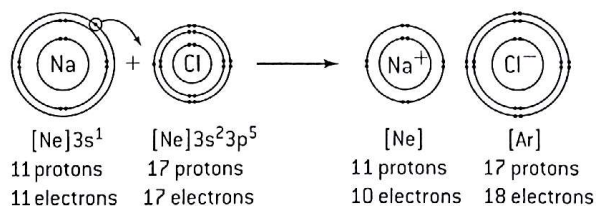


## Ionic bonding

### IONIC BOND

When atoms combine they do so by trying to achieve a noble gas configuration. Ionic compounds are formed when electrons are transferred from one atom to another to form ions with complete outer shells of electrons. In an ionic compound the positive and negative ions are attracted to each other by strong electrostatic forces, and build up into a strong lattice. Ionic compounds have high melting points as considerable energy is required to overcome these forces of attraction.



The classic example of an ionic compound is sodium chloride  $\text{Na}^+\text{Cl}^-$ , formed when sodium metal burns in chlorine. Chlorine is a covalent molecule, so each atom already has a noble gas configuration. However, the energy given out when the ionic lattice is formed is sufficient to break the bond in the chlorine molecule to give atoms of chlorine. Each sodium atom then transfers one electron to a chlorine atom to form the ions.

The charge carried by an ion depends on the number of electrons the atom needed to lose or gain to achieve a full outer shell.

Cations			Anions		
Group 1	Group 2	Group 3	Group 15	Group 16	Group 17
+1	+2	+3	-3	-2	-1
$\text{Li}^+$ $\text{Na}^+$ $\text{K}^+$	$\text{Mg}^{2+}$ $\text{Ca}^{2+}$	$\text{Al}^{3+}$	$\text{N}^{3-}$ $\text{P}^{3-}$	$\text{O}^{2-}$ $\text{S}^{2-}$	$\text{F}^-$ $\text{Cl}^-$ $\text{Br}^-$

Thus, in magnesium chloride, two chlorine atoms each gain one electron from a magnesium atom to form  $\text{Mg}^{2+}\text{Cl}_2^-$ . In magnesium oxide two electrons are transferred from magnesium to oxygen to give  $\text{Mg}^{2+}\text{O}^{2-}$ . Transition metals can form more than one ion. For example, iron can form  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and copper can form  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ .

### FORMULAS OF IONIC COMPOUNDS

It is easy to obtain the correct formula as the overall charge of the compound must be zero.

lithium fluoride $\text{Li}^+\text{F}^-$	magnesium chloride $\text{Mg}^{2+}\text{Cl}_2^-$	aluminium bromide $\text{Al}^{3+}\text{Br}_3^-$
sodium oxide $\text{Na}^+_2\text{O}^{2-}$	calcium sulfide $\text{Ca}^{2+}\text{S}^{2-}$	iron(III) oxide $\text{Fe}^{3+}_2\text{O}^{2-}_3$
potassium nitride $\text{K}^+_3\text{N}^{3-}$	calcium phosphide $\text{Ca}^{2+}_3\text{P}^{3-}_2$	iron(II) oxide $\text{Fe}^{2+}\text{O}^{2-}$

Note: the formulas above have been written to show the charges carried by the ions. Unless asked specifically to do this it is common practice to omit the charges and simply write  $\text{LiF}$ ,  $\text{MgCl}_2$ , etc.

### IONS CONTAINING MORE THAN ONE ELEMENT (POLYATOMIC IONS)

In ions formed from more than one element the charge is often spread (delocalized) over the whole ion. An example of a positive ion is the ammonium ion  $\text{NH}_4^+$ , in which all four N-H bonds are identical. Negative ions are sometimes known as acid radicals as they are formed when an acid loses one or more  $\text{H}^+$  ions.

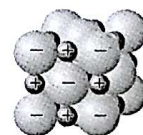
hydroxide $\text{OH}^-$		carbonate $\text{CO}_3^{2-}$	{ from carbonic acid, $\text{H}_2\text{CO}_3$ }
nitrate $\text{NO}_3^-$	(from nitric acid, $\text{HNO}_3$ )	hydrogencarbonate $\text{HCO}_3^-$	
sulfate $\text{SO}_4^{2-}$	{ from sulfuric acid, $\text{H}_2\text{SO}_4$ }	ethanoate $\text{CH}_3\text{COO}^-$	(from ethanoic acid, $\text{CH}_3\text{COOH}$ )
hydrogensulfate $\text{HSO}_4^-$		phosphate $\text{PO}_4^{3-}$	(from phosphoric acid $\text{H}_3\text{PO}_4$ )

The formulas of the ionic compounds are obtained in exactly the same way. Note: brackets are used to show that the subscript covers all the elements in the ion e.g. sodium nitrate,  $\text{NaNO}_3$ , ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$  and calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ .

### IONIC BOND AND PROPERTIES OF IONIC COMPOUNDS

Ionic compounds are formed between metals on the left of the periodic table and non-metals on the right of the periodic table; that is, between elements in groups 1, 2, and 3 with a low electronegativity (electropositive elements) and elements with a high electronegativity in groups 15, 16, and 17. Generally the difference between the electronegativity values needs to be greater than about 1.8 for ionic bonding to occur.

Ions in solid ionic compounds are held in a crystal lattice. The ionic bond is the sum of all the electrostatic attractions (and repulsions) within the lattice. A large amount of energy is required to break the lattice so ionic compounds tend to have high melting points. Many are soluble in water as the hydration energy of the ions provides the energy to overcome the lattice enthalpy. Solid ionic compounds cannot conduct electricity as the ions are held in fixed positions. When molten the ions are free to move and conduct electricity as they are chemically decomposed at the respective electrodes.



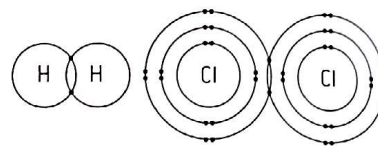
NaCl

Sodium chloride (melting point  $801^\circ\text{C}$ )  
Ions held strongly in ionic lattice

# Covalent bonding

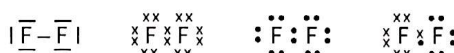
## SINGLE COVALENT BONDS

Covalent bonding involves the sharing of one or more pairs of electrons so that each atom in the molecule achieves a noble gas configuration. The simplest covalent molecule is hydrogen. Each hydrogen atom has one electron in its outer shell. The two electrons are shared and attracted electrostatically by both positive nuclei resulting in a directional bond between the two atoms to form a molecule. When one pair of electrons is shared the resulting bond is known as a single covalent bond. Another example of a diatomic molecule with a single covalent bond is chlorine,  $\text{Cl}_2$ .



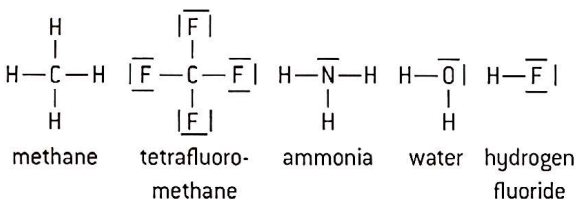
## LEWIS STRUCTURES

In the Lewis structure (also known as electron dot structure) all the valence electrons are shown. There are various different methods of depicting the electrons. The simplest method involves using a line to represent one pair of electrons. It is also acceptable to represent single electrons by dots, crosses or a combination of the two. The four methods below are all correct ways of showing the Lewis structure of fluorine.



Sometimes just the shared pairs of electrons are shown, e.g.  $\text{F}-\text{F}$ . This gives information about the bonding in the molecule, but it is not the Lewis structure as it does not show all the valence electrons.

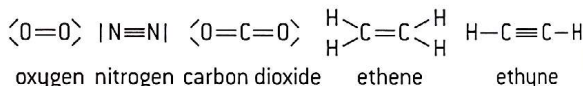
## SINGLE COVALENT BONDS



The carbon atom (electron configuration  $1s^2 2s^2 2p^2$ ) has four electrons in its outer shell and requires a share in four more electrons. It forms four single bonds with elements that only require a share in one more electron, such as hydrogen or chlorine. Nitrogen ( $1s^2 2s^2 2p^3$ ) forms three single bonds with hydrogen in ammonia leaving one non-bonded pair of electrons (also known as a lone pair). In water there are two non-bonded pairs and in hydrogen fluoride three non-bonded pairs.

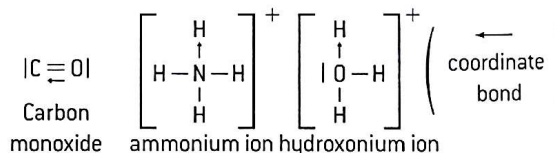
## MULTIPLE COVALENT BONDS

In some compounds atoms can share more than one pair of electrons to achieve an noble gas configuration.

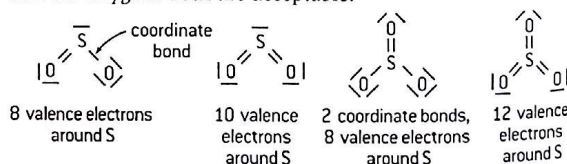


## COORDINATE (DATIVE) BONDS

The electrons in the shared pair may originate from the same atom. This is known as a coordinate covalent bond.



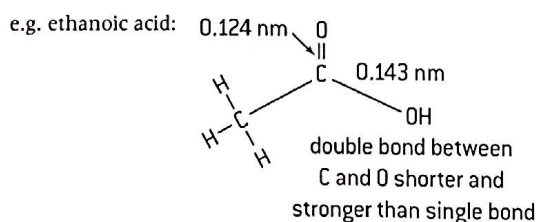
Sulfur dioxide and sulfur trioxide are both sometimes shown as having a coordinate bond between sulfur and oxygen or they are shown as having double bonds between the sulfur and the oxygen. Both are acceptable.



## BOND LENGTH AND BOND STRENGTH

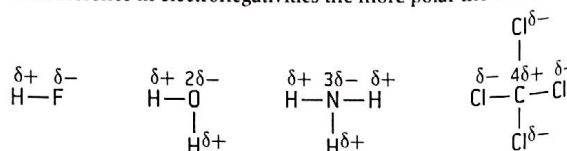
The strength of attraction that the two nuclei have for the shared electrons affects both the length and strength of the bond. Although there is considerable variation in the bond lengths and strengths of single bonds in different compounds, double bonds are generally much stronger and shorter than single bonds. The strongest covalent bonds are shown by triple bonds.

		Length / nm	Strength / $\text{kJ mol}^{-1}$
Single bonds	Cl-Cl	0.199	242
	C-C	0.154	346
Double bonds	C=C	0.134	614
	O=O	0.121	498
Triple bonds	C $\equiv$ C	0.120	839
	N $\equiv$ N	0.110	945



## BOND POLARITY

In diatomic molecules containing the same element (e.g.  $\text{H}_2$  or  $\text{Cl}_2$ ) the electron pair will be shared equally, as both atoms exert an identical attraction. However, when the atoms are different the more electronegative atom exerts a greater attraction for the electron pair. One end of the molecule will thus be more electron rich than the other end, resulting in a polar bond. This relatively small difference in charge is represented by  $\delta^+$  and  $\delta^-$ . The bigger the difference in electronegativities the more polar the bond.





# Shapes of simple molecules and ions

## VSEPR THEORY

The shapes of simple molecules and ions can be determined by using the **valence shell electron pair repulsion (VSEPR)** theory. This states that pairs of electrons arrange themselves around the central atom so that they are as far apart from each other as possible. There will be greater repulsion between non-bonded pairs of electrons than between bonded pairs. Since all the electrons in a multiple bond must lie in the same direction, double and triple bonds count as one pair of electrons. Strictly speaking the theory refers to electron domains, but for most molecules this equates to pairs of electrons.

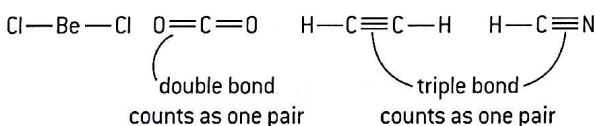
This results in five basic shapes depending on the number of pairs. For 5 and 6 electron domains the octet needs to be expanded and this can only happen if there are readily available d orbitals present that can also be utilized. For Standard Level only 2, 3 and 4 electron domains need to be considered.

No. of electron domains	Shape	Name of shape	Bond angle(s)
2		linear	180°
3		trigonal planar	120°
4		tetrahedral	109.5°
5		trigonal bipyramidal	90°, 120°, 180°
6		octahedral	90°, 180°

## WORKING OUT THE ACTUAL SHAPE

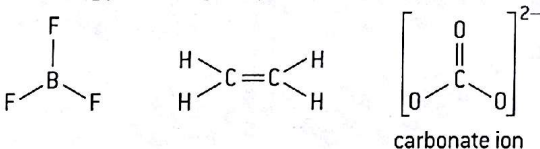
To work out the actual shape of a molecule calculate the number of pairs of electrons around the *central* atom, then work out how many are bonding pairs and how many are non-bonding pairs. (For ions, the number of electrons that equate to the charge on the ion must also be included when calculating the total number of electrons.)

### 2 ELECTRON DOMAINS



### 3 ELECTRON DOMAINS

3 bonding pairs – trigonal planar

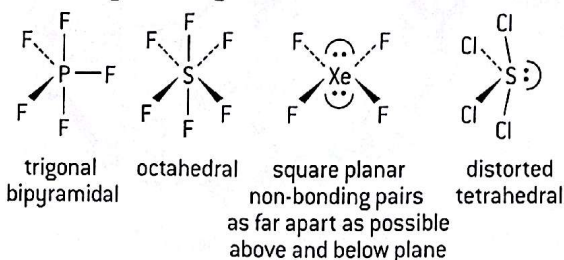


2 bonding pairs, 1 non-bonded pair – bent or V-shaped



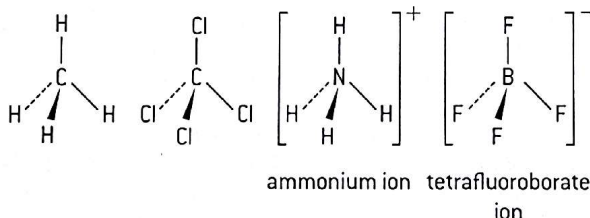
### 5 AND 6 ELECTRON DOMAINS

5 and 6 negative charge centres

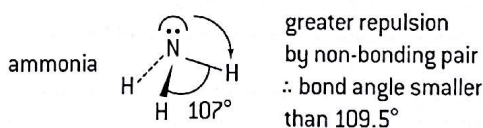


### 4 ELECTRON DOMAINS

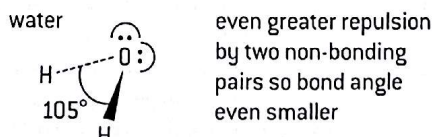
4 bonding pairs – tetrahedral



3 bonding pairs, 1 non-bonding pair – trigonal pyramidal



2 bonding pairs, 2 non-bonding pairs – bent or V-shaped



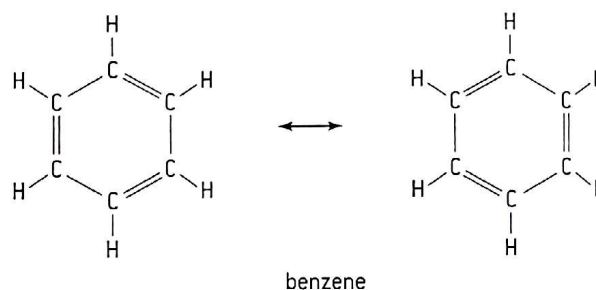
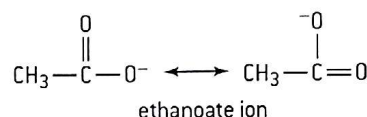
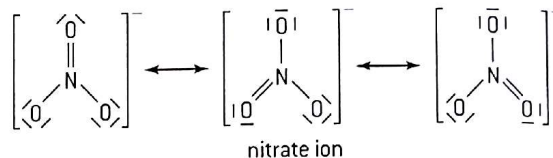
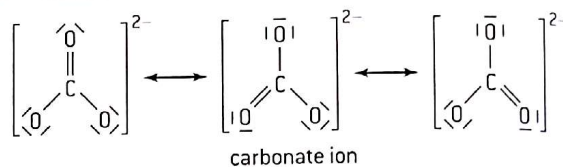
# Resonance hybrids and allotropes of carbon

## RESONANCE STRUCTURES

When writing the Lewis structures for some molecules it is possible to write more than one correct structure. For example, ozone can be written:



These two structures are known as resonance hybrids. They are extreme forms of the true structure, which lies somewhere between the two. Evidence that this is true comes from bond lengths, as the bond lengths between the oxygen atoms in ozone are both the same and are intermediate between an O=O double bond and an O-O single bond. Resonance structures are usually shown with a double headed arrow between them. Other common compounds which can be written using resonance structures are shown here.

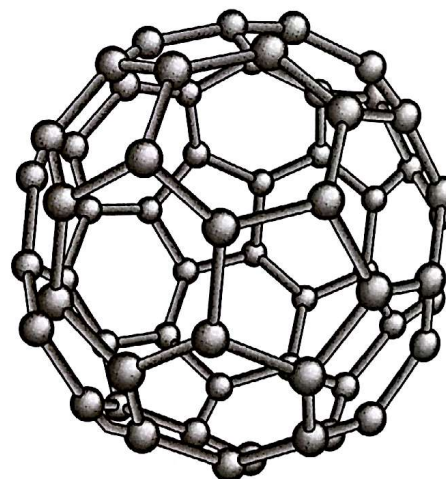
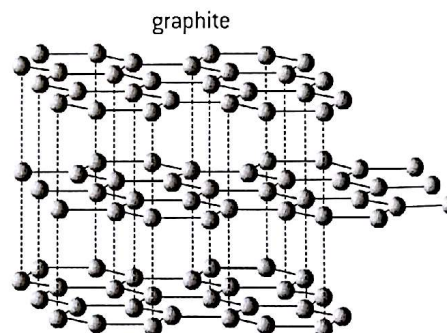
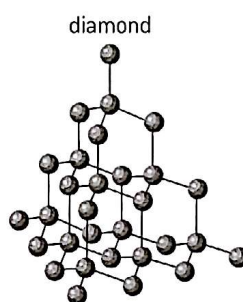


## ALLOTROPE OF CARBON

Allotropes occur when an element can exist in different crystalline forms. In diamond each carbon atom is covalently bonded to four other carbon atoms to form a giant covalent structure. All the bonds are equally strong and there is no plane of weakness in the molecule so diamond is exceptionally hard, and because all the electrons are localized it does not conduct electricity. Both silicon and silicon dioxide, SiO<sub>2</sub>, form similar giant tetrahedral structures.

In graphite each carbon atom has very strong bonds to three other carbon atoms to give layers of hexagonal rings. There are only very weak bonds between the layers. The layers can slide over each other so graphite is an excellent lubricant and because the electrons are delocalized between the layers it is a good conductor of electricity. In 2010 the Nobel prize for Physics was awarded for the discovery of graphene. Graphene is a single layer of hexagonally arranged carbon atoms, i.e. it is essentially a form of graphite which is just one atom thick. It is extremely light, functions as a semiconductor and is 200 times stronger than steel. More recently chemists have developed a new magnetic form of graphene which is called graphone.

A third allotrope of carbon is buckminsterfullerene, C<sub>60</sub>. Sixty carbon atoms are arranged in hexagons and pentagons to give a geodesic spherical structure similar to a football. Following the initial discovery of buckminsterfullerene many other similar carbon molecules have been isolated. This has led to a new branch of science called nanotechnology.



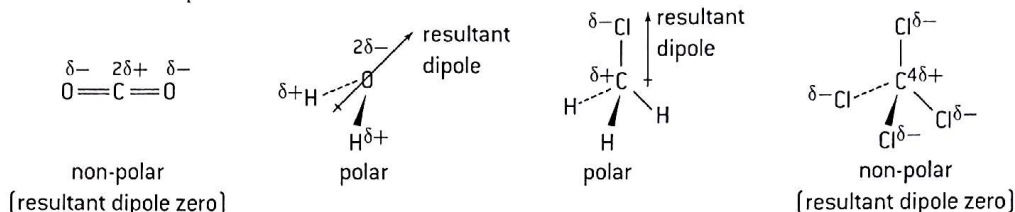
buckminsterfullerene, C<sub>60</sub>



# Intermolecular forces

## MOLECULAR POLARITY

Whether a molecule is polar, or not, depends both on the relative electronegativities of the atoms in the molecule and on its shape. If the individual bonds are polar then it does not necessarily follow that the molecule will be polar as the resultant dipole may cancel out all the individual dipoles.



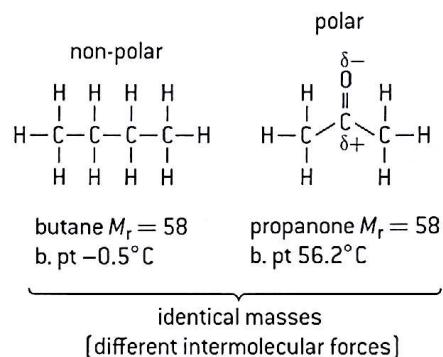
## LONDON DISPERSION FORCES

Even in non-polar molecules the electrons can at any one moment be unevenly spread. This produces temporary instantaneous dipoles. An instantaneous dipole can induce another dipole in a neighbouring particle resulting in a weak attraction between the two particles. London dispersion forces increase with increasing mass.

	increasing London dispersion forces →			
$M_r$	$\text{F}_2$	$\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$
b. pt / °C	38.0	70.9	160	254
	-188	-34.0	58.0	183
	→ increasing London dispersion forces			
$M_r$	$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$
b. pt / °C	16.0	30.0	44.0	58.0
	-162	-88.6	-42.2	-0.5

## DIPOLE-DIPOLE FORCES

Polar molecules are attracted to each other by electrostatic forces. Although still relatively weak the attraction is stronger than London dispersion forces.



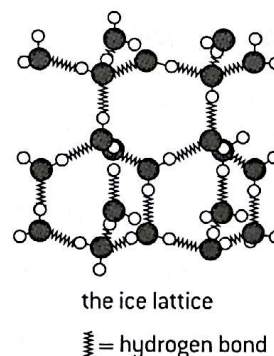
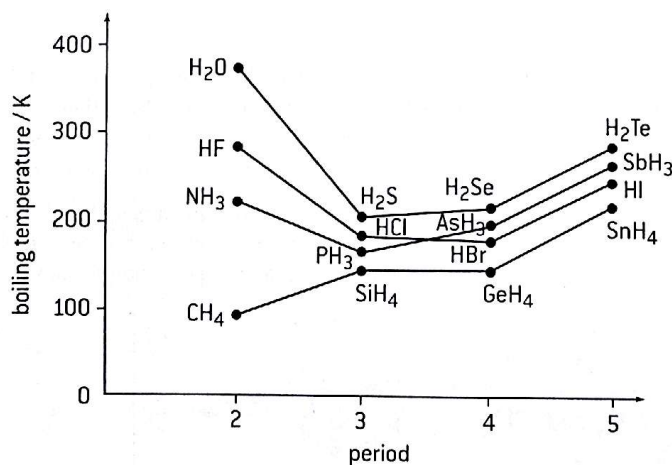
## INTERMOLECULAR FORCES

The covalent bonds between the atoms *within* a molecule are very strong. The forces of attraction *between* the molecules are much weaker. These intermolecular forces depend on the polarity of the molecules. Be careful with the terminology. The weakest intermolecular forces are called London dispersion forces. This description refers to instantaneous dipole-induced dipole forces that exist between any atoms or groups of atoms and should be used for non-polar entities. A more general inclusive term is van der Waals' forces which includes dipole-dipole and dipole-induced dipole as well as London dispersion forces.

## HYDROGEN BONDING

Hydrogen bonding occurs when hydrogen is bonded directly to a small highly electronegative element, such as fluorine, oxygen, or nitrogen. As the electron pair is drawn away from the hydrogen atom by the electronegative element, all that remains is the proton in the nucleus as there are no inner electrons. The proton attracts a

non-bonding pair of electrons from the F, N, or O resulting in a much stronger dipole-dipole attraction. Water has a much higher boiling point than the other group 16 hydrides as the hydrogen bonding between water molecules is much stronger than the dipole-dipole bonding in the remaining hydrides. A similar trend is seen in the hydrides of group 15 and group 17. Hydrogen bonds between the molecules in ice result in a very open structure. When ice melts the molecules can move closer to each other so that water has its maximum density at  $4^\circ\text{C}$ .



# Physical properties related to bonding type

## MELTING AND BOILING POINTS

When a liquid turns into a gas the attractive forces between the particles are completely broken so boiling point is a good indication of the strength of intermolecular forces. When solids melt, the crystal structure is broken down, but there are still some attractive forces between the particles. Melting points do give an indication of the strength of intermolecular forces but they are also determined by the way the particles pack in the crystal state. They are also affected by impurities. Impurities weaken the structure and result in lower melting points.

Covalent bonds are very strong so macromolecular covalent structures have extremely high melting and boiling points. For example, diamond, which has a giant tetrahedral structure, melts in the region of 4000°C and silicon dioxide, SiO<sub>2</sub>, which has a similar structure, melts at over 1600°C. Graphite has very strong bonds between the carbon atoms in its hexagonal layers and has a similar melting point to diamond. Metals (see next page) and ionic compounds also tend to have relatively high melting and boiling points due to ionic attractions. Although it might be expected that ionic compounds with smaller more highly charged ions have higher melting points and boiling points the facts do not support this.

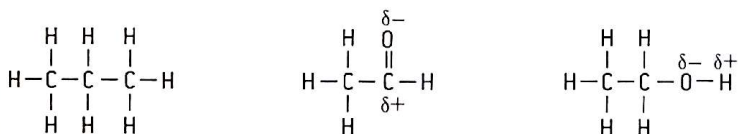
Ionic compound	Melting point / °C	Boiling point / °C
LiCl	605	1382
NaCl	801	1413
KCl	770	1420
MgCl <sub>2</sub>	714	1412

The melting and boiling points of simple covalent molecules depend on the type of forces of attraction between the molecules. These follow the order:

hydrogen bonding > dipole-dipole > London dispersion forces

The weaker the attractive forces the more volatile the substance.

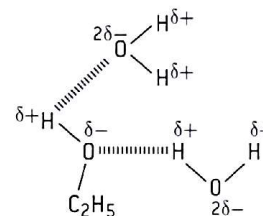
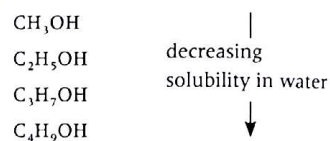
For example, propane, ethanal and ethanol have similar molar masses but there is a considerable difference in their melting points.



Compound	propane	ethanal	ethanol
<i>M<sub>r</sub></i>	44	44	46
<i>M. pt</i> / °C	-42.2	20.8	78.5
<b>Polarity</b>	non-polar	polar	polar
<b>Bonding type</b>	London dispersion	dipole-dipole	hydrogen bonding

## SOLUBILITY

'Like tends to dissolve like'. Polar substances tend to dissolve in polar solvents, such as water, whereas non-polar substances tend to dissolve in non-polar solvents, such as heptane or tetrachloromethane. Organic molecules often contain a polar head and a non-polar carbon chain tail. As the non-polar carbon chain length increases in an homologous series the molecules become less soluble in water. Ethanol itself is a good solvent for other substances as it contains both polar and non-polar ends.

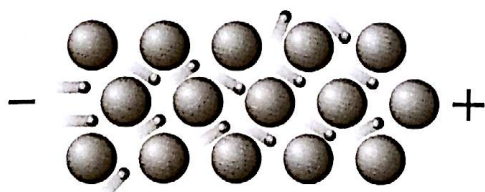


Ethanol is completely miscible with water as it can hydrogen-bond to water molecules.

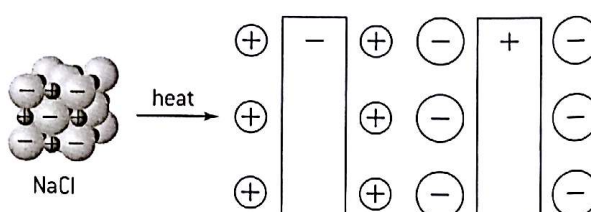
## CONDUCTIVITY

For conductivity to occur the substance must possess electrons or ions that are free to move. Metals (and graphite) contain delocalized electrons and are excellent conductors. Molten ionic salts also conduct electricity, but are chemically decomposed in the process. Where all the electrons are held in fixed positions, such as diamond or in simple molecules, no electrical conductivity occurs.

When a potential gradient is applied to the metal, the delocalized electrons can move towards the positive end of the gradient carrying charge.



When an ionic compound melts, the ions are free to move to oppositely charged electrodes. Note: in molten ionic compounds it is the ions that carry the charge, not free electrons.

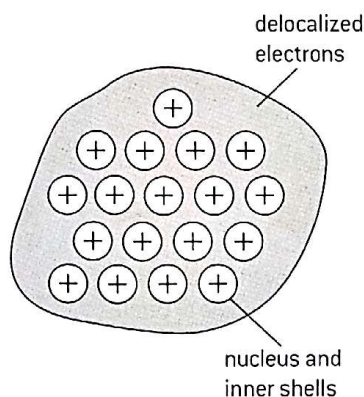




# Metals and alloys

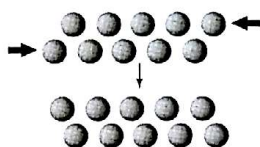
## METALLIC BONDING

The valence electrons in metals become detached from the individual atoms so that metals consist of a close packed lattice of positive ions in a 'sea' of delocalized electrons. A metallic bond is the attraction that two neighbouring positive ions have for the delocalized electrons between them.



Generally the strength of a metallic bond depends on the charge of the ions and the radius of the metal ion.

Metals are malleable, that is, they can be bent and reshaped under pressure. They are also ductile, which means they can be drawn out into a wire.



Metals are malleable and ductile because the close-packed layers of positive ions can slide over each other without breaking more bonds than are made.

## MELTING POINTS OF METALS

Although most metals tend to have quite high melting points, mercury is a liquid at room temperature and the group 1 elements (alkali metals) all melt below 181 °C. The trend in group 1 clearly follows the pattern that the smaller the metal ion formed when the valence electrons delocalize the stronger the metallic bond and the higher the melting point.

	Li	Na	K	Rb	Cs
<b>M. pt / °C</b>	181	97.8	63.5	39.3	28.5

However this logic only just holds true across period 3 (Na to Al) even though the charge on the ion is also increasing at the same time as the size of the ion is decreasing. It breaks down in group 14 as tin, which has a smaller ionic radius than lead, has a lower boiling point.

	Na	Mg	Al	Sn	Pb
<b>M. pt / °C</b>	97.8	650	660	232	328

This is because the melting point does not only depend upon the size and charge of the ion formed when the valence electrons are delocalized but also on the way in which the atoms are arranged in the solid metal.

## ALLOYS

Alloys are sometimes termed a metallic solid solution. They are usually made up of more than one metal although steel is an alloy of iron and carbon. Some common alloys are brass, bronze, solder, pewter and amalgams.

Alloy	Principal metal	Added metal(s)
Brass	copper	zinc
Bronze	copper	tin
Solder	lead	tin (some may have more tin than lead)
Pewter	tin	copper, antimony, bismuth or lead
Amalgams	mercury	e.g. tin, silver, gold or sodium

The addition of another metal to a metallic element alters its properties. The added metals are likely to have a different radius and may have a different charge and so distort the structure of the original metal as the bonding is less directional. One obvious example of this is that alloys may have lower melting points than their component metals. For example, before copper and plastic were used for water piping lead tended to be used (the origin of the word *plumber*). Lead melts at 328 °C and when pipes were being joined or repaired there was a danger of melting the actual pipe if too much heat was employed. Solder has a much lower melting point (typically 180–190 °C) and can be used to weld lead pipes together or to secure wires to terminals in an electrical circuit.

Generally alloys are less ductile and less malleable than pure metals as the added impurities disturb the lattice. This also tends to make alloys harder than the pure metals they are derived from. For example, aluminium is a soft, ductile and malleable metal. When it is alloyed with another soft metal such as copper the resulting aluminium alloy is much harder and stronger and yet still retains much of its low density. Small amounts of carbon added to iron produce steel with a high tensile strength. If chromium is also added it produces stainless steel, an alloy of steel with a much increased resistance to corrosion.

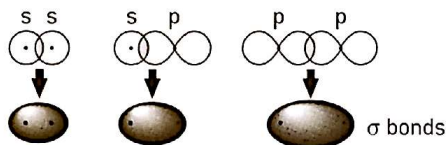
# HL Molecular orbitals

## COMBINATION OF ATOMIC ORBITALS TO FORM MOLECULAR ORBITALS

Although the Lewis representation is a useful model to represent covalent bonds it does make the false assumption that all the valence electrons are the same. A more advanced model of bonding considers the combination of atomic orbitals to form molecular orbitals.

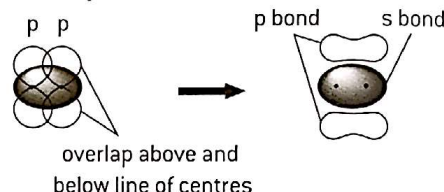
### $\sigma$ bonds

A  $\sigma$  (sigma) bond is formed when two atomic orbitals on different atoms overlap along a line drawn through the two nuclei. This occurs when two s orbitals overlap, an s orbital overlaps with a p orbital, or when two p orbitals overlap 'head on'.



### $\pi$ bonds

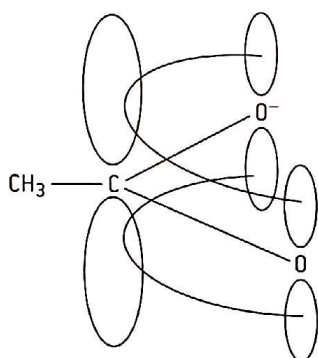
A  $\pi$  (pi) bond is formed when two p orbitals overlap 'sideways on'. The overlap now occurs above and below the line drawn through the two nuclei. A  $\pi$  bond is made up of two regions of electron density.



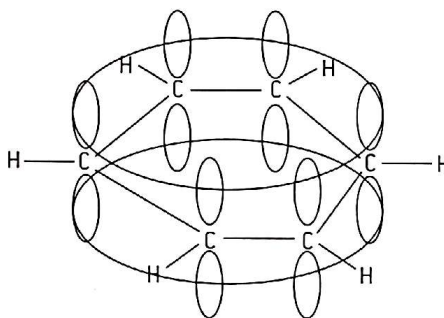
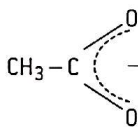
## DELOCALIZATION OF ELECTRONS

Resonance involves using two or more Lewis structures to represent a particular molecule or ion where the structure cannot be described by using a single Lewis structure. They can also be explained by the delocalization of electrons. For example, in the ethanoate ion the carbon atom and the two oxygen atoms each have a p orbital containing one electron after the  $\sigma$  bonds have been formed. Instead of forming just one double bond between the carbon atom and one of the oxygen atoms the electrons can delocalize over all three atoms. This is energetically more favourable than forming just one double bond.

Delocalization can occur whenever alternate double and single bonds occur between carbon atoms. The delocalization energy in benzene is about  $150 \text{ kJ mol}^{-1}$ , which explains why the benzene ring is so resistant to addition reactions.



ethanoate ion shown as



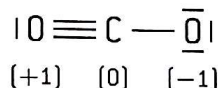
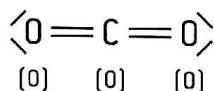
benzene ring shown as



## FORMAL CHARGE

Formal charge is a technique used in chemistry that is based on a false assumption but which can be useful for determining which of several potential Lewis structures is preferred when two or more are possible. It assumes that all atoms in a molecule or ion have the same electronegativity (the false assumption) and is equal to the (Number of Valence electrons) - (Number of Non-bonding electrons) -  $\frac{1}{2}$  (Number of Bonding electrons). This can be described by the formula  $FC = V - N - \frac{1}{2}B$  although note that this formula is not given in the IB data booklet. The preferred structure is the one where the individual atoms have the lowest possible formal charge.

For example, consider two possible structures for carbon dioxide, both of which obey the octet rule.



Formal charges

$$\text{C} = 4 - 0 - (\frac{1}{2} \times 8) = 0$$

$$\text{O} = 6 - 4 - (\frac{1}{2} \times 4) = 0$$

$$\text{C} = 4 - 0 - (\frac{1}{2} \times 8) = 0$$

$$\text{O} = 6 - 2 - (\frac{1}{2} \times 6) = +1 \text{ (O with triple bond)}$$

$$\text{O} = 6 - 6 - (\frac{1}{2} \times 2) = -1 \text{ (O with single bond)}$$

Both give a total formal charge of zero but the preferred structure is the first one with the two double bonds as the individual atoms have the lowest formal charges.

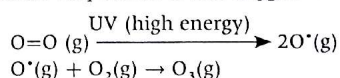


# HL Oxygen and ozone

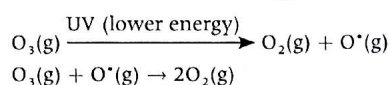
## IMPORTANCE OF THE OZONE LAYER

From the Lewis structures of both oxygen and ozone it can be seen that the double bond in oxygen is stronger than the 'one and a half' bond between the oxygen atoms in ozone.

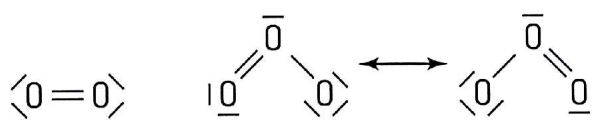
This difference in bond enthalpies helps to protect us from the Sun's harmful ultraviolet radiation. The ozone layer occurs in the stratosphere between about 12 km and 50 km above the surface of the Earth. Stratospheric ozone is in dynamic equilibrium with oxygen and is continually being formed and decomposed. The strong double bond in oxygen is broken by high energy ultraviolet light from the Sun to form atoms. These oxygen atoms are called radicals as they possess an unpaired electron and are very reactive. One oxygen radical can then react with an oxygen molecule to form ozone.



The weaker bonds in ozone require ultraviolet light of less energy to break them. When they are broken the reverse process happens and the ozone breaks down back to an oxygen molecule and an oxygen radical. The radical can then react with another ozone molecule to form two oxygen molecules.



Overall the rate of production of ozone is equal to the rate of ozone destruction – this process, during which a wide range of ultraviolet light is absorbed, is known as a steady state. Human-made pollutants such as CFCs and oxides of nitrogen can disrupt this process and in recent years large 'holes' in the ozone layer have appeared – particularly in winter and early spring over the South and North Poles.



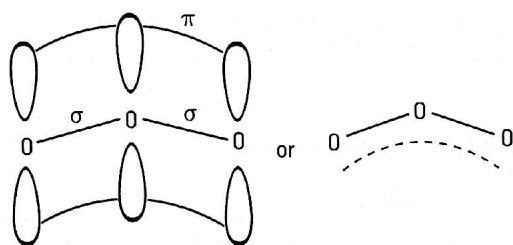
Lewis structures of oxygen and ozone

## WAVELENGTH OF UV LIGHT NECESSARY FOR $\text{O}_2$ AND $\text{O}_3$ DISSOCIATION

The bond enthalpy for the  $\text{O}=\text{O}$  double bond is given as  $498 \text{ kJ mol}^{-1}$  in the IB data booklet. For just one double bond this equates to  $8.27 \times 10^{-19} \text{ J}$ . The wavelength of light that corresponds to this enthalpy value ( $E$ ) can be calculated by combining the expressions  $E = h\nu$  and  $c = \lambda\nu$  to give  $\lambda = \frac{hc}{E}$  where  $h$  is Planck's constant and  $c$  is the velocity of light.

$$\lambda = \frac{6.63 \times 10^{-34} (\text{J s}) \times 3.00 \times 10^8 (\text{m s}^{-1})}{8.27 \times 10^{-19} (\text{J})} = 241 \text{ nm}$$

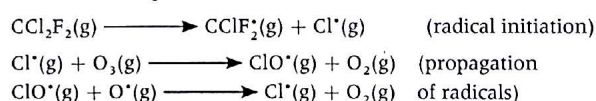
This is in the high energy region of the ultraviolet spectrum. Ozone is described above as two resonance hybrids. An alternative bonding model is to consider the  $\pi$  electrons to be delocalized over all three oxygen atoms. In both models the bond order is 1.5, i.e. with an enthalpy between an  $\text{O}-\text{O}$  single bond ( $144 \text{ kJ mol}^{-1}$ ) and an  $\text{O}=\text{O}$  double bond ( $498 \text{ kJ mol}^{-1}$ ) so ultraviolet light with a longer wavelength (lower energy) is absorbed in breaking the ozone bonds. The actual wavelength required is 330 nm. Working backwards this gives the strength of the  $\text{O}-\text{O}$  bond in ozone as  $362 \text{ kJ mol}^{-1}$ .



delocalized  $\pi$  bond in ozone

## CATALYSIS AND OZONE DESTRUCTION BY CFCs AND $\text{NO}_x$

CFCs catalyse the destruction of ozone because the high energy ultraviolet light in the stratosphere causes the homolytic fission of the  $\text{C}-\text{Cl}$  bond to produce chlorine radicals. Note that it is the  $\text{C}-\text{Cl}$  bond that breaks, not the  $\text{C}-\text{F}$  bond, as the  $\text{C}-\text{Cl}$  bond strength is weaker. These radicals then break down ozone molecules and regenerate more radicals so that the process continues until the radicals eventually escape or terminate. It has been estimated that one molecule of a CFC can catalyse the breakdown of up to 100 000 molecules of ozone.

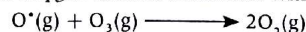


Evidence to support this mechanism is that the increase in the concentration of chlorine monoxide in the stratosphere over the Antarctic has been shown to mirror the decrease in the ozone concentration.

Nitrogen oxides also catalytically decompose ozone by a radical mechanism. The overall mechanism is complex. Essentially oxygen radicals are generated by the breakdown of  $\text{NO}_2$  in ultraviolet light.



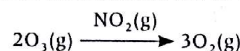
The oxygen radicals then react with ozone



The nitrogen oxide can also react with ozone to regenerate the catalyst



The overall reaction can be simplified as:

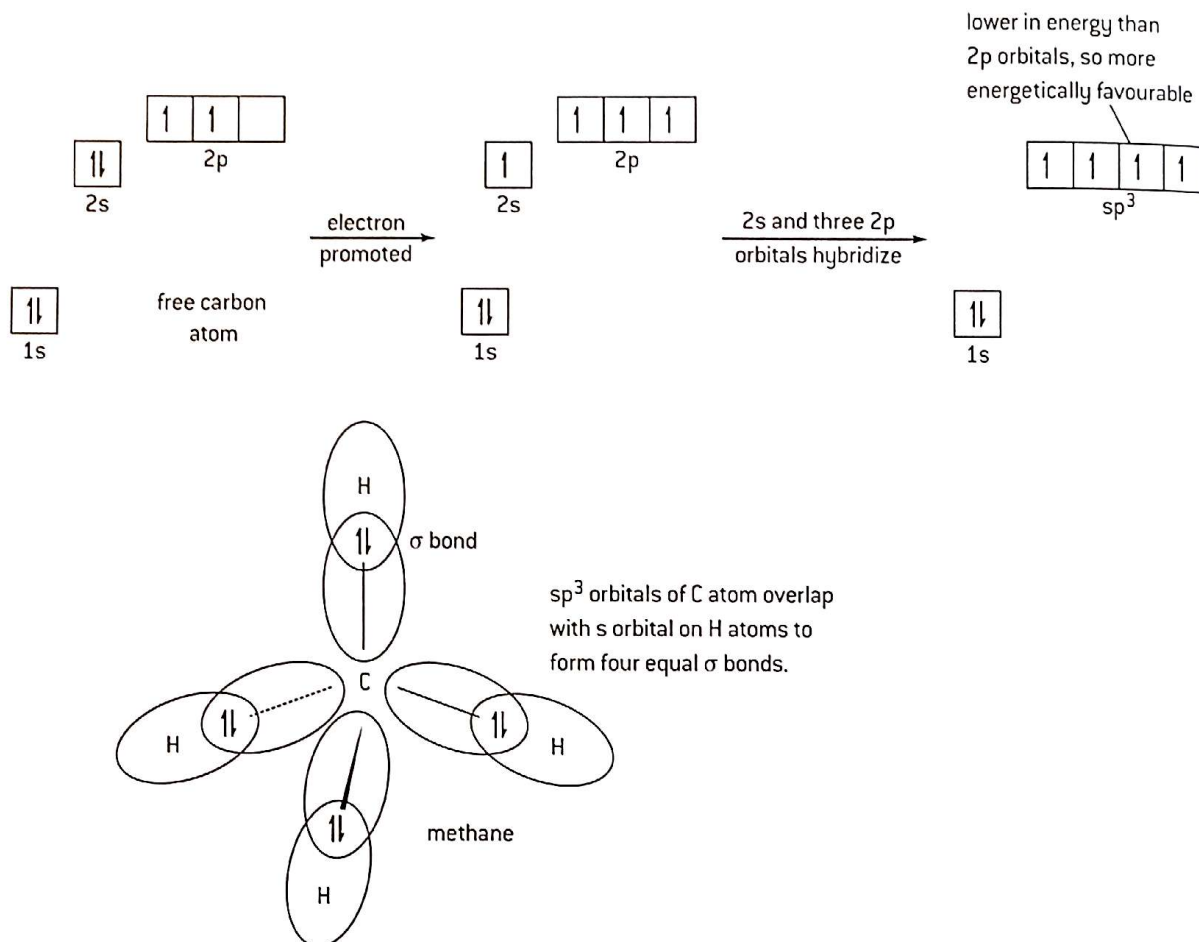


# HL Hybridization (1)

## $sp^3$ HYBRIDIZATION

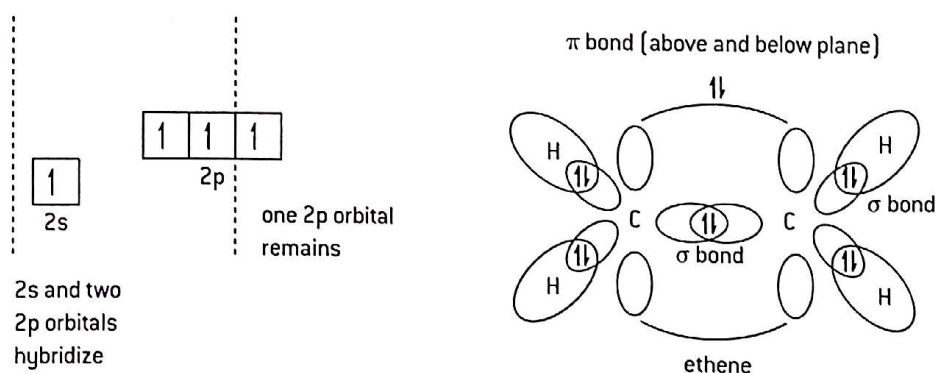
Methane provides a good example of  $sp^3$  hybridization. Methane contains four equal C-H bonds pointing towards the corners of a tetrahedron with bond angles of  $109.5^\circ$ . A free carbon atom has the configuration  $1s^2 2s^2 2p^2$ . It cannot retain this configuration in methane. Not only are there only two unpaired electrons, but the p orbitals are at  $90^\circ$  to each other and will not give bond angles of  $109.5^\circ$  when they overlap with the s orbitals on the hydrogen atoms.

When the carbon bonds in methane one of its 2s electrons is promoted to a 2p orbital and then the 2s and three 2p orbitals hybridize to form four new hybrid orbitals. These four new orbitals arrange themselves to be as mutually repulsive as possible, i.e. tetrahedrally. Four equal  $\sigma$  bonds can then be formed with the hydrogen atoms.



## $sp^2$ HYBRIDIZATION

$sp^2$  hybridization occurs in ethene. After a 2s electron on the carbon atom is promoted the 2s orbital hybridizes with two of the 2p orbitals to form three new planar hybrid orbitals with a bond angle of  $120^\circ$  between them. These can form  $\sigma$  bonds with the hydrogen atoms and also a  $\sigma$  bond between the two carbon atoms. Each carbon atom now has one electron remaining in a 2p orbital. These can overlap to form a  $\pi$  bond. Ethene is thus a planar molecule with a region of electron density above and below the plane.

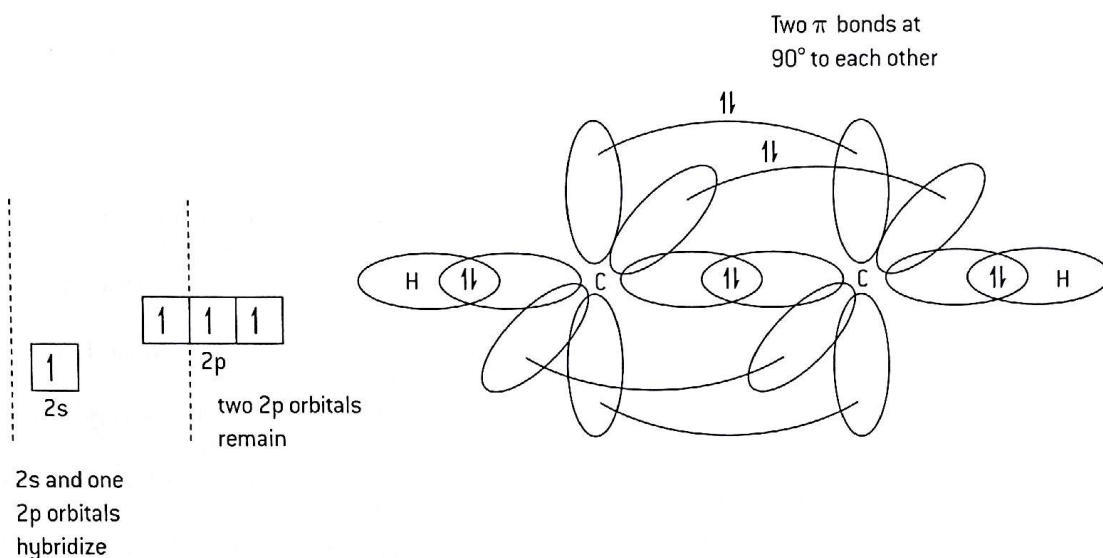




# HL Hybridization (2)

## sp HYBRIDIZATION

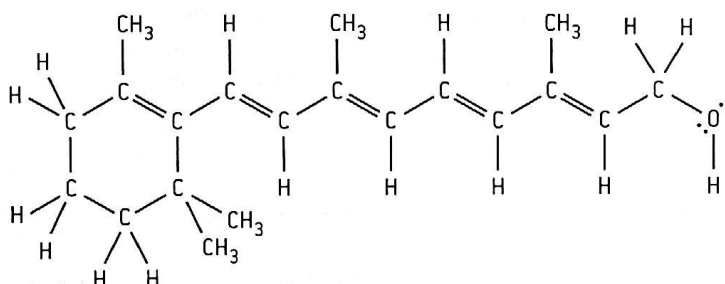
sp hybridization occurs when the 2s orbital hybridizes with just one of the 2p orbitals to form two new linear sp hybrid orbitals with an angle of 180° between them. The remaining two p orbitals on each carbon atom then overlap to form two  $\pi$  bonds. An example is ethyne.



## PREDICTING THE TYPE OF BONDING AND HYBRIDIZATION IN MOLECULES

In carbon compounds containing single, double or triple bonds the numbers of each different type of bond ( $\sigma$  or  $\pi$ ) and the type of hybridization shown by each carbon atom can be deduced.

Vitamin A contains 5 C=C double bonds, 15 C-C bonds, 29 C-H bonds, 1 C-O bond and 1 O-H bond.



Each single bond is a  $\sigma$  bond and each double bond contains one  $\sigma$  and one  $\pi$  bond so there is a total of 51  $\sigma$  bonds and 5  $\pi$  bonds in the molecule. Each carbon atom either side of a double bond is  $sp^2$  hybridized so 10 of the carbon atoms are  $sp^2$  hybridized. The remaining 10 carbon atoms are  $sp^3$  hybridized. The oxygen atom, which has four pairs of electrons around it, is also  $sp^3$  hybridized.

## RELATIONSHIP BETWEEN TYPE OF HYBRIDIZATION, LEWIS STRUCTURE, AND MOLECULAR SHAPES

Molecular shapes can be arrived at either by using the VSEPR theory or by knowing the type of hybridization. Hybridization can take place between any s and p orbital in the same energy level and is not just restricted to carbon compounds. If the shape and bond angles are known from using Lewis structures then the type of hybridization can be deduced. Similarly if the type of hybridization is known the shape and bond angles can be deduced.

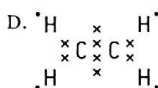
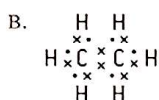
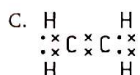
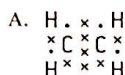
Hybridization	Regular bond angle	Examples
$sp^3$	109.5°	
$sp^2$	120°	
$sp$	180°	

# MULTIPLE CHOICE QUESTIONS – CHEMICAL BONDING AND STRUCTURE

1. What are the correct formulas of the following ions?

	Nitrate	Phosphate	Carbonate	Ammonium
A.	$\text{NO}_3^-$	$\text{PO}_4^{3-}$	$\text{CO}_3^-$	$\text{NH}_3^+$
B.	$\text{NO}_3^{2-}$	$\text{PO}_3^{2-}$	$\text{CO}_3^{2-}$	$\text{NH}_3^+$
C.	$\text{NO}_3^-$	$\text{PO}_4^{3-}$	$\text{CO}_3^{2-}$	$\text{NH}_4^+$
D.	$\text{NO}_3^{2-}$	$\text{PO}_3^{2-}$	$\text{CO}_3^{2-}$	$\text{NH}_4^+$

2. Which is the correct Lewis structure for ethene?



3. Given the following electronegativities, H: 2.2 N: 3.0 O: 3.5 F: 4.0, which bond would be the most polar?

A. O-H in  $\text{H}_2\text{O}$

C. N-O in  $\text{NO}_2$

B. N-F in  $\text{NF}_3$

D. N-H in  $\text{NH}_3$

4. Which substance is made up of a lattice of positive ions and free moving electrons?

A. Graphite

C. Sulfur

B. Sodium chloride

D. Sodium

5. When  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , are arranged in order of **increasing** bond angle, what is the correct order?

A.  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$

C.  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$

B.  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$

D.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$

6. Which order is correct when the following compounds are arranged in order of **increasing** melting point?

A.  $\text{CH}_4 < \text{H}_2\text{S} < \text{H}_2\text{O}$

C.  $\text{CH}_4 < \text{H}_2\text{O} < \text{H}_2\text{S}$

B.  $\text{H}_2\text{S} < \text{H}_2\text{O} < \text{CH}_4$

D.  $\text{H}_2\text{S} < \text{CH}_4 < \text{H}_2\text{O}$

7. Which species contain a coordinate covalent bond?

I.  $\text{HCHO}$

II.  $\text{CO}$

III.  $\text{H}_3\text{O}^+$

A. I and II only

C. II and III only

B. I and III only

D. I, II and III

8. Which is the correct order for **decreasing** H-N-H bond angles in the species  $\text{NH}_2^-$ ,  $\text{NH}_3$  and  $\text{NH}_4^+$  (largest bond angle first)?

A.  $\text{NH}_3$ ,  $\text{NH}_2^-$ ,  $\text{NH}_4^+$

C.  $\text{NH}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{NH}_3$

B.  $\text{NH}_4^+$ ,  $\text{NH}_3$ ,  $\text{NH}_2^-$

D.  $\text{NH}_2^-$ ,  $\text{NH}_3$ ,  $\text{NH}_4^+$

9. Which is the correct order for **increasing** intermolecular forces of attraction (smallest force first)?

A. Covalent bonds, hydrogen bonds, dipole-dipole, London dispersion forces

B. London dispersion forces, dipole-dipole, hydrogen bonds, covalent bonds

C. London dispersion forces, hydrogen bonds, dipole-dipole, covalent bonds

D. Covalent bonds, dipole-dipole, hydrogen bonds, London dispersion forces

10. Which statement best explains why alloys tend to be less malleable than pure metals?

A. The added metal has more valence electrons so increases the amount of delocalization.

B. The added metal prevents the layers from being drawn out into a wire.

C. The added metal disturbs the lattice so the layers are less able to slide over each other.

D. The added metal acts as an impurity and so lowers the melting point.

HL

11. Which of the following species contains at least one atom that is  $\text{sp}^2$  hybridized?

A. hydrogen cyanide,  $\text{HCN}$

B. 2-methylpropane,  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$

C. propanone,  $\text{CH}_3\text{COCH}_3$

D. ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$

12. How many  $\sigma$  and  $\pi$  bonds are present in propanal,  $\text{CH}_3\text{CHCHO}$ ?

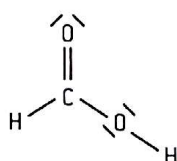
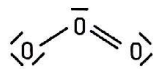
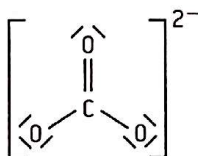
A.  $8\sigma$  and  $2\pi$

C.  $5\sigma$  and  $1\pi$

B.  $8\sigma$  and  $1\pi$

D.  $9\sigma$  and  $1\pi$

13. Which species have delocalized electrons?



A. I and II only

C. II and III only

B. I and III only

D. I, II and III

14. What is the formal charge on the oxygen atom in the hydronium ion  $\text{H}_3\text{O}^+$ ?

A. -2

C. 0

B. -1

D. +1

15. Which describes the shape of the  $\text{SF}_4$  molecule?

A. Tetrahedral

C. Square planar

B. Distorted tetrahedral

D. Trigonal bipyramidal

16. Which statements about graphene are correct?

I. It can be considered as a single layer of graphite

II. The hybridization of the carbon atoms is  $\text{sp}^2$

III. It is an allotrope of carbon

A. I and II only

B. I and III only

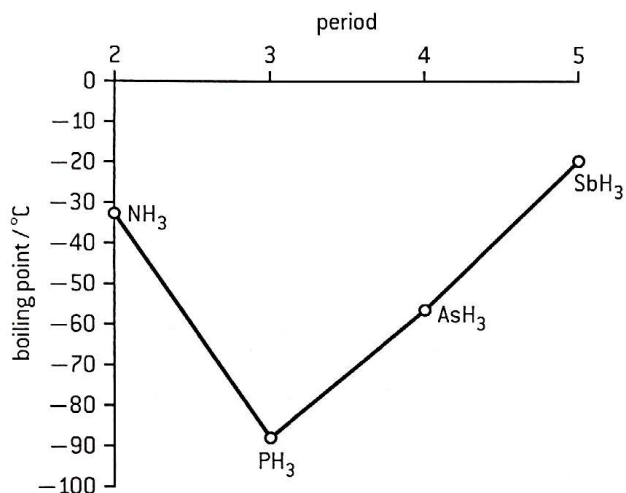
C. II and III only

D. I, II and III



## SHORT ANSWER QUESTIONS – CHEMICAL BONDING AND STRUCTURE

1.  $\text{PF}_3$ ,  $\text{SF}_2$  and  $\text{SiF}_4$  have different shapes. Draw their Lewis structures and use the VSEPR theory to predict the name of the electron domain geometry and the molecular shape of each molecule. [8]
2. a) (i) Draw the Lewis structure of  $\text{NH}_3$ , state its molecular shape and deduce and explain the  $\text{H}-\text{N}-\text{H}$  bond angle in  $\text{NH}_3$ . [4]  
(ii) The graph below shows the boiling points of the hydrides of group 15. Discuss the variation in the boiling points. [4]



- b) Explain, using diagrams, why  $\text{CO}$  and  $\text{NO}_2$  are polar molecules but  $\text{CO}_2$  is a non-polar molecule. [5]

3. Ethane,  $\text{C}_2\text{H}_6$ , and disilane,  $\text{Si}_2\text{H}_6$ , are both hydrides of group 14 elements with similar structures but with different chemical properties.
  - a) Deduce the Lewis (electron dot) structure for  $\text{Si}_2\text{H}_6$  showing all valence electrons. [1]
  - b) State and explain the  $\text{H}-\text{Si}-\text{H}$  bond angle in  $\text{Si}_2\text{H}_6$ . [2]
  - c) State which of the bonds,  $\text{Si}-\text{H}$  or  $\text{C}-\text{H}$ , is more polar. Explain your choice. [2]
  - d) Predict, with an explanation, the polarity of the two molecules. [2]
  - e) Explain why disilane has a higher boiling point than ethane. [2]
4. a) State and explain which of propan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , and methoxyethane,  $\text{CH}_3\text{OCH}_2\text{CH}_3$ , is more volatile. [3]  
b) Propan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ , and hexan-1-ol,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$ , are both alcohols. State and explain which compound is more soluble in water. [2]  
c) Graphite is used as a lubricant and is an electrical conductor. Diamond is hard and does not conduct electricity. Explain these statements in terms of the structure and bonding of these allotropes of carbon. [6]
5. a) State the **full** and the **condensed** electron configuration for chlorine. [2]  
b) Deduce the orbital diagram for silicon using a box ☐ to represent an orbital and  $\uparrow$  and  $\downarrow$  to represent electrons with opposite spins. [2]  
c) Explain why chlorine forms an ionic compound with sodium but a covalent compound with silicon. [2]

HL

6. a) Ozone and sulfur hexafluoride are greenhouse gases.
  - (i) Draw the Lewis structure of sulfur hexafluoride. [1]
  - (ii) Explain why sulfur can expand its octet whereas oxygen cannot. [1]
  - (iii) Deduce the electron domain geometry for both ozone and sulfur hexafluoride and deduce their molecular shape. [2]
  - (iv) Deduce the bond angles in ozone and sulfur hexafluoride. [2]
- b) Another greenhouse gas is dichlorodifluoromethane,  $\text{CCl}_2\text{F}_2$ . This gas can also cause destruction of the ozone layer.
  - (i) Determine the wavelength of light required to break the  $\text{C}-\text{F}$  and the  $\text{C}-\text{Cl}$  bonds. [4]
  - (ii) Suggest why dichlorodifluoromethane is unreactive in the atmosphere near the surface of the Earth but reactive in the ozone layer. [2]
7. Two Lewis structures that obey the octet rule can be proposed for the nitronium ion,  $\text{NO}_2^+$ .
 

$$\left[ \text{O}=\text{N}=\text{O} \right]^+$$

I

$$\left[ \text{O} \equiv \text{N} - \text{O} \right]^+$$

II
8. a) Describe the bonding within the carbon monoxide molecule. [2]  
b) Describe the delocalization of  $\pi$  (pi) electrons and explain how this can account for the structure and stability of the carbonate ion,  $\text{CO}_3^{2-}$ . [3]  
c) Explain the meaning of the term hybridization. State the type of hybridization shown by the carbon atoms in carbon dioxide, diamond, graphite and the carbonate ion. [5]  
d) (i) Explain the electrical conductivity of molten sodium oxide and liquid sulfur trioxide. [2]  
(ii) Samples of sodium oxide and solid sulfur trioxide are added to separate beakers of water. Deduce the equation for each reaction and predict the electrical conductivity of each of the solutions formed. [3]

Deduce the formal charge for each atom in both of the two proposed structures and determine which structure is the most likely. [4]