Your notes

Cambridge (CIE) A Level Chemistry

Intermolecular Forces, Electronegativity & Bond Properties

Contents

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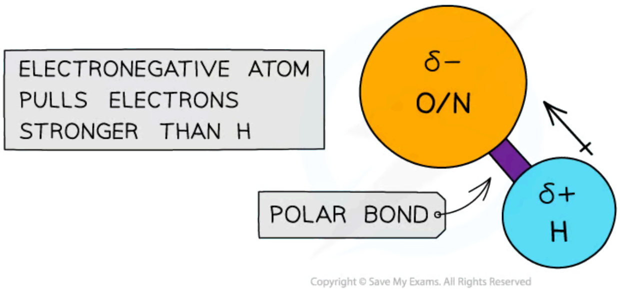
Hydrogen Bonding

- **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 occur, two conditions must be met:
  1. A molecule must contain a highly electronegative atom (O, N, or F) with a lone pair of electrons.
  2. A hydrogen atom must be covalently bonded to O, N, or F, making the bond highly polar.
- When hydrogen is covalently bonded to an **electronegative** atom (O, N, or F) the bond becomes very 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

Polarity of the OH bond



The electronegative atoms O or N have a stronger pull on the electrons in the covalent bond with hydrogen, causing the bond to become polarised

- The strongest hydrogen bonds are formed when the angle between the covalent bond (e.g., O-H) and the hydrogen bond is 180°, as this linear arrangement maximizes the electrostatic attraction.
- The number of hydrogen bonds depends on:
  - The number of hydrogen atoms attached to O or N in the molecule
  - The number of **lone pairs** on the O or N

Hydrogen bonding in ammonia

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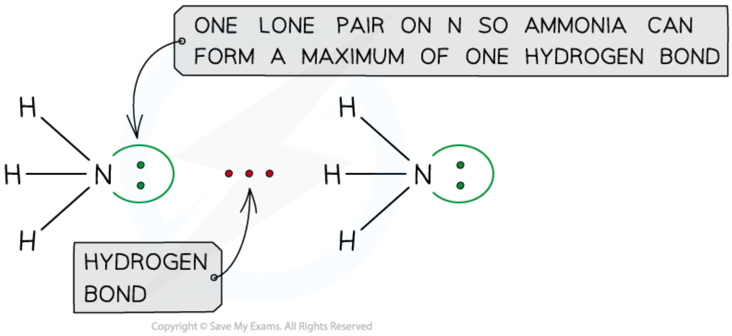
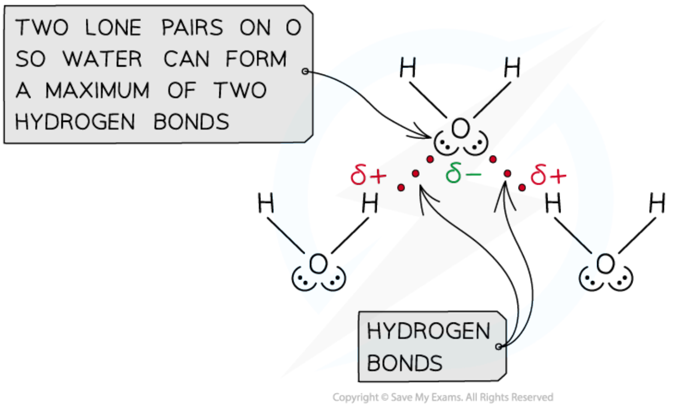


Ammonia can form a maximum of one hydrogen bond per molecule

Hydrogen bonding in water



Water can form a maximum of two hydrogen bonds per molecule. Two hydrogen bonds on the δ– oxygen atom and one on each δ+ hydrogen atom

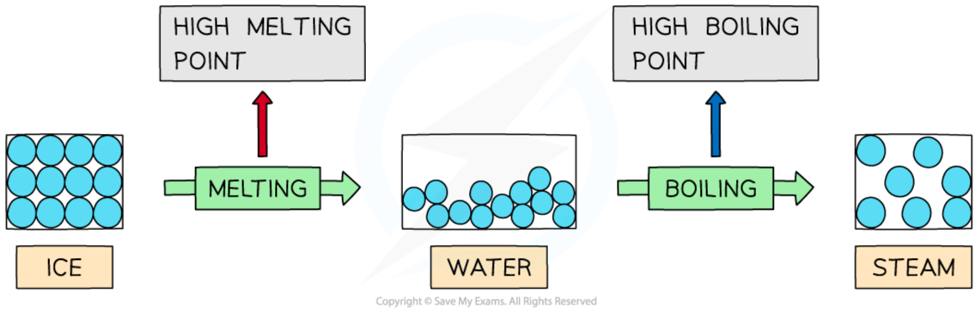
Properties of water

- Hydrogen bonding in water, causes it to have **anomalous properties** such as high melting and boiling points, high surface tension and anomalous density of ice compared to water

High melting & boiling points

- Water has high **melting** and **boiling points** which is caused by the **strong intermolecular forces** of hydrogen bonding between the molecules
- In **ice** (solid H_2O) and water (liquid H_2O) the molecules are tightly held together by hydrogen bonds
- A lot of energy is therefore required to break the water molecules apart and melt or boil them

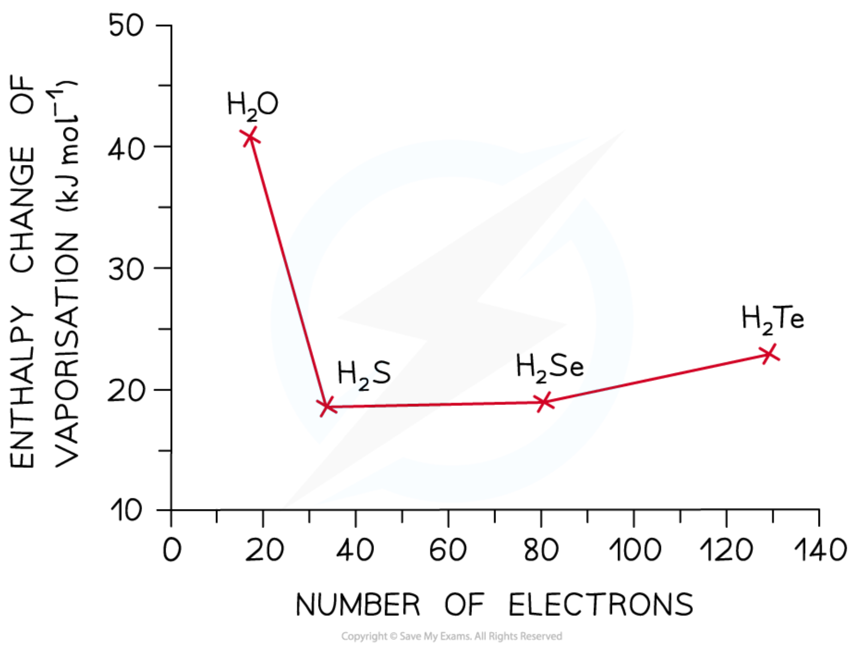
Changing states and hydrogen bonding



Hydrogen bonds are strong intermolecular forces which are difficult to break causing water to have high melting and boiling points

- 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 **increased instantaneous dipole – induced dipole forces** as the molecules become larger
- Based on this, H_2O would 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

Graph of enthalpy of vaporisation for different 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 those of the strong hydrogen bonds, which cause the high boiling points

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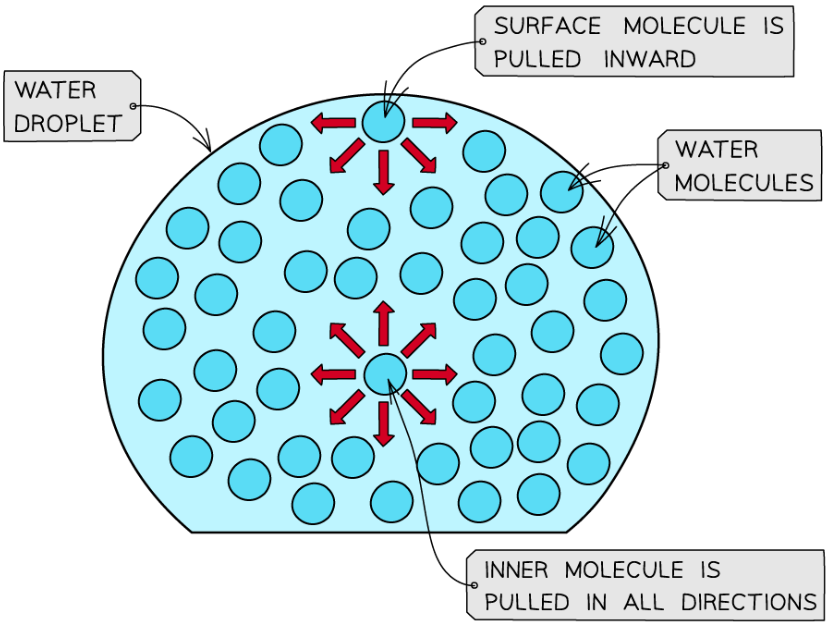
High surface tension

- 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** on the **surface molecules** causing the surface them to become compressed and more tightly together at the surface
- This increases water's **surface tension**

The effect of hydrogen bonding in water

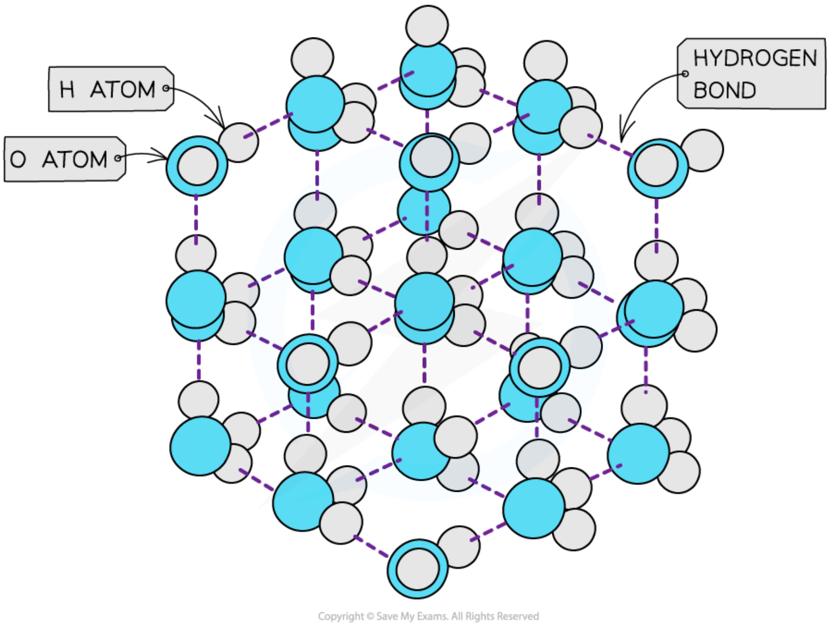


The surface molecules are pulled downwards due to the hydrogen bonds with other molecules, whereas the inner water molecules are pulled in all directions

Density

- **Solids** are **denser** than their **liquids** as the particles in solids are more **closely packed** together than in their liquid state
- In ice however, the water molecules are packed in a **3D hydrogen-bonded** network in a **rigid lattice**
- Each oxygen atom is surrounded by hydrogen atoms
- This way of packing the molecules in a solid 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

Structure and density of water



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

Examiner Tips and Tricks

Ice floats on water because of ice's lower density.

Your notes

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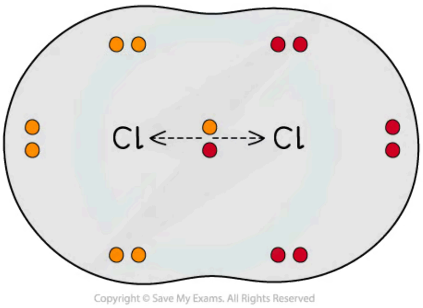
Bond Polarity & Dipole Moments

- **Electronegativity** is the ability of an atom to draw a pair of electrons towards itself in a covalent bond
- Electronegativity **increases** across a Period and **decreases** going down a Group

Polarity

- When two atoms in a covalent bond have the **same electronegativity** the covalent bond is **nonpolar**

Bonding electrons in a chlorine molecule

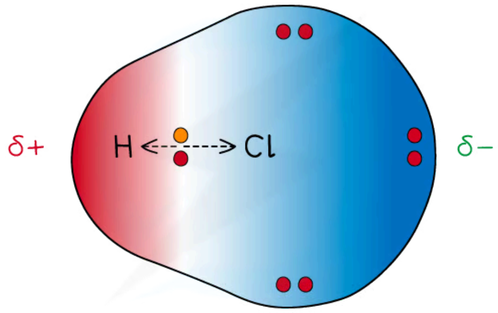


The two chlorine atoms have similar electronegativities so the bonding electrons are shared equally between the two atoms

- When two atoms in a covalent bond have **different electronegativities** the covalent bond is **polar** and the electrons will be drawn towards the **more electronegative** atom
- As a result of this:
  - The negative charge centre and positive charge centre do not **coincide** with each other
  - This means that the **electron distribution** is **asymmetric**
  - The **less electronegative** atom gets a partial charge of δ+ (**delta positive**)
  - The **more electronegative** atom gets a partial charge of δ- (**delta negative**)
- The greater the difference in **electronegativity** the more polar the bond becomes

Bonding electrons in a hydrogen chloride molecule

Your notes



Cl has a greater electronegativity than H causing the electrons to be more attracted towards the Cl atom which becomes delta negative and the H delta positive

Dipole moment

- The **dipole moment** is a measure of how **polar** a bond is
- The **direction** of the dipole moment is shown by the following sign in which the **arrow** points to the **partially negatively charged end** of the dipole:

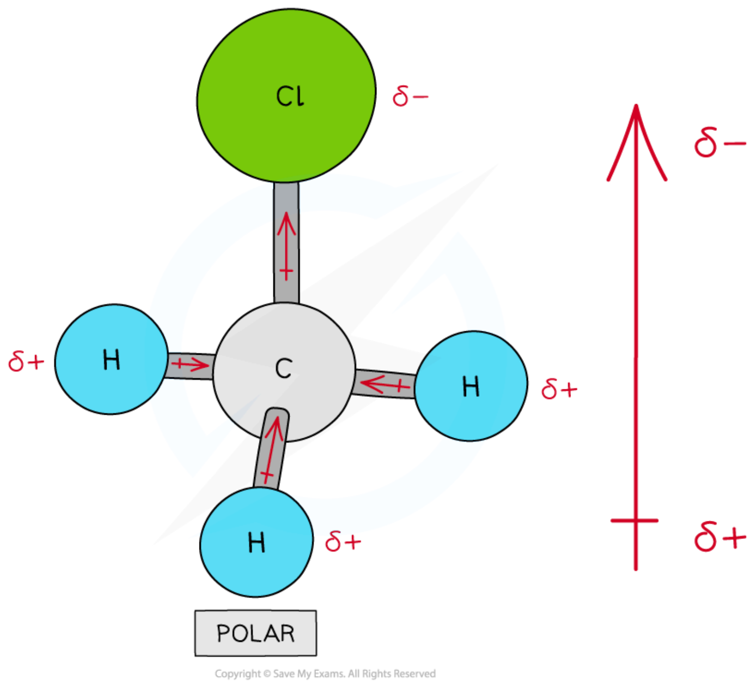
Representing dipoles

The sign shows the direction of the dipole moment and the arrow points to the delta negative end of the dipole

Assigning polarity to molecules

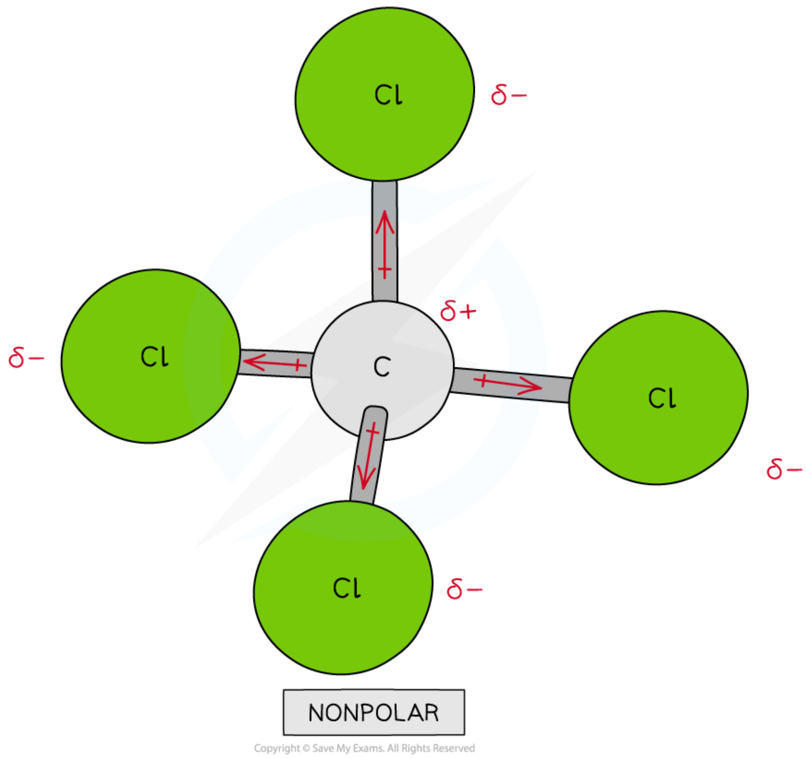
- To determine whether a molecule with **more than two atoms** is polar, the following things have to be taken into consideration:
  - The polarity of each bond
  - How the bonds are arranged in the molecule
- Some molecules have **polar bonds** but are overall not **polar** because the polar bonds in the molecule are arranged in such a way that the individual dipole moments **cancel each other out**

Polarity in chloromethane



There are four polar covalent bonds in CH3Cl which do not cancel each other out causing CH3Cl to be a polar molecule; the overall dipole is towards the electronegative chlorine atom

Polarity in tetrachloromethane



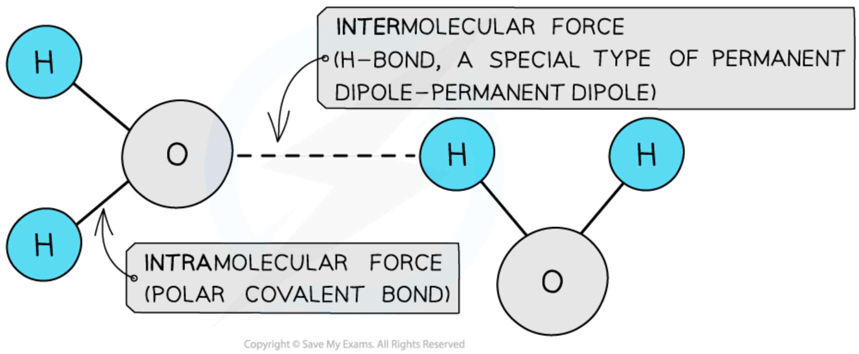
Though CCl4 has four polar covalent bonds, the individual dipole moments cancel each other out causing CCl4 to be a nonpolar molecule

Your notes

Van der Waals' Forces & Dipoles

- Covalent bonds are strong **intramolecular forces**
- Molecules also contain weaker **intermolecular forces** which are forces **between** molecules
- These intermolecular forces are called **van der Waals' forces**
- There are two types of van der Waals' forces:
    - **Instantaneous** (temporary) **dipole – induced dipole forces** also called **London dispersion forces**
    - **Permanent dipole – permanent dipole forces**

Intermolecular and intramolecular forces in water

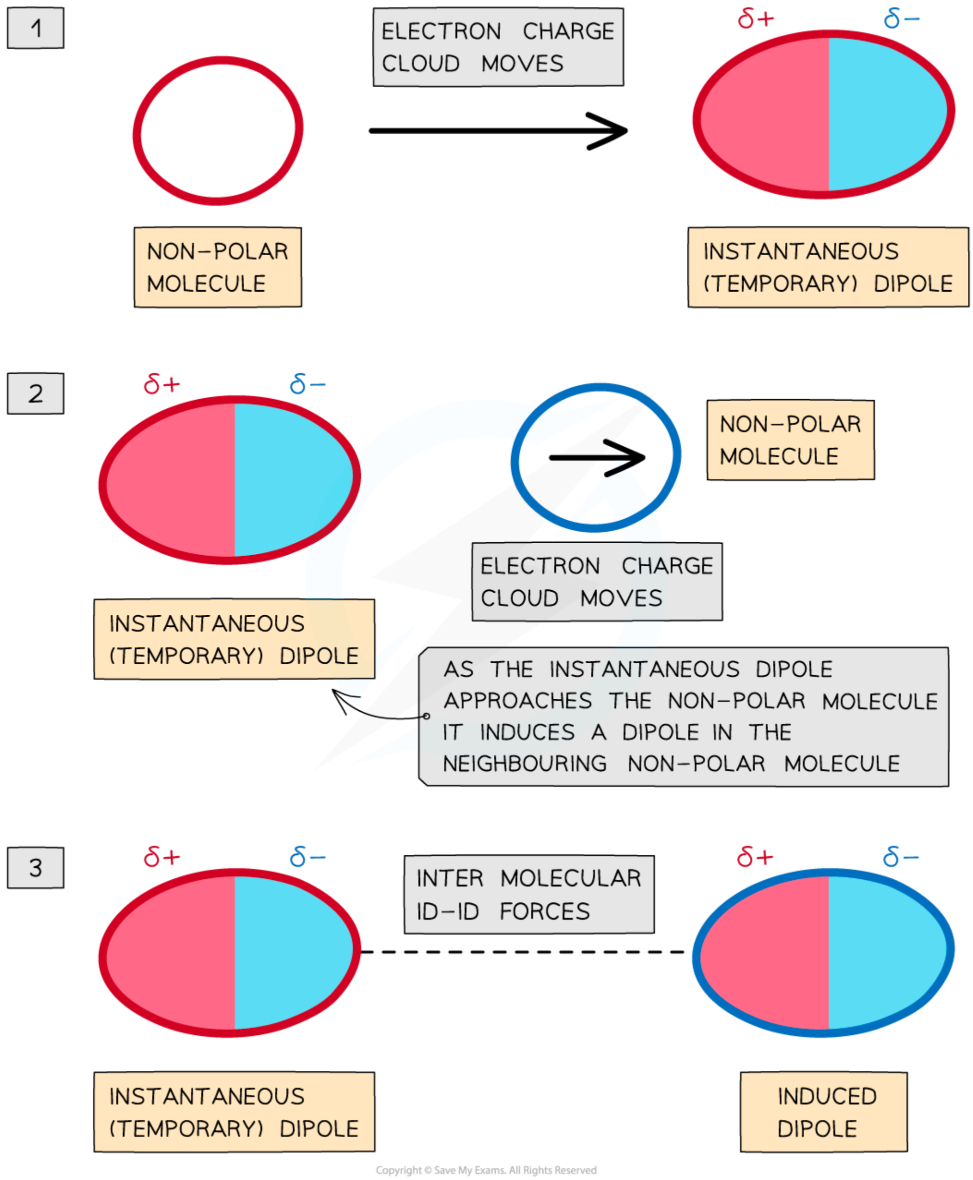


The polar covalent bonds between O and H atoms are intramolecular forces and the permanent dipole – permanent dipole forces between the molecules are intermolecular forces as they are a type of van der Waals' force

Instantaneous dipole – induced dipole (id – id)

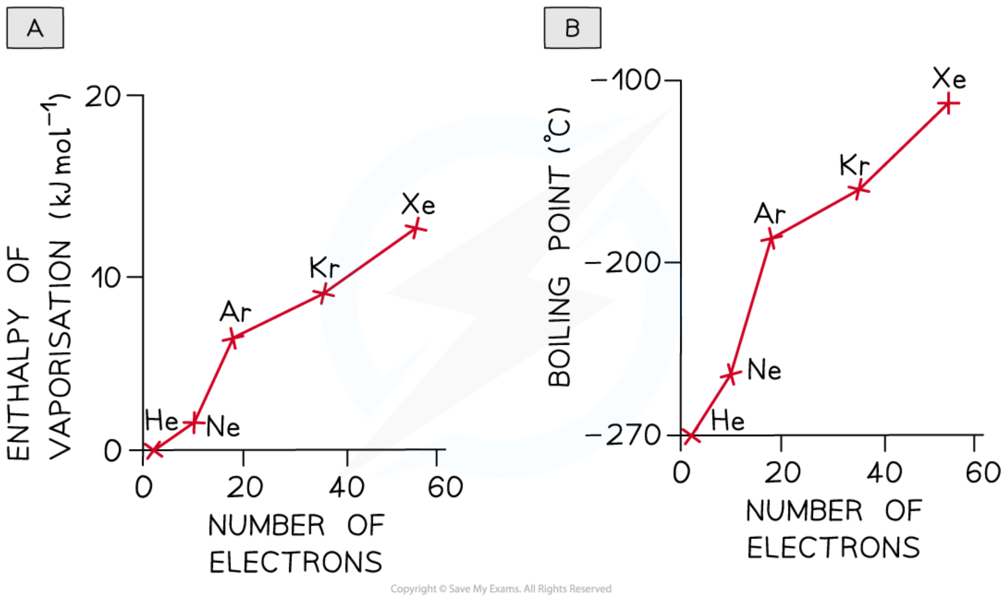
- **Instantaneous dipole – induced dipole forces** or **London dispersion forces** exist between all atoms or molecules
- The **electron charge cloud** in non-polar molecules or atoms are constantly moving
- During this movement, the electron charge cloud can be more on one side of the atom or molecule 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**

Instantaneous dipoles

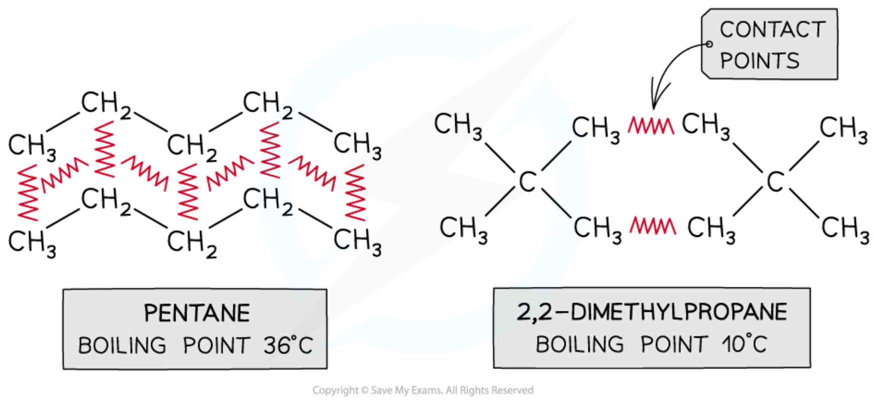


Id-id (London dispersion) forces between two non-polar molecules

- Id - id forces increase with:
  - Increasing number of electrons (and **atomic number**) in the molecule
  - Increasing the places where the molecules come close together



Going down the Group, the id-id forces increase due to the increased number of electrons in the atoms

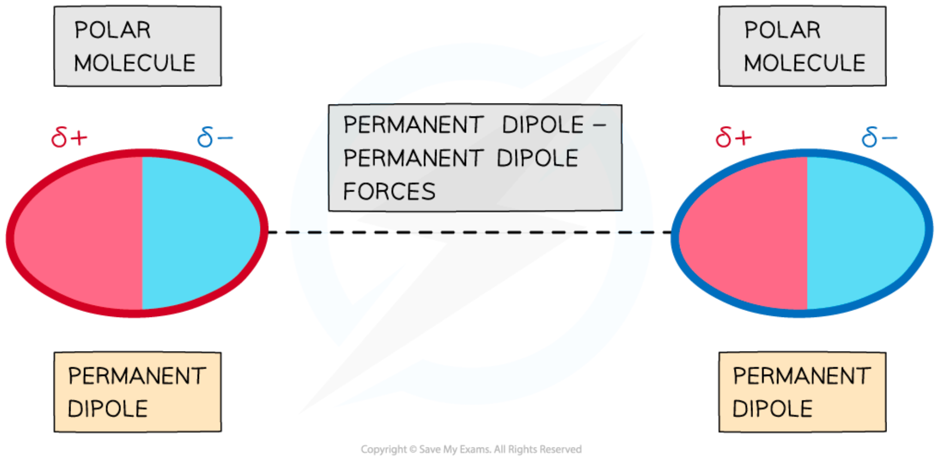


The increased number of contact points in pentane means that it has more id-id forces and therefore a higher boiling point

Permanent dipole - permanent dipole (pd - pd)

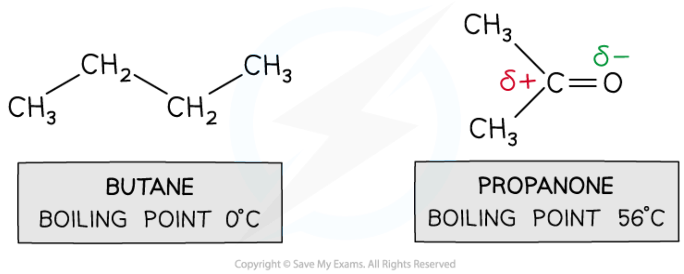
- **Polar molecules** have **permanent dipoles**
- The molecule will always have a **negatively** and **positively charged end**
- Forces between two molecules that have permanent dipoles are called **permanent dipole - permanent dipole forces**
- The **δ+ end of the dipole** in one molecule and the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

Your notes



The delta negative end of one polar molecule will be attracted onwards the delta positive end of a neighbouring polar molecule

- For small molecules with **the same number of electrons,** pd - pd forces are **stronger** than id - id
  - Butane and propanone have the same number of electrons
  - Butane is a nonpolar molecule and will have id - id forces
  - Propanone is a polar molecule and will have pd - pd 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

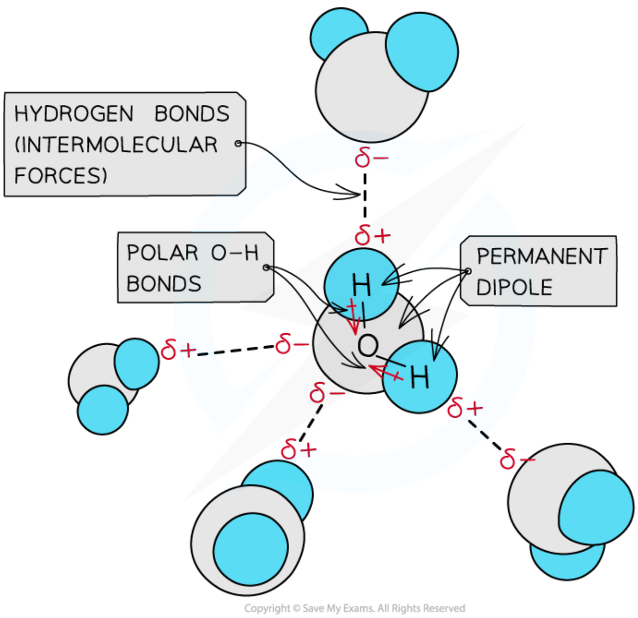
Examiner Tips and Tricks

Remember this difference: intramolecular forces are forces **within** a molecule, whereas intermolecular forces are forces **between** a molecule.

Hydrogen Bonding as a Permanent Dipole

- **Hydrogen bonding** is an **intermolecular force** between molecules with an -OH/-NH group and molecules with an N/O atom
- Hydrogen bonding is a special case of a **permanent dipole – dipole force** between molecules
  - Hydrogen bonds are **stronger** forces than pd - pd forces
- The hydrogen is bonded to an O/N atom which is so **electronegative**, that almost all the electron density from the covalent bond is drawn towards the O/N atom
- This leaves the H with a **large delta positive** and the O/N with a **large delta negative charging** resulting in the formation of a **permanent dipole** in the molecule
- A **delta positive H** in one molecule is **electrostatically attracted** to the **delta negative O/N** in a neighbouring molecule

Hydrogen bonds in water molecules



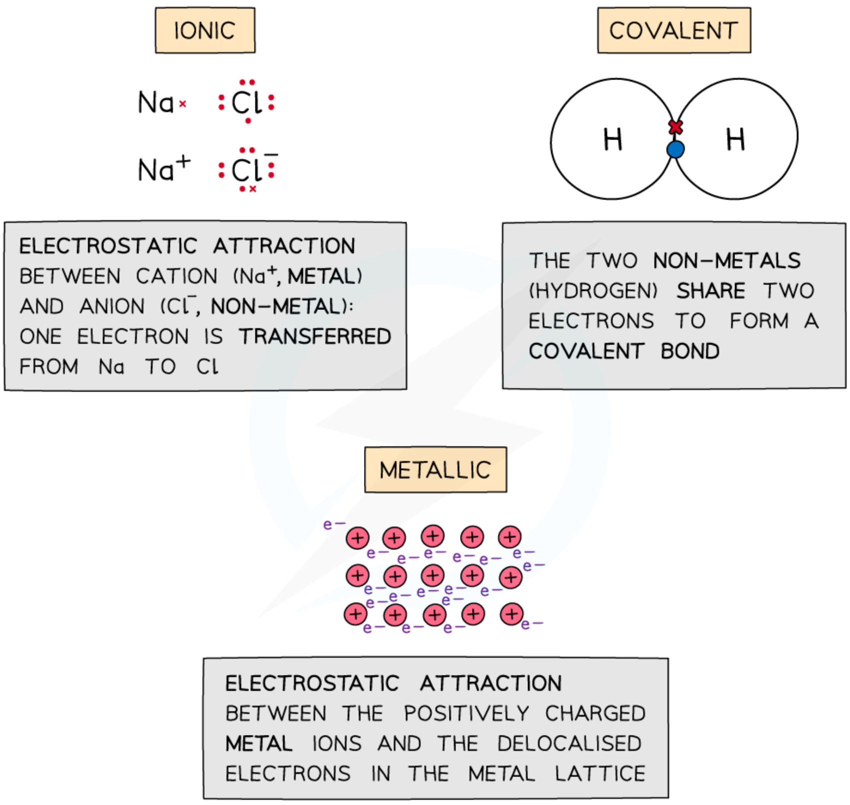
Hydrogen bonding in water occurs between the oxygen lone pair of one water molecule and the δ+ hydrogen atoms of another water molecule

Comparing Bonds & Intermolecular Forces

Intramolecular forces

- **Intramolecular forces** are forces **within** a molecule
- **Ionic bonding** is the **electrostatic attraction** between **positive** (cations) and **negative** (anions) ions in an ionic **crystal lattice**
  - These ions are formed by transferring the electrons from one species to the other
- **Covalent bonds** are formed when the outer electrons of two atoms are **shared**
- **Metallic bonding** is the **electrostatic attraction** of positively charged metal ions and their delocalised electrons in a **metal lattice**

Intramolecular forces

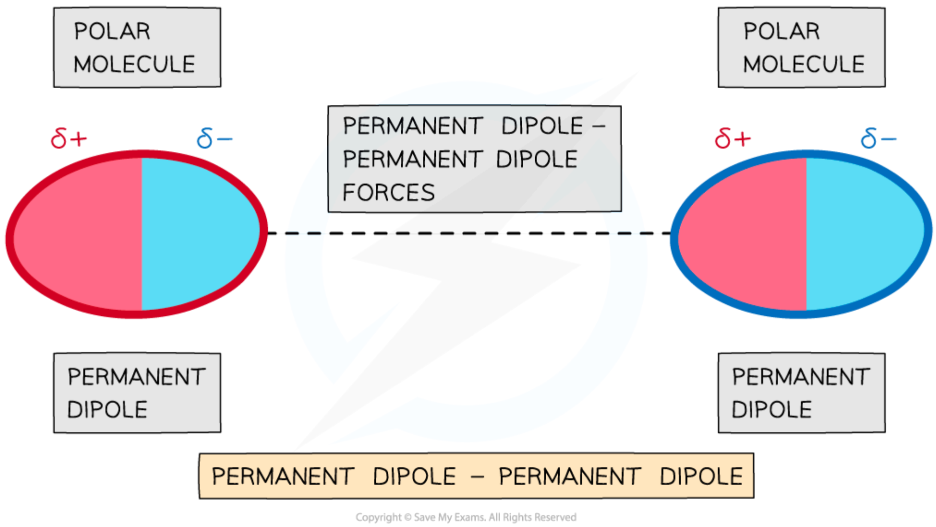


The three types of intramolecular forces are ionic, covalent and metallic bonding

Intermolecular forces

- **Intermolecular forces** are forces **between** molecules and are also called **van der Waals' forces**
- **Permanent dipole – permanent dipole** are the attractive forces between two neighbouring molecules with a permanent dipole
- **Hydrogen bonds** are a special type of **permanent dipole – permanent dipole** forces
- **Instantaneous dipole – induced dipole** (London dispersion) forces are the attractive forces between a temporary dipole and a neighbouring molecule with an induced dipole

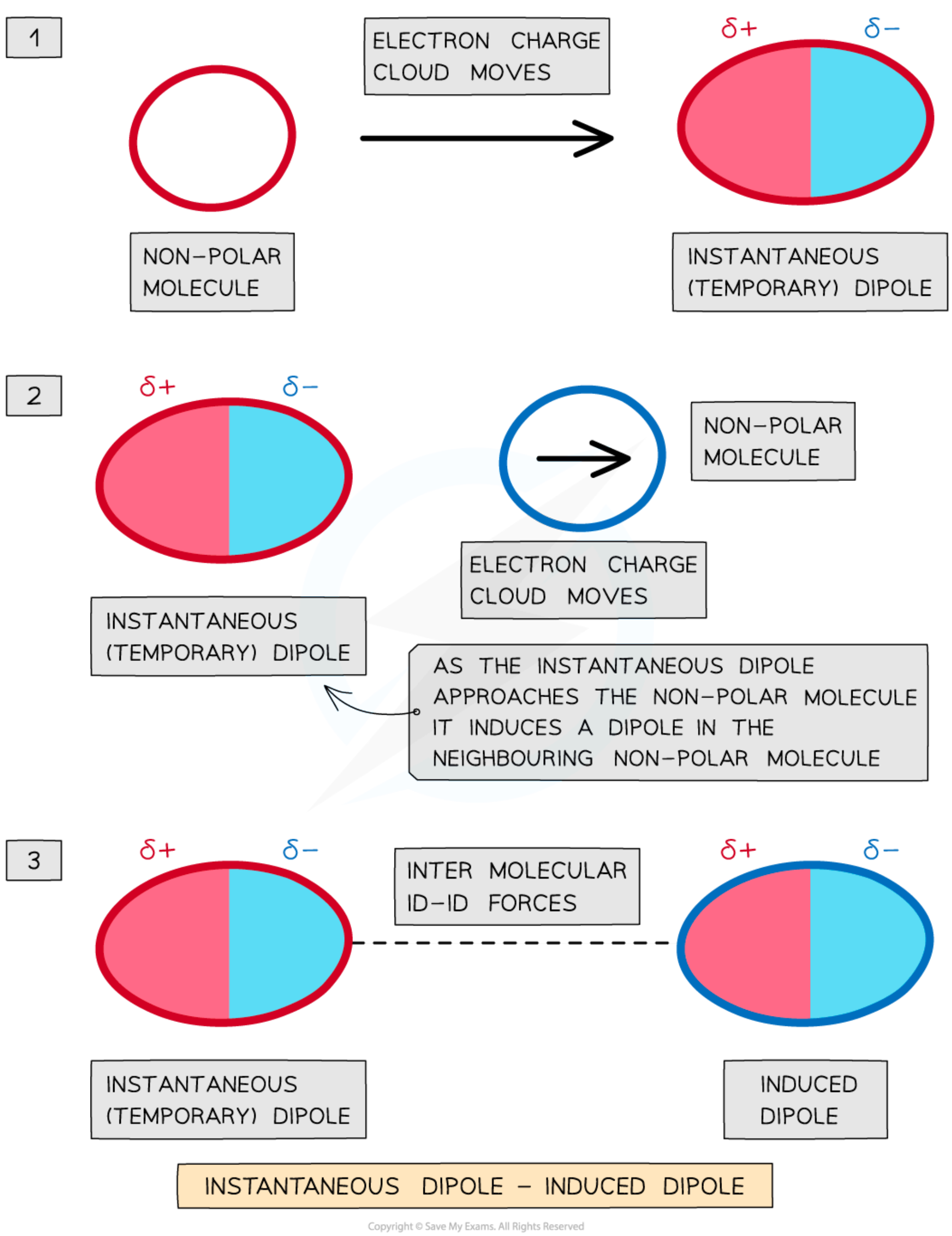
Permanent dipoles as intermolecular forces



Permanent dipole – permanent dipole are the intermolecular forces that occur between two neighbouring molecules with a permanent dipole

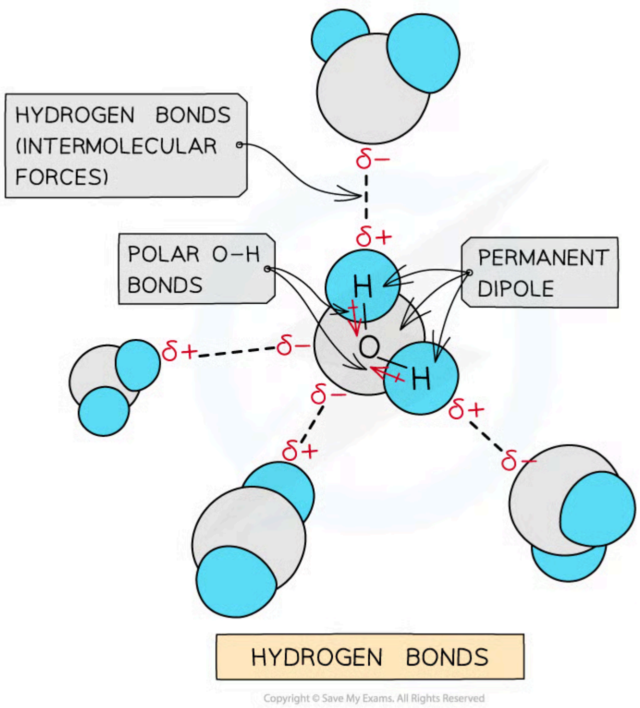
Instantaneous dipoles as intermolecular forces

Your notes



Instantaneous dipole – induced dipole (London dispersion) forces are the intermolecular forces that occur between a temporary dipole and a neighbouring molecule with an induced dipole

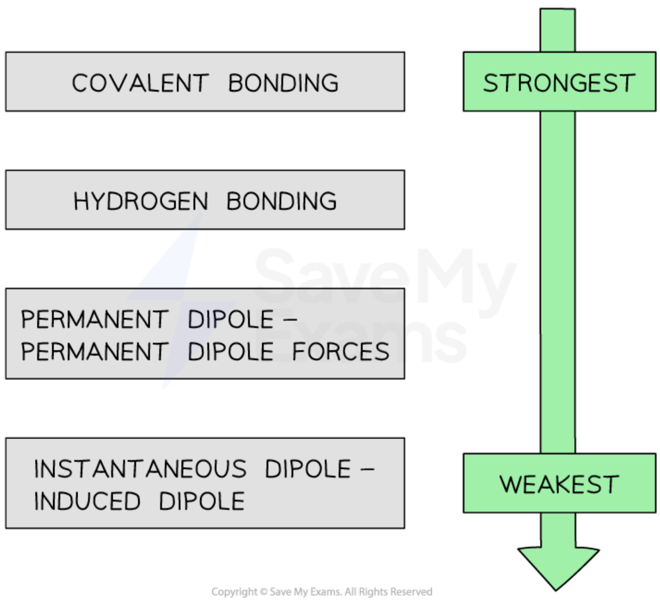
Hydrogen bonding as an intermolecular force



Hydrogen bonds are a special type of permanent dipole – permanent dipole forces

- In general, **intramolecular forces** are **stronger** than intermolecular forces
- The strengths of the types of bond or force are as follows:

The varying strengths of different types of bonds



In general, covalent bonding is the strongest force while instantaneous dipole – induced dipole is the weakest force

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