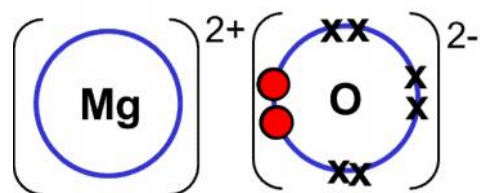


## 2. Bonding

### Ionic Bonding

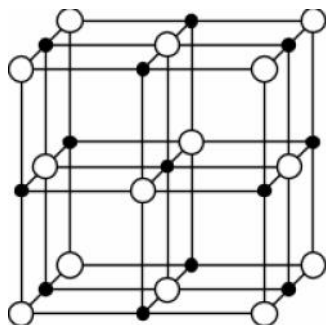
Metal atoms lose electrons to form +ve ions.  
Non-metal atoms gain electrons to form -ve ions.



Mg goes from  $1s^2 2s^2 2p^6 3s^2$   
to  $Mg^{2+} 1s^2 2s^2 2p^6$

O goes from  $1s^2 2s^2 2p^4$  to  
 $O^{2-} 1s^2 2s^2 2p^6$

Ionic crystals have the structure of giant lattices of ions



**An ionic bond** is the strong **electrostatic force** of attraction between **oppositely charged ions** formed by electron transfer.

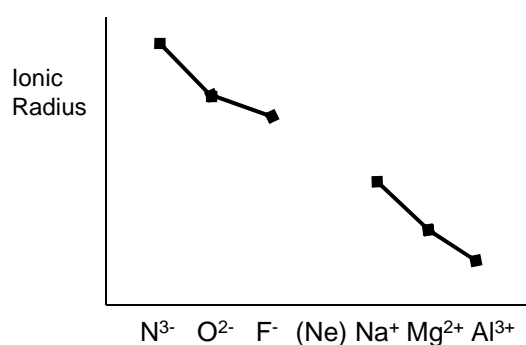
Ionic bonding is stronger and the melting points higher when **the ions are smaller** and/ or have **higher charges**. E.g. MgO has a higher melting point than NaCl as the ions involved ( $Mg^{2+}$  &  $O^{2-}$  are smaller and have higher charges than those in NaCl,  $Na^+$  &  $Cl^-$ )

### Ionic Radii

Positive ions are smaller compared to their atoms because it has one less shell of electrons and the ratio of protons to electrons has increased so there is greater net force on remaining electrons holding them more closely.

The negative ions formed from groups five to seven are larger than the corresponding atoms.

The negative ion has more electrons than the corresponding atom but the same number of protons. So the pull of the nucleus is shared over more electrons and the attraction per electron is less, making the ion bigger.



$N^{3-}$ ,  $O^{2-}$ ,  $F^-$  and  $Na^+$ ,  $Mg^{2+}$ ,  $Al^{3+}$  all have the same electronic structure (of the noble gas Ne)

There are increasing numbers of protons from N to F and then Na to Al but the same number of electrons. The effective nuclear attraction per electron therefore increases and ions get smaller

Within a group the size of the ionic radii increases going down the group. This is because as one goes down the group the ions have more shells of electrons.

## Ionic Bonding

### Evidence for the existence of ions

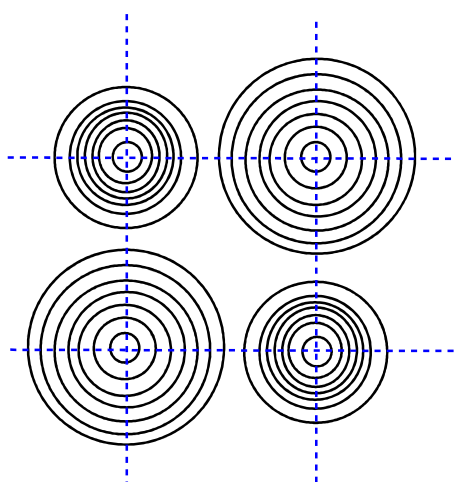
#### X-ray diffraction: Electron density map of NaCl

These maps show the likelihood of finding electrons in a region

The contours are lines of equal electron density

The maps show that for NaCl

- The ions are arranged in a regular pattern.
- The chloride ions are larger than the sodium ions

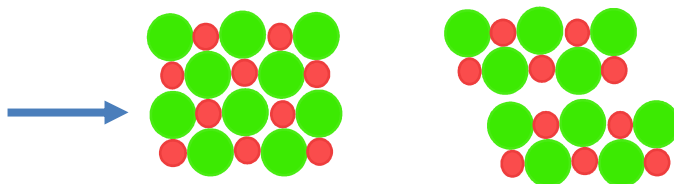


The ions are discrete or separate, because the electron density falls to zero between the ions

The electron density map does not, however, show the edge of the ion and so it is difficult to measure the radius of the ion from an electron density map

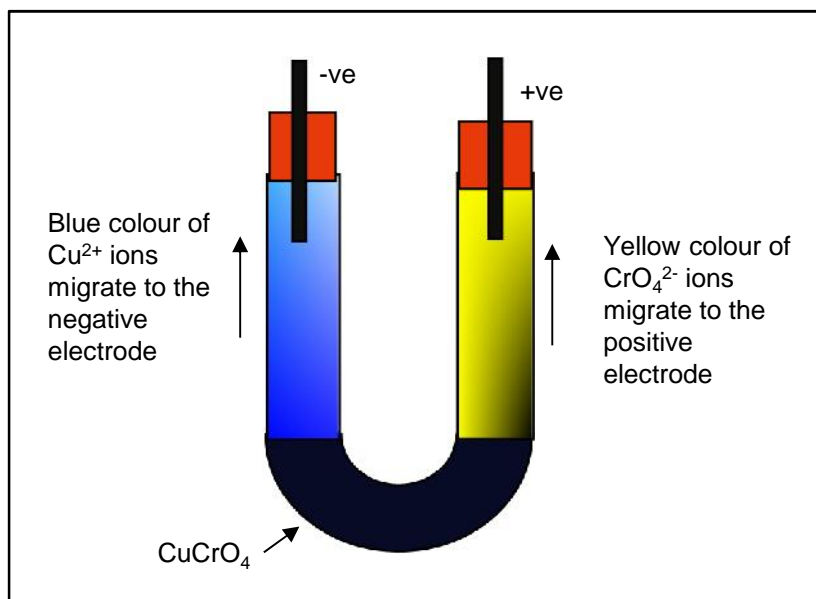
### Physical properties of Ionic Compounds

- high melting points ( there are strong attractive forces between the ions)
- non conductor of electricity when solid (ions are held together tightly and can not move)
- conductor of electricity when in solution or molten. ( ions are free to move)
- brittle / easy to cleave apart



A little force will push the ions along and ions will be next to similar ions. There will be a force of repulsion between like ions, pushing the layers apart

### Migration of ions



Blue colour of  $\text{Cu}^{2+}$  ions migrate to the negative electrode

Yellow colour of  $\text{CrO}_4^{2-}$  ions migrate to the positive electrode



A drop of potassium Manganate solution, which is purple, is placed on moist filter paper on a microscope slide and the ends of the slide are connected to a 24 V DC power supply. After ten minutes the purple colour of the  $\text{MnO}_4^-$  ion has migrated to the positive electrode

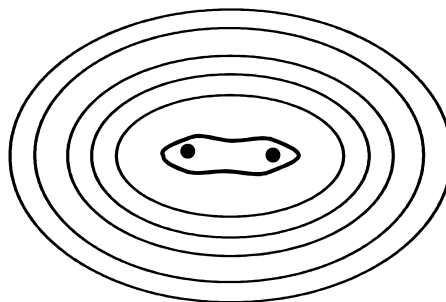
## Covalent Bonding

A covalent bond is strong and is caused by the electrostatic attraction between the bonding shared pair of electrons and the two nuclei.

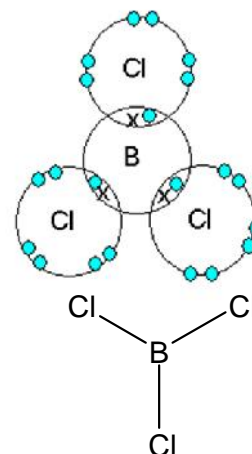
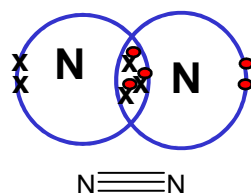
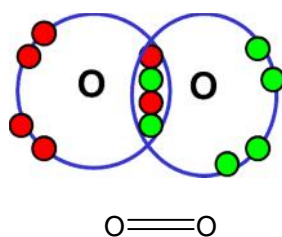
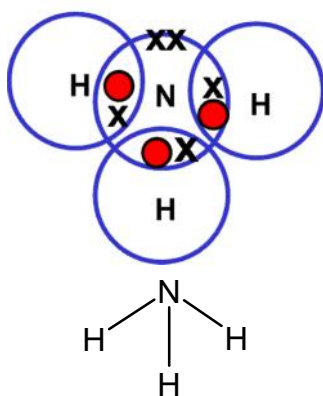
The strength of covalent bond can be demonstrated by the high melting points of giant atomic structures like diamond and graphite. They have high melting points because they contain many strong covalent bonds in a macromolecular structure. It takes a lot of energy to break the many strong bonds.

The X-ray diffractions for the hydrogen molecule show high concentration of negative charge between H nuclei. This negative charge is strongly attracted by both nuclei so attractive interactions exceed repulsive ones

In a covalent compound there is significant electron density between the atoms



## Electron Configuration Diagrams



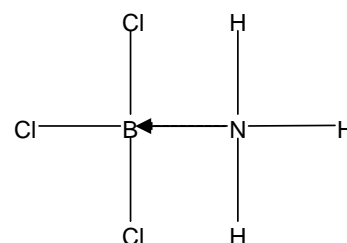
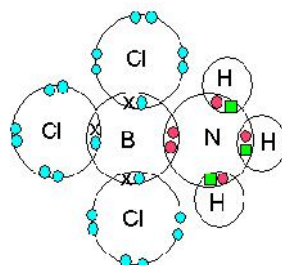
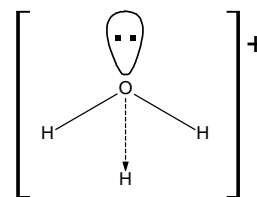
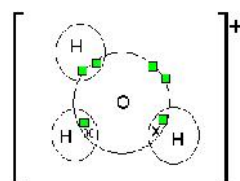
### Effect of multiple bonds on bond strength and length.

Nuclei joined by multiple (i.e. double and triple) bonds have a **greater electron density** between them. This causes an **greater force of attraction** between the nuclei and the electrons between them, resulting in a **shorter bond length** and **greater bond strength**.

## Dative Covalent bonding

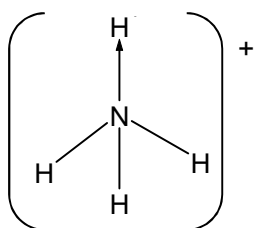
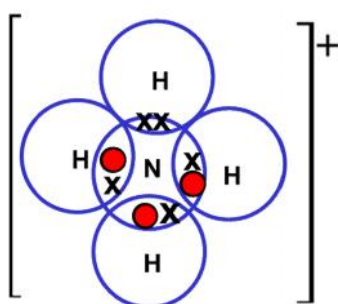
A **Dative covalent bond** forms when the **shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**. A **dative covalent bond** is also called co-ordinate bonding.

Common examples you should be able to draw that contain dative covalent bond (e.g.  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{NH}_3\text{BF}_3$ )

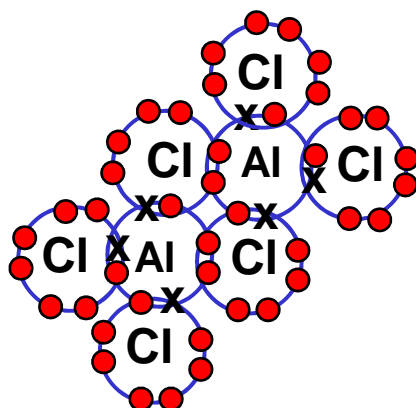


The direction of the arrow goes from the atom that is providing the lone pair to the atom that is deficient

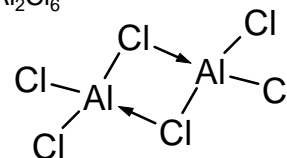
The ammonium ion  $\text{NH}_4^+$



The dative covalent bond acts like an ordinary covalent bond when thinking about shape so in  $\text{NH}_4^+$  the shape is tetrahedral



Two aluminium chloride ( $\text{AlCl}_3$ ) molecules join together through two dative bonds to form the dimer  $\text{Al}_2\text{Cl}_6$



## Shape of molecules

Name	No bonding pairs	No lone pairs	Diagram	Bond angle	Examples
linear	2	0		180	CO <sub>2</sub> , CS <sub>2</sub> , HCN, BeF <sub>2</sub>
Trigonal planar	3	0		120	BF <sub>3</sub> , AlCl <sub>3</sub> , SO <sub>3</sub> , NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
Tetrahedral	4	0		109.5	SiCl <sub>4</sub> , SO <sub>4</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>
Trigonal pyramidal	3	1		107	NCl <sub>3</sub> , PF <sub>3</sub> , ClO <sub>3</sub> , H <sub>3</sub> O <sup>+</sup>
Bent	2	2		104.5	OCl <sub>2</sub> , H <sub>2</sub> S, OF <sub>2</sub> , SCl <sub>2</sub>
Trigonal Bipyramidal	5	0		120 and 90	PCl <sub>5</sub>
Octahedral	6	0		90	SF <sub>6</sub>

### How to explain shape

1. State number of bonding pairs and lone pairs of electrons.
2. State that electron pairs repel and try to get as far apart as possible (or to a position of minimum repulsion.)
3. If there are no lone pairs state that the electron pairs repel equally
4. If there are lone pairs of electrons, then state that lone pairs repel more than bonding pairs.
5. State actual shape and bond angle.

**Remember lone pairs repel more than bonding pairs and so reduce bond angles (by about 2.5° per lone pair in above examples)**

Occasionally more complex shapes are seen that are variations of octahedral and trigonal bipyramidal where some of the bonds are replaced with lone pairs. You do not need to learn the names of these but ought to be able to work out these shapes using the method below



Square planar  
Bond angle  $90^\circ$

e.g.  $\text{XeF}_4$

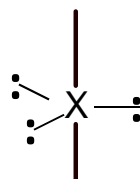


Xe has 8 electrons in its outer shell. 4 F's add 4 more electrons. This makes a total of 12 electrons made up of 4 bond pairs and 2 lone pairs. This means it is a variation of the 6 bond pair shape (octahedral)



Bond angle  $\sim 89^\circ$   
(Reduced by lone pair)

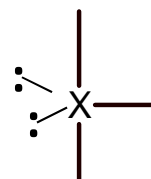
e.g.  $\text{BrF}_5$



Bond angle  $180^\circ$

e.g.  $\text{I}_3^-$

Cl has 7 electrons in its outer shell. 3 F's add 3 more electrons. This makes a total of 10 electrons made up of 3 bond pairs and 2 lone pairs. This means it is a variation of the 5 bond pair shape (trigonal bipyramidal)



Bond angle  $\sim 89^\circ$   
(Reduced by lone pairs)

e.g.  $\text{ClF}_3$



I has 7 electrons in its outer shell. 4 F's add 4 more electrons. Remove one electron as positively charged. This makes a total of 10 electrons made up of 4 bond pairs and 1 lone pair. This means it is a variation of the 5 bond pair shape (trigonal bipyramidal)



Bond angles  $\sim 119^\circ + 89^\circ$   
(Reduced by lone pair)

e.g.  $\text{SF}_4$  &  $\text{IF}_4^+$



## Electronegativity and intermediate bonding

### Definition

**Electronegativity** is the relative tendency of an **atom in a covalent bond** in a molecule to **attract electrons** in a covalent bond to itself.

F, O, N and Cl are the most electronegative atoms

Electronegativity is measured on the **Pauling scale** (ranges from 0 to 4)

The **most** electronegative element is **fluorine** and it is given a value of 4.0

### Factors affecting electronegativity

Electronegativity increases across a period as the **number of protons increases** and the atomic radius decreases because the **electrons in the same shell** are pulled in more.

It decreases down a group because the **distance** between the nucleus and the outer electrons **increases and the shielding** of inner shell electrons increases

### Intermediate bonding

Ionic and covalent bonding are the extremes of a continuum of bonding type. Differences in electronegativity between elements can determine where a compound lies on this scale

A compound containing elements of similar electronegativity and hence a **small electronegativity difference** will be purely **covalent**

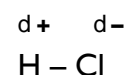
A compound containing elements of very different electronegativity and hence a very **large electronegativity difference** (> 1.7) will be **ionic**

### Formation of a permanent dipole – (polar covalent) bond

A **polar covalent bond** forms when the elements in the bond have **different electronegativities**. (Of around 0.3 to 1.7)

When a bond is a **polar covalent bond** it has an **unequal distribution of electrons** in the bond and produces a **charge separation, (dipole)** + - ends.

The element with the larger electronegativity in a polar compound will be the - end



## Polar and Non Polar molecules

### Symmetric molecules

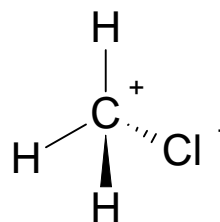
A symmetric molecule (**all bonds identical and no lone pairs**) will **not** be polar **even if individual bonds within the molecular ARE polar**.

The individual dipoles on the bonds '**cancel out**' due to the symmetrical shape of the molecule. There is no **NET** dipole moment: the **molecule is NON POLAR**

e.g.  $\text{CCl}_4$  will be non-polar whereas  $\text{CH}_3\text{Cl}$  will be polar



$\text{CO}_2$  is a symmetrical molecule and is a non-polar molecule

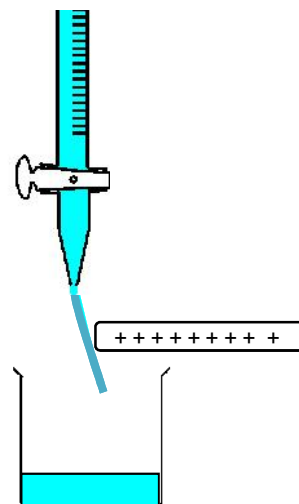


## Experiment effect of charged rod on polar/non-polar liquids

In this experiment, a charged rod (formed by rubbing a plastic rod) is brought close to a jet of liquid flowing from a burette.

If the liquid is polar, the jet of liquid will be attracted to the electrostatic force of the rod. The dipoles in the polar molecules will all align and the negative end  $-$  will be attracted to the positive rod (or vice versa). The stronger the dipole the more the deflection of the jet.

Non-polar liquids will not be deflected and attracted to the charged rod

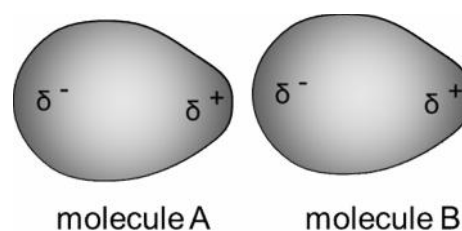


## Intermolecular Forces

### London Forces

London forces occur between **all molecular substances** and noble gases. **They do not occur in ionic substances.**

**London Forces** are also called **instantaneous, induced dipole-dipole interactions**. They occur between all simple covalent molecules and the separate atoms in noble gases. In any molecule the electrons are moving constantly and randomly. As this happens the electron density can fluctuate and parts of the molecule become more or less negative i.e. small temporary or transient dipoles form. These temporary dipoles can cause dipoles to form in neighbouring molecules. These are called induced dipoles. The induced dipole is always the opposite sign to the original one.



### Main factor affecting size of London Forces

The **more electrons** there are in the molecule the higher the chance that temporary dipoles will form. This makes the **London forces stronger between the molecules** and more energy is needed to break them so boiling points will be greater.

The increasing boiling points of the halogens down the group 7 series can be explained by the increasing number of electrons in the bigger molecules causing an increase in the size of the London forces between the molecules. This is why  $I_2$  is a solid whereas  $Cl_2$  is a gas.

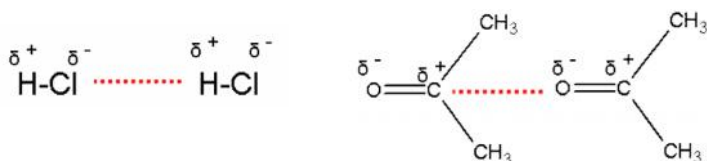
The increasing boiling points of the alkane homologous series can be explained by the increasing number of electrons in the bigger molecules causing an increase in the size of the London forces between molecules.

The **shape** of the molecule can also have an effect on the size of the London forces. Long **straight chain** alkanes have a **larger surface area of contact between molecules** for London forces to form than compared to spherical shaped **branched alkanes** and so have stronger London forces.



## Permanent dipole-dipole forces

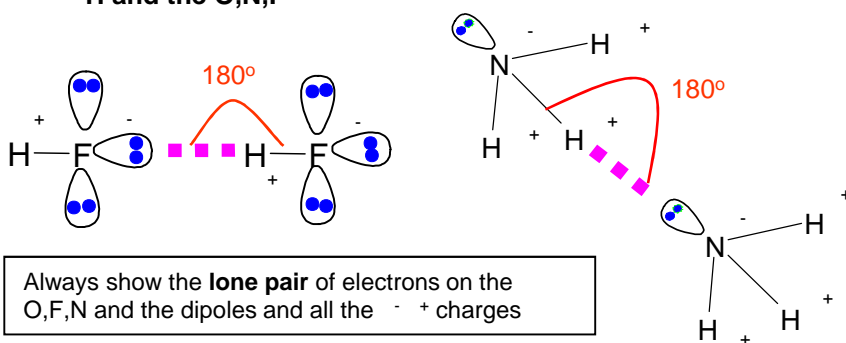
- Permanent dipole-dipole forces occurs between polar molecules
- It is stronger than van der waals and so the compounds have higher boiling points
- Polar molecules have a permanent dipole. (commonly compounds with C-Cl, C-F, C-Br H-Cl, C=O bonds)
- Polar molecules are asymmetrical and have a bond where there is a significant **difference in electronegativity** between the atoms.



Permanent dipole forces occur in addition to London forces

## Hydrogen bonding

It occurs in compounds that have a **hydrogen atom attached to one of the three most electronegative atoms of nitrogen, oxygen and fluorine**, which must have an available lone pair of electrons. e.g. a **-O-H -N-H F- H** bond. There is a **large electronegativity difference** between the **H and the O,N,F**



Always show the **lone pair** of electrons on the O,F,N and the dipoles and all the  $\delta^-$   $\delta^+$  charges

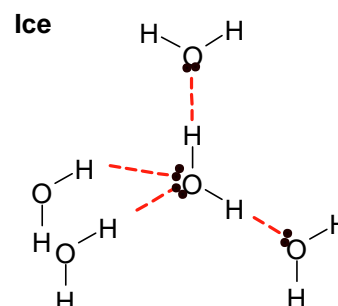
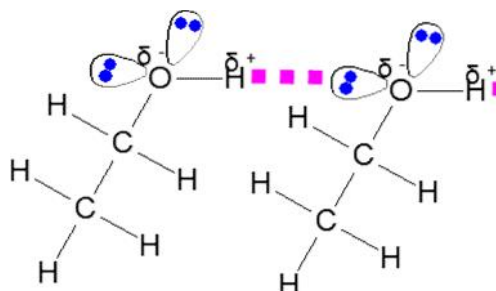
Hydrogen bonding occurs in addition to London forces

The hydrogen bond should have an bond angle of  $180^\circ$  with one of the bonds in one of the molecules

The bond angle is  $180^\circ$  around the H atom because there are two pairs of electrons around the H atom involved in the hydrogen bond. These pairs of electrons repel to a position of minimum repulsion, as far apart as possible.

Alcohols, carboxylic acids, proteins, amides all can form hydrogen bonds

Alcohols form hydrogen bonds. This means alcohols have higher boiling points and relatively low volatility compared to alkanes with a similar number of electrons

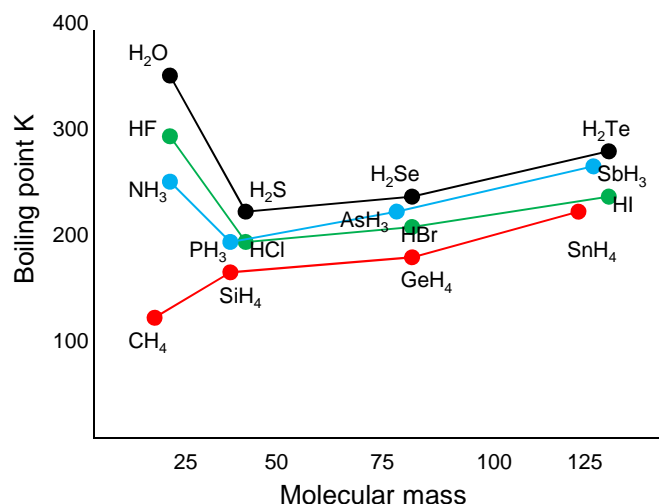


In ice the molecules are held further apart by the hydrogen bonds than in liquid water and this explains the lower density of ice

Hydrogen bonding is stronger than the other two types of intermolecular bonding.

The **anomalously high** boiling points of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HF}$  are caused by the hydrogen bonding between these molecules in addition to their London forces. The additional forces require more energy to break and so have higher boiling points

The general increase in boiling point from  $\text{H}_2\text{S}$  to  $\text{H}_2\text{Te}$  or from  $\text{HCl}$  to  $\text{HI}$  is caused by increasing London forces between molecules due to an increasing number of electrons.



## Solvents and Solubility

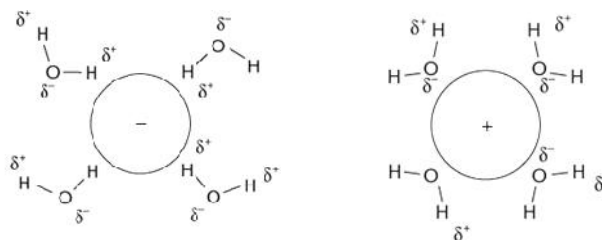
Solubility of a solute in a solvent is a complicated balance of energy required to break bonds in the solute and solvent against energy given out making new bonds between the solute and solvent.

### Ionic substances dissolving in water

When an ionic lattice dissolves in water it involves breaking up the bonds in the lattice and forming new bonds between the metal ions and water molecules.

The **negative** ions are attracted to the  $\delta^+$  **hydrogens** on the **polar water** molecules and the positive ions are attracted to the  $\delta^-$  oxygen on the polar water molecules.

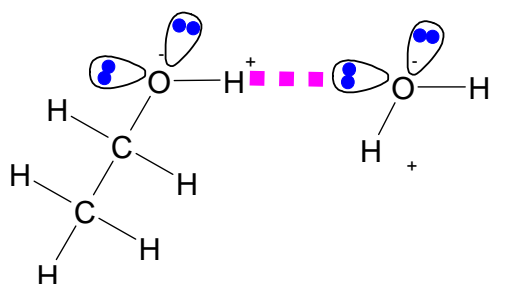
hydration of the ions



The higher the **charge density** the greater the hydration enthalpy (e.g. **smaller ions** or **ions with larger charges**) as the ions attract the water molecules more strongly.

### Solubility of simple alcohols

The smaller alcohols are soluble in water because they can form hydrogen bonds with water. The longer the hydrocarbon chain the less soluble the alcohol.



### Insolubility of compounds in water

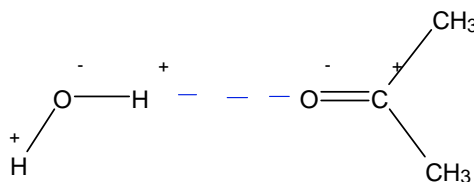
Compounds that cannot form hydrogen bonds with water molecules, e.g. polar molecules such as haloalkanes or non polar substances like hexane will be insoluble in water.

## Solubility in non-aqueous solvents

Compounds which have similar intermolecular forces to those in the solvent will generally dissolve

**Non-polar solutes will dissolve in non-polar solvents.** e.g. Iodine which has only London forces between its molecules will dissolve in a non polar solvent such as hexane which also only has London forces.

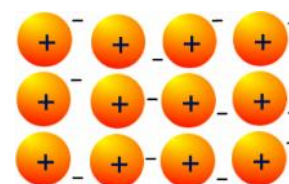
Propanone is a useful solvent because it has both polar and non polar characteristics. It can form London forces with some non polar substances such as octane with its CH<sub>3</sub> groups. Its polar C=O bond can also hydrogen bond with water.



## Metallic bonding

Metals consist of giant lattices of metal ions in a sea of delocalised electrons

Definition: A **metallic bond** is the **electrostatic force** of attraction between the **positive metal ions** and the **delocalised electrons**



sodium

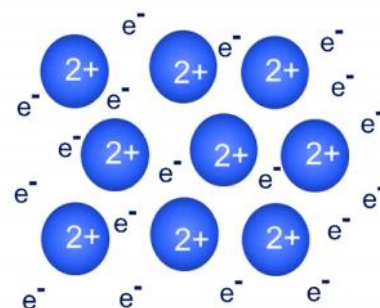
The three main factors that affect the strength of a **metallic bond** are:

1. Number of protons/ Strength of nuclear attraction.  
*The more protons the stronger the bond*
2. Number of delocalised electrons per atom (the outer shell electrons are delocalised)  
*The more delocalised electrons the stronger the bond*
3. Size of ion.  
*The smaller the ion, the stronger the bond.*

Metals have high melting points because the strong electrostatic forces between positive ions and sea of delocalised electrons require a lot of energy to break

### Example

**Mg has stronger metallic bonding than Na and hence a higher melting point.** The **Metallic** bonding gets stronger because in Mg there are more electrons in the outer shell that are released to the sea of electrons. The Mg ion is also smaller and has one more proton. There is therefore a stronger electrostatic attraction between the **positive metal ions** and the **delocalised electrons** and **higher** energy is needed to break bonds.



magnesium

Metals can conduct electricity well because the delocalised electrons can move through the structure

Metals are malleable because the positive ions in the lattice are all identical. So the planes of ions can slide easily over one another. The attractive forces in the lattice are the same whichever ions are adjacent

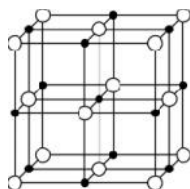
## 2B Structure: ionic, metallic, molecular and giant covalent (macromolecular).

You should be able to draw the following diagrams or describe the structure in words to show the four different types of crystal. You should also be able to explain the properties of these solids.

**Giant lattices** are present in:

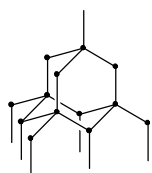
- ionic solids (giant ionic lattices)
- covalently bonded solids, such as diamond, graphite and silicon(IV) oxide (giant covalent lattices)
- solid metals (giant metallic lattices)

### Ionic: sodium chloride



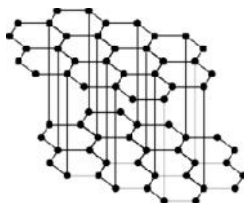
Giant Ionic lattice showing alternate  $\text{Na}^+$  and  $\text{Cl}^-$  ions

### Giant Covalent: diamond



Tetrahedral arrangement of carbon atoms. 4 covalent bonds per atom

### Giant Covalent: Graphite

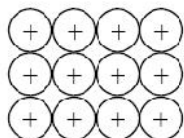


Planar arrangement of carbon atoms in layers. 3 covalent bonds per atom in each layer. 4<sup>th</sup> outer electron per atom is delocalised. Delocalised electrons between layers.

Both these macromolecular structures have very high melting points because of strong covalent forces in the giant structure. It takes a lot of energy to break the **many strong** covalent bonds

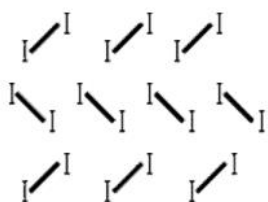
### Metallic: magnesium or sodium

Use this diagram for any metal



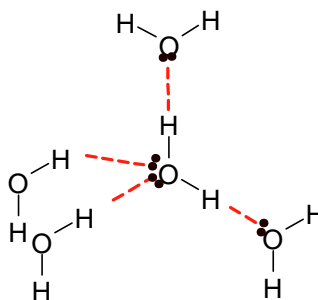
Giant metallic lattice showing close packing magnesium ions

### Molecular: Iodine



Regular arrangement of  $\text{I}_2$  molecules held together by weak London forces

### Molecular: Ice



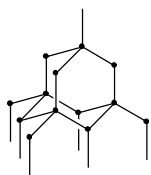
This is a difficult diagram to draw.

The main point to show is a central water molecule with two ordinary covalent bonds and two hydrogen bonds in a tetrahedral arrangement

The molecules are held further apart than in liquid water and this explains the lower density of ice

# Carbon Allotropes

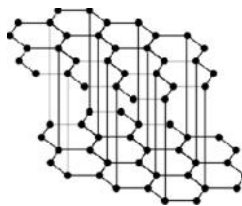
## Macromolecular: diamond



Tetrahedral arrangement of carbon atoms. 4 covalent bonds per atom

Diamond cannot conduct electricity because all 4 electrons per carbon atoms are involved in covalent bonds. They are localised and cannot move

## Macromolecular: Graphite



Planar arrangement of carbon atoms in layers. 3 covalent bonds per atom in each layer. 4<sup>th</sup> outer electron per atom is delocalised. Delocalised electrons between layers.

Graphite can conduct electricity well between layers because one electron per carbon is free and delocalised, so electrons can move easily along layers.

It does not conduct electricity between layers because the energy gap between layers is too large for easy electron transfer.

Both these macromolecular structures have very high melting points because of strong covalent forces in the giant structure. It takes a lot of energy to break the **many strong** covalent bonds

## Graphene

Graphene is a new substance that is a one layer of graphite. i.e. 3 covalent bonds per atom and the 4<sup>th</sup> outer electron per atom is delocalised.

These have very high tensile strength because of the strong structure of many strong covalent bonds

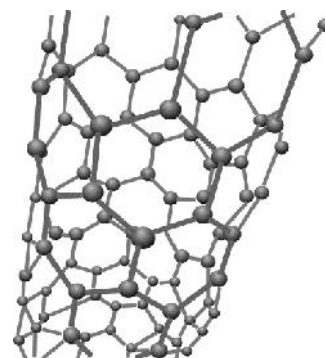
Graphene can conduct electricity well along the structure because one electron per carbon is free and delocalised, so electrons can move easily along the structure.

## Carbon nanotubes

These have very high tensile strength because of the strong structure of many strong covalent bonds

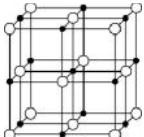
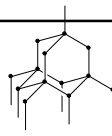
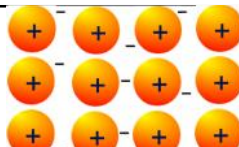
Nanotubes can conduct electricity well along the tube because one electron per carbon is free and delocalised, so electrons can move easily along the tube.

Nanotubes have potentially many uses. One being the potential to us as vehicles to deliver drugs to cells.



There are delocalized electrons in buckminsterfullerene.

## Bonding and Structure

Bonding	Structure	Examples
Ionic : <b>electrostatic force</b> of attraction between <b>oppositely charged ions</b>	 <p style="text-align: center;"><b>Giant Ionic Lattice</b></p>	<b>Sodium chloride</b> Magnesium oxide
Covalent : <b>shared pair</b> of electrons	<b>Simple molecular:</b> With intermolecular forces (London forces, permanent dipoles, hydrogen bonds) between molecules	<b>Iodine</b> <b>Ice</b> Carbon dioxide Water Methane
Covalent : <b>shared pair</b> of electrons	<b>Macromolecular:</b> giant molecular structures.	 <p><b>Diamond</b> <b>Graphite</b> Silicon dioxide Silicon</p>
<b>Metallic: electrostatic force</b> of attraction between the <b>metal positive ions</b> and the <b>delocalised electrons</b>	 <p style="text-align: center;"><b>Giant metallic lattice</b></p>	<b>Magnesium, Sodium</b> (all metals)

Only use the words **molecules** and **intermolecular forces** when talking about simple molecular substances

Property	Ionic	Molecular (simple)	Macromolecular	Metallic
<b>boiling and melting points</b>	high- because of giant lattice of ions with strong electrostatic forces between oppositely charged ions.	low- because of weak intermolecular forces between molecules (specify type e.g London forces/hydrogen bond)	high- because of many strong covalent bonds in macromolecular structure. Take a lot of energy to break the many strong bonds	high- strong electrostatic forces between positive ions and sea of delocalised electrons
<b>Solubility in water</b>	Generally good	generally poor	insoluble	insoluble
<b>conductivity when solid</b>	poor: ions can't move/ fixed in lattice	poor: no ions to conduct and electrons are localised (fixed in place)	diamond and sand: poor, because electrons can't move (localised) graphite: good as free delocalised electrons between layers	good: delocalised electrons can move through structure
<b>conductivity when molten</b>	good: ions can move	poor: no ions	poor	(good)
<b>general description</b>	crystalline solids	mostly gases and liquids	solids	shiny metal Malleable as the positive ions in the lattice are all identical. So the planes of ions can slide easily over one another -attractive forces in the lattice are the same whichever ions are adjacent