# CAIE Chemistry A-level

## 3: Chemical Bonding

Notes

## Electronegativity and Bonding

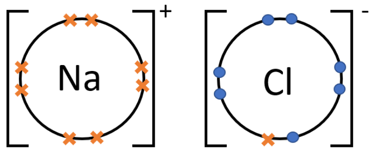
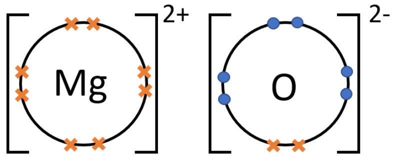
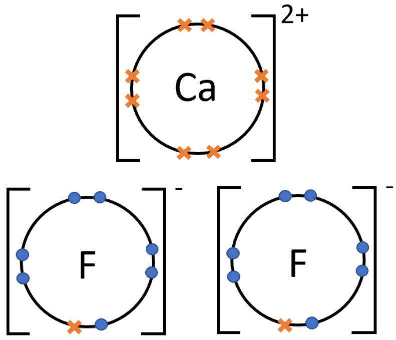
Electronegativity is the **power of an atom** to attract electrons to itself in a bond.

Moving **across a period** the electronegativity increases due to the net charge on the nucleus increasing. This attracts the bonding pair of electrons more strongly.
Moving **down a group**, electronegativity decreases due to the bonding pair of electrons being increasingly further from the nucleus attraction.

## Ionic Bonding

An ionic bond is formed when electrons are transferred from a metal to a non-metal, forming an ionic compound. The compound is held together by the **electrostatic attraction** between **the positively charged metal ions and negatively charged non-metal ions.**

**Dot and cross diagrams** are often used to represent ionic bonding. For one species electrons are shown as dots and the other as crosses. Typically only outer shell electrons are shown and charges are shown outside square brackets surrounding the ion.

| Compound | Ions | Formation of ions | Dot and cross diagram |
|---|---|---|---|
| Sodium chloride (NaCl) | $Na^+$ and $Cl^-$ | Na donates an electron to Cl |  |
| Magnesium oxide (MgO) | $Mg^{2+}$ and $O^{2-}$ | Mg donates 2 electrons to O |  |
| Calcium fluoride ($CaF_2$) | $Ca^{2+}$ and $F^-$ | Ca donates 2 electrons to 2 F |  |

In ionic compounds, ions are surrounded on all sides by oppositely charged ions forming a **giant ionic lattice**.

## Metallic Bonding

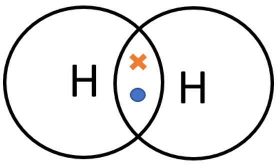
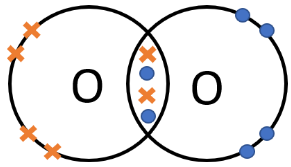
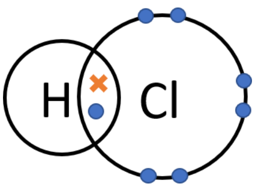
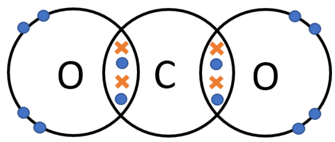
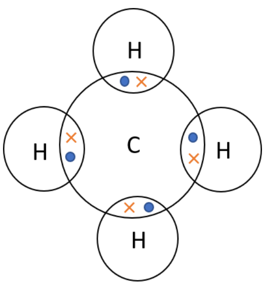
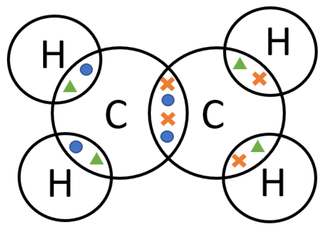
In metals, positive metal ions (cations) are fixed in a **lattice** and surrounded by mobile **delocalised electrons**. The strong electrostatic attraction between the positive metal ions and the sea of negative delocalised electrons hold the metal together.

## Covalent Bonding

A covalent bond is a chemical bond where electron pairs are shared between atoms. A covalent bond is the strong electrostatic attraction between a **shared pair of electrons** and the nuclei of the bonding atoms. This is because the negative electrons are attracted to the positive protons in the nuclei and this overcomes the repulsion between the two nuclei.

Similarly to ionic bonding, **dot and cross diagrams** can be used to represent covalent bonding. The circles (or outer shells) must overlap and this overlap must contain a dot and cross to represent the shared pair of electrons.

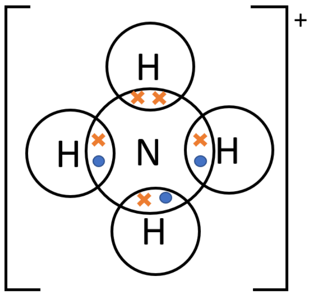
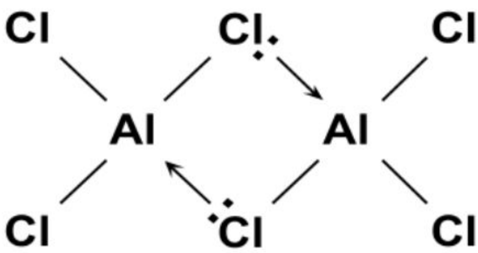
Below are examples of covalent compounds:

| Compound | Dot and cross diagram | Compound | Dot and cross diagram |
|---|---|---|---|
| Hydrogen ($H_2$) |  | Oxygen ($O_2$) |  |
| Hydrogen chloride (HCl) |  | Carbon dioxide ($CO_2$) |  |
| Methane ($CH_4$) |  | Ethene ($C_2H_4$) |  |

**Elements in period three can often expand their octet** including the compounds sulfur dioxide ($SO_2$), phosphorus pentachloride ($PCl_5$) and sulfur hexafluoride ($SF_6$).

## Coordinate (Dative Covalent) Bonding

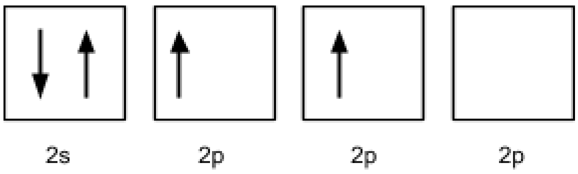
A dative covalent bond has **one atom which supplies both of the shared electrons**. In the dative covalent bond A→B, A donates a pair of electrons to B. Examples are shown below:

| **Compound** | **Dot and cross diagram** |
|---|---|
| Ammonium ion ($NH_4^+$) |  |
| $Al_2Cl_6$ |  |

## Sigma Bond ($\sigma$)

A sigma bond is a **single covalent bond** formed when **two orbitals overlap end-to-end**. The pair of electrons are found between the two nuclei.

Below is a diagram showing the electrons in the second shell of carbon:




Carbon forms 4 covalent bonds rather than 2 because this releases more energy and makes the molecule more stable. A small amount of energy is used to **promote** one of the 2s electrons to the empty 2p orbital (as these have a similar energy) to give 4 unpaired electrons. The carbon atom is now in an excited state. **Hybridisation** occurs when the electrons are rearranged again into four identical $sp^3$ hybrids. The sigma bond forms when two orbitals from different atoms **overlap end-to-end**.

The process of promoting an electron, hybridisation and formation of the molecular orbitals follows the same pattern in all covalently-bound molecules.

## Pi Bond (π)

A pi bond is a covalent bond formed when **2 orbitals overlap sideways**. The pi bond is the region **above and below a sigma bond** where this pair of electrons can be found.

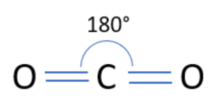
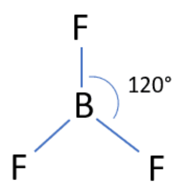
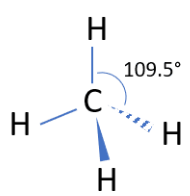
When a pi bond forms between two carbons, first a 2s electron is **promoted** to the empty 2p orbital to give 4 unpaired electrons. The carbon atom is now in an excited state. **Hybridisation** of three orbitals (rather than 4 when forming a sigma bond) forms $sp^2$ hybrids. **End-to-end overlap** of two $sp^2$ hybrids from different carbon atoms forms a sigma bond. The p orbital in each carbon contains an unpaired electron. These orbitals **overlap sideways** to form a pi bond.

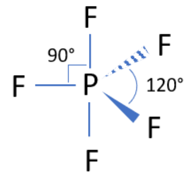
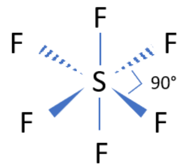
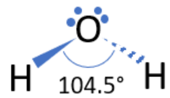
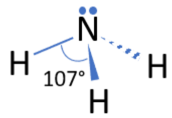
## Shapes of Molecules

The shape of a molecule is determined by the **arrangement of electrons** around the central atom. Electron pairs are regions of negative charge so they repel each other and arrange themselves as far apart as possible. **Lone pairs are more repulsive than bonding pairs** so the order of repulsion is:

| | |
|---|---|
| **Greatest repulsion** | Lone pair - Lone pair |
| | Lone pair - Bonding pair |
| **Lowest repulsion** | Bonding pair - Bonding pair |

When drawing the shapes of molecules, a bond in the plane of the paper is a normal line. A bold wedge shows the bond is coming towards you and a dotted wedge shows the bond is going away from you. Dots are used to represent electrons in a lone pair.

| Number of lone pairs (lp) and bonding pairs (bp) | Shape name | Bond angle | Example compound and diagram |
|---|---|---|---|
| 2 bp | Linear | 180° | $CO_2$   |
| 3 bp | Trigonal planar | 120° | $BF_3$   |
| 4 bp | Tetrahedral | 109.5° | $CH_4$   |

| | | | |
|---|---|---|---|
| 5 bp | Trigonal bipyramidal | 90° and 120° | $PF_5$  |
| 6 bp | Octahedral | 90° | $SF_6$  |
| 2 bp, 2 lp | Non-linear or V-shaped | 104.5° | $H_2O$  |
| 3 bp, 1 lp | Pyramidal | 107° | $NH_3$  |

Ions have the same shapes and bond angles as molecules. For example, the ammonium ion ($NH_4^+$) has 4 bonding pairs so has a tetrahedral shape and a bond angle of 109.5°.

## Intermolecular Forces

**Intermolecular forces** of attraction occur **between** neighbouring molecules.

### Electronegativity

Electronegativity is the ability of an atom to **attract a bonding pair of electrons** in a covalent bond. Electronegativity increases towards the top right of the periodic table. More electronegative atoms are better at attracting the bonding electrons in a covalent bond.

A polar bond is a bond with a **permanent charge difference** (or permanent dipole). This occurs when the two bonding atoms in a covalent bond are different because one atom is more electronegative than the other so it will attract the bonding electrons towards itself. If two atoms in a covalent bond are exactly the same, the electronegativity of both atoms will be the same so the bond will be non-polar.

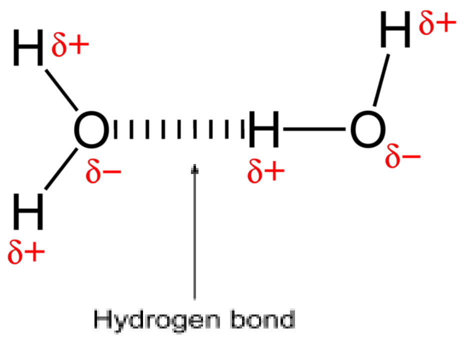
A polar molecule must contain **polar bonds** and be **non-symmetrical**. If a polar molecule is symmetrical, the dipoles will cancel each other out.
The oxygen in non-metal oxides is very electronegative. This causes a permanent dipole across the covalent bond so the atom that oxygen is bonded to becomes partially positive.

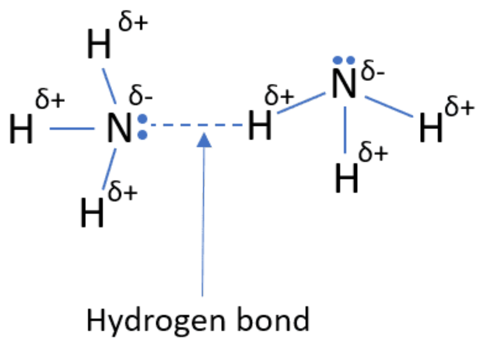
When the oxide is added to water, lone pairs of oxygen in the water are attracted to the partially positive atom in the oxide causing **hydrolysis**. Below are examples of this reaction:

$$P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$$
$$Cl_2O(g) + H_2O(l) \rightarrow 2HClO(aq)$$

### Hydrogen Bonding

Molecules containing **N-H**, **O-H** or **F-H** bonds can form hydrogen bonds. This is because oxygen, nitrogen and fluorine are **very electronegative** meaning they draw the bonding electrons towards them to create a strong dipole (a charge difference across the bond). A hydrogen bond is the attraction between the partially positive hydrogen ($H^{\delta+}$) and a lone pair on $O^{\delta-}$, $N^{\delta-}$, or $F^{\delta-}$. Water ($H_2O$) and ammonia ($NH_3$) are examples of compounds that form hydrogen bonds:




Hydrogen bonds are the reason that water has such anomalous properties, like its high melting and **boiling point** for a molecule its size, its **high surface tension** and its **higher density** as a liquid than a gas. When boiling water the relatively strong hydrogen bonds need to be broken rather than just van der waals or permanent dipoles, meaning its b.p is higher than other molecules its size. Hydrogen bonds mean water molecules are attracted to each other so the surface tension is higher so animals like water striders can walk on water surfaces. The hydrogen bonding in water causes water molecules in **ice** to align in an **open lattice structure.** This means water expands as it freezes so **ice is less dense than water**.

### Reactivity

The reactivity of covalent compound is affected by three factors:

- **Bond energy**: the amount of energy needed to break one mole of a given gaseous covalent bond to produce gaseous atoms. Bond energies given in the data book are an average and don't consider the specific molecule the bond is found in.
- **Bond length**: the distance between two nuclei in a covalent bond. A longer bond means the shared pair of electrons is further from at least one nucleus so the attraction and bond strength decreases with increasing bond length.
- **Bond polarity**: if the electronegativities of the bonding atoms are different, the bond will be polar and the bonding atoms will have partial charges.

The strength of a bond rather than polarity typically determines the rate of a reaction. A **stronger bond** means the compound is **less reactive**. Polarity may mean molecules are attracted to each other which triggers the reaction.

### Van der Waals Forces

Dispersion forces, also known as London forces, are a type of van der Waals force found between **symmetrical, non-polar molecules**. There are no permanent dipoles but electrons are mobile and in an instant, they may be **unevenly distributed**. This creates a **temporary dipole**, with the side containing more electrons becoming partially negative. The temporary dipole can **induce dipoles in neighbouring molecules** as the partial negative charge repels electrons. These opposite partial charges will remain attracted to each other.

Permanent dipole-dipole forces are another type of van der Waals forces found between **polar molecules**. The permanent dipole in these molecules means the partial charges are more strongly attracted to one another. Molecules with permanent dipole-dipole forces usually have higher boiling points than those which only have London forces between them. However, $CCl_4$ has a higher boiling point than $CHCl_3$ because $CCl_4$ is a bigger molecule with more electrons so the increased London forces compensate for the lack of permanent dipole-dipole forces.

Elements in Group 18 exist as single atoms so the only forces between the atoms are London forces. These forces are **relatively weak** so require little energy to break meaning Group 18 elements have low boiling points. Boiling point increases down the group because the **number of electrons and atomic radius increases** meaning there are stronger temporary dipoles and stronger London forces between the atoms.

$Br_2$ is liquid at room temperature because although it only has London forces between molecules, it contains lots of electrons meaning strong temporary dipoles between molecules.