Edexcel International AS Chemistry

Your notes

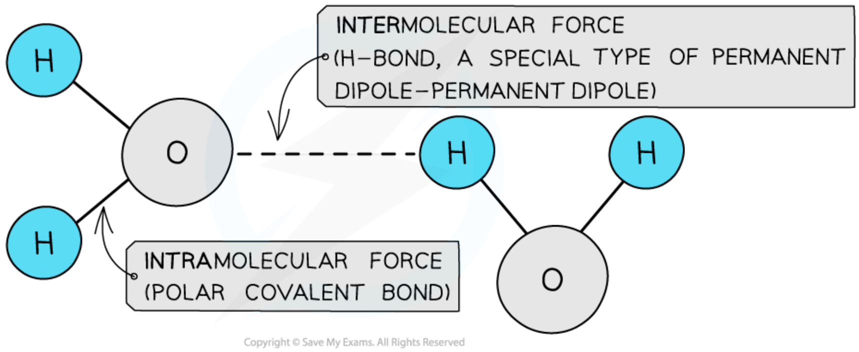
Intermolecular Forces

Contents

Intermolecular Forces – Introduction

Intramolecular forces

- **Intramolecular forces** are forces **within** a molecule and are usually covalent bonds
- **Covalent bonds** are formed when the outer electrons of two atoms are **shared**
- Single, double, triple and co-ordinate bonds are all types of intramolecular forces



Intermolecular forces

- Molecules also contain weaker **intermolecular forces** which are forces **between** the molecules
- There are three types of intermolecular forces:
  - **Induced dipole – dipole forces** also called **van der Waals** or **London dispersion forces**
  - **Permanent dipole – dipole forces** are the attractive forces between two neighbouring molecules with a permanent dipole
  - **Hydrogen Bonding** are a special type of **permanent dipole – permanent dipole** forces
  - **Intramolecular forces** are **stronger** than intermolecular forces
    - For example, a hydrogen bond is about one tenth the strength of a covalent bond
  - The strengths of the types of bond or force are as follows:

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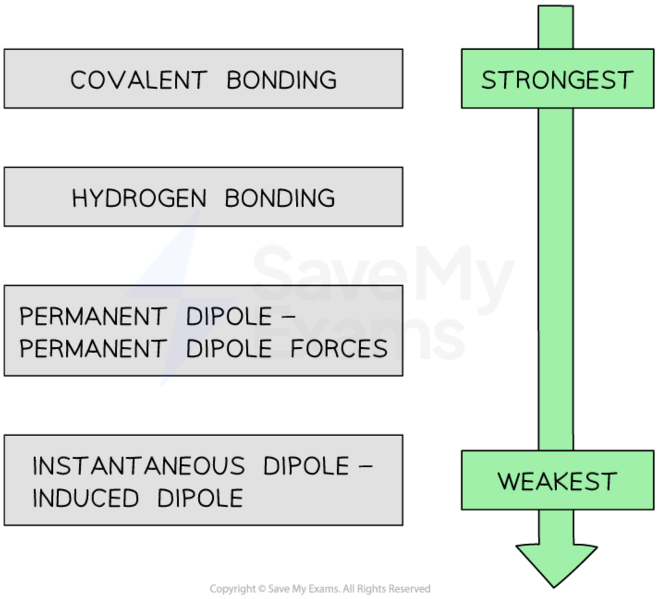
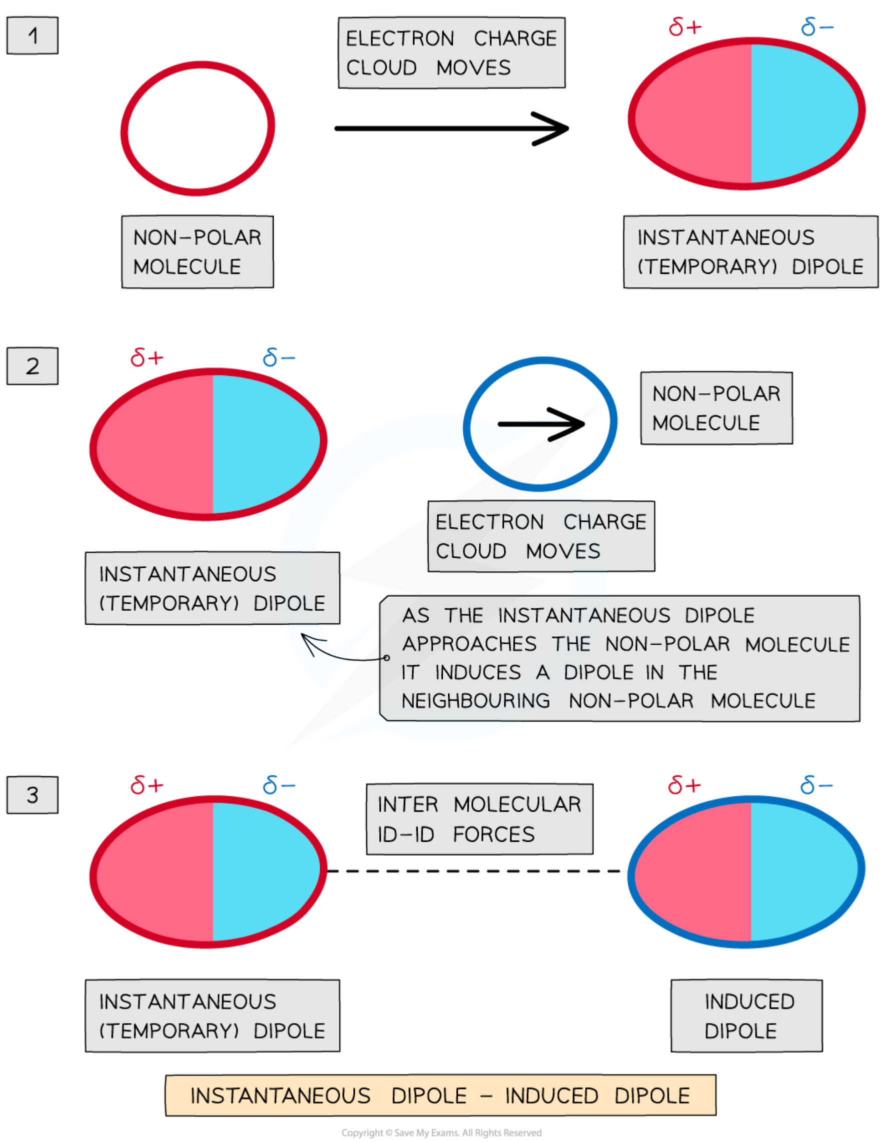


The varying strengths of different types of bonds

Induced dipole-dipole forces:

- **Induced dipole - dipole forces** exist between all atoms or molecules
  - They are also known as **London dispersion forces**

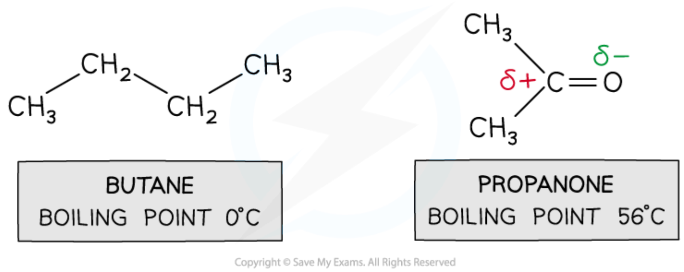


- The **electron charge cloud** in non-polar molecules or atoms are constantly moving
- During this movement, the electron charge cloud can be more on one side of the atom or molecule than the other
- This causes a **temporary dipole** to arise
- This **temporary dipole** can **induce** a dipole on neighbouring molecules
- When this happens, the **δ+ end of the dipole** in one molecule and the **δ- end of the dipole** in a neighbouring molecule are **attracted** towards each other
- Because the electron clouds are moving constantly, the dipoles are only **temporary**

Relative strength

- For small molecules with **the same number of electrons,** permanent dipoles are **stronger** than induced dipoles

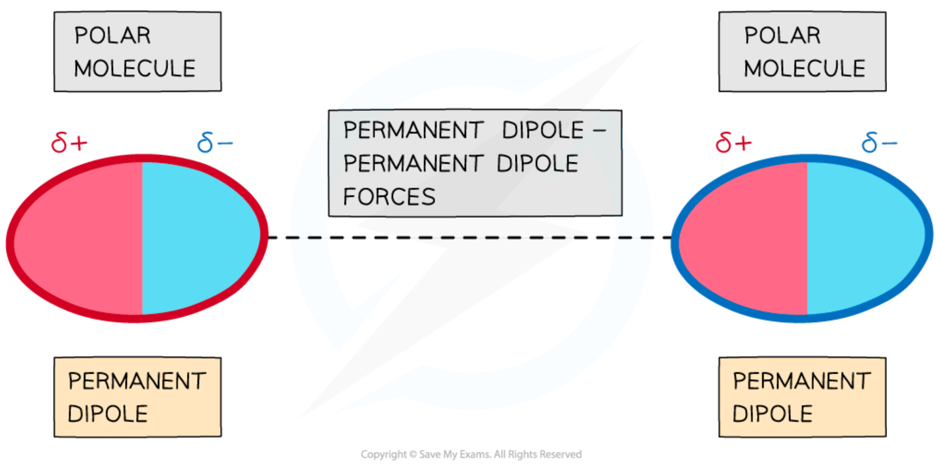
- Butane and propanone have the same number of electrons
- Butane is a nonpolar molecule and will have induced dipole forces
- Propanone is a polar molecule and will have permanent dipole forces
- Therefore, more energy is required to break the intermolecular forces between propanone molecules than between butane molecules
- So, propanone has a higher boiling point than butane



Pd-pd forces are stronger than id-id forces in smaller molecules with an equal number of electrons

Permanent dipole - dipole forces:

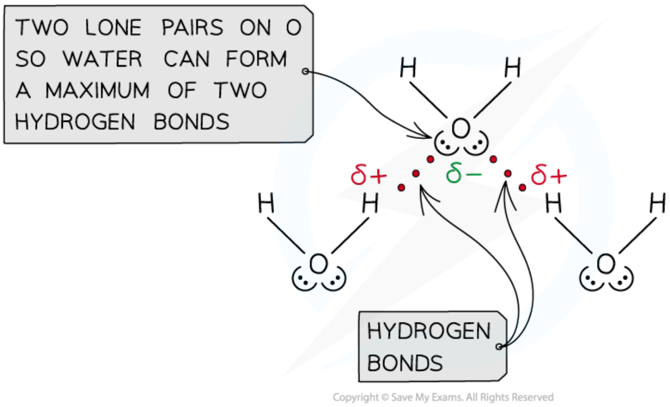
- **Polar molecules** have **permanent dipoles**
- The molecule will always have a **negatively** and **positively charged end**



- Forces between two molecules that have permanent dipoles are called **permanent dipole - dipole forces**
- The **δ+ end of the dipole** in one molecule and the **δ- end of the dipole** in a neighbouring molecule are **attracted** towards each other

Hydrogen bonding

- **Hydrogen bonding** is the **strongest** form of **intermolecular bonding**
  - Intermolecular bonds are bonds **between** molecules
  - Hydrogen bonding is a type of **permanent dipole – permanent dipole** bonding
- For hydrogen bonding to take place the following is needed:
  - A species which has an **O, N or F** (very **electronegative**) atom bonded to a hydrogen
- When hydrogen is covalently bonded to an **O**, **N** or **F**, the bond becomes highly **polarised**
- The H becomes so **δ+** charged that it can form a bond with the **lone pair** of an **O**, **N or F** atom in another molecule
- For example, in water
  - Water can form two hydrogen bonds, because the O has two lone pairs



Hydrogen bonding in water

Examiner Tips and Tricks

Make sure to use a **dashed, straight line** when drawing your intermolecular forces! Hydrogen bonds should **start at the lone pair** and go **right up to the delta positive atom** - it must be really clear where your H bond starts and ends.

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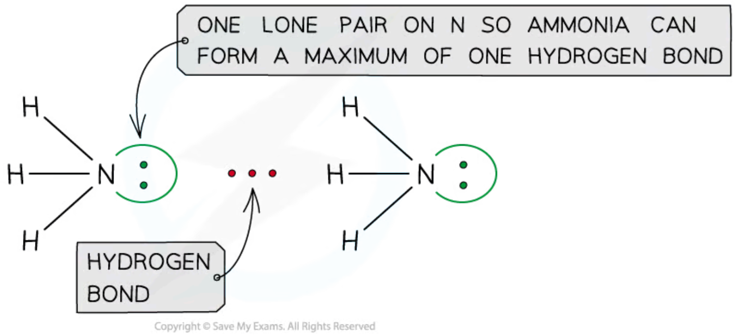
Molecular Interactions

Examples of compounds that can form hydrogen bonds are:

- Alcohols (contains an O-H bond)
- Ammonia (contains an N-H bond)
- Amines (contains an N-H bond)
- Carboxylic acids (contains an O-H bond)
- Hydrogen fluoride (contains an H-F bond)
- Proteins (contains an N-H bond)



Ammonia can form a maximum of one hydrogen bond per molecule

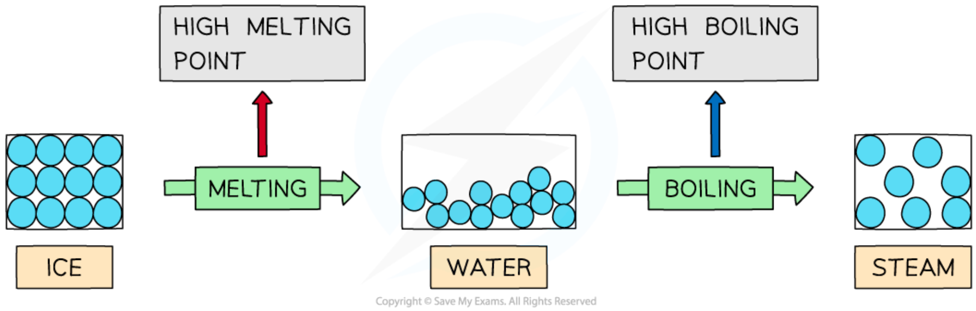
Anomalous Properties of Water

Properties of water

- Hydrogen bonding in water, causes it to have **anomalous properties** such as high melting and boiling points, high surface tension and a higher density in the liquid than the solid

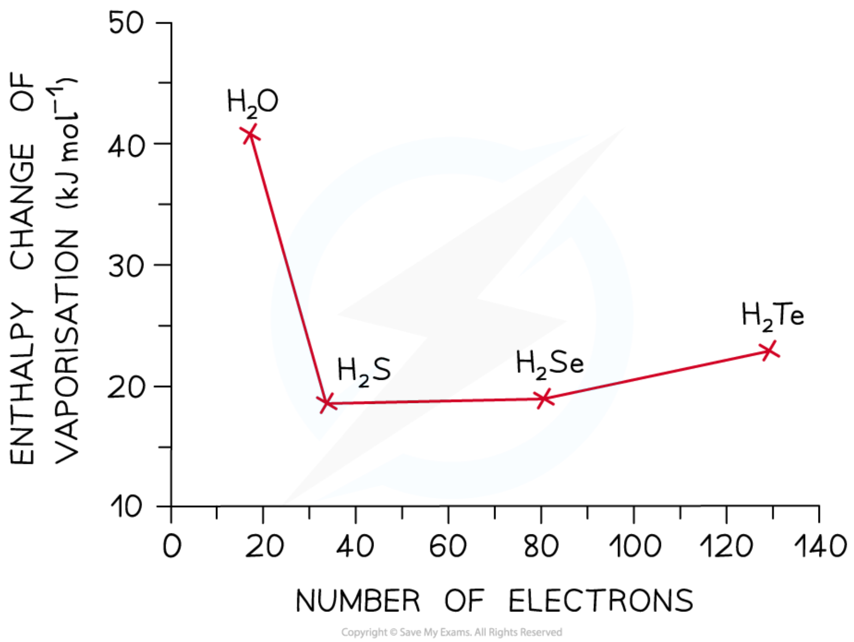
High melting & boiling points

- Water has high **melting** and **boiling points** due to the the **strong intermolecular forces** of hydrogen bonding between the molecules in both ice (solid H_2O) and water (liquid H_2O)
- A lot of energy is therefore required to separate the water molecules and melt or boil them



Hydrogen bonds are strong intermolecular forces which are harder to break causing water to have a higher melting and boiling point than would be expected for a molecule of such a small size

- The graph below compares the **enthalpy of vaporisation** (energy required to boil a substance) of different hydrides
- The enthalpy changes **increase** going from H_2S to H_2Te due to the increased number of electrons in the Group 16 elements
- This causes an increase in the **instantaneous dipole - induced dipole forces (dispersion forces)** as the molecules become larger
- Based on this, H_2O should have a much lower enthalpy change (around 17 kJ mol^{-1})
- However, the enthalpy change of vaporisation is almost 3 times **larger** which is caused by the **hydrogen bonds** present in water but not in the other hydrides



The high enthalpy change of evaporation of water suggests that instantaneous dipole-induced dipole forces are not the only forces present in the molecule – there are also strong hydrogen bonds, which cause the high boiling point

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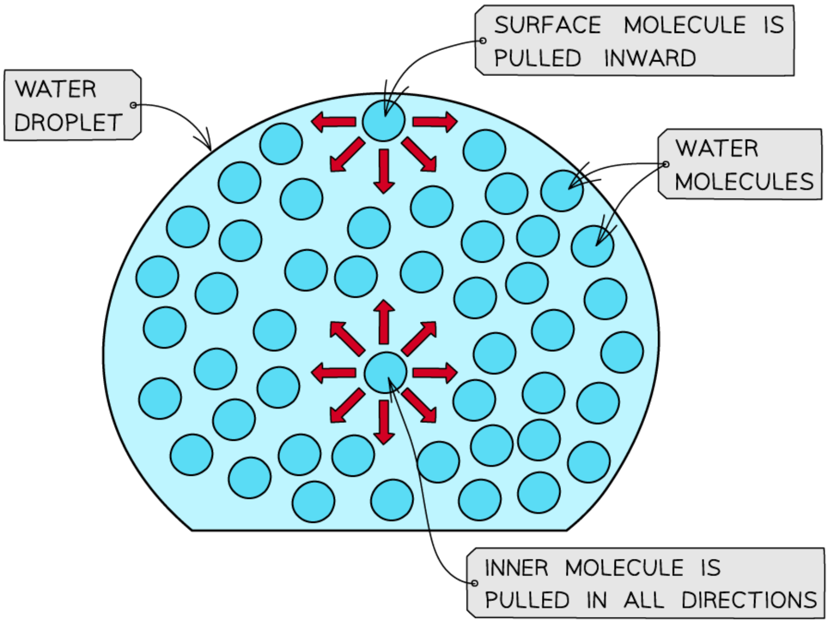
High surface tension

- Water has a **high surface tension**
- **Surface tension** is the ability of a **liquid surface** to resist any **external forces** (i.e. to stay unaffected by forces acting on the surface)
- The water molecules at the **surface** of liquid are bonded to other water molecules through **hydrogen bonds**
- These molecules **pull downwards** the **surface molecules** causing the surface of them to become compressed and more tightly together at the surface
- This increases water's **surface tension**



The surface molecules are pulled downwards due to the hydrogen bonds with other molecules, whereas the inner water molecules are pulled in all directions

Density

- **Solids** are **denser** than their **liquids** as the particles in solids are more **closely packed** together than in their liquid state
- The water molecules are packed into an open lattice
- This way of packing the molecules and the relatively long **bond lengths** of the hydrogen bonds means that the water molecules are slightly further apart than in the liquid form
- Therefore, ice has a lower density than liquid water by about 9%

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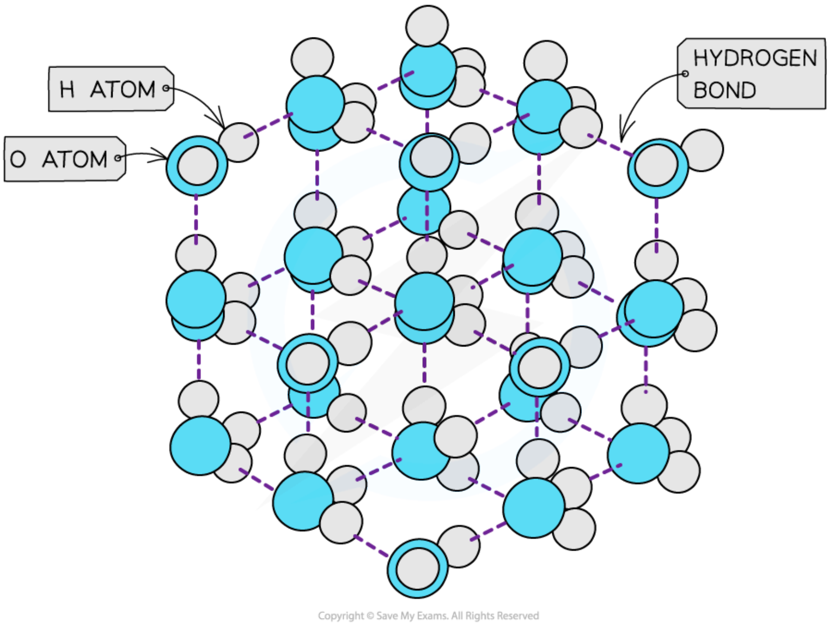

The 'more open' structure of molecules in ice causes it to have a lower density than liquid water

Examiner Tips and Tricks

The H-O-H bond angle in water is 104.5° but in ice, this increases to closer to the undistorted tetrahedral bond angle of 109.5°. This is because the lone pairs of electrons on the oxygen atom are drawn towards the δ+ on the hydrogen atom on a neighbouring water molecule, away from the oxygen atom. This reduces the repulsion of the bonded electron pairs around the oxygen, increasing the bond angle.

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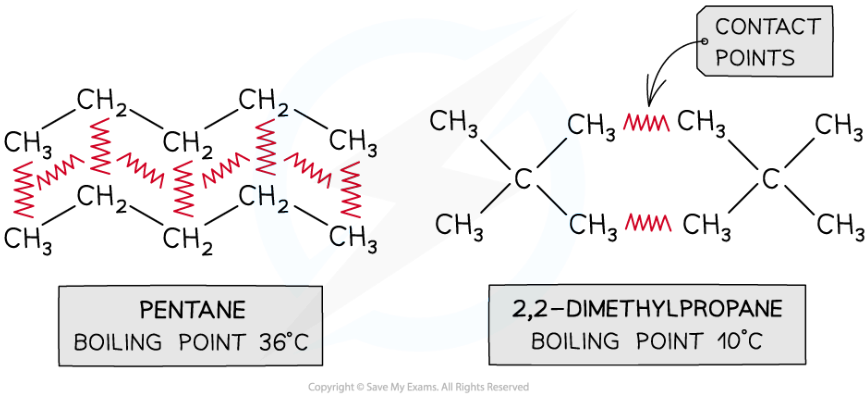
Physical Properties & Intermolecular Forces

Branching

- The larger the surface area of a molecule, the more contact it will have with adjacent molecules
- The surface area of a molecule is **reduced by branching**
- The greater its ability to induce a dipole in an adjacent molecule, the greater the **London (dispersion) forces** and the higher the melting and boiling points
- This point can be illustrated by comparing different isomers containing the same number of electrons:



Boiling points of molecules with the same numbers of electrons but different surface areas

Number of electrons

- The greater the number of electrons (or the greater the molecular mass) in a molecule, the greater the likelihood of a distortion and thus the greater the frequency and magnitude of the temporary dipoles
- The dispersion forces between the molecules are stronger and the enthalpy of vaporisation, melting and boiling points are larger
- The greater boiling points of the noble gases illustrate this factor:

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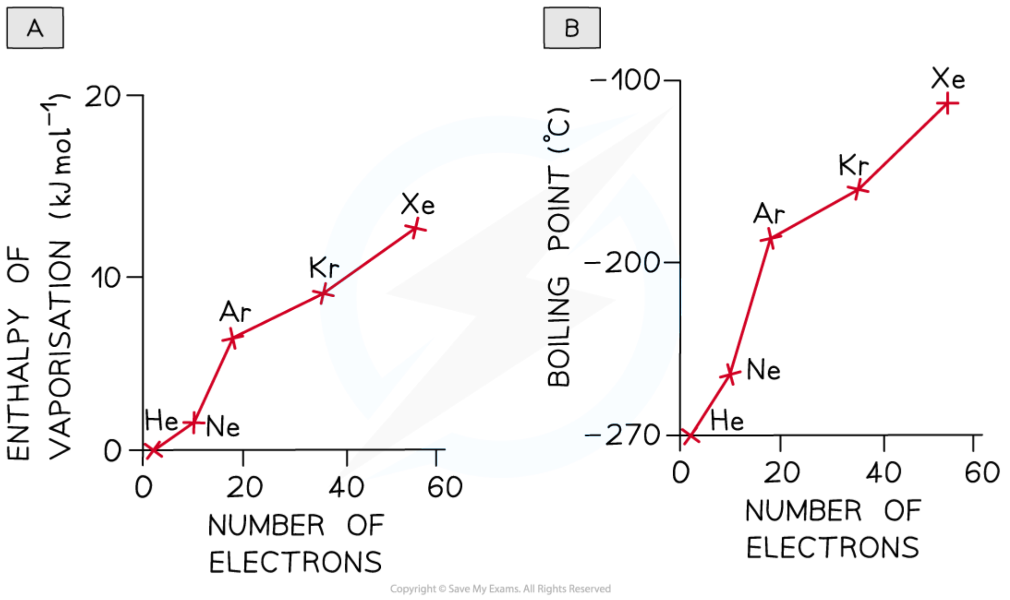
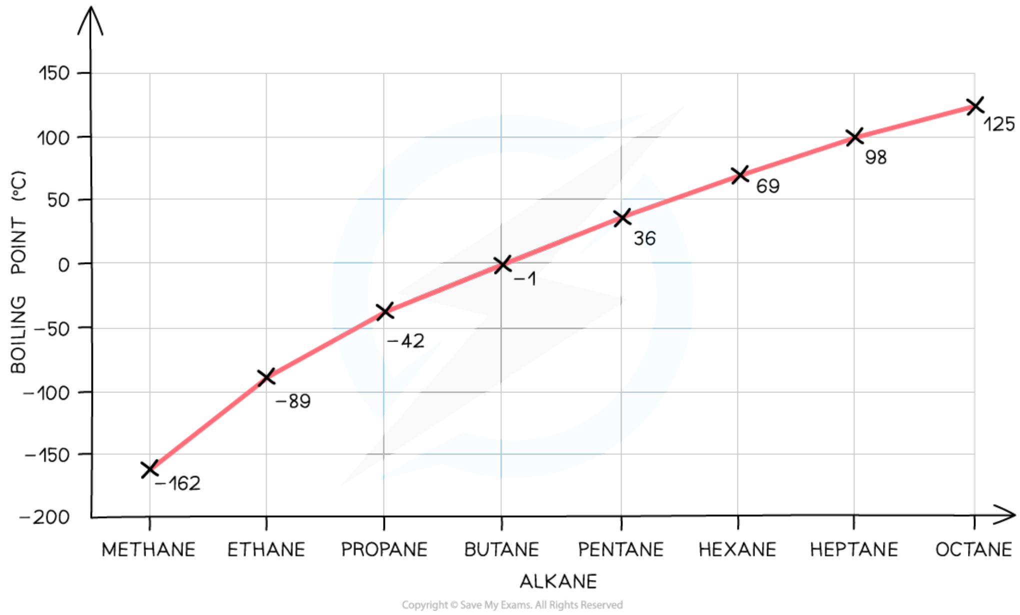


As the number of electrons increases more energy is needed to overcome the forces of attraction between the noble gases atoms



Graph showing the increase in boiling point as the number of electrons increases

Alcohols

- Hydrogen bonding occurs between molecules where you have a hydrogen atom attached to one of the very electronegative elements - fluorine, **oxygen** or nitrogen
- In an alcohol, there are **O–H bonds** present in the structure

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- Therefore hydrogen bonds set up between the slightly positive hydrogen atoms (δ+ H) and lone pairs on oxygens in other molecules
- The hydrogen atoms are slightly positive because the bonding electrons are pulled away from them towards the very electronegative oxygen atoms
- In **alkanes**, the only intermolecular forces are **temporary induced dipole-dipole forces**
- Hydrogen bonds are much stronger than these and therefore it takes more energy to separate alcohol molecules than it does to separate alkane molecules
- Therefore, the boiling point of alkanes is lower than the boiling point of the respective alcohols
- For example, the boiling point of propane is -42 °C and the boiling point of propanol is 97 °C

Hydrogen Halides

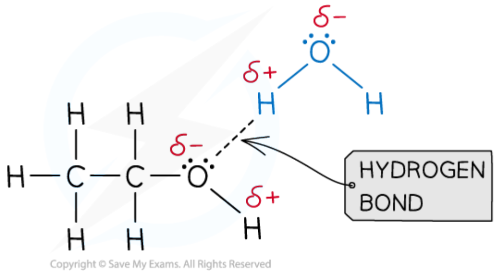
- The boiling points of the hydrogen halides are as follows

Hydrogen Halide	Boiling Point (K)
HF	293
HCl	188
HBr	207
HI	238

- The boiling points of the rest of the hydrogen halides **increase** as the molecules become larger
- The extra electrons allow greater temporary dipoles and so increase the amount of London dispersion forces between the molecules
- Hydrogen fluoride also has hydrogen bonding between the HF molecules
- The bond is very polar so that the hydrogen has a significant amount of positive charge and the fluorine a significant amount of negative charge. In addition, the fluorine has small intense lone pairs
- Hydrogen bonds can form between the hydrogen on one molecule and a lone pair on the fluorine in its neighbour

Solvent Choice

- The general principle is that 'like dissolves like' so non-polar substances mostly dissolve in non-polar solvents, like hydrocarbons, and they form dispersion forces between the solvent and the solute
- Polar covalent substances generally dissolve in polar solvents as a result of dipole-dipole interactions or the formation of hydrogen bonds between the solute and the solvent
- A good example of this is seen in organic molecules such as alcohols and water:

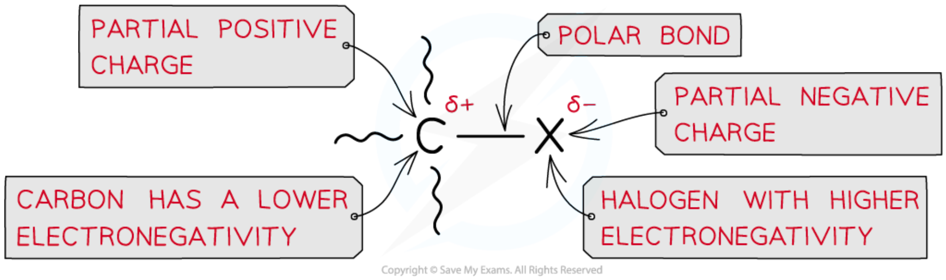


Hydrogen bonds form between ethanol and water

- As covalent molecules become larger, their solubility can decrease as the polar part of the molecule is only a smaller part of the overall structure
  - This effect is seen in alcohols, for example, where ethanol, C_2H_5OH, is readily soluble but hexanol, $C_6H_{13}OH$, is not
- Polar covalent substances are unable to dissolve well in non-polar solvents as their dipole-dipole attractions are unable to interact well with the solvent
- Giant covalent substances generally don't dissolve in any solvents as the energy needed to overcome the strong covalent bonds in the lattice structures is too great

Haloalkanes

- Even though haloalkanes contain a polar bond, they are only partially soluble in water as they can not form hydrogen bonds
- This is because there are no H-F, H-O or H-N bonds within the molecule



Due to the large difference in electronegativity between the carbon and halogen atoms, the C–X bond is polar

Ionic compounds

- Many ionic compounds will dissolve in **polar** solvents, e.g. water
- Solubility is dependent on two main factors:
  1. Breaking down the ionic lattice
  2. The polar molecules attract and surround the ions
- Polar molecules, such as water, can break down or disrupt the ionic lattice and surround each ion in solution
- The δ+ end of the polar molecule can surround the negative anion
- The δ- end of the polar molecule can surround the positive cation
- The solubility of an ionic compound depends on the relative strength of the electrostatic forces of attraction within the ionic lattice and the attractions between the ions and the polar molecule
- In general, the greater the ionic charge, the less soluble an ionic compound is
  - For example, 356.9 g of sodium chloride, NaCl, will dissolve in one dm^3 of water while only 74.4 g of calcium chloride will dissolve in one dm^3 of water
  - This is a general rule, though and there are many exceptions

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