

## 2.26 Intermolecular Forces

**Intermolecular** forces are the relatively weak forces that exist between molecules. These govern the physical properties such as boiling point, melting point, solubility in solvents and viscosity.

**Intramolecular** forces are the forces within a molecule i.e. covalent bonds which are strong. These generally govern the chemical properties of a compound.

Remember molecules are covalently bonded substances. Intermolecular forces are only important between covalent molecules. They are not important in substances with ionic or metallic bonding.

There are three main types of intermolecular forces: London forces, permanent dipole bonding, and hydrogen bonding.

### London Forces

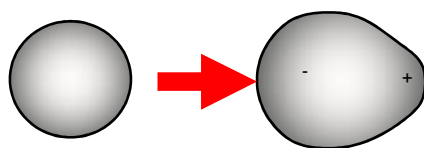
There are various different names for this type of force. They are also called **instantaneous, induced dipole-dipole interactions**, or **dispersion forces** or by some exam boards **Van der Waals Forces**

Van der Waals more correctly is used to describe all the different types of intermolecular forces. Some exam boards use it to just mean these weak dispersion forces

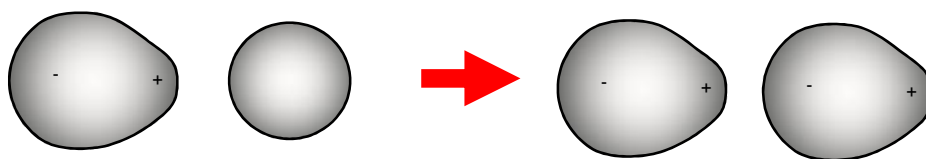
London forces occur between **all molecular substances** and separate atoms in noble gases. In theory they can occur between ions but they are insignificant compared to the ionic attractions so in exam answers do not say that they occur in ionic or metallic substances.

#### How do London forces occur?

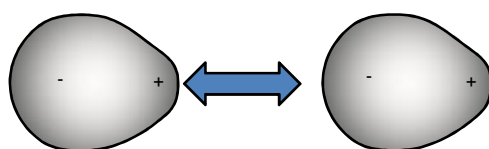
In any molecule the electrons are moving constantly and randomly. As this happens the electron density can fluctuate and parts of the molecule temporarily become more or less negative i.e. small temporary or transient dipoles form.



These temporary dipoles can cause the opposite charge dipoles to form in neighbouring molecules. These are called induced dipoles. The induced dipole is always the opposite sign to the original one.



There is then an attractive force between the opposite dipoles in the neighbouring molecules



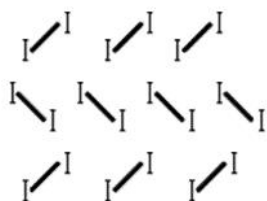
### Main factor affecting size of London Forces

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.

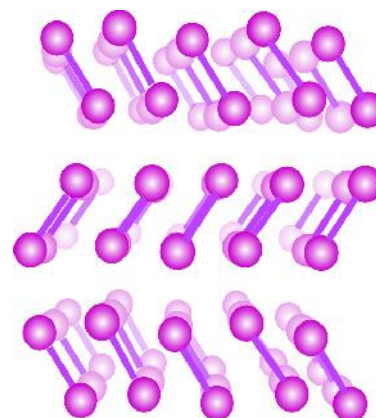
Element	No of electrons in molecule	Boiling Point (°C)	Physical State
Fluorine	18	-188	Gas
Chlorine	34	-35	Gas
Bromine	70	59	Liquid
Iodine	106	184	Solid

#### Molecular: Iodine



There are covalent bonds between the iodine atoms in the  $I_2$  molecule

The crystals contain a regular arrangement of  $I_2$  molecules held together by weak London intermolecular forces



#### Properties of molecular crystals

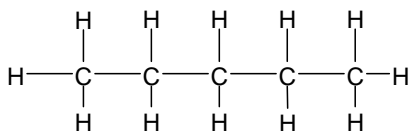
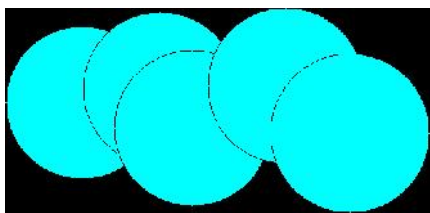
Low melting and boiling points because the London forces are weak

Non conductor of electricity in any state because no charged particles are present

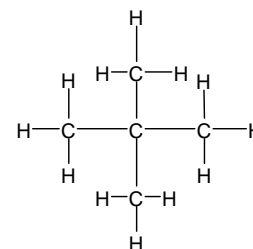
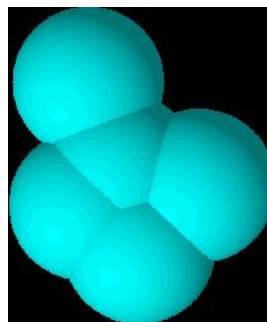
Low solubility in water because iodine cannot form strong forces (hydrogen bonds) with water

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 .



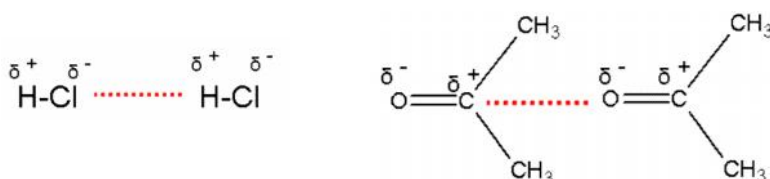
Pentane B.p.36 °C



2,2 Dimethylpropane  
B.p.10 °C

## Permanent dipole-dipole forces

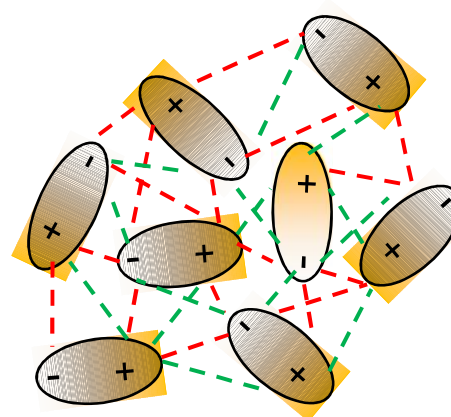
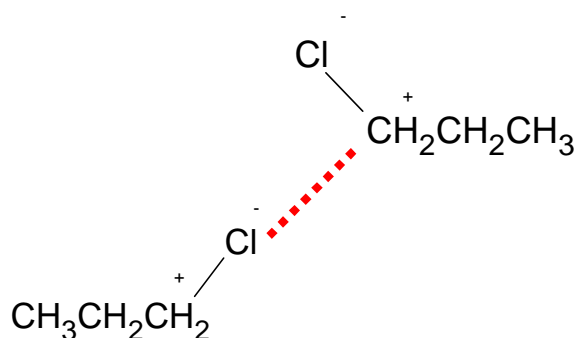
- Permanent dipole-dipole forces occurs between polar molecules
- It is stronger than van der waals and so the compounds have higher boiling points
- Polar molecules have a permanent dipole. (commonly compounds with C-Cl, C-F, C-Br H-Cl, C=O bonds)
- Polar molecules are asymmetrical and have a polar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



Permanent dipole forces occur in addition to London forces

These permanent dipole-dipole forces of attraction between molecules are stronger than London forces and they occur in addition to London Forces.

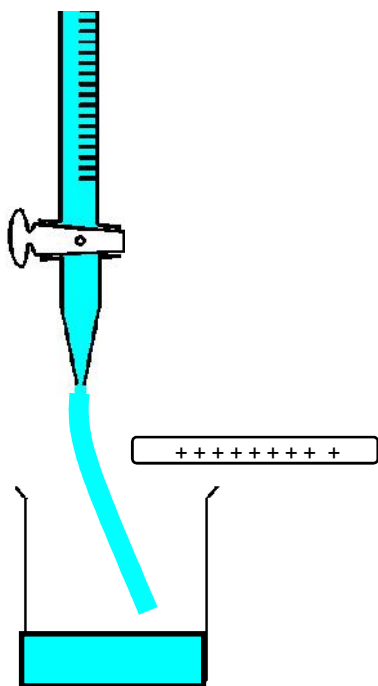
E.g. in 1-chloro propane there are both London forces and permanent dipole attractions, so its boiling point is higher than an alkane with similar numbers of electrons



Attraction - - - - -  
Repulsion - - - - -

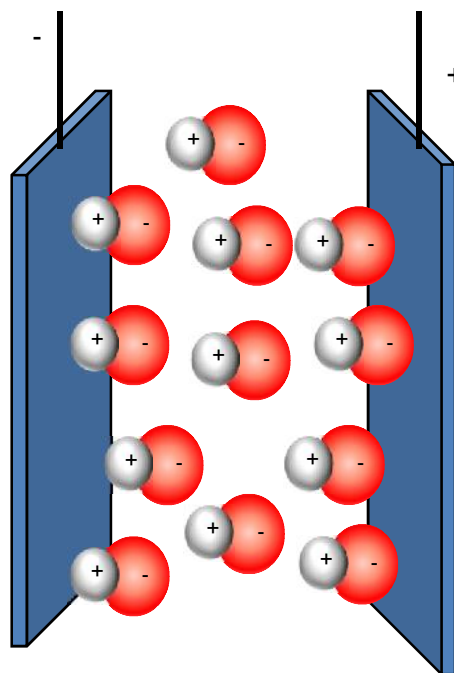
Interaction of many dipoles in a liquid.

Typical compounds that have permanent dipoles include HCl, HBr, halogenoalkanes, ketones, aldehydes.



A jet of a polar Compound issued from a burette will be attracted towards a charged rod.

The stronger the dipole the bigger the deflection



In a charged field all the dipoles will align

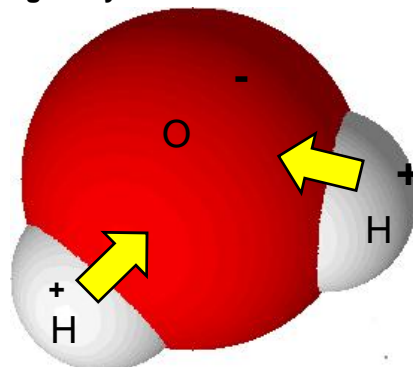
## Hydrogen bonding

Hydrogen bonding 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**

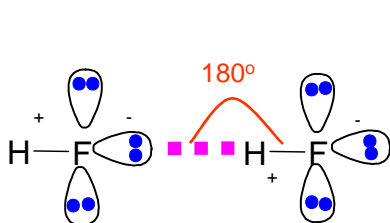
Hydrogen bonding occurs in addition to London forces

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

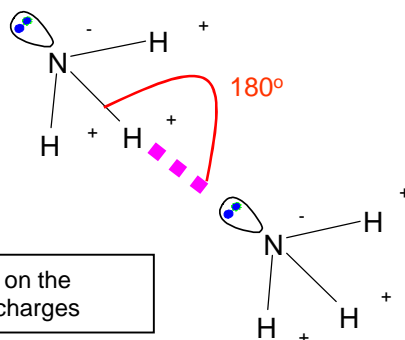
The small size of the hydrogen atom and the oxygen, nitrogen, fluorine atoms allow the atoms to approach each other closely, which makes the force of attraction strong. The force of attraction is also made strong because the difference in electronegativity is significant.



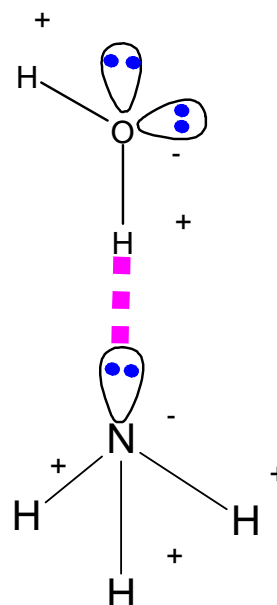
### Drawing diagrams to illustrate hydrogen bonding



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



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



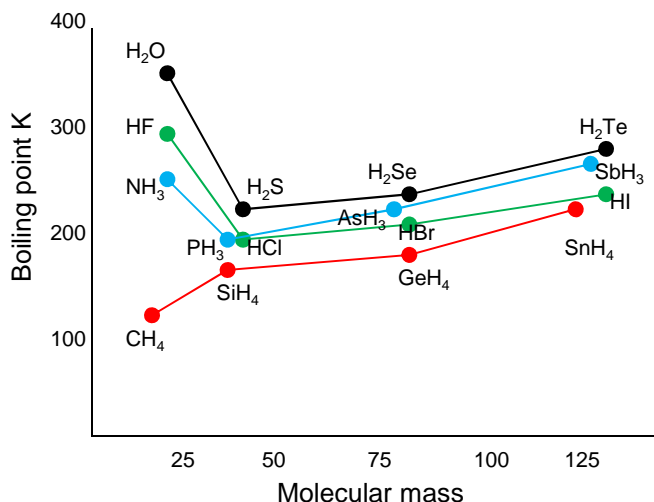
The bond angle is  $180^\circ$  around the H atom because there are two pairs of electrons around the H atom involved in the hydrogen bond. These pairs of electrons repel to a position of minimum repulsion, as far apart as possible.

### Properties of compounds with Hydrogen Bonding

- They have higher boiling points compared to compounds with other types of intermolecular forces
- They tend to be soluble in other compounds with hydrogen bonds (water, ethanol) e.g. ammonia, HF, carboxylic acids will dissolve in water and ethanol.
- They can have higher viscosity: the stronger the hydrogen bonding the more viscous the liquid.
- Higher surface tension

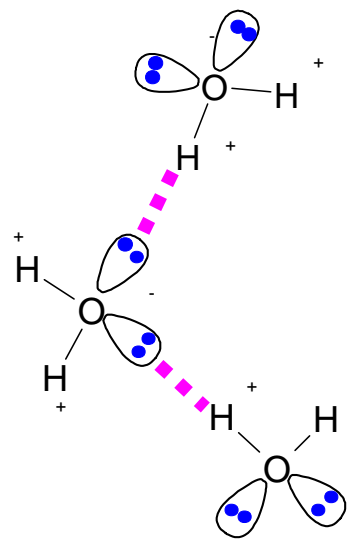
The **anomalously high** boiling points of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HF}$  are caused by the hydrogen bonding between these molecules in addition to their London forces. The additional forces require more energy to break and so have higher boiling points

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.



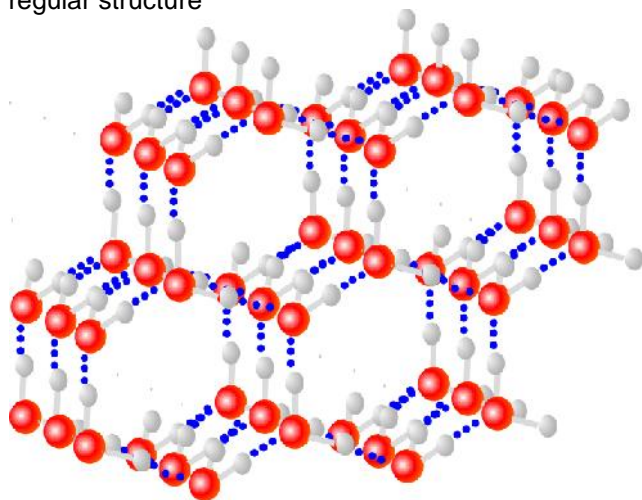
## Hydrogen bonding in Water

Water can form two hydrogen bonds per molecule, because the electronegative oxygen atom has two lone pairs of electrons on it. It can therefore form stronger hydrogen bonding and needs more energy to break the bonds, leading to a higher boiling point.



## Ice

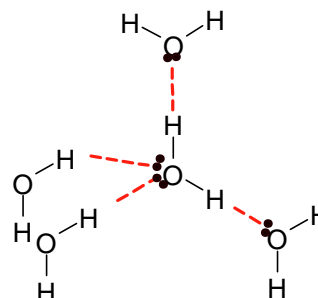
In ice the hydrogen bonds hold the water molecules together in a regular structure



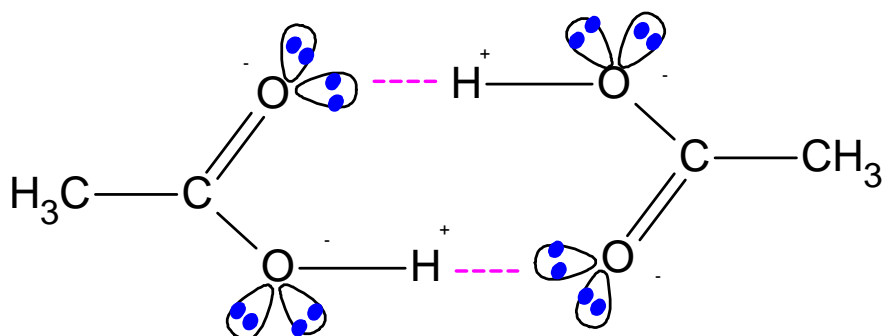
The molecules are held further apart than in liquid water and this explains the lower density of ice

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



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



Hydrogen bonding in solid ethanoic acid can cause a dimer to form. (This means two ethanoic acid molecules are bonded together to appear as one molecule)

Solid Ethanoic therefore appears to have Mr of 120

## 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.

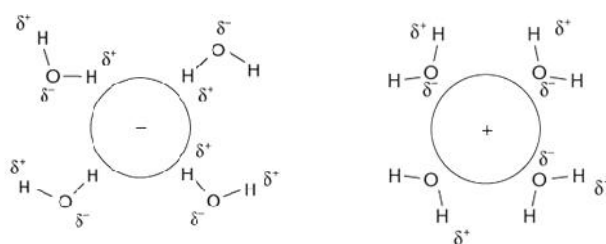
If the solute cannot form strong enough bonds with the water to compensate for the energy needed to break the hydrogen bonds in water, it will not dissolve.

### 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



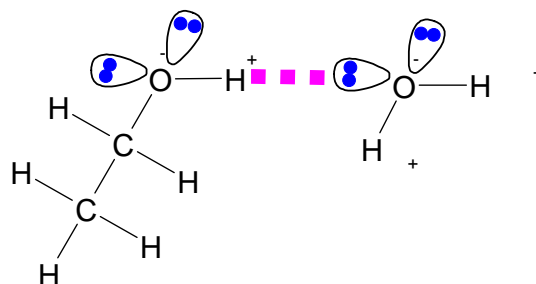
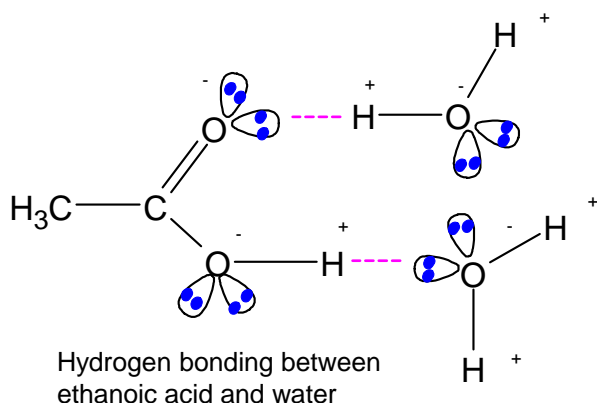
The higher the **charge density** the greater the hydration enthalpy (e.g. **smaller ions** or **ions with larger charges**) as the ions attract the water molecules more strongly.

### Solubility of polar molecules in Water

Molecules with significant hydrogen bonding can dissolve in water because they can form hydrogen bonds with the water molecules

### 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 halogenoalkanes 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.

