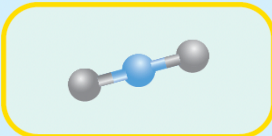
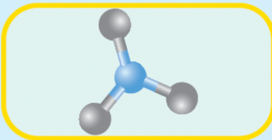
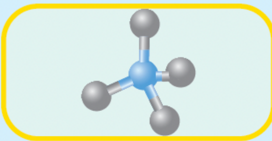
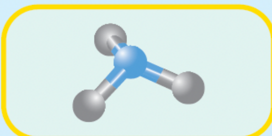
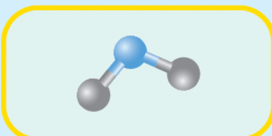
Chapter 9: Molecular Shapes and Intermolecular Forces

- We use a theory called VSEPR (pronounced 'vesper') theory to **predict the shape of a molecule.**
- **VSEPR** stands for **v**alence-**s**hell **e**lectron-**p**air **r**epulsion theory.
- The VSEPR theory is based on the fact that **electron pairs in the valence shell** (the outermost energy level) **repel each other.**
- Since electron pairs repel each other, they'll **arrange themselves as far away from each other as possible.**

Bond pair of electrons = when electrons are **shared between atoms**
Lone pair of electrons = aren't shared and aren't involved in a bond (i.e. belong to one atom only)
Lone pairs have **extra repulsion power** – i.e. they repel other electron pairs to a greater extent than bond pairs do.

Determining the shape of a molecule

Step 1: Count valence electrons of central atom
Step 2: Add one electron for each bonding atom
Step 3: Divide total by 2 to find the number of electron pairs
Step 4**:** Identify types of electron pairs and predict shape (using the table below).

Total number of electron pairs around central atom	Number of bond pairs	Number of lone pairs	Shape of molecule	Diagrams	Bond angle
2	2	0	Linear		180°
3	3	0	Trigonal planar		120°
4	4	0	Tetrahedral		109.5°
4	3	1	Pyramidal		107°
4	2	2	V-shaped/ bent		104.5°

For Leaving Cert we can think of **the central atom in a molecule as the atom of which there is only one.**

What shape is a molecule of BeH_2?

Step 1: 2
Step 2: 2 + 2 = 4
Step 3: 4 ÷ 2 = 2 pairs
Step 4: Be is bonded to two hydrogen atoms – therefore, both pairs of electrons must be bond pairs.
A molecule with two bond pairs and zero lone pairs is **linear**, with a bond angle of **180º**.

What shape is a molecule of BCl_3?

Step 1: 3
Step 2: 3 + 3 = 6
Step 3: 6 ÷ 2 = 3 electron pairs
Step 4: B is bonded to three Cl atoms. Therefore, all three electron pairs are bond pairs.

A molecule with three bond pairs **is trigonal planar,** with a bond angle of **120º**.

What shape is a molecule of CH_4?

Step 1: 4
Step 2: 4 + 4 = 8
Step 3: 8 ÷ 2 = 4 electron pairs
Step 4: C is bonded to four H atoms. Therefore, all, four electron pairs must be bond pairs.

A molecule with four bond pairs is **tetrahedral**, with a bond angle of 109.5º.

What shape is a molecule of H_2O?

Step 1: 6
Step 2: 6 + 2 = 8
Step 3: 8 ÷ 2 = 4 electron pairs
Step 4: The O atom is bonded to two H atoms, so two of these electron pairs must be bond pairs. **Any remaining pairs are lone pairs.**

A molecule with two bond pairs and two lone pairs is **V-shaped**. We draw H_2O in a V-shaped shape, with a bond angle of **104.5º**.

What shape is a molecule of NH_3?

Step 1: 5
Step 2: 5 + 3 = 8
Step 3: 8 ÷ 2 = 4 electron pairs
Step 4: The N atom is bonded to three H atoms, so three electron pairs must be bond pairs, and therefore the remaining pair must be a lone pair.

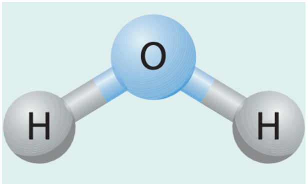
A molecule with three bond pairs and one lone pair is **pyramidal**, with a bond angle of **107º**.

AB_3 = pyramidal / trigonal planar
AB_2 = linear / V-shaped
AB_4 = tetrahedral

If a molecule has non-polar bonds only, then the molecule is also non-polar.
If a molecule has polar bonds, it may be polar or non-polar.

A polar molecule must have two characteristics:
1. It must contain polar covalent bonds.
2. The centres of positive and negative charge must not coincide (the molecule must not be symmetrical).

Determine if the molecule below is polar or non-polar.

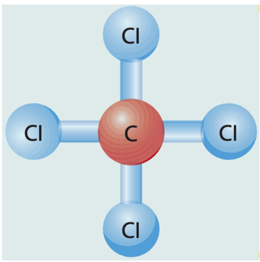


Step 1: Determine if the bonds are polar or non-polar
Step 2: Determine if the centres of negative and positive charge coincide (if the molecule is symmetrical)

1. The O-H bonds in a water molecule are polar covalent.
2. We can see that the centre of negative charge in this water molecule is at the O atom. The positive charge is midway between the hydrogen atoms. The centres of negative and positive charges are not in the same place – they do not coincide.

The partial positive and partial negative poles are in different parts of the molecule – therefore, the molecule has two poles – i.e. is polar.

Determine if this molecule is polar or non-polar.



1. The C-Cl bonds are polar covalent (electronegativity difference of 0.61).
2. The centre of positive charge is in the centre of the molecule – at the carbon atom. The centre of negative charge is also in the centre of the molecule – midway between all four chlorine atoms.

The partial positive and partial negative poles of this molecule coincide and ‘cancel’ each other out. Therefore, this molecule is not a polar molecule.

A molecule will be non-polar if:

1. It contains only pure/non-polar covalent bonds.
2. It contains polar covalent bonds but the centres of negative and positive charge coincide (the molecule is symmetrical).

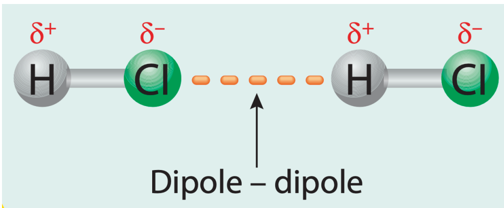
Intermolecular forces

Intermolecular forces are the forces between molecules.

1. Permanent dipole-dipole forces

Permanent dipole-dipole forces exist between the negative pole of one polar molecule and the positive pole of another polar molecule.

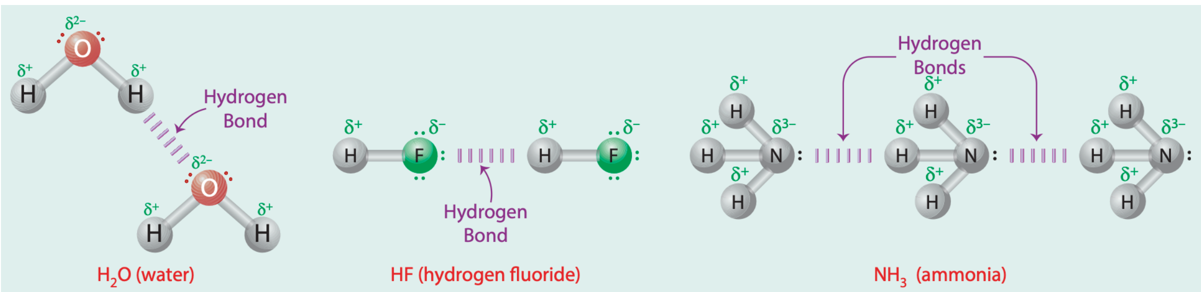
- Large electronegativity differences between atoms in a molecule results in a **dipole** – i.e. there are two poles of charge in the molecule: one partially positive, one partially negative.
- The slightly positively charged end of one molecule is attracted to the slightly negatively charged end of the other.
- This force of attraction between molecules is called a permanent dipole-dipole force.
- Since the δ^+ and δ^- charged poles are permanent, these intermolecular forces are also permanent.



Permanent dipole-dipole forces: hydrogen bonding

Hydrogen bonds are a specific type of permanent dipole-dipole attraction between a hydrogen atom of one molecule and a small, highly electronegative atom (nitrogen, oxygen or fluorine) of a neighbouring molecule.

- Hydrogen bonds are a special type of permanent dipole-dipole intermolecular force that occurs between **the hydrogen of one molecule and the nitrogen, oxygen or fluorine of another.**
- Atoms of nitrogen, oxygen and fluorine are all **very small and highly electronegative**. The large difference in electronegativity between **H and N**, **O or F** causes a **very strong dipole**. Essentially, hydrogen bonds are a **stronger type** of permanent dipole-dipole force.
- For **a compound to have hydrogen bonding between its molecules** it must contain a hydrogen atom **directly bonded** to a nitrogen, oxygen or fluorine molecule. It's not just the presence of these atoms in a molecule – they must be **directly bonded to each other**.

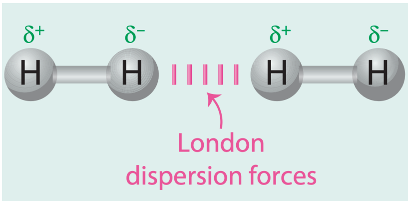


**Note that HF is an exception to the rule of thumb electronegativity rule – it is covalent, despite H and F having an electronegativity difference of 1.78.*

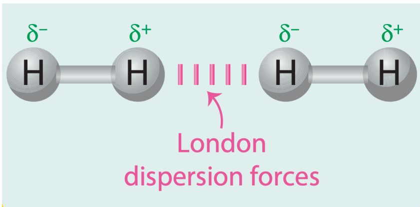
2. London dispersion forces

London dispersion forces are weak, temporary forces of attraction between neighbouring molecules as a result of temporary dipoles.

- London dispersion forces are similar to permanent dipole-dipole forces except that they're **temporary**.
- They're still a force of attraction between the partially positive end of a molecule and the partially negative end of a neighbouring molecule, except that **the partial charges are very short-lived, and therefore the attraction between molecules is also short-lived.**
- Temporary dipoles form because electrons within molecules (and atoms) move around. This causes temporary dipoles, i.e. cause one end of the molecule to be temporarily δ^+ and the other to be temporarily δ^-.
- This can induce dipoles in neighbouring molecules.



Since there isn't a large enough electronegativity difference for the electrons to be permanently attracted towards one end of the molecule, they continue to move, and the next moment the partial charges could look like this:



All molecules have London dispersion forces between them. For non-polar molecules – e.g. H_2, O_2, Cl_2 – they're the only type of intermolecular forces between molecules.

3. Ion-dipole forces

Ion-dipole forces are forces of attraction between an ion and a molecule with a dipole.

The strength of ion-dipole attractions depends on (1) the size of the charge on the ion; (2) the strength of the dipole on the molecule; (3) the distance between the ion and the dipole.

Intermolecular forces and physical properties: melting and boiling points

Intermolecular forces have a significant effect on physical properties, such as **the melting or boiling point** of the substance. This is because **attractive forces between molecules make molecules more difficult to separate**.

Comparing compounds with different IMFs:

Stronger intermolecular force = higher boiling point, e.g. H_2O (with hydrogen bonds between its molecules) has a higher boiling point than H_2 (with only London dispersion forces between its molecules)

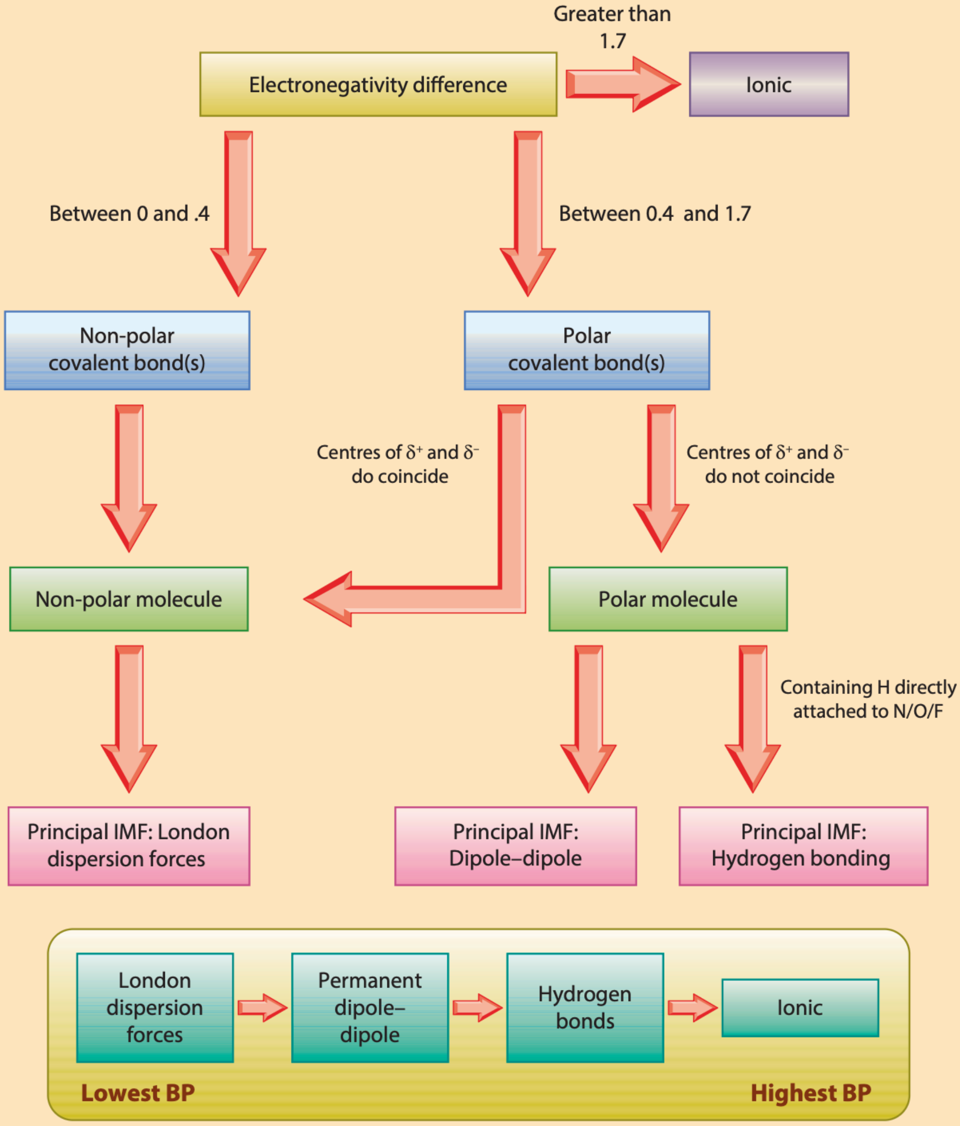
It's important to note that this rule only applies to **comparable substances** – i.e. substances with molecules of similar relative molecular mass (M_r).

Comparing compounds with the same IMFs:

Larger molecule = higher boiling point, e.g. O_2 has a higher boiling point than H_2.
This is because….

- The **strength of intermolecular forces increases as the size of the molecule increases.**
- Larger molecules have more electrons = can form stronger dipoles (dipoles with a greater imbalance of electrons).
- Stronger dipoles can induce stronger dipoles in neighbouring molecules.
- This increases the strength of the intermolecular forces.

Crack it!



For any two compounds that have the same IMFs between their molecules, compare the size of the molecules (larger molecule = stronger IMF = higher BP).

Intermolecular forces and physical properties: solubility

Like dissolves like

Polar solute in a polar solvent
For example, polar ammonia will dissolve in polar water (the partial positive and negative charges on one will attract the partial positive and negative charges on the other).

Ionic solute in a polar solvent
The ionic bonding in the ionic compound is overcome by the strong attraction between the charged ions and the partial charges on the polar molecules. There are ion-dipole forces between the ions and polar molecules.

Non-polar solute in polar solvents
Non-polar substances have no charged ions or permanently partially charged molecules. The molecules of the polar solvent will be more attracted to each other than they are to the non-polar (not charged) solute. The solute molecules will remain close together, and not disperse, i.e. not form a solution.

Non-polar solute in non-polar solvent
In the absence of stronger polar attractions, the non-polar solvent and solute will be attracted to each other by London dispersion forces.

Effect of molecular shape on physical properties

The shape of its molecules determines some physical properties of the compound.
For example, a molecule with intramolecular polar covalent bonds may be symmetrical – i.e. be a non-polar molecule. As a result it will have only London dispersion forces and have relatively low melting points and boiling points, as well as being insoluble in water.