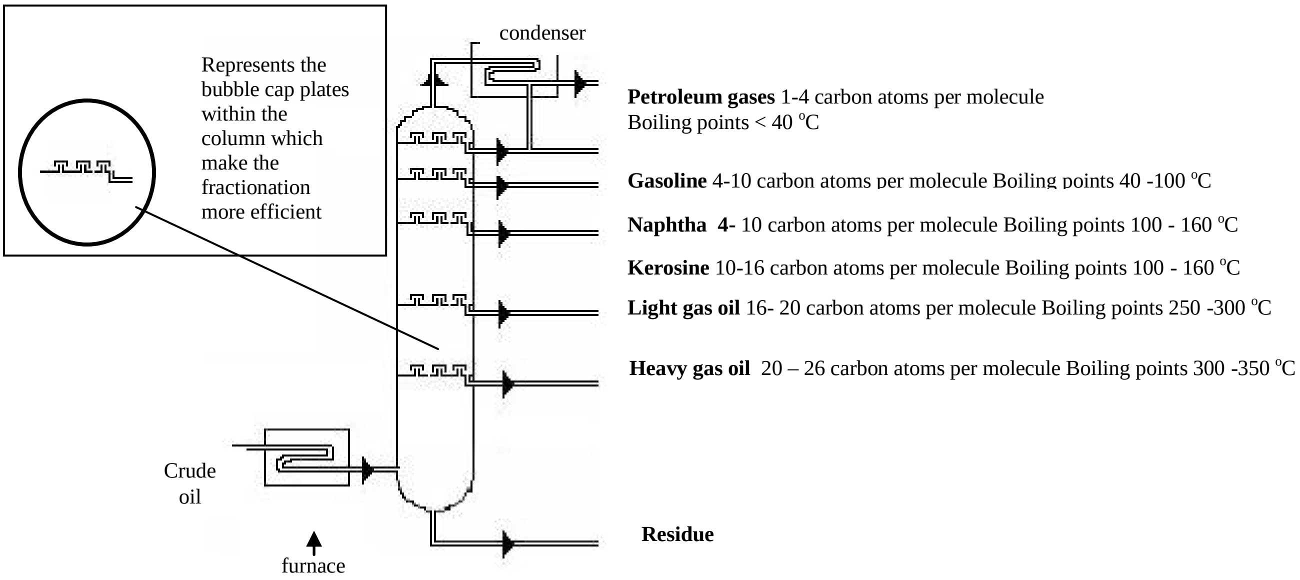
The result is the formation of ions. Many organic reactions involve ions.

Topic 7.2 (b)

Crude oil (petroleum) is a complex mixture of hydrocarbons. The first process is the primary fractional distillation to separate the hydrocarbons into simpler mixtures depending upon their boiling points.

A simplified diagram of the primary distillation of petroleum

This process is fractional distillation or fractionation. The lower the boiling point the higher the point in the fractionation column from which they are removed.



Some uses of fractions:

- Petroleum (or refinery) gases fraction is used for fuels and as feedstocks in some petrochemical processes.
- The gasoline fraction is used for petrol and some petrochemicals.
- The naphtha fraction is used as a feedstock for petrochemical manufacture.
- The kerosene fraction is used for the production of aviation fuel and some chemical processes.
- The gas oil fractions are used for diesel fuel, heating and lubricating oils.
- The residue is used for the production of bitumen, waxes and less volatile lubricating oils.

Cracking.

The hydrocarbon fractions from the primary distillation of crude oil are of limited use without further processes. The gasoline fraction on its own can only produce a fraction of the petrol required by society. It is therefore necessary to process the fractions containing less useful large molecules to produce smaller more useful molecules. This process is called cracking. In particular, cracking produces unsaturated alkene molecules such as ethene and propene which are the basis of the manufacture of many polymers.

In thermal cracking the molecules are broken down by heat and the reaction involves free radicals. Many modern plants employ catalytic cracking in which the catalyst is a fluidized bed of zeoloites. Zeolites are complex aluminosilicates and the mechanism of cracking involves an ionic mechanism.

The cracking process also results in branched chain alkanes, cycloalkanes and some aromatic compounds to form.

The conditions of he cracking plant are adjusted so that the yield of the most useful molecules is greatest. Students should be able to write an equation for an example of cracking.

e.g. $C_{14}H_{30} \rightarrow C_{10}H_{22} + 2C_2H_4$

Topic 7.2 (c)

Chlorination of alkanes

Alkanes are chlorinated in the presence of UV light.
A photon of light causes homolytic fission of the chlorine molecule.

$$Cl_2 + hf \rightarrow 2Cl^{\cdot}$$

The term 'hf' represents the energy of a photon of the radiation. The symbol 'h' is Planck's constant and 'f' is the frequency of the radiation.

The species , $Cl^{\cdot}$, is a chlorine free radical. Each chlorine atom retains one of the shared pair of electrons in the Cl-Cl bond in the chlorine molecule to become two chlorine radicals.
Free radicals are very reactive and react with a hydrocarbon such as methane in a chain reaction as follows.

$Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$ chain initiation

$Cl^{\cdot} + CH_4 \rightarrow {}^{\cdot}CH_3 + HCl$
$^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$ } chain propagation

$^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow C_2H_6$ chain termination

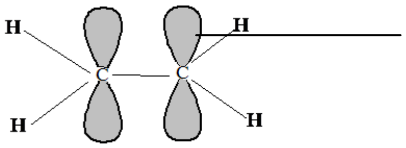
Further substitution can give CH_2Cl_2, $CHCl_3$ and CCl_4.
e.g.

$$CH_3Cl + Cl^{\cdot} \rightarrow HCl + {}^{\cdot}CH_2Cl$$
$${}^{\cdot}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\cdot}$$

The stages above make up the **reaction mechanism**. This mechanism is called ***free radical substitution*.**

Topic 7.2 (d)

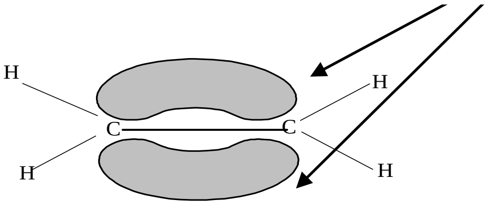
In ethene the double bond between the carbon atoms is made up a sigma bond and a pi bond and can be represented as



unused p-orbital which can overlap with the p-orbital from the other carbon

the Greek for "p" is "π" and so it is called a pi-bond.

π-orbital



The pi bond is made by the overlap of two p orbitals.

The p-bond is a region of high electron density.

Topic 7.2(e)

Electrophilic addition

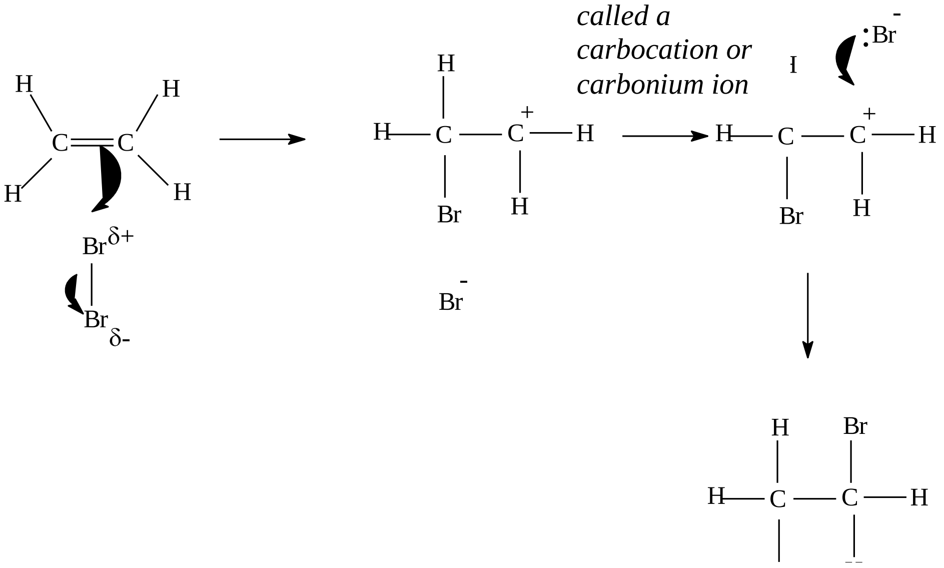
The carbon-carbon double bond adds on a molecule of chlorine or bromine.

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

ethene 1,2-dibromoethane

The reaction mechanism involves the formation of ions. The carbon-carbon double bond is a region of high electron density which can polarise a halogen molecule.

The mechanism below shows how a bromine molecule is polarised by an ethene molecule.. The curly arrows show the movement of a pair of electrons.



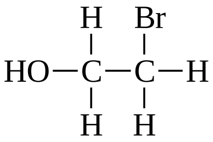
This ion is called a carbocation or carbonium ion

The resulting bromide ion is now a nucleophile which attacks the positive centre of the carbonium ion.

Product is 1,2-dibromoethane.

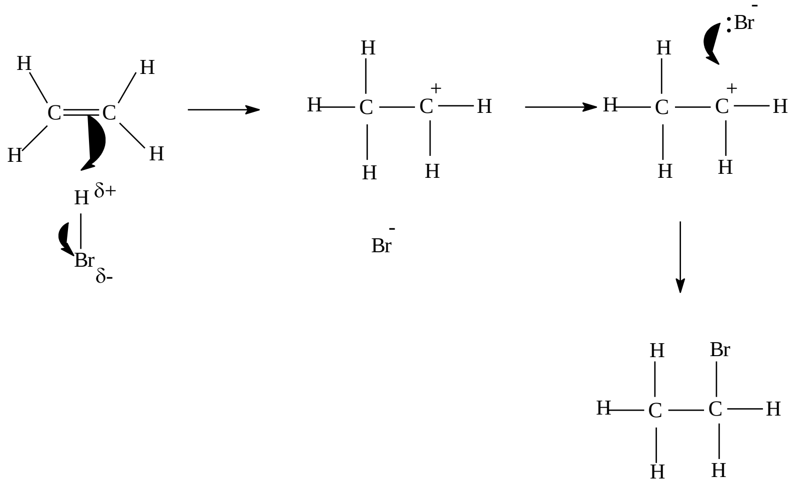
This mechanism is called ***electrophilic addition***. The initial stage is equivalent to the addition of a Br^+ ion. Br^+ is an electrophile. This reaction is the basis of a test-tube reaction to test for the presence of a carbon-carbon double bond. Bromine, aqueous bromine or bromine in an organic solvent will react with any carbon-carbon double bond and in doing so the brown colour of the bromine will be removed. See previous.

If bromination is carried out in water, the carbocation is attacked by any nucleophile and water is the one with the greatest concentration. The main product is 2-bromoethanol.



$$\begin{array}{ccccc} & & H & & Br \\ & & | & & | \\ HO & - & C & - & C - H \\ & & | & & | \\ & & H & & H \end{array}$$

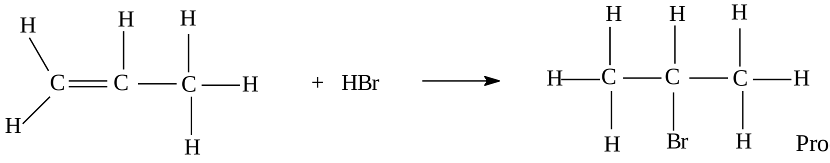
The mechanism for the addition of hydrogen bromide to ethene is similarly an **electrophilic addition**.



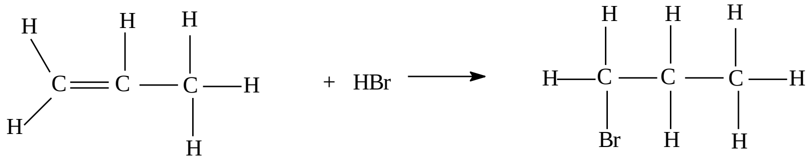
bromoethane

A different situation occurs when the alkene is not symmetrical.

If hydrogen bromide is added to propene then two reactions are possible.



Product 2-bromopropane

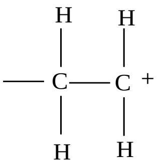


Product 1-bromopropane

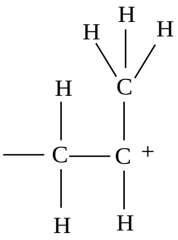
Which one of these is favoured?

The answer lies in the relative stability of the possible carbocations.

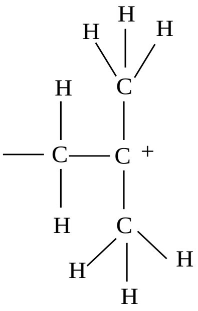
Carbocations are described in terms of the number of carbon atoms attached to the carbon atom carrying the positive charge.



Primary carbocation



Secondary carbocation

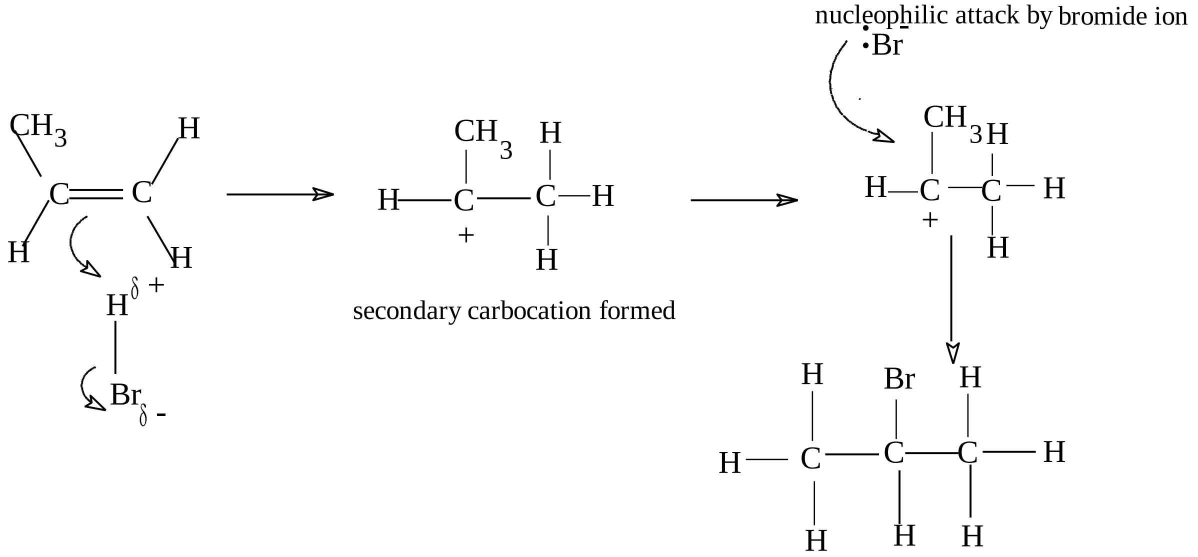


Tertiary carbocation

The order of relative stability is:

***tertiary* is more stable than *secondary* which is more stable than *primary*.**

The addition of hydrogen bromide to propene leads to 2-bromopropane being the major product since that would be formed from the secondary carbocation.



Topic 7.2 (f)

Catalytic hydrogenation.

In the presence of a catalyst, alkenes add on molecular hydrogen.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

Suitable catalysts are platinum, palladium and nickel. Platinum and palladium are effective at room temperature. Nickel is usually preferred as being the cheapest catalyst. Nickel on a support usually requires elevated temperatures of up to 300 °C. A form of very fine nickel particles called Raney nickel (after its inventor M. Raney) is commonly used and is effective at room temperature or a low temperature and at atmospheric pressure.

Unsaturated oils and fats are hydrogenated in the presence of nickel in process known as *hardening*.

Formation of ethene by an elimination reaction

Bromoethane eliminates HBr when the vapour is passed over heated sodalime and ethene is formed..

$$CH_3\text{-}CH_2Br + NaOH \rightarrow CH_2{=}CH_2 + NaBr + H_2O$$

Topic 7.2 (g)

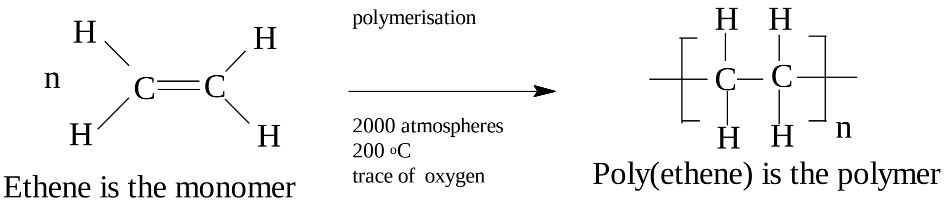
Polymerisation of alkenes and substituted alkenes.

Polymerisation is the combination of a very large number of molecules called monomers to form a large molecule called the polymer. Ethene and other alkenes form a large number of addition polymers in which no there molecules are eliminated in the polymerisation process.

Poly(ethene) or Polythene.

Poly(ethene) was discovered accidentally in equipment used for high pressure experiments with ethene in 1932.

When ethene is subjected to a pressure of about 2000 atmospheres and a temperature of around 200 °C and in the presence of a trace of oxygen, poly(ethene) is formed.



This type of polymerisation is **addition polymerisation** no small molecules are eliminated. The production of polyamides and polyesters belong to condensation polymerisation.

This type of poly(ethene) is low density poly(ethene), LDPE.

It is formed by a free radical mechanism.

The trace of oxygen reacts with some of the ethene to form free radicals. This the chain initiation process resulting in a species with an unpaired electron (say $Sp^{\cdot}$**)**.

Then follows chain propagation.

$$Sp^{\cdot} + CH_2 – CH_2 \rightarrow SCH_2 – CH_2^{\cdot}$$

$$SpCH_2 – CH_2^{\cdot} + CH_2 – CH_2 \rightarrow SpCH_2 – CH_2\text{-}CH_2 – CH_2^{\cdot}$$

Followed by more chain lengthening stages.

Chain termination ends with two radicals reacting.

The product consists of chains containing thousands of ethene molecules linked together.

Uses of low density poly(ethene)

It can be stretched into fine, tough, films and made into can be stretched into fine, tough, films.

High density poly(ethene)

In 1953 Karl Ziegler discovered that poly(ethene) with a more crystalline structure could be made by using metal catalysts. Similar work was done with propene by Giulio Natta.

In 1963 they were jointly awarded the Nobel Prize for Chemistry.

These catalysts are now known as Ziegler-Natta catalysts and contain compounds such as titanium(III) chloride, titanium(IV) chloride and aluminium triethyl.

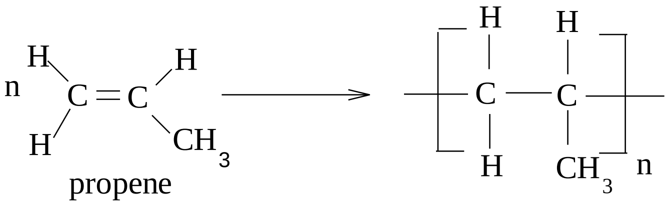
In this reaction the polymerisation is carried out in a solvent at a temperature of 50-75 °C and only a slight pressure and a colloidal suspension of the Ziegler-Natta catalyst.

The difference between the low density form and the high density form is that the low density polymer tends to have side chains which keep the chains apart. The high density form has very few side chains and as a result has significant order in the packing of the hydrocarbon chains.

This makes the polymer highly crystalline and makes it suitable for uses above 100 °C.
It is used for containers, water pipes, wire and cable insulation.

Polymers of substituted alkenes

The simplest such polymer is poly(propene).

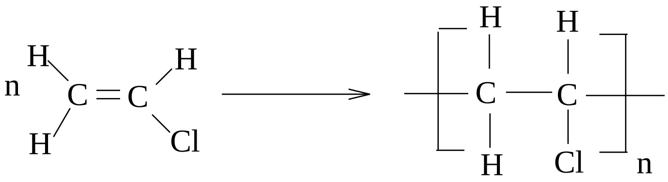


propene Poly(propene)

Poly(propene) is used for food and other containers such as mixing bowls and buckets. Its relatively high temperature resistance allows it to be used in hospital equipment which can be sterilised and in some building components. It can be extruded to form fibres which can be used in ropes and as carpet fibres.

Poly(chloroethene) or PVC

This is most useful polymer formed by free radical addition polymerisation.
The monomer is chloroethene or vinyl chloride and the polymers is poly(chloroethene) or polyvinylchloride.

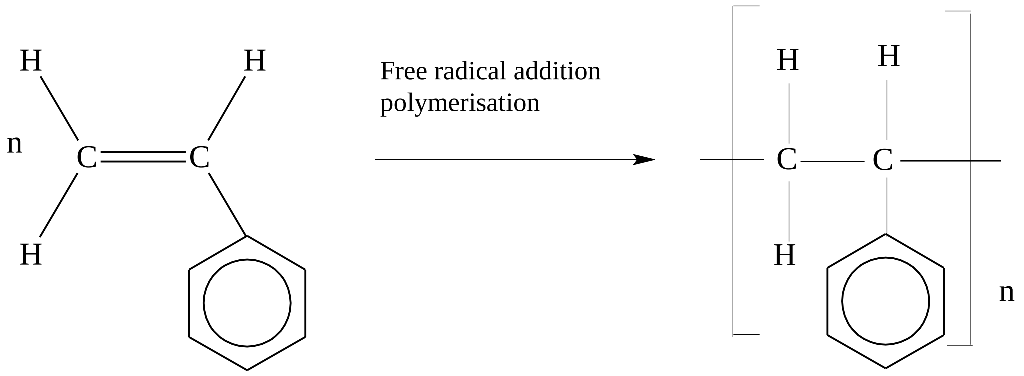


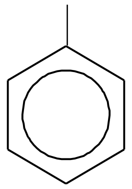
chloroethene poly(chloroethene) or PVC

The manufacture is exclusively a free radical process in which the initiator is an organic peroxide.
The reaction is carries out at a temperature between 40 and 80 °C, the precise temperature can be controlled to give a polymer of the desired molar mass.

The polymer is a hard rigid solid but its properties are modified by the addition of other chemicals called plasticizers which allow it to become soft enough for the manufacture of films, artificial leather etc.
Uses include cable insulation, pipes, fittings, packaging, flooring, artificial leather, moulded articles etc.

Poly(phenylethene) or polystyrene





is the phenyl group C_6H_5

The monomer phenylethene or styrene is volatile colourless liquid. The resulting polymer is a hard common everyday plastic. Polystyrene is used in toys, and the housings of electrical goods such as computers and kitchen appliances. Many of the plastic components of motor cars use polystyrene. The other familiar form is expanded polystyrene foam. This made by blowing gas through the molten material and is a familiar packing material.

7.3 Halogenoalkanes

Candidates should be able to:

(a) *describe the formation of a chloroalkane by direct chlorination of alkanes;*

(b) *describe the substitution reaction between* OH^- *and 1-chlorobutane and explain this on the basis of the recalled mechanism.,*

(d) *show an awareness of the wide use of halogenoalkanes as solvents, the toxicity of some of them, the use of CFCs as refrigerants and in aerosols; and their use in anaesthetics as well as the adverse environmental effects of CFCs;*

(e) *understand the adverse environmental effects of CFCs and explain these in terms of the relative bond strengths of the C - H, C - F, and C - Cl bonds involved;*

(f) *show an awareness of the use of organohalogen compounds as pesticides and polymers and assess their environmental impact.*

Topic 7.3

(a) Students should know the direct chlorination of alkanes to form chloroalkanes.

$$Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$$

The reaction takes place in uv light and further substitution takes place.

Details of the free radical mechanism of this reaction have already been discussed.

Larger alkanes also undergo this reaction.

e.g. $$C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$$

(b) The nucleophilic substitution of chloroalkanes.

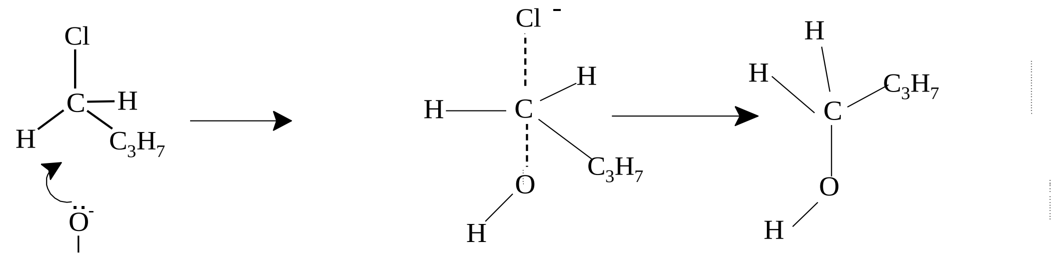
When 1-chlorobutane is warmed with aqueous sodium hydroxide butan-1-ol is formed.

$$C_4H_9Cl + NaOH \rightarrow C_4H_9OH + NaCl$$

The mechanism for the reaction is called nucleophilic substitution.

The nucleophile is OH^- from the alkali.

Cl^-



Nucleophilic attack by the hydroxide ion

Formation of a transition state in which a partial bond is forming between the carbon and the oxygen atom and the carbon-chlorine bond breaking.

Formation of product with the chloride ion leaving

Topic 7.3 (d) and (e)

Many halogenoalkanes are excellent solvents and are used industrially as degreasing agents.

Most of them are volatile and health and safety authorities are very concerned with pollution by VOCs (Volatile organic compounds).

The cheapest halogen is chlorine and chloroalkanes are used extensively as solvents.

The more common ones are tetrachloroethene, C_2Cl_4; chloromethane, CH_3Cl; dichloromethane, CCl_2H_2;1,1,2-trichloroethene, $CCl_2{=}CHCl$; tetrachloromethane, CCl_4; 1,1,1, trichloromethane, CCl_3CH_3; Exposure to the vapours of these chemicals can be harmful to the nervous system and to internal organs such as liver and kidneys. Carbon tetrachloride (tetrachloromethane, CCl_4) was once used in fire extinguishers but not only is its vapour very toxic but in use on a fire can produce the toxic gas phosgene. For many years chlorofluorohydrocarbons were used as refrigerants and aerosol propellants.

These have been banned because of their effect upon the ozone layer.

In the upper atmosphere stable CFC molecules encounter uv radiation which ruptures the carbon chlorine bond to form a chlorine radical. This then reacts with an ozone molecule

e.g. $CF_2Cl_2 + hf \rightarrow Cl + CF_2Cl$

then one reaction which can occur with ozone is

$Cl + O_3 \rightarrow ClO + O_2$

O_2 | 2O this reaction is occurring all the time under the influence of uv light

$ClO + O \rightarrow O_2 + Cl$ the chlorine radical is regenerated setting up a chain reaction.

Visit http://www.bom.gov.au/lam/Students_Teachers/ozanim/ozoanim.shtml for an animated explanation.

CFCs are gradually being replaced by other molecules which are said to be safer.

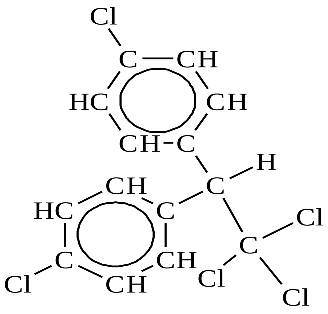
The carbon-chlorine bond is much weaker than the carbon-fluorine bond. (338 kJ mol^{-1} compared with 484 kJ mol^{-1}).

Suggested alternatives are HCFCs and HFCs.

HCFCs are hydrochlorofluorocarbons. They all contain at least one hydrogen atom and this causes them to be much less stable in the lower atmosphere than CFCs. Fewer of the HCFC molecules reach the stratosphere where they can deplete the ozone layer. The carbon –hydrogen bond strength is 412 kJ mol^{-1}.
One adverse property is that HCFCs are potent greenhouse gases.
HFCs are hydrofluorocarbons and contain no chlorine and as the carbon-fluorine bonder is strong they are unlikely to form radicals which can destroy the ozone layer.

Topic 7.3 (f)

Organ-chlorine compounds have been used as pesticides. The best know is DDT the use of which has been restricted because it persists in the environment and being fat soluble builds up in the food chain.



DDT

Creatures at the end of the food chain suffered because of its use.

One example was the peregrine falcon which failed to hatch its eggs due to extreme thinness of the egg shell as a result of accumulation of DDT.

Concern has also been shown concerning polymers containing chlorine such as poly(chloroethene) or PVC.

The monomer chloroethene is extremely toxic.

Combustion of PVC may lead to high concentrations of carbon monoxide, carbon dioxide and hydrogen chloride. The hydrogen chloride produces a highly acidic environment. It has also been established that under some circumstances highly toxic dioxins are formed.

Visit http://archive.greenpeace.org/toxics/html/content/pvc1.html

7.4 Alcohols

Candidates should be able to:

(a) *describe the physical properties of the lower alcohols, solubility in water and relatively low volatility, and relate this to the existence of hydrogen bonding;*

(b) *recall a method for the industrial preparation of ethanol from ethene;*

(c) *recall the dehydration reaction (elimination) of primary alcohols ;*

(d) *show awareness of the importance of ethanol-containing drinks in society, their ethanol content, breathalysers, and the effects of ethanol excess.*

(a) Alcohols

The first few members of the aliphatic monohydric alcohols are as shown in the table below.

formula	CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH	$C_5H_{11}OH$
name	methanol	ethanol	propan-1-ol	butan-1-ol	pentan-1-ol
bp./ °C	64.7	78.3	117.7	97.2	138
solubility in water	very soluble	very soluble	very soluble	soluble	sparingly soluble

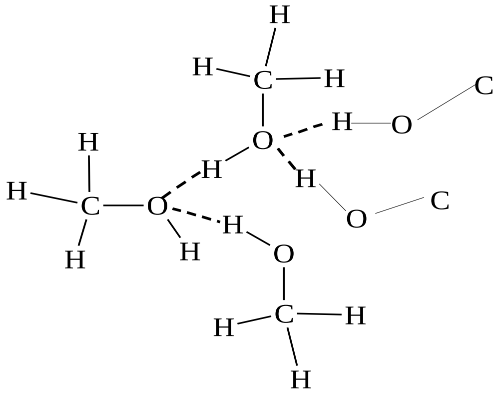
formula	$CH_3CH(OH)CH_3$	$CH_3CH_2CH(OH)CH_3$
name	propan-2-ol	butan-2-ol
bp./ °C	82.4	99.5
solubility in water	very soluble	soluble

The solubility tends to decrease as the molar mass increases. This is due to the increasing effect of the hydrocarbon chain over the effect of the –OH group which can hydrogen bond with water molecules. Pentan1-ol is only sparingly soluble and higher alcohols are immiscible with water.

The boiling points of the alcohols are much higher than would be expected from their molar masses. The boiling point of ethene (M_r = 30) is -88.6 °C whereas the boiling point of methanol (M_r = 32) is 64.7 °C.

The explanation is that the –OH group hydrogen bonds with the hydroxy group of neighbouring molecules thereby increasing the intermolecular forces significantly.

The diagram aims to show how some of the hydrogen bonds form in liquid methanol.



(b) Industrial manufacture of ethanol from ethene.

Steam and ethene are passed over a catalyst of phosphoric acid

$$CH_2{=}CH_2(g) + H_2O(g) \quad | \quad CH_3CH_2OH(g)$$

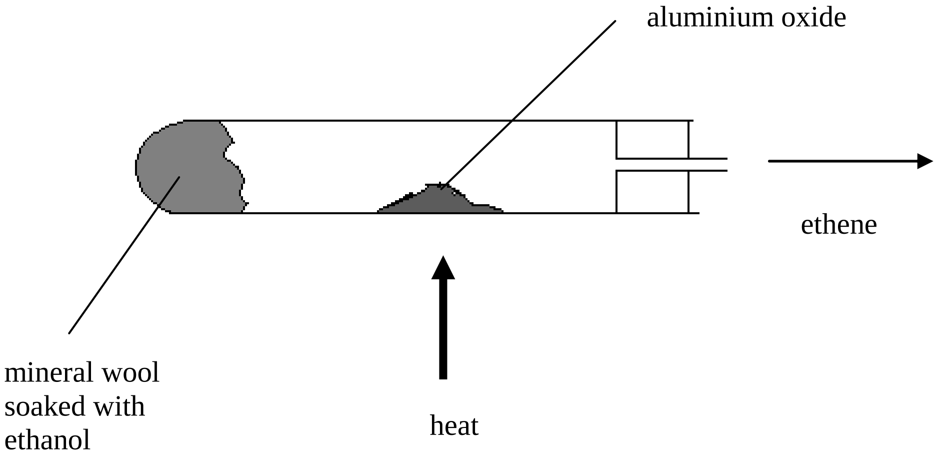
A temperature of 300°C, a pressure of 60-70 atmospheres, and a steam:ethene ratio of 0.6:1 are used.
For efficient conversion, the steam and ethene are recycled as there is only about 5% conversion per pass.
Note the theoretical atom economy is 100%.

(c) The dehydration of alcohols.

Many alcohols may be dehydrated to form an alkene.

e.g. $CH_3CH_2OH(g) \rightarrow H_2O(g) + CH_2{=}CH_2(g)$

This reaction can be performed in the lab by passing ethanol vapour over heated aluminium oxide.



Alternately the alcohol may be heated with concentrated sulfuric acid (in excess) at about 170 ^oC

$$\underset{\text{propan-1-ol}}{CH_3CH_2CH_2OH} \xrightarrow{\text{concentrated sulfuric acid}} \underset{\text{propene}}{CH_3CH{=}CH_2} + H_2O$$

Topic 7.4 (d)

For some people ethanol can become an addictive drug leading to chronic alcoholism. Candidates must understand the role of ethanol as a drug in society. Ethanol-containing drinks are socially acceptable in many cultures although banned in other countries such as the Moslem countries in the Middle East. For most people a moderate consumption of ethanol is part of their social life.

The ethanol content of alcoholic drinks varies according to the type of drink.

Drink	**Approximate % of ethanol**
Beers	3 - 5
Wines	8-13
Fortified wines e.g. sherry	15 -17
Spirits e.g. whisky	40

Candidates should know that a regular excess of ethanol may have a permanent damaging effect upon the body although there is some evidence that small regular amounts of alcohol (especially red wine) may have a beneficial effect upon health.

Ethanol slows down speed of reaction and the dangers of drinking and driving are very well known. In some countries it is an offence to have any alcohol in the blood stream when in charge of a motor vehicle. In the UK the present legal limit is 80 mg of ethanol per 100 cm^3 of blood but many people would like to see the limit lowered or even reduced to zero.

The introduction of the breathalyser in 1967 made it easy for the police to make a judgement as to whether a driver was over the limit. The original breathalyser used the fact that acidified dichromate(VI) ions oxidise ethanol and a colour change occurs in the instrument. Later models are more sophisticated. Police officers at the roadside administer a screening breath test using a digital breathalyser. This uses a "traffic light" system under which green indicates no alcohol present, amber some alcohol but below the legal limit, and red alcohol possibly above the legal limit.

If the reading is red, the person is arrested on suspicion of drink-driving and required to take a further test at a police station. At the police station, the person is required to provide two breath samples for the Intoximeter equipment which is accurate and is used to provide blood alcohol concentration evidence in court. The reading that is used is the *lower* of the two samples.

TOPIC 8 Analytical Techniques

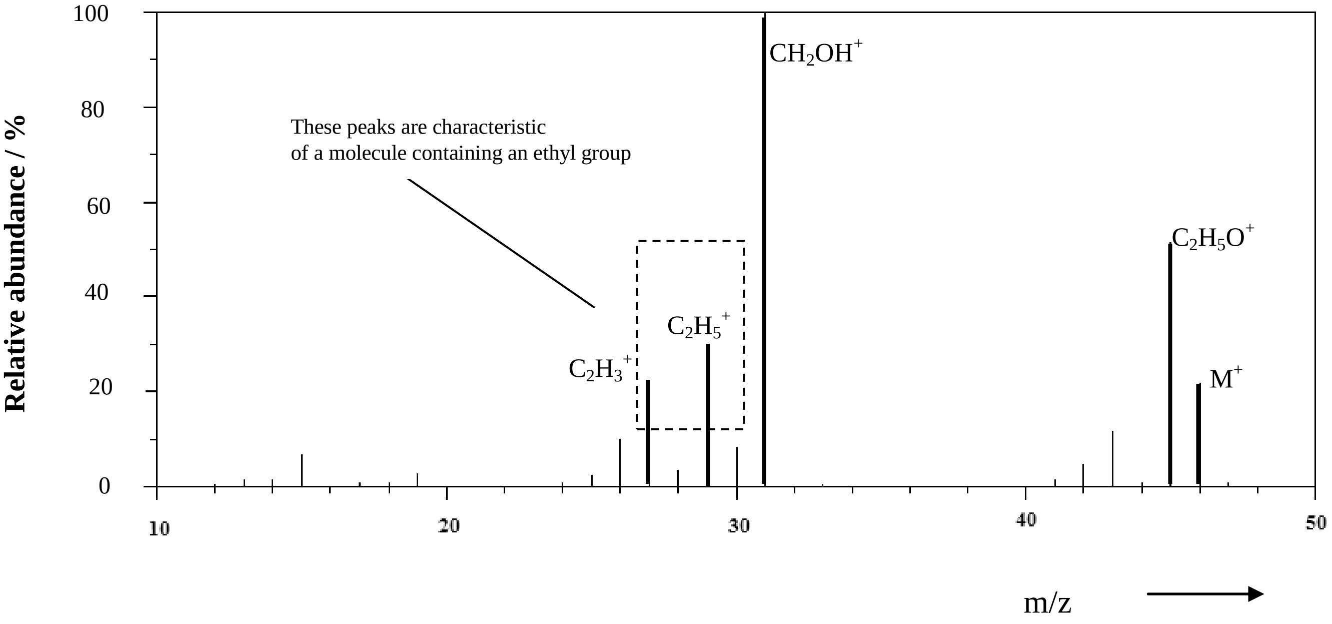
Candidates should be able to:

(a) *use* ***given*** *mass spec data in the elucidation of structure;*

(b) *use given characteristic i.r. vibrational frequencies (expressed in cm^{-1}), to identify simple groupings in organic molecules.*

(a) When an organic compound is introduced into a mass spectrometer, not only does the molecule become ionised but the molecule also breaks up giving rise to a variety of fragments all forming positive ions. From the fragmentation pattern it is sometimes possible to gather information about the structure of the molecule.

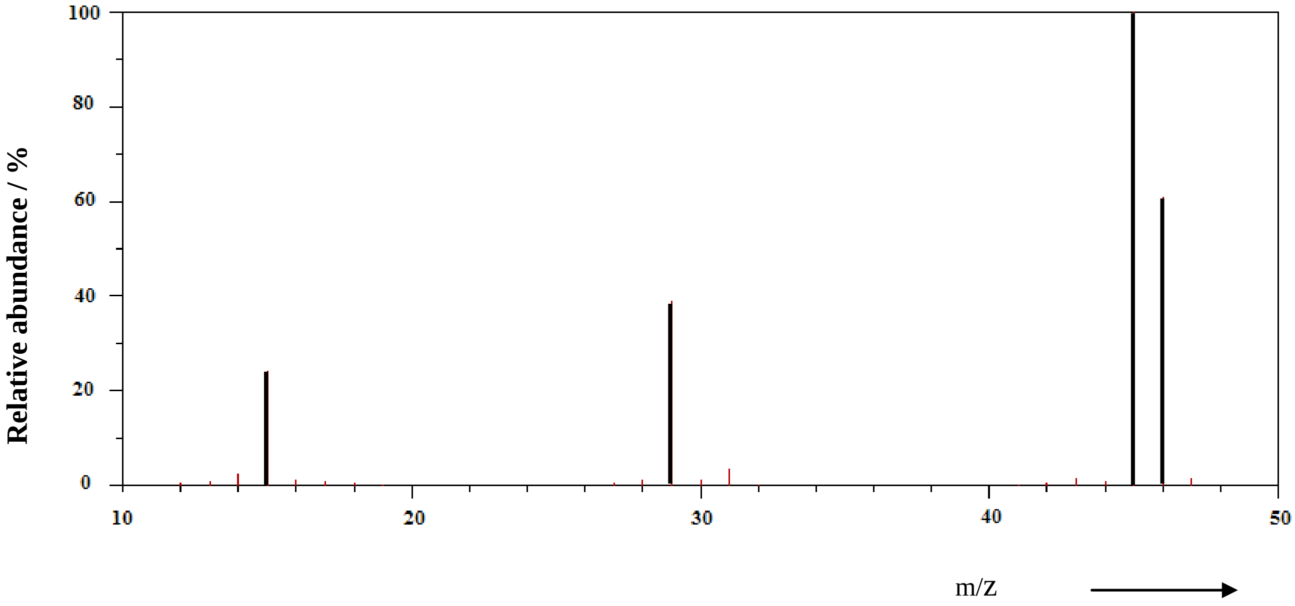
Look at the mass spectrum of ethanol below. The main peaks are emphasise



There is the expected molecular ion peak at 46 corresponding to $C_2H_5OH^+$: the other peaks are due to fragmentations in the mass spectrometer and give evidence as to the structure of the parent molecule. The pattern often depends on the stabilities of the ions produced. The ion m/z equals 31 is stabilised by the presence of the oxygen atom. Some fragments are radicals which are not recorded by the mass spectrometer.

Students should be able to use mass spectra to suggest fragmentations and elucidate structures. Note that in compounds containing chlorine or bromine peaks will double up because of the naturally occurring isotopes ^{35}Cl and ^{37}Cl and ^{79}Br and ^{81}Br.

Mass spectrum of methoxymethane



If we look at the mass spectrum of methoxymethane, CH_3OCH_3, which is isomeric with ethanol, a completely different fragmentation pattern is observed.

Suggest the ions which produce the peaks emphasised.

(b) Infrared Spectroscope

Bonds in molecules vibrate and bend and the frequencies of these movements are within the infrared region of the electromagnetic spectrum.

When organic molecules are exposed to infrared radiation in an infrared spectrometer the bonds absorb radiation of characteristic frequencies.

In the examination candidates will be given infrared data in the form.

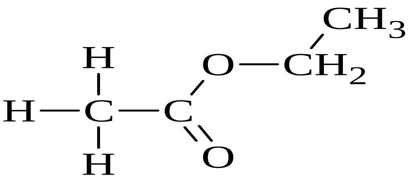
Infrared Spectroscopy characteristic absorption values

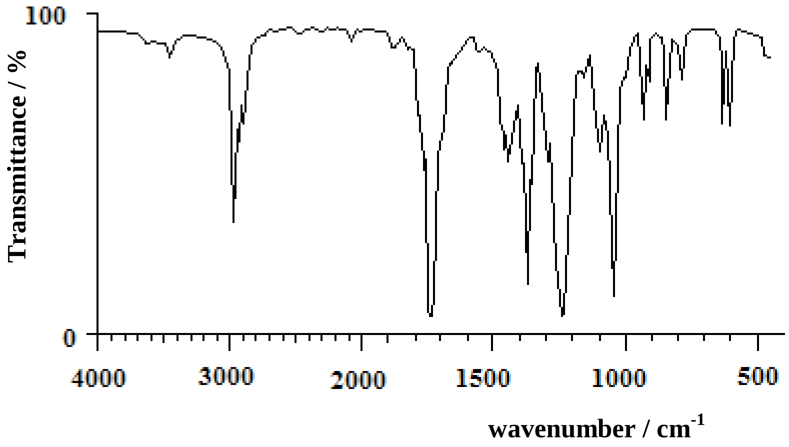
Bond	**Wavenumber/cm^{-1}**
C – Br	500 to 600
C – Cl	650 to 800
C – O	1000 to 1300
C = C	1620 to 1670
C = O	1650 to 1750
C ≡ N	2100 to 2250
C – H	2800 to 3100
O – H	2500 to 3550
N – H	3300 to 3500

Wavenumber is the reciprocal of the wavelength in cm and like frequency is directly proportional to the energy of the radiation.

The IR spectrum of ethyl ethanoate is shown below

Ethyl ethanoate is an ester with the structure





The infrared spectrum of ethyl ethanoate

The trough at 1740 cm^{-1} is the stretching frequency of >C=O group (see table 1650 -1750) and at 1240 $cm^{-1}$is the absorption due to >C-O (see table 1000 -1300). This is the >C-O stretching frequency and is usually very prominent in esters.

The trough around 3000 cm^{-1} could be due to C-H or O-H, in fact in this case it is C-H and in this compound the O-H absorption is missing. (Students would not be expected to know this).

The specification emphasises that students are required to identify **simple** groupings in organic molecules.