# UNIT 3 - CHEMICAL BONDING

When elements form compounds, they either gain, lose or share electrons to get to the nearest stable noble gas electron configuration. There are exceptions to this rule for some Group 15, 16, and 17 elements.

The first type of chemical bonding is ionic bonding. Ionic bonding is the electrostatic attraction between positively and negatively charged ions (cations and anions) in an ionic crystal lattice.

The second type of chemical bonding is covalent bonding, which occurs when the outer electrons of two atoms are shared.

Ionic and covalent bonds are usually very strong and it takes an immense amount of energy to break them. The third type of bonding occurs between metals and is called metallic bonding.

Anion - a negatively charged ion

Cation - a positively charged ion

Lattice - a regular repeating arrangement of atoms, molecules, or ions in three dimensions throughout the whole crystal structure.

Although strong covalent bonds keep together the atoms within molecules, the forces between molecules are weak. These forces are called **van der Waals' forces**, the general term used to describe all **intermolecular forces**. There are several types of van der Waals forces, including

- Dipole (instantaneous dipole-induced dipole (id-id) forces. These are also called London dispersion forces)
- Permanent dipole-permanent dipole (pd-pd)
- Hydrogen bonding, which is a stronger form of permanent dipole-dipole forces

Van der Waals' forces - weak forces of attraction between molecules involving either instantaneous (id-id) or permanent dipole-permanent dipole (pd-pd) forces (including hydrogen bonding). The expression covers all types of intermolecular forces.

Intermolecular forces - the weak forces between molecules

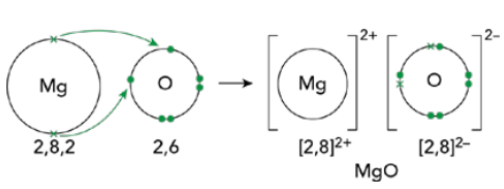
**Ionic Bonding**

*How are ions formed?*

One way to form an ion is for an element to gain or lose one or more electrons:

- Positive ions are formed when an element loses electrons. Metal atoms usually lose electrons to form cations
- Negative ions are formed when an element gains electrons. Non-metal atoms usually gain electrons to form anions

The charge of the ion depends on how many electrons are lost or gained, for example, iron (III) loses three electrons, and so will be written as $Fe^{3+}$.




When metals combine with non-metals, the valence electrons of the metals are transferred to the valence shell of the non-metal. As a result of this, the metal and non-metal atoms usually end up with complete outer shells.

The strong force of attraction between the positive and negative ions in the ionic crystal lattice results in an ionic bond. An ionic bond is sometimes referred to as an electrovalent bond.

*Dot and cross diagrams*

Dot and cross diagrams help keep the electrons from separate elements distinguishable from each other so it is visible to the reader which element donated what electron, and which element gained the electron. Dot and cross diagrams are usually asked in exams, and you can either be asked to draw all the shells of each element or just the valence shells since this is the shell that donates and receives electrons from other elements.

Ionic bond - the electrostatic attraction between oppositely charged ions (cations and anions)

Electrovalent bond - another name for the ionic bond

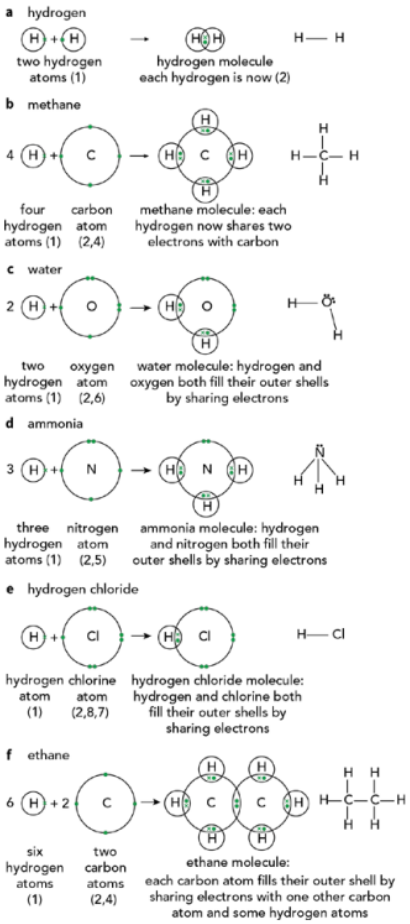
Dot and cross diagram - a diagram showing the arrangement of the outer shell electrons in an ionic or covalent element or compound. The electrons are shown as dots or crosses to show their origin (which element they're from)

Properties of Ionic Bonds

- High melting and boiling points
- High enthalpy change of vaporization
- Most ionic compounds are soluble in water because they are polar
- Ionic compounds conduct electricity when in liquid states (otherwise their electrons are locked in a regular lattice arrangement and cannot move about and carry a charge)

**Covalent Bonding**

*Single covalent bonds*




When two nonmetal atoms combine, they share one or more pairs of electrons. A shared pair of electrons is called a single covalent bond, or a *bond pair*. A single covalent bond is represented by a single line, for example, the single covalent bond between two chlorine atoms: Cl—Cl.

When chlorine atoms, for example, combine, not all the electrons are used in the bonding process. The pairs of valence electrons not used in bonding are called lone pairs.

Covalent bonding - the electrostatic attraction between the nuclei of two atoms and a shared pair of electrons.

Lone pairs - pairs of electrons in the outer shell of an atom that is not involved in bonding.

*Multiple covalent bonds*

Double covalent bonds

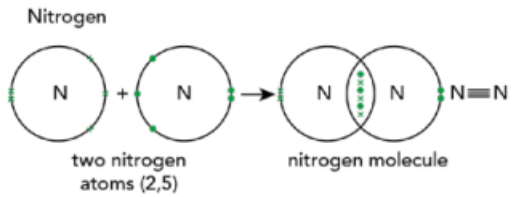
Some atoms can bond together by sharing two pairs of electrons. We call this a double covalent bond, and this is represented by a double line between the atoms, for example, between two oxygen atoms: O=O.

Double covalent bond - two shared pairs of electrons bonding two atoms together, represented by a double line between the two atoms involved in the bonding process, e.g. Oxygen: O=O.

To form an oxygen molecule, each oxygen atom has to gain two electrons to complete its valence shell, so two pairs of electrons are shared and two covalent bonds are formed.

For carbon dioxide ($CO_2$), each oxygen atom needs two electrons, but the carbon atom needs four, so two oxygen atoms each form two bonds with carbon so that the carbon gains a full outer shell.

In ethene, two hydrogen atoms share a pair of electrons with each carbon atom, this leaves each carbon atom with two outer shell electrons for bonding with each other. A double bond is formed between the two carbon atoms.




Triple covalent bond

Some atoms can also share three electron pairs, which is known as a triple covalent bond.

For nitrogen to become a molecule, it needs to gain three electrons, so 3 pairs of electrons are shared and covalent bonds are formed.

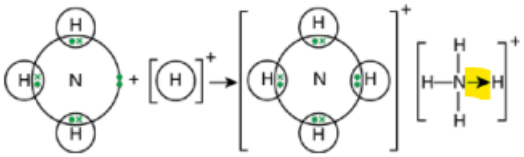
*Coordinate bonding (dative covalent bonding)*

A coordinate bond, or dative covalent bond, is formed when one atom provides both the electrons needed for the bond. For dative covalent bonding to occur, two conditions need to be met:

1) One atom must have a lone pair of electrons
2) A second atom must have an unfilled orbital to accept the lone pair. In other words, an electron-deficient compound

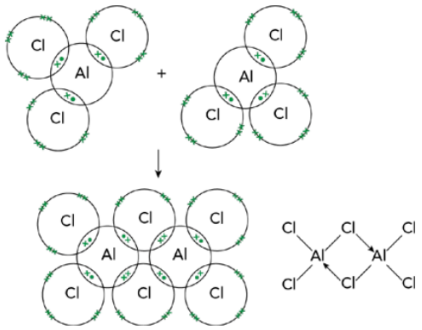
Coordinate bonding - the sharing of a pair of electrons between two atoms where both the electrons in the bond come from the same element. Also known as dative covalent bonding.

Electron-deficient - an atom or molecule that has less than its usual share of electrons



An example of this is the ammonium ion, $NH^{4+}$. It is formed when ammonia combines with a hydrogen ion. The hydrogen ion is electron deficient and has space for two more electrons in its valence shell (basically it started as having no electrons whatsoever; it had an empty valence shell). The nitrogen atom in the ammonia molecule has a lone pair of electrons, which provides the two electrons hydrogen needs to have a full outer shell.

A dative bond is shown in a display formula with an arrow going from the donating element to the element receiving electrons. Here, from nitrogen to hydrogen.



Another molecule with dative bonds is aluminum chloride.

<u>Properties of Covalent Compounds</u>

- Low melting points
- Low boiling points
- Low enthalpy change of vaporization
- Some are soluble in water because they are polar (e.g. HCl), and some aren't because they are non-polar (e.g. iodine ($I_2$))
- Covalent compounds cannot conduct electricity

*Bond length and bond energy*

In general, <u>double bonds are shorter than single bonds</u>, because they have a greater quantity or negative charge between the two atoms' nuclei. The greater force of attraction between the electrons and the nuclei pulls the atoms closer together, resulting in a stronger bond.

We measure the strength of a bond through bond energy, which is the energy needed to break one mole of a given covalent bond (in a gaseous state).

Bond energy - the energy required to break one mole of a particular covalent bond in a gaseous state. The units of bond energy are kilojoules per mole, kJ $mol^{-1}$.

The distance from the nucleus of one atom to another depends on the two atoms forming the bond. The internuclear distance between two covalently bonded atoms is called the bond length.

Bond length - the distance between the nuclei of two covalently bonded atoms.

| Bond | Bond energy / kJ $mol^{-1}$ | Bond length / nm |
|---|---|---|
| C–C | 350 | 0.154 |
| C=C | 610 | 0.134 |
| C–O | 360 | 0.143 |
| C=O | 740 | 0.116 |

★ The greater the size of the atom, the greater the bond length
★ The greater the bond length, the smaller the bond energy

Bond strength can influence the reactivity of a compound. If the bond energy is extremely strong, for example in nitrogen (which has a triple bond: N≡N), it will require a large amount of energy to overcome the bond, therefore, the element will be less reactive than one that has a lower bond energy. The polarity of the bond and whether the bond is a σ bond or a π bond both play a large part in determining chemical reactivity.

## Shapes of Molecules

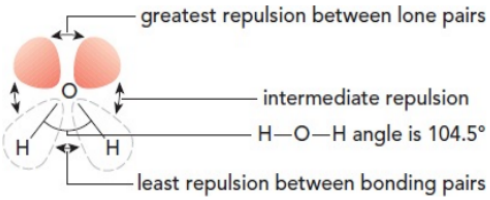
*Valence Shell Electron Pair Repulsion Theory (VSEPR)*

VSEPR:

- The valence shell electrons are the electrons in the main outer shell
- Pairs of electrons repel each other because they have the same charge
- A lone pair of electrons repel each other more than a bonded pair of electrons
- Repulsion between multiple and simple bonds is treated the same as repulsion between single bonds. Repulsions between pairs of double bonds are greater
- The shape of a molecule can be deduced by this theory, with the most stable shape that minimizes the forces of repulsion

The shape and bond angles of covalently bonded molecules depend on two things:

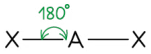
1) The number of pairs of electrons around each atom
2) Whether these pairs are lone pairs or bonding pairs




Lone pairs of electrons have a more concentrated electron charge cloud than bond pairs. The charges of lone pairs are wider and slightly closer to the nucleus, resulting in a different amount of repulsion between different types of electron pairs.

This diagram shows the repulsion between lone and bonding pairs of electrons in a water molecule. The repulsion of the lone pairs is greater than the repulsion of the bond pairs, which is why the bonds between the H atoms seem to be being pushed downwards due to the repulsion force.

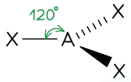
*Working out the shapes of molecules*




LINEAR

Linear: for this structure, electron pairs have minimum repulsion and are located as far apart as possible, resulting in a linear structure with a bond angle of 180°.

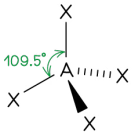
- 2 Bond Pairs
- No lone pairs
- 180° bond angle




TRIGONAL PLANAR

Trigonal Planar: the central atom is surrounded by three pairs of electrons. Placing the electron pairs in this arrangement (forming a triangle) minimizes the electron pair repulsion.

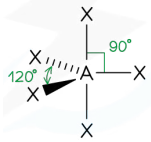
- 3 Bond Pairs
- No lone pairs
- 120° bond angle




TETRAHEDRAL

Tetrahedral: the four bonding pairs of electrons in this structure repel each other equally, and two of these bonds are in different planes, with the dotted line showing the bond projecting INTO the paper, and the solid triangle showing the bond projecting OUT of the paper.

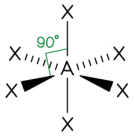
- 4 Bond Pairs
- No lone pairs
- 109.5° bond angle




TRIGONAL BIPYRAMIDAL

Trigonal Bipyrimidal:

- 5 Bond Pairs
- No lone pairs
- 90° bond angle (with 120° between the two projecting bonds)

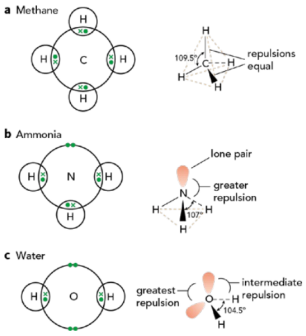



OCTAHEDRAL

Octahedral:

- 6 bond pairs
- No lone pairs
- 90° bond angle (the same bond angle for all bonds, all planes)

The shapes of molecules, however, are not constricted to just regular shapes. If the compound has an element that contains lone pairs, the bond angle will change. One lone pair of electrons decreases the bond angle by 2.5°.



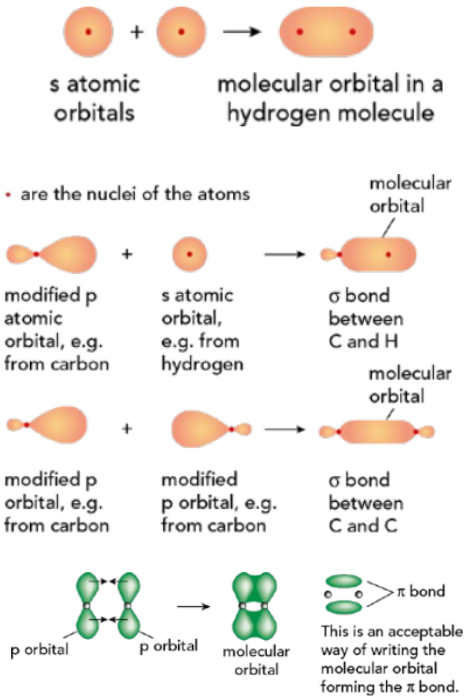

Ammonia for example, without a lone pair, would have a tetrahedral structure. But since it has one lone pair of electrons, the bond angle will decrease by 2.5: 109.5 - 2.5 = 107°. So the bond angle for ammonia would be 107°. Similarly, for water, $H_2O$ would, without any lone pairs, be a tetrahedral structure. Water has <u>two</u> lone pairs, so the bond angle would decrease by 5° (because 2.5 x 2 = 5). So: 109.5° - 5 = <u>104.5</u>°.

**σ bonds and π bonds**

Single covalent bonds are formed when two nonmetal atoms combine (when their orbitals overlap). This combined orbital is called a molecular orbital.

The amount of overlaps of the atomic orbitals determines the strength of the bond: the greater the overlap, the stronger the bond. The diagram adjacent shows two hydrogen atoms combining to form a molecular orbital.

★ The merging of atomic orbitals is called hybridization. Mixing an s orbital with three, two, or one ρ orbitals forms $sp^3$, $sp^2$, and sp atomic orbitals




★ Sigma (σ bonds) are formed from the linear overlap of atomic orbitals (head-on overlap), whilst ρi (π bonds) are formed from the sideways overlap of atomic orbitals.

P orbitals can also overlap linearly to form covalent bonds. When ρ orbitals are involved in forming single bonds, they become modified to inclined some s orbital character. The orbital is slightly altered to make the lobes of the ρ orbitals bigger.

<u>$sp^3$ hybridization</u>

★ When one 's' orbital mixes with three 'ρ' orbitals to form four new orbitals named $sp^3$.

This kind of orbital is 25% s orbital and 75% ρ orbital. This kind of hybridization is why molecules form tetrahedral structures.

<u>$sp^2$ hybridization</u>

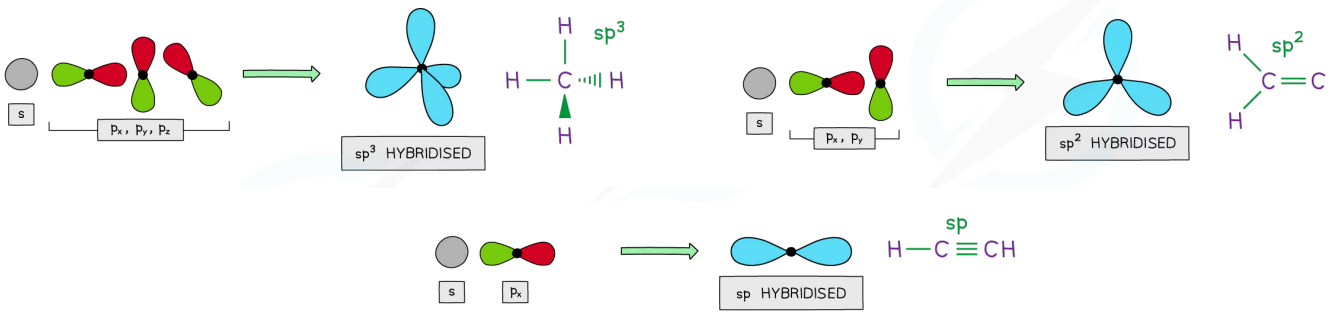
★ When one 's' orbital merges with two 'ρ' orbitals to form three new orbitals

$sp^2$ hybridization is always in one plane and forms the trigonal planar structure in compounds.

<u>sp hybridization</u>

★ When one 's' orbital merges with one 'ρ' orbital to form two new orbitals

This type of hybridization always forms a linear structure in compounds.



## Metallic Bonding

**Metallic bonding - the strong electrostatic force of attraction between positively charged cations and a sea of delocalized electrons**

The strength of metallic bonds increases as the number of delocalized electrons per atom increases. This means that the more electrons a metal can lose, the stronger its metallic bonding will be. For example, Aluminum is in Group 3, so it can lose 3 electrons. Compared to let's say Sodium (which can only lose 1 electron), Aluminum has stronger metallic bonding because it has more delocalized electrons.

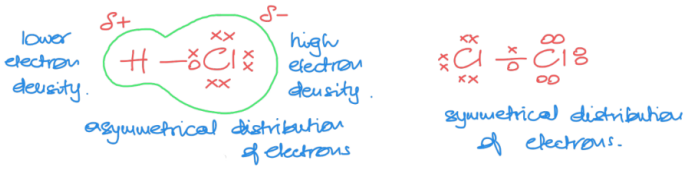
Metallic bonding gives metals their unique properties:

- It gives metals their high melting and boiling points because of how much energy it takes to overcome the strong electrostatic forces of attraction between the cations and electrons
- The delocalized electrons are free to move around and carry a charge, which allows metals to conduct electricity. Again, metals with more delocalized electrons can conduct more electricity.
- Metals are also excellent conductors of heat because of how the vibrations pass through the atoms that are packed closely together. This is also why most metals are sonorous (make a ringing sound when struck)

## Intermolecular Forces

**Electronegativity - the ability of an atom to attract electrons in a chemical bond**

The four most electronegative elements are Fluorine, Oxygen, Nitrogen, and Chlorine (in that order. You can use the acronym FONCl to remember this).




*What makes a bond polar?*

- Asymmetrical distribution of electrons

If one of the elements in a molecule is more electronegative than the other, it will pull the electrons toward its nucleus, resulting in uneven electron distribution.

| Non-polar Bond | Polar Bond |
|---|---|
| Similar atoms with the same electronegativity (e.g. diatomic molecules like $Cl_2$) | Different atoms with different electronegativities (e.g. HCl, HBr – the electronegativity difference is great) |
| Equal pull on the bond pair | Unequal pull on the bond pair |
| Equal distribution of electrons | Unequal distribution of electrons |

<u>Electronegativity — Periodicity</u>

Electronegativity **increases** across a Period
Electronegativity **decreases** down a group

<u>Factors Influencing Electronegativity</u>

- Nuclear charge: atoms in the same period with a greater nuclear charge are more likely to attract the bonding pair of electrons.
- Atomic radius: atoms in the same group where the valence electrons are further from the nucleus are less likely to attract the bonding pair of electrons because the pull of the nucleus on the is weaker.
- Shielding: the greater the number of inner electron shells and sub-shells, the lower the effective nuclear charge on the bonding electrons due to shielding.

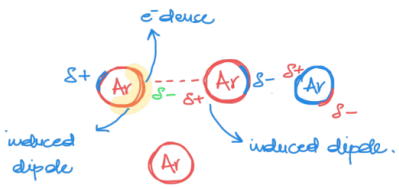
<u>The Pauling Scale</u>

This is the most commonly used scale to measure electronegativity. It has no units. The difference in the electronegativity values based on the Pauling scale can be used to determine where a substance is ionic or covalent.

- Metals have relatively low Pauling values while non-metals have higher values. Therefore, if a substance is ionic (metal + non-metal), the electronegativity difference will be greater than 1.8.
- If the substance is covalent, the electronegativity difference will be less than 1.8 (because non-metals have similar Pauling values)
- Some compounds are not entirely covalent and have some ionic character in them. These have intermediate electronegativity differences, e.g. 1.0

Instantaneous-Induced Dipole Forces (id-id)

Instantaneous dipole–induced dipole forces are sometimes called temporary dipole–induced dipole forces or London Dispersion forces.




The electron charge clouds in a non-polar molecule or atom are constantly moving. Oftentimes more of the charge cloud is on one side of the molecule than the other meaning that one end of the molecule has, for a short time, more negative charge than the other. A temporary dipole is established. This dipole can **induce** a dipole on neighboring molecules. As a result of this, there are forces of attraction between the δ+ end of the dipole in one molecule and the δ– end of the dipole in a neighboring molecule. These dipoles are always temporary because the electron clouds are always moving.

(id-id) forces can increase by:
- Increasing the number of electrons and protons in the molecule
- Increasing the number of contact points between the molecules (contact points - places where molecules come close together)

Permanent dipole-Permanent Dipole (pd-pd) forces

Molecules with pd-pd forces are considered polar.
The attractive force between the δ+ charge on one molecule and the δ– charge on a neighboring molecule causes a weak attractive force between the molecules.

(pd-pd) forces are stronger than (id-id) forces and so require more energy to overcome.

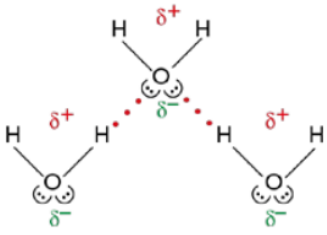
- Polar molecules are often hydrophilic, meaning they are soluble in water. This is because water is also polar. Non-polar molecules are hydrophobic, meaning they do not mix with water. They repel water molecules and clump together. Oil is a non-polar substance, which is why it doesn't mix with water.

Hydrogen Bonding

Hydrogen bonding is the strongest form of intermolecular bonding. It is a type of permanent dipole-permanent dipole bonding.

For hydrogen bonding to occur between two molecules:

- One molecule must have a hydrogen atom covalently bonded to F, O, or N (the three most electronegative atoms)
- A second molecule must have an F, O, or N atom with an available lone pair of electrons.




For hydrogen bonding to happen, the molecules must have:

- An H atom covalently bonded to a highly electronegative atom, e.g. N, O, or F
- Another highly electronegative atom with a lone pair of electrons.

When a hydrogen atom is covalently bonded to a very electronegative atom, the bond is highly polarised. The δ+ charge on the hydrogen atom is high enough for a bond to be formed with a lone pair of electrons on the F, O, or N atom of a neighboring molecule.

Intermolecular forces and Boiling points

(id-id) – weakest IMF → lowest boiling points
(pd-pd) – strong IMF → moderate boiling point
Hydrogen bonding – strongest IMF → very high boiling point