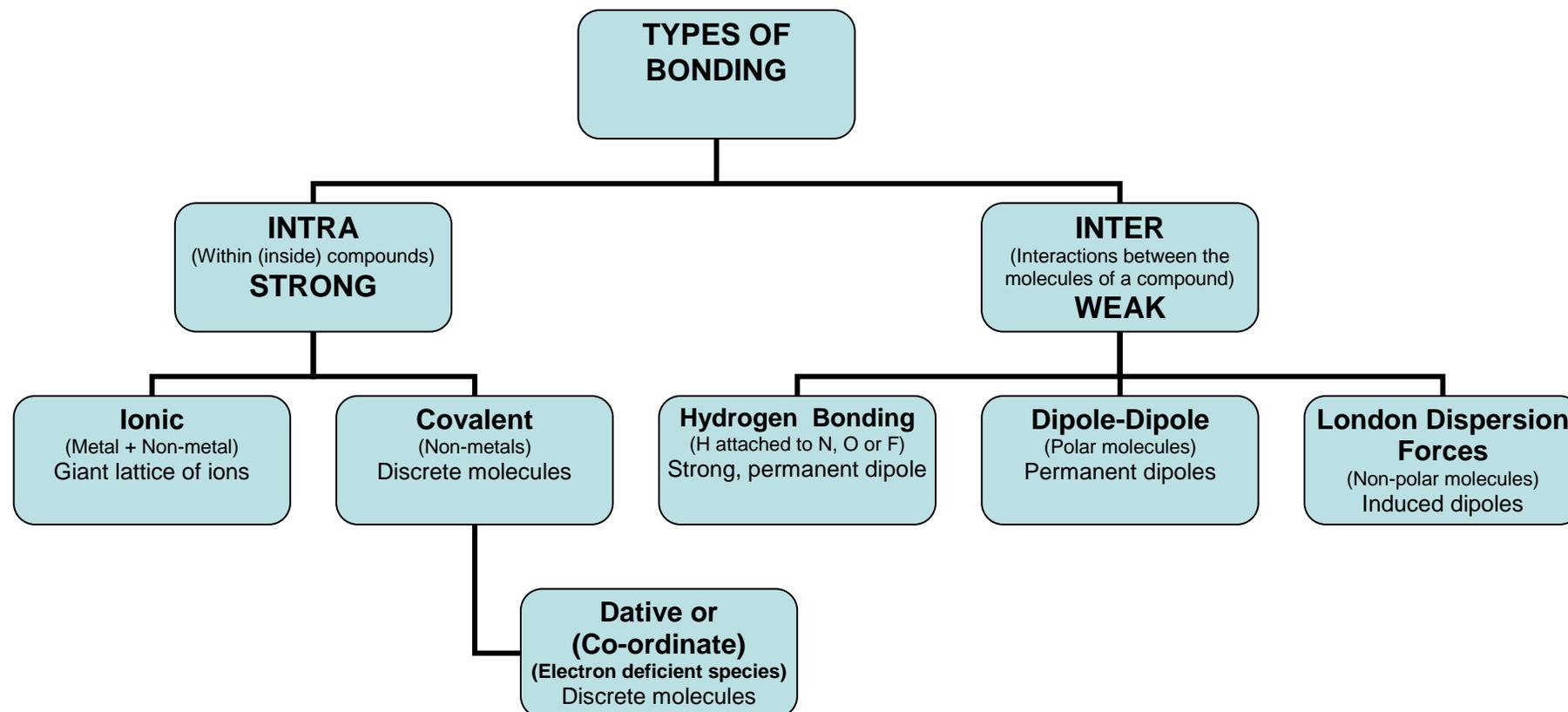**Revised August 2011**

HONORS TOPIC 9: Chemical Bonding

- **Introduction**

In the study of bonding we will consider several different types of chemical bond and some of the theories associated with them.

```
                          TYPES OF
                          BONDING


         INTRA                              INTER
   (Within (inside) compounds)       (Interactions between the
         STRONG                       molecules of a compound)
                                            WEAK


   Ionic          Covalent      Hydrogen Bonding    Dipole-Dipole    London Dispersion
(Metal + Non-metal) (Non-metals)  (H attached to N, O or F)  (Polar molecules)      Forces
Giant lattice of ions Discrete molecules Strong, permanent dipole Permanent dipoles  (Non-polar molecules)
                                                                                    Induced dipoles


                    Dative or
                  (Co-ordinate)
              (Electron deficient species)
                Discrete molecules
```

To help distinguish the difference in strength of intra and inter bonds consider the process of boiling of water. When water boils the product is steam (gaseous water). The products are not hydrogen and oxygen. This is because the weak inter molecular forces are broken not the much stronger intra molecular forces.

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- **Intra Bonding**

<u>Ionic</u> (the transfer of electrons between atoms to form ions that form giant ionic lattices)

Atoms have equal numbers of protons and electrons and consequently have no overall charge. When atoms lose or gain electrons, (in order to achieve full s and p sub-shells or a "noble gas structure" and stability), the proton/electron numbers are unbalanced causing the particles to become charged. These charged particles are called *ions*. Since metals have a tendency to lose electrons to form positive ions and non-metals the opposite, the ionic bond is usually formed between metals & non-metals. The strong electrostatic forces between the charged particles are called *ionic bonds*. Since the electrostatic forces are large the bond is a strong one.

Task 9a

List the ions present and hence the formula of the following compounds;
Sodium chloride, calcium chloride, iron(III) bromide, sodium oxide.

<u>Covalent</u> (the sharing of electrons between atoms to form discrete molecules)

In covalent bonding atoms once again want to achieve full s and p sub-shells, this time by joining together and sharing valence electrons. When they do so they form *molecules*. One shared pair of electrons represents a single covalent bond; two shared pairs represent a double bond, etc. These bonds usually occur between atoms that are non-metals. Any electron pairs that occur in the valence shell of an atom but do not form a bond with another atom are called *non-bonding electrons* or *lone pairs*.

<u>Lewis structures of covalently bonded molecules</u>

Lewis structures use dots to represent valence electrons in atoms when they form molecules. As discussed above, when atoms form molecules they share electrons to achieve full s and p sub-shells. In the case of hydrogen this is two (a duet), in the case of the second period non-metal elements this is eight (octet rule). Some elements in the third period can have more than eight electrons in their outer shells (expanded octet rule).

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Drawing Lewis structures

1. Calculate the total number of valence shell electrons (taking into account any charges present by adding for negative charges, and subtracting for positive charges).

2. In a species with more than two atoms, decide which atom is the central one (this is usually obvious, but if in doubt it will be the least electronegative atom but never hydrogen). Use one pair of electrons to form a covalent bond between the terminal (outer) atoms that are bonded to the central atom.

3. Arrange the remaining electrons to complete the octets of the terminal atoms and then place any remaining electrons on the central atom, if necessary expanding the central atoms' octet.

4. If the central atom lacks an octet, form multiple bonds (double or triple*) by converting non-bonding electrons from terminal atoms into bonding pairs. (Some atoms are exceptions and remain electron deficient).

5. One bonding pair of electrons represents one covalent bond that in turn can be represented by a single line (—) etc.

Task 9b

Draw Lewis diagrams for each of these species;

F_2, O_2, N_2, HCl, HF, H_2O, NH_3, CBr_4, PF_5, PCl_6^-, NH_4^+

*Sigma (σ) and Pi (π) bonds - the shared pair of electrons that make up a covalent bond can be classified in two ways; as either a sigma bond or a pi bond. A single bond is always a sigma (covalent) bond, a double bond is made up of a sigma and a pi, and a triple bond is made up of a sigma plus two pi bonds.

- **Shapes of covalently bonded molecules and ions**

The shapes of covalently bonded molecules and ions can be determined by considering the number of electron pairs around the central atom. The electron pairs repel one another and try to get as far apart as possible. This theory is called *Valence Shell Electron Pair Repulsion* theory or VSEPR. There are some standard shapes for specific numbers of electron pairs and some simple deviations from this theory when non-bonding (lone) pairs are present around the central atom. Those shapes, their names, bond angles and other relevant information are listed on the table on the next page.

Notes

A non-bonding pair will repel more strongly than a bonding pair. When comparing bond angles it can be seen that this has the effect of altering the bond angles and the shape of molecules that have a similar total number of electron pairs around the central atom, but where the total is made up of different combinations of bonding and lone pairs.

For the purposes of predicting shape multiple bonds can be considered as single bonds (or single negative centers). For example, a double bond is considered to be just one bonding pair when predicting shape. For example, carbon dioxide can be considered to be surrounded by two electron pairs (negative centers) and is therefore linear, even though there are actually two bonding pairs on either side of the carbon atom.

Predicting shapes of molecules

1. Draw the Lewis dot structure for the molecule.
2. Count the electron pairs (both bonding and non-bonding) around the central atom.
3. Use the table below to recall the correct shape, name and bond angles that correspond to the position of the atoms in the structure that arranges them in a way that minimizes repulsion (i.e., keep them as far apart as possible).

Task 9c

Draw Lewis structures and sketch the shapes for the following. In each case identify the number of bonding & lone pairs pairs around the central atom, and predict bond angles;

PCl_6^-, ICl_3, BrF_5, SO_3^{2-}, CH_4, NH_4^+, ICl_4^-, SO_2
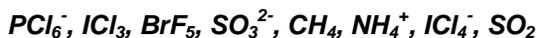
Revised August 2011
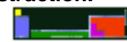
| Number of electron pairs around central atom		Full description of the molecule					
BONDING (B)	LONE (E)	Example	Bond angles °	Geometry of Electron Pairs	Geometry of Atoms	3D Shape	Type (A is central)
2	0	$BeCl_2$	180	Linear	**Linear**		AB_2
3	0	BF_3	120	Trigonal planar	**Trigonal Planar**		AB_3
2	1	SO_2	Slightly less than 120	Trigonal planar	**Bent or V Shaped**		AB_2E
4	0	CH_4	109.5	Tetrahedral	**Tetrahedral**		AB_4
3	1	NH_3	107.5	Tetrahedral	**Trigonal Pyramidal**		AB_3E
2	2	H_2O	104.5	Tetrahedral	**Bent or V Shaped**		AB_2E_2
5	0	PCl_5	120 in plane. 90 perpendicular to plane	Trigonal bipyramidal	**Trigonal Bipyramidal**		AB_5
4	1	SF_4	Complex	Trigonal bipyramid	**Seesaw**		AB_4E
3	2	ClF_3	Approx. 90	Trigonal bipyramidal	**T-Shaped**		AB_3E_2
2	3	XeF_2	180	Trigonal bipyramid	**Linear**		AB_2E_3
6	0	SF_6	90	Octahedral	**Octahedral**		AB_6
5	1	BrF_5	Approx. 90	Octahedral	**Square Pyramidal**		AB_5E
4	2	XeF_4	90	Octahedral	**Square Planar**		AB_4E_2

Resonance structures & bond length

Occasionally when drawing a Lewis structure that involves multiple bonds, it may be possible to draw a number of different (but still feasible) Lewis structures. In such a case we call the various structures resonance structures. For example, carbon dioxide has three possible Lewis structures.
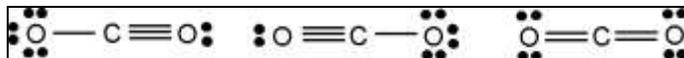
The carbonate ion provides another example. The Lewis structure for the carbonate ion can be represented by the diagram below.
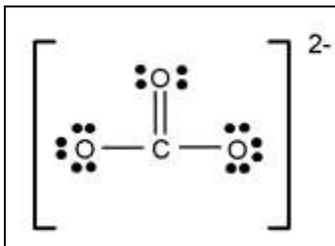
However, it would be equally correct to have created the double bond on the right hand oxygen or the left hand oxygen rather than the oxygen at the top of the diagram and hence get a total of three different resonance structures. The reality is that the structure is an "average" of all three possible resonance structures and each bond is really one and one third covalent bonds rather than any combination of two singles and one double.

If a multiple bond (double or triple) is created between two atoms the bond length observed will be shorter than the corresponding single bond. This is because a double bond is stronger than a single bond and hence pulls the atoms closer together. A triple bond is correspondingly shorter and stronger than a double bond. Evidence for the "one and one third" bond order in the carbonate ion is that all the bonds are found to be the same length, not the different lengths that one would expect to find if a combination of double and single bonds were present.
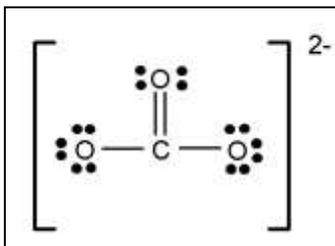
Formal charge

The formal charges of each atom within a structure can be calculated using the formula below.

$$\left(\begin{array}{l}\text{Formal Charge on an atom} \\ \text{within a Lewis structure}\end{array}\right) = \left(\begin{array}{l}\text{The number of} \\ \text{valence electrons} \\ \text{around that atom} \\ \text{in the free atom}\end{array}\right) - \left(\begin{array}{l}\text{The number of} \\ \text{non bonding electrons} \\ \text{around that atom} \\ \text{in Lewis structure}\end{array}\right) - \frac{1}{2}\left(\begin{array}{l}\text{The number of} \\ \text{bonding electrons} \\ \text{around that atom} \\ \text{in Lewis structure}\end{array}\right)$$

The formal charge of an atom within a Lewis structure is generally used in one of two ways.

(i)   To suggest where charges may most reasonably lay (for example where the 2-charge of the carbonate ion actually resides)

Using the Lewis structure for the carbonate ion (CO_3^{2-}) as an example it is possible to determine the formal charges on the atoms and therefore the most likely separation of charge.
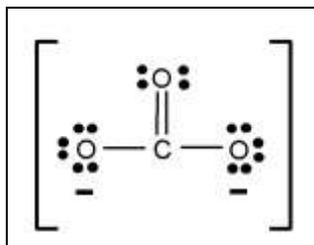

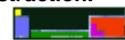Carbon atom   Formal charge = 4 – 0 – ½ (8) = 0
Oxygen atom in C=O   Formal charge = 6 – 4 – ½ (4) = 0
Each oxygen atom in C-O   Formal charge = 6 – 6 – ½ (2) = -1

Note that the sum of the formal charges adds up to the total charge on the ion or molecule.

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    (ii)   To help select the most plausible structure from a set of resonance structures

Again, calculate the formal charge on an atom within a Lewis structure, apply the following formula. Using the two possible Lewis structures for CH_2O with formal charges added as an example, it is possible to determine the most likely Lewis structure for the compound.

Again, the sum of the formal charges adds up to the total charge on the species.

In order to determine which structure is most likely, choose the structure with zero formal charges, and/or formal charges with absolute values as low as possible, and/or keep any negative formal charges on the most electronegative atoms. Since the first structure has no formal charges it is considered to be the most plausible.

If you can draw a Lewis structure that uses all of the valence electrons and fulfils the octets, do NOT seek alternative, "better" structures with lower formal charges unless the question leads you down that path.

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Dative or Co-ordinate bonding (electron deficient species)

Occasionally when drawing a Lewis structure you may encounter a molecule with a central atom that does not have a complete octet of electrons surrounding it. One such example is BF_3. In this molecule the boron atom has only six electrons surrounding it rather than the usually required eight.
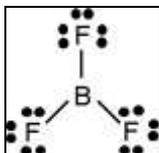
The boron atom is said to be electron deficient. It can make up the octet by forming bonds with other compounds that have non-bonding pairs of electrons, e.g. ammonia (NH_3).
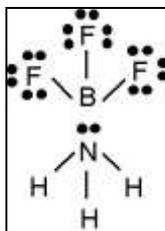

The new, shared pair (covalent bond) formed is made up by using both the electrons from one species (in this case the nitrogen atom in the ammonia molecule) rather than one from each species as in a normal covalent bond. This type of covalent bond is called a **dative** or **co-ordinate** bond.

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- **Electron clouds and the sliding scale of bonding type**

An electron cloud diagram can be thought of as a probability map of where an electron may be found at any one time. In separate atoms this is very simple.
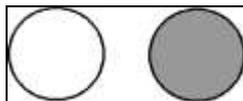
When a chemical bond forms there is a redistribution of the outer electron clouds.

Electrons may be completely transferred (100% ionic bonding)
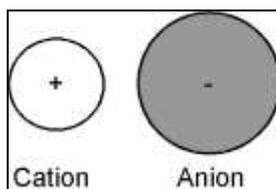
Or completely equally shared (100% covalent, non-polar covalent bonding)

In the simplest terms it is possible to think of compounds being either 100% ionic or 100% covalent but actually it is necessary to consider these two situations being at the extremities of a sliding scale. In fact, most bonds are intermediate between the two, with a largely covalent substance actually having a degree of ionic behavior, and vice-versa.

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Ionic substance with some covalent character

If the cation is small and highly charged it will have the ability to distort the charge cloud around the anion thus;
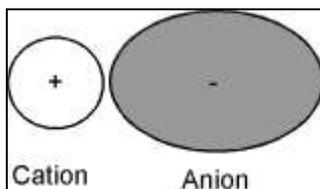
Comparing this diagram with the charge cloud representations of 100% ionic bonding and 100% covalent bonding it is possible to observe the ionic bond beginning to acquire some covalent character. Fajans rules help to assess the degree of distortion (POLARISATION). Distortion will be at a maximum when;

1. The cation is small and highly charged, i.e., has a high charge density.
2. When the anion is large and highly charged, i.e., electrons are more loosely held.

Covalent substance with some ionic character (Polar Covalent)

Electronegativity is the ability of an atom within a covalent bond to attract electrons to itself. When, in a covalent bond, one atom has a higher electronegativity than the other, the electrons are attracted toward that atom leading to a charge cloud distortion thus;

Comparing this diagram with the first two charge cloud representations, it is possible to observe the covalent bond beginning to acquire some ionic character. Using the Pauling scale it is possible to make predictions about the degree of ionic and covalent character in a compound. By considering differences in electronegativity and by using the table below, one can predict the % of covalent and ionic character present in a bond between two atoms.

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Electronegativity difference between the atoms in the covalent bond	Approximate Percentage of ionic character
0.1	0.5
0.5	6
1.0	22
1.5	43
2.0	63
2.5	79
3.0	89

A difference of approximately 1.7 marks the boundary between predominately ionic or covalent character.
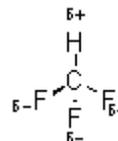
- **Polar bonds and Polar molecules**

In order for a substance to be "polar", bonds within the molecule must carry different charges (i.e., a dipole moment must exist) **AND** the dipoles that are present must **NOT** cancel out due to symmetry. The dipole moment can be indicated by an arrow that points toward the negative charge center with the tail of the arrow indicating the positive charge center, or by using $\delta+$ and $\delta-$ to indicate small areas of positive and negative charge.

For example, consider 2-pentanone and trifluoromethane that are both polar. Like water, (which is also polar), opposite ends of the molecules carry different charges and there is no canceling of the dipoles.
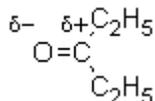
"polar", 2-pentanone   "polar", trifluoromethane

Now consider hexane and carbon tetrachloride, neither are polar molecules but for different reasons.

In Hexane (C_6H_{14}), carbon and hydrogen have very similar electronegativities and as a result the bonds are effectively non-polar. Carbon tetrachloride (CCl_4) on the other hand has four polar C-Cl bonds but because of its symmetrical shape is non-polar overall. The partial positive charge is
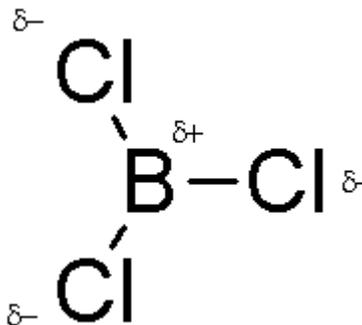
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located at the center of the molecule and the partial negative charges equally spread around it, causing the dipoles to cancel.

Examples of other compounds that are non-polar as a result of symmetry and the cancellation of dipoles are CO_2 and BCl_3.

$$\overset{\delta-}{O} = \overset{\delta+\ \ \delta+}{C} = \overset{\delta-}{O}$$
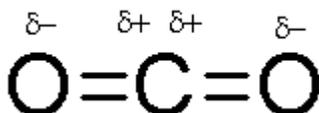
"non-polar", carbon dioxide

$$\overset{\delta-}{Cl}\ \ \ \ \ \ \ \overset{\delta+}{B} - \overset{\delta-}{Cl}\ \ \overset{\delta-}{Cl}$$

"non-polar", boron trichloride

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- **Inter Bonding**

Hydrogen Bonding

Hydrogen is an exceptional element in that when it forms a covalent bond its electron is held to one side of the nucleus leaving the other side completely exposed. Any approaching negatively charged group can get very close to the hydrogen nucleus and this produces an unexpectedly large electrostatic attraction. These electrostatic attractions are exaggerated when H is bonded to a more electronegative element that is small enough to allow a significant intermolecular interaction, i.e., F, O or N. Such intermolecular, electrostatic attractions are called *hydrogen bonds.*

The occurrence of hydrogen bonds has two important consequences;

(i)   It gives substances containing them anomalously high boiling points

(ii)   Substances containing them tend to be more viscous

Both are explained by the increased attraction between molecules caused by hydrogen bonding making it more difficult to separate them. For example, in water, black dots represent oxygen atoms and white dots represent hydrogen atoms.

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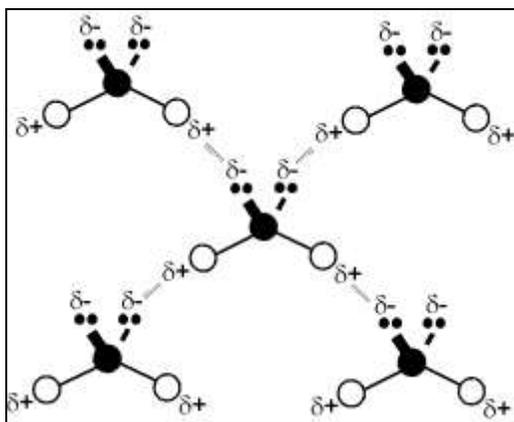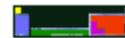
Dipole-Dipole interactions

When molecules that have permanent dipoles come together, they will arrange themselves so that the negative and the positive ends of the molecules attract one another.
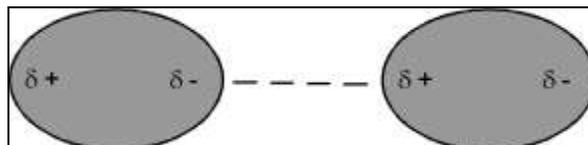
The attractions are called *dipole-dipole interactions*. The molecules eventually align in order to find the best compromise between attraction and repulsion.
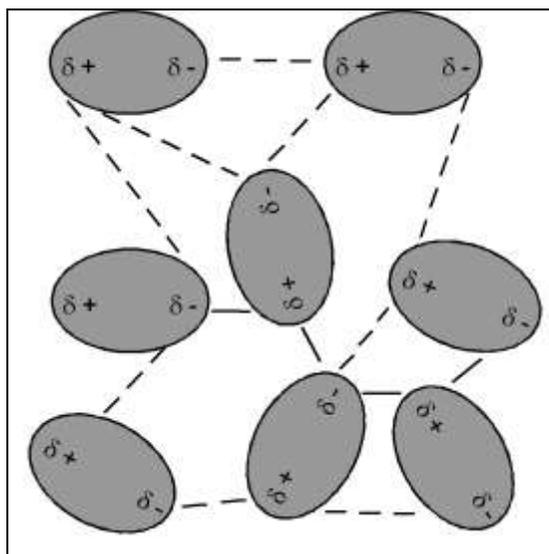
London Dispersion Forces (LDF's)

These are small electrostatic forces that are caused by movement of electrons within the covalent bonds of molecules that would otherwise have no permanent dipole. As one molecule approaches another the electrons of one or both are temporarily displaced owing to their mutual repulsion. This movement causes small, temporary dipoles to be set up which attract one another. These attractions are called *London Dispersion Forces*.

These dispersion forces increase with the size of the molecule and with its surface area. Large molecules with big surface areas have more electrons which have greater POLARIZABILITY. This leads to more dispersion forces, greater attraction and therefore higher boiling points.
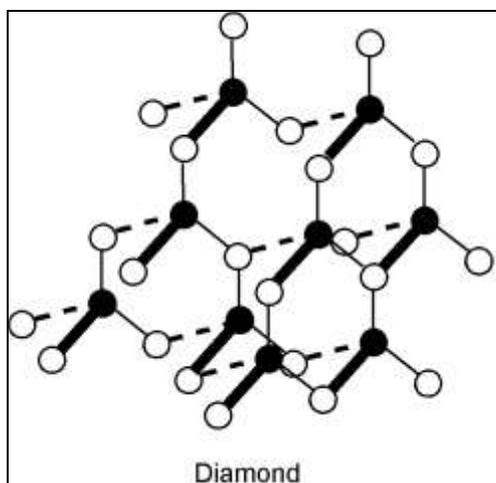
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- **Other aspects of bonding theory**

The solid state

Variations in bond type lead to different structures in solids. Four different types of solid structure and their properties are considered here.

Giant atomic structures (diamond and graphite)

These structures are made of carbon atoms covalently bonded together in a continuous network.

Diamond

The diamond structure is based upon the tetrahedral unit where all of the carbon atoms are bonded to one another with very strong covalent bonds in a huge macro structure. This makes diamond very strong and hard and gives it a high melting and boiling point.
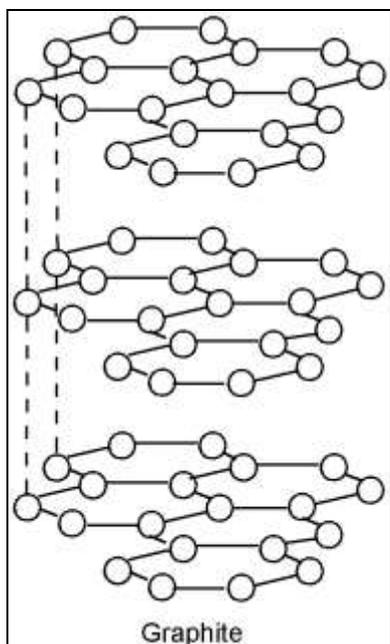
Graphite

Graphite has a layered structure where each carbon atom is bonded to three others in each plane. The structure leads to specific properties;

(i)   It will conduct electricity only in one plane

In the graphite structure each carbon is only bonded to three others. This leaves one of the outer electrons "free". Each carbon atom has one such "free" electron and these are spread out over each layer (delocalized). This leads to a "sea" of electrons similar to that in the metallic structure and graphite's ability to conduct electricity along the layers. Since the electrons cannot move between layers there is no conduction in the vertical plane.

(ii)   It can be used as a lubricant

Weak dispersion forces hold the layers in graphite together represented by the dotted lines on the diagram. As a result they can slide over one another, making graphite a good lubricant.

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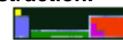
Ionic structures (sodium chloride)
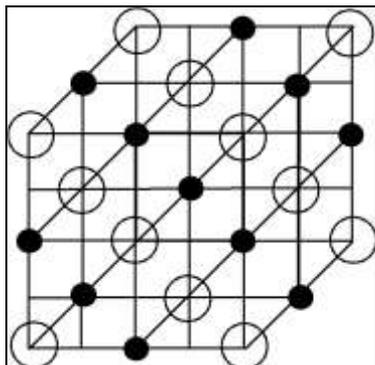
In the ionic structure the lattice of ions is held together by strong electrostatic interactions between them. The strong bonds give ionic solids high melting points. They can only conduct electricity when molten or in solution since in the solid the ions are rigidly held and cannot move.

The charged particles present in an ionic solid explain how and why ionic solids dissolve in water. When an ionic solid dissolves the polar water molecules penetrate the lattice and attach themselves to the ions. The process is called *hydration* and the ions are said to be *hydrated*.

Hydrated Anion

Lattice being attacked by water molecules

Hydrated cation

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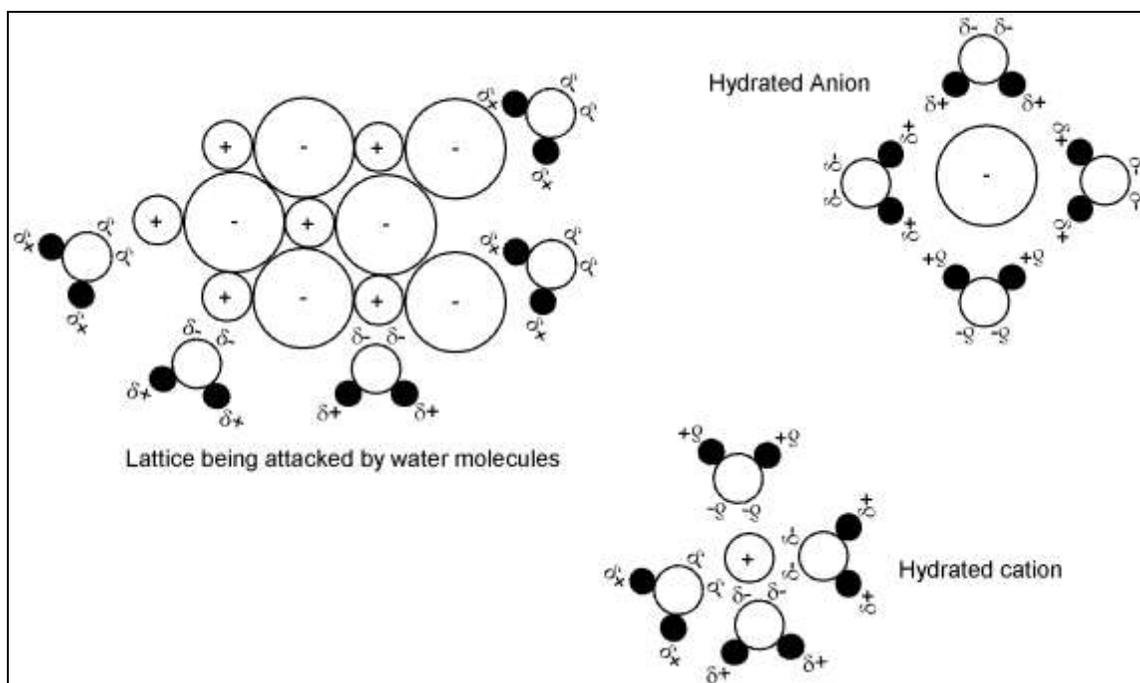
Molecular structures (iodine)
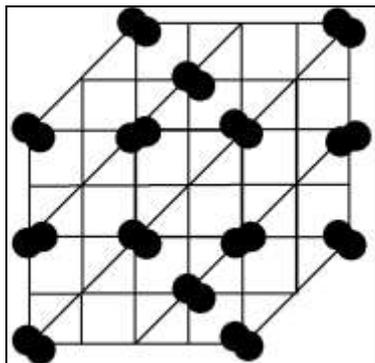
Iodine is held in a similar lattice structure to NaCl but in this case only weak dispersion forces hold the I_2 molecules in place. This means that solid iodine has a very low melting point since there is only a weak interaction between its molecules. In addition there are no charged particles present making iodine a non-conductor.

Metal structures (metallic bonding)

A metals' structure can be considered to be a close packed lattice of positive atoms/ions surrounded by a "sea" of moving electrons. These electrons and their movement cause metals to be good conductors of electricity. The close packed atoms/ions make them good conductors of heat.

The metallic bond is the electrostatic attraction between the positive and negative charges. The flexibility of these bonds makes metals malleable & ductile.

The liquid state

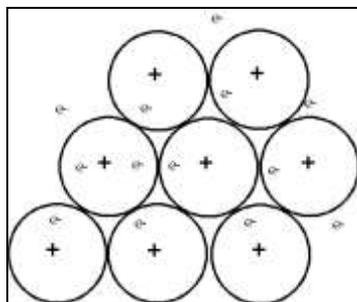In a gas the molecules possess enough energy to overcome the intermolecular forces, and hence move around freely. When a gas is cooled the kinetic energy of its molecules falls and the intermolecular forces become increasingly important. Cooling eventually leads to them having insufficient energy to overcome these forces and the gas condenses to form a liquid.

In a solid the particles have a regular ordered structure and move very little around fixed positions. As solids are heated the particles gain energy and can break away from this ordered arrangement forming a liquid.

The liquid represents the molecules at an intermediate state between the ordered state of the solid and the disordered state of the gas.

Vapor pressure

Consider a liquid in a sealed container. Even if the liquid is below its boiling point a few of the molecules will possess enough energy to overcome the intermolecular forces holding them together and escape into the vapor phase above the liquid. The weaker the intermolecular forces

between the molecules, the easier this process will be and the more molecules will enter the vapor phase. This causes a relatively high vapor pressure. So, in summary, weak intermolecular forces cause liquids to have low boiling points, they are said to be volatile and will have high vapor pressures, and vice-versa.

The gaseous state

Boiling points of the noble gases

On descending group 18 the atoms of the elements get bigger, have more electrons and larger surface areas. This increases the London dispersion forces between them, making them more difficult to separate and increasing their boiling points.

Group 18 Element	He	Ne	Ar	Kr	Xe
Boiling Point / ^{o}C	-269	-246	-186	-152	-108

Boiling points of the Hydrides of Groups 14, 15, 16 and 17

Group 14 hydride	CH_4	SiH_4	GeH_4	SnH_4
Boiling Point / ^{o}C	-161	-112	-90	-

The boiling point increases due to increased size and London dispersion forces.

Group 15 hydride	NH_3	PH_3	AsH_3	SbH_3
Boiling Point / ^{o}C	-33	-87	-60	-25

A similar pattern (of increase in size, dispersion forces and boiling points) is observed here except for ammonia. The ammonia molecules are attracted to one another by hydrogen bonds giving ammonia a much higher boiling point than would normally be predicted.

Group 16 hydride	H_2O	H_2S	H_2Se	H_2Te
Boiling Point / ^{o}C	100	-65	-45	-15

Group 17 hydride	HF	HCl	HBr	HI
Boiling Point / ^{o}C	20	-85	-69	-35

Revised August 2011
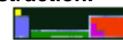
The patterns in groups 16 and 17 resemble that of group 15, with water and hydrogen fluoride respectively exhibiting the higher boiling points associated with hydrogen bonding.

Boiling Points of Group 14, 15, 16 & 17 Hydrides

	Period 2	Period 3	Period 4	Period 5
Boiling Point of group 14 hydrides in oC	-161	-112	-90	-50
Boiling Point of group 15 hydrides in oC	-33	-87	-60	-25
Boiling Point of group 16 hydrides in oC	100	-65	-45	-15
Boiling Point of group 17 hydrides in oC	20	-85	-69	-35
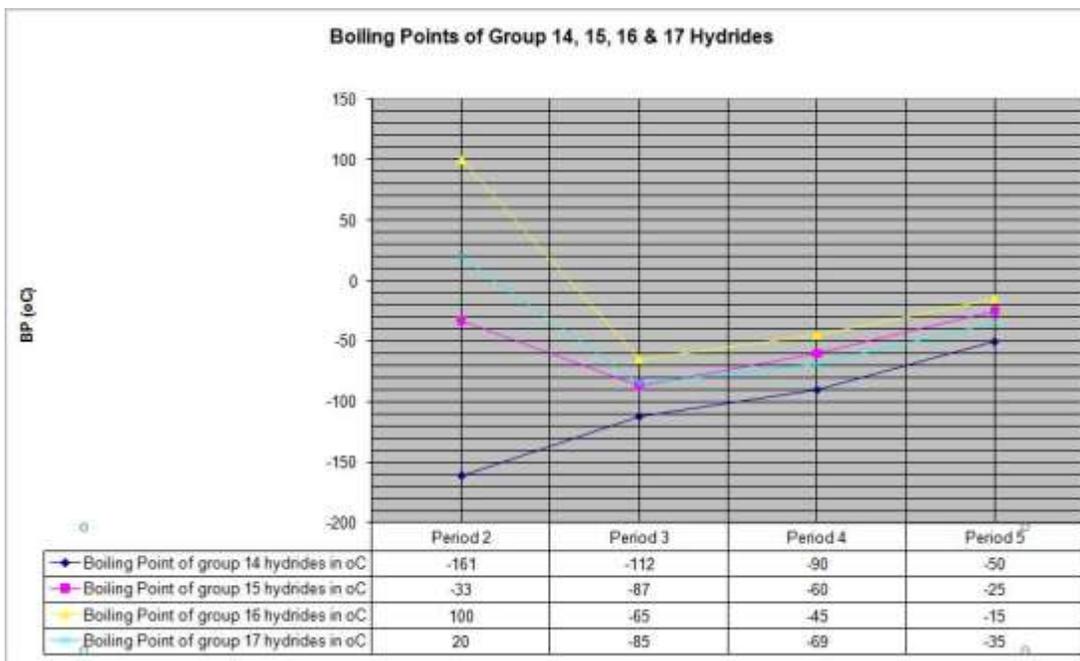
Revised August 2011

- **Summary of bonding and the relationship to properties**

Substances

IONIC (GIANT lattice)	DISCRETE COVALENT (INDIVIDUAL molecules)	GIANT COVALENT (MACRO molecular)	METALS/ALLOYS (MIXTURES of metals)
+ve ion and –ve ion formed via transfer of electrons held together in giant lattice with strong electrostatic interaction	Small groups of atoms covalently bonded together by sharing electrons	Massive structures of atoms covalently bonded together	Close packed array of atoms (ions) with "sea" of free moving electrons
Metal + Non-Metal e.g. KCl, MgF_2, Na_2SO_4 etc.	Non-Metal + Non-Metal (compounds/polyatomic ions) e.g. CO_2, PCl_6^- (Lewis structures/shape)	Elements and some compounds e.g. Graphite & diamond (carbon), Si, SiO_2	Metals e.g. Na, Al, Au, Stainless Steel (Fe/C/Cr), Bronze (Cu/Sn), Brass (Cu/Zn)
STRONG bonds high m.p/b.p poor conductors of electricity when solid (ions NOT free to move), good when liquid or in solution (dissolved) will dissolve in polar solvents	Strong covalent bond within the molecule, but molecules attracted to one another with **WEAK IMF** low m.p/b.p, often liquids or gases at RT; **LDF – (induced dipoles) Dipole – (perm. dipoles) H-Bonds – (H - N/O/F)** poor conductors	STRONG bonds high m.p/b.p hard poor conductors	STRONG (but flexible) bonds high m.p/b.p good conductors of electricity ("sea" of electrons) and heat (close packed) malleable (can be shaped), ductile (can be drawn into thin wires), luster (shiny),