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.

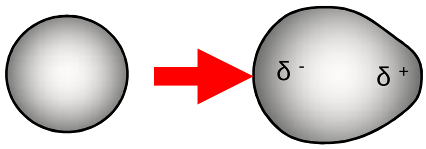
London Forces

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**

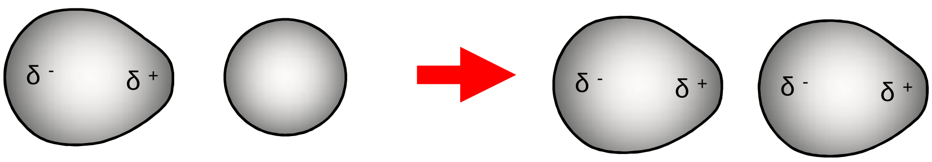
Van der Waals more correctly is used to describe all the different types of intermolecular forces. Some exam boards use it to just mean these weak dispersion forces

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.

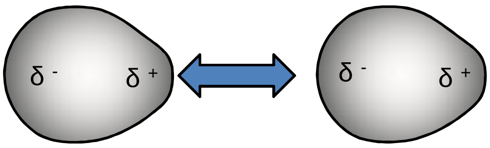
How do London forces occur?
In any molecule the electrons are moving constantly and randomly. As this happens the electron density can fluctuate and parts of the molecule temporarily become more or less negative i.e. small temporary or transient dipoles form.



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

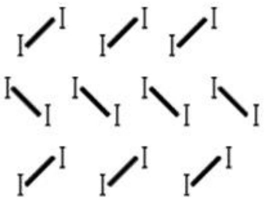


Main factor affecting size of London Forces
The **more electrons** there are in the molecule the higher the chance that temporary dipoles will form. This makes the **London forces stronger between the molecules** and more energy is needed to break them so boiling points will be greater.

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.

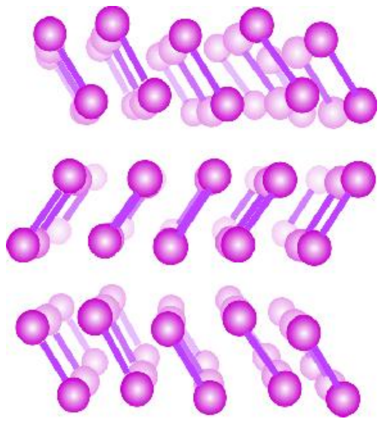
Element	No of electrons in molecule	Boiling Point (°C)	Physical State
Fluorine	18	-188	Gas
Chlorine	34	-35	Gas
Bromine	70	59	Liquid
Iodine	106	184	Solid

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

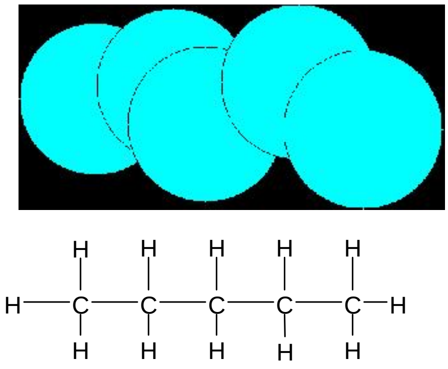
Low melting and boiling points because the London forces are weak

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

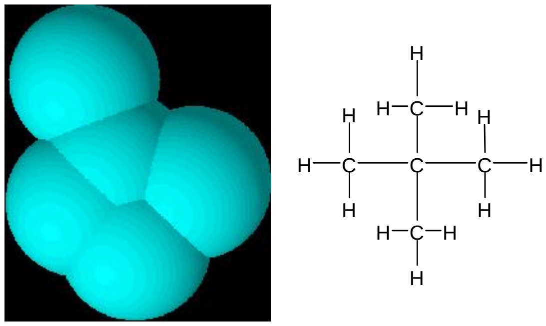
Low solubility in water because Iodine cannot form strong forces (hydrogen bonds) with water

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 .



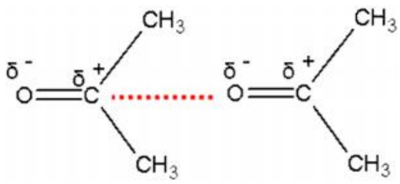
Pentane B.p.36 ºC



2,2 Dimethylpropane
B.p.10 ºC

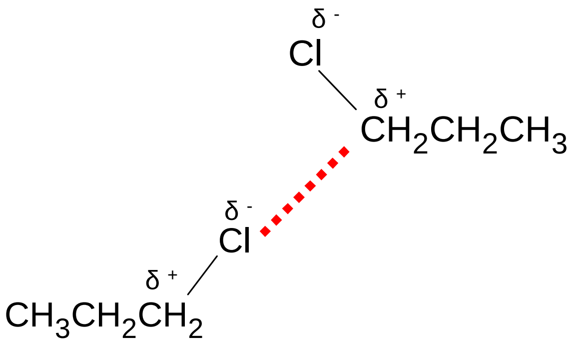
Permanent dipole-dipole forces

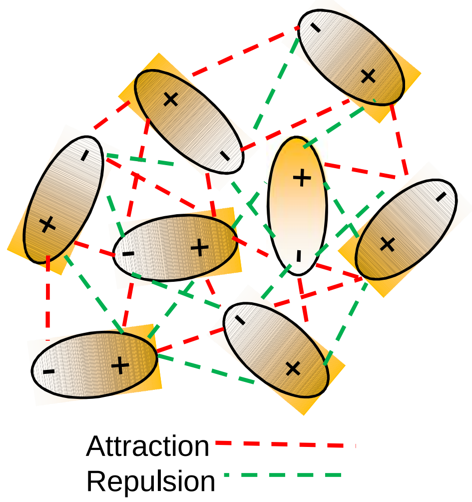
•Permanent dipole-dipole forces occurs between polar molecules
•Polar molecules have a permanent dipole. (commonly compounds with C-Cl, C-F, C-Br H-Cl, C=O bonds)
•Polar molecules are asymmetrical and have a polar bond caused by a significant **difference in electronegativity** between the atoms.



Permanent dipole forces occur in addition to London forces

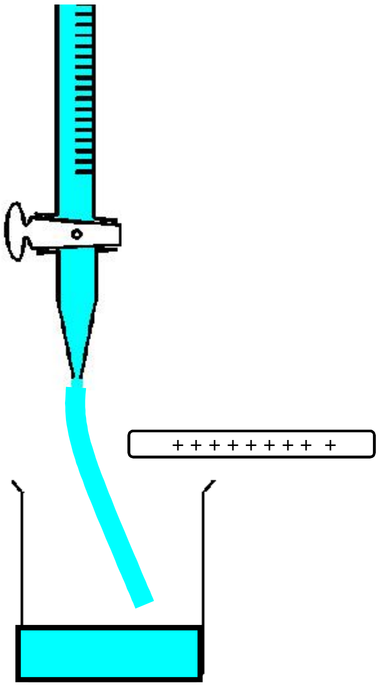
These permanent dipole-dipole forces of attraction between molecules are stronger than London forces and they occur in addition to London Forces.
E.g. in 1-chloro propane there are both London forces and permanent dipole attractions, so its boiling point is higher than an alkane with similar numbers of electrons





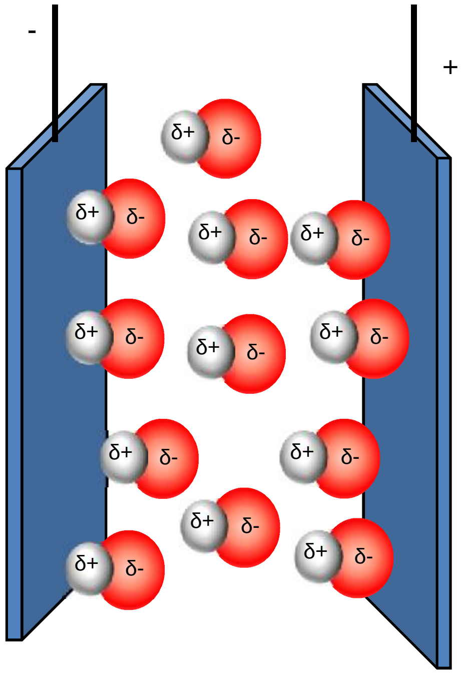
Interaction of many dipoles in a liquid.

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

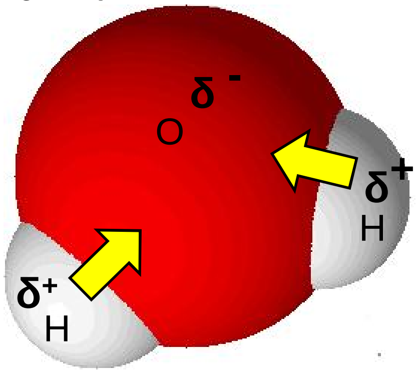
Hydrogen bonding

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**

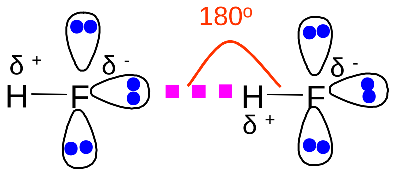
Hydrogen bonding occurs in addition to London forces

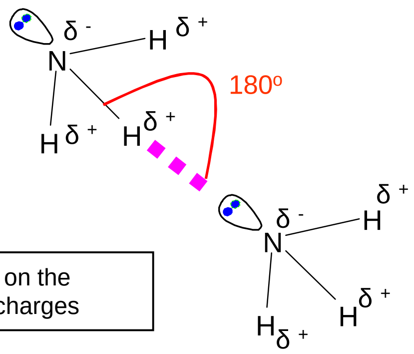
Hydrogen bonding is stronger than the other two types of intermolecular bonding.

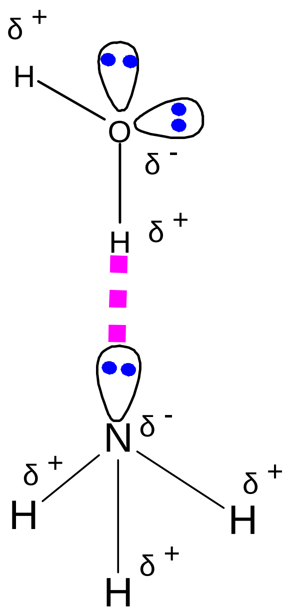
The small size of the hydrogen atom and the oxygen, nitrogen, fluorine atoms allow the atoms to approach each other closely, which makes the force of attraction strong. The force of attraction is also made strong because the difference in electronegativity is significant.



Drawing diagrams to illustrate hydrogen bonding







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

The hydrogen bond should have an bond angle of 180º with one of the bonds in one of the molecules

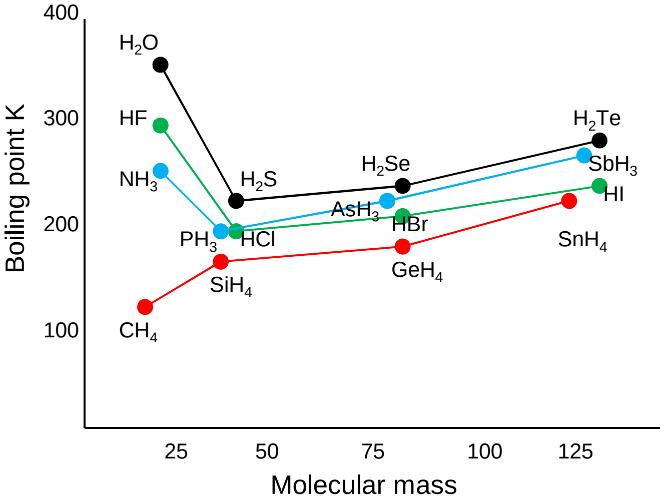
The bond angle is 180º around the H atom because there are two pairs of electrons around the H atom involved in the hydrogen bond. These pairs of electrons repel to a position of minimum repulsion, as far apart as possible.

Properties of compounds with Hydrogen Bonding

- They have higher boiling points compared to compounds the other types of intermolecular forces
- They tend to be soluble in other compounds with hydrogen bonds (water, ethanol) eg 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

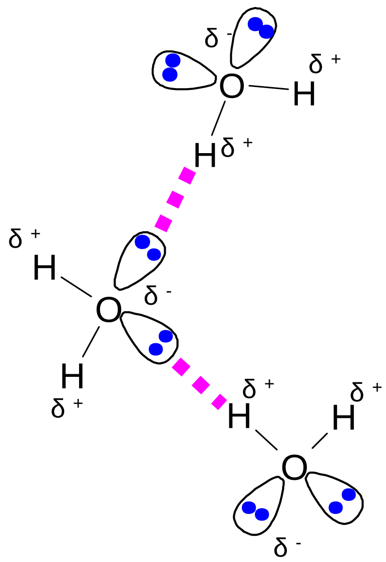
The **anomalously high** boiling points of H_2O, NH_3 and HF are caused by the hydrogen bonding between these molecules in addition to their London forces. The additional forces require more energy to break and so have higher boiling points

The general increase in boiling point from H_2S to H_2Te or from HCl to HI is caused by increasing London forces between molecules due to an increasing number of electrons.



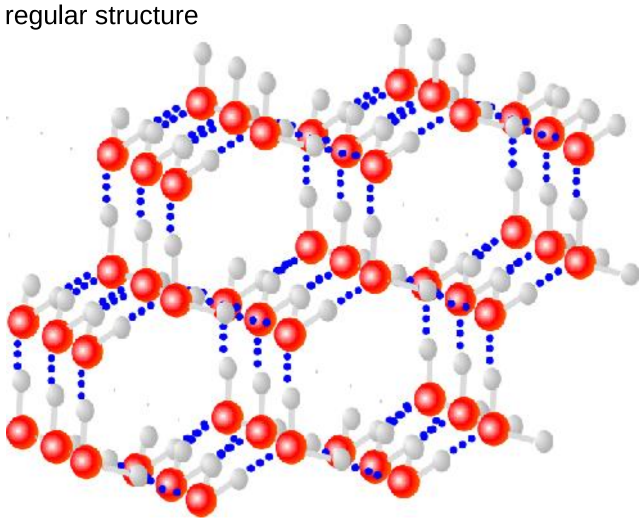
Hydrogen bonding in Water

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.

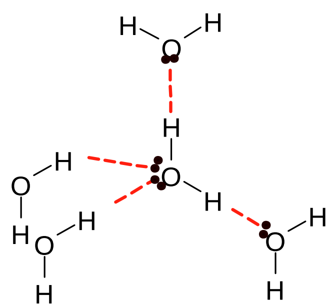


Ice

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



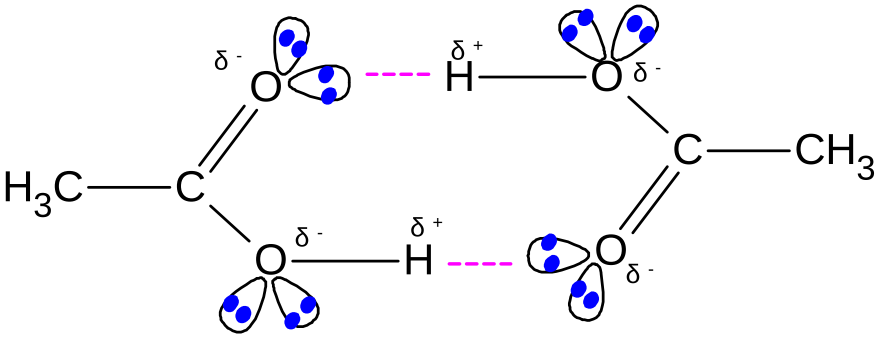
The molecules are held further apart than in liquid water and this explains the lower density of ice



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.

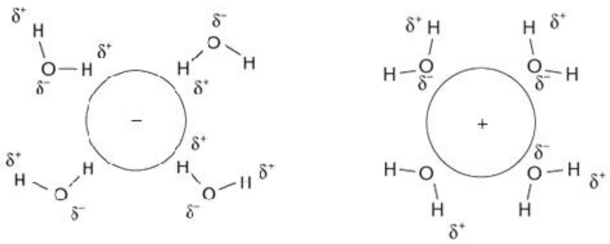
If the solute cannot form strong enough bonds with the water to compensate for the energy needed to break the hydrogen bonds in water, it will not dissolve.

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 **δ^+ hydrogens** on the **polar water** molecules and the positive ions are attracted to the δ^- oxygen on the polar water molecules.

hydration of the ions



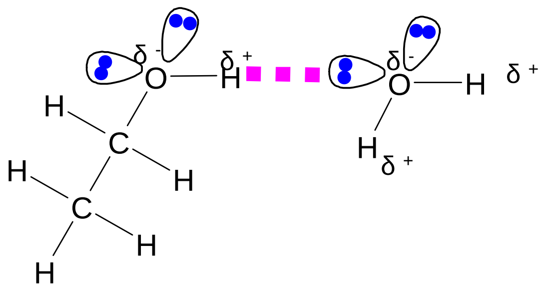
The higher the **charge density** the greater the hydration enthalpy (e.g. **smaller ions** or **ions with larger charges**) as the ions attract the water molecules more strongly.

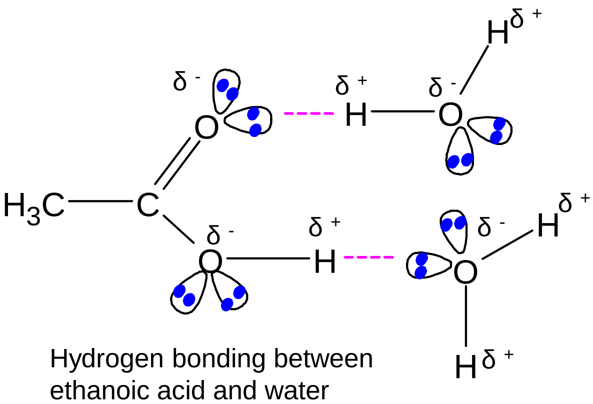
Solubility of polar molecules in Water

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.





Hydrogen bonding between ethanoic acid and water

Insolubility of compounds in water

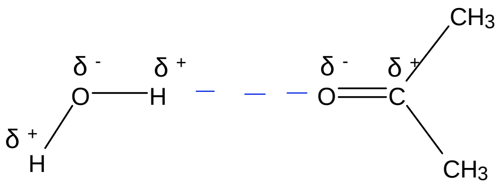
Compounds that cannot form hydrogen bonds with water molecules, e.g. polar molecules such as halogenoalkanes or non polar substances like hexane will be insoluble in water.

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_3 groups. Its polar C=O bond can also hydrogen bond with water.



Intermolecular Forces Questions

London Forces

1) a) Explain how transient, induced dipole-dipole interactions form between molecules
b) Explain why the boiling points of alkanes increase as you increase the number of carbon atoms.
c) Explain why the boiling points of group 7 elements increase as you descend group 7
d) Explain why a branched compound dimethylpropane has a lower boiling point than pentane even though they have the same molecular mass.

Permanent Dipole forces

2) a) Describe what is meant by the term polar bond and how one forms.
b) Explain how permanent dipole forces occur between molecules of HCl. Use a diagram to illustrate your answer.
c) Draw a diagram to show the permanent dipole foces that occurs between two molecules of chloroethane (CH_3CH_2Cl) [You will need to draw the molecules using displayed formulae]
d) Hydrogen bromide has a higher boiling point than hydrogen chloride. By considering the likely strengths of the permanent dipoles and London forces in these molecules explain whether this difference in boiling point would be due to permanent dipole forces or London forces.

Hydrogen Bonding

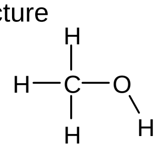
3) a) Describe how hydrogen bonds form between molecules of Hydrogen Fluoride. Use a diagram to illustrate your answer (include all lone-pair electrons and partial charges in your diagram).

b) Explain why the boiling point of hydrogen fluoride is higher than that of hydrogen chloride.

4) a) Draw a diagram to show the hydrogen bonding that forms between two molecules of Ammonia (NH_3) Show all lone pairs and partial charges

b) Nitrogen and Chlorine have the same electronegativity. Find out why Ammonia can hydrogen bond but hydrogen chloride only forms permanent dipole bonding.

5)a) Methanol has the structure



Explain why the O–H bond in a methanol molecule is polar.

b) Draw a diagram to show the intermolecular bonding that occurs between two molecules of methanol. Show all lone pairs and partial charges

c) The boiling point of methanol is +65 °C; the boiling point of oxygen is –183 °C. Methanol and oxygen each have an Mr value of 32. Explain, in terms of the intermolecular forces present in each case, why the boiling point of methanol is much higher than that of oxygen.

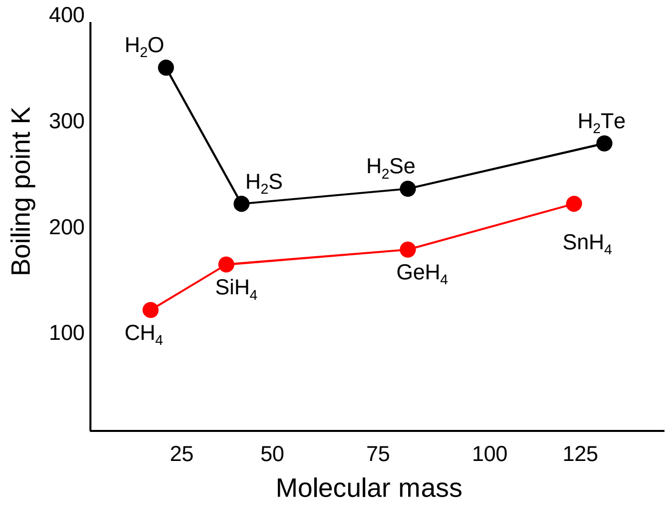
d) Methanol can dissolve in water because it can form hydrogen bonds with water. Draw a diagram to show how this occurs.

6 Two students were having a discussion about hydrogen bonding. One thinks that hydrogen bonding is just a stronger version of permanent dipole forces. The other thinks that hydrogen bonding is like a weak covalent bond. Who is right or are they both correct? Research and then give reasons for your answer.

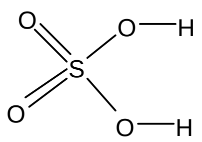
General questions

7 (a) Explain why the boiling temperature of PH_3 is greater than that of CH_4.
(b) Explain why the boiling temperature of NH_3 is greater than that of PH_3

8)a) Explain the trends in the boiling points of the group 4 and group 6 hydrides shown on the graph.
b) Estimate the boiling point of water if hydrogen bonding did not occur



9) Sufuric acid is a liquid. Its displayed formula is drawn below.



The electronegativity values for hydrogen, sulfur and oxygen are 2.1, 2.5 and 3.5 respectively.
a) Indicate the polarity of each bond present in the formula given.
b) Describe the different types of intermolecular bonding that will occur between sulfuric acid molecules. In your answer, identify the relevant parts of the molecule will be involved in the different types of intermolecular bonding.
c) Which of the different types of intermolecular bonding will be the strongest?

10) The melting and boiling points of organic chemicals are due to various types of intermolecular and ionic interactions. Discuss the following varying boiling points of the following compounds and account for the differences in terms of the bonding present.

Propane ($CH_3CH_2CH_3$) = 231K, Ethanal(CH_3CHO) = 294K,

Ethanol (CH_3CH_2OH)=351K, methanoic acid (HCOOH)= 373K,

Chloromethane (CH_3Cl)= 249K, ethylamine ($CH_3CH_2NH_2$) = 290K,

methoxymethane (CH_3OCH_3)= 248K, Sodium Methanoate ($HCOO^-Na^+$) = melting point 526K

11) 1-chloroethane does not dissolve in water. Propanone and propana-1-ol do dissolve in water. Explain the difference in solubility