Edexcel International AS Chemistry

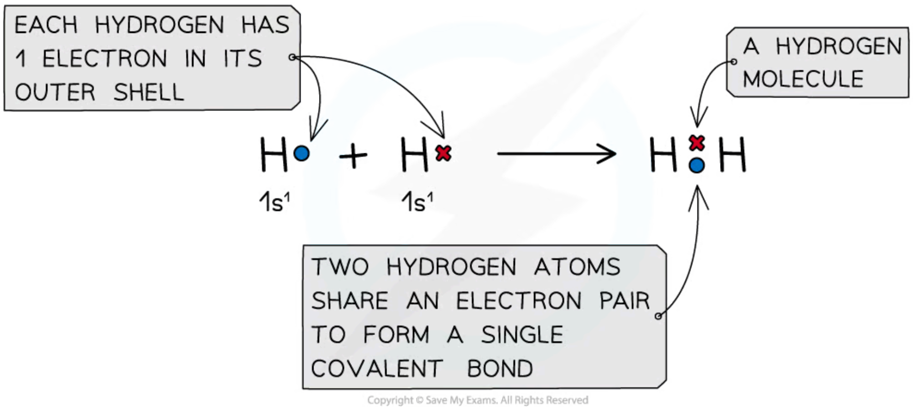
Your notes

Covalent Bonding & Structure

Contents

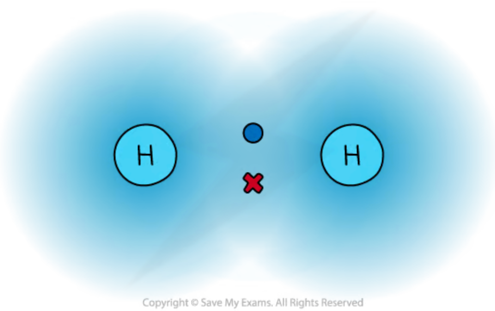
Evidence of Covalent Bonding

- **Covalent** bonding occurs between two **non-metals**
- A covalent bond involves the **electrostatic attraction** between nuclei of two atoms and the electrons of their outer shells
- **No electrons** are **transferred** but only **shared** in this type of bonding
- When a covalent bond is formed, two **atomic orbitals** overlap and a **molecular orbital** is formed
- Covalent bonding happens because the electrons are more stable when attracted to two nuclei than when attracted to only one



The positive nucleus of each atom has an attraction for the bonding electrons shared in the covalent bond

- In a normal covalent bond, each atom provide one of the electrons in the bond. A covalent bond is represented by a short straight line between the two atoms, H-H
- Covalent bonds should not be regarded as shared electron pairs in a fixed position; the electrons are in a state of constant motion and are best regarded as **charge clouds**

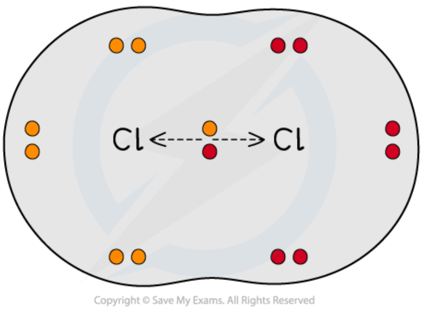


A representation of electron charge clouds. The electrons can be found anywhere in the charge clouds

Bond Polarity

Non-metals are able to **share** pairs of electrons to form different types of covalent bonds Sharing electrons in the covalent bond allows each of the 2 atoms to achieve an electron configuration similar to a noble gas This makes each atom more stable

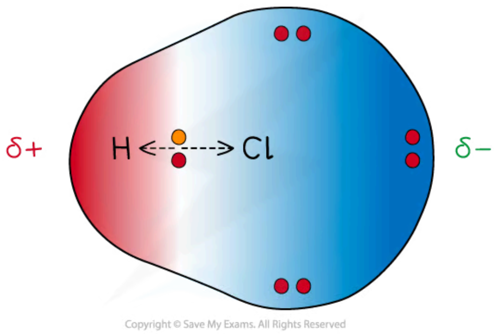
- When two atoms in a covalent bond have the **same electronegativity** the covalent bond is **nonpolar**



The two chlorine atoms have identical 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 until the bond becomes ionic



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

The octet rule

- In some instances, the central atom of a covalently bonded molecule can accommodate **more** or **less** than 8 electrons in its outer shell
    - Being able to accommodate **more** than 8 electrons in the outer shell is known as **'expanding the octet rule'**
        - Atoms from Period 3 onwards can accommodate more than 8 electrons as the d-orbitals are accessible
        - Common examples of elements that can have an 'expanded octet' are phosphorous and sulfur
        - For example, PCl_5, which has 10 electrons around the central phosphorus atom
        - In SF_6, there are 12 electrons around the central sulfur atom
    - Accommodating **less** than 8 electrons in the outer shell means that the central atom is **'electron deficient'**
        - Boron has 3 electrons in its outer shell, $2s^2 2p^1$
        - When it forms a covalent compound, these three electrons are paired
        - For example, BF_3 which has 6 electrons around the central boron atom

Covalent bonding & simple covalent lattice structures

- Covalent bonding can be responsible for substances that have many different structures and therefore different physical properties
- Small molecules such as H_2O and N_2 are simple units made from covalently bonded atoms
- These simple molecules contain **fixed numbers** of atoms
- **Simple covalent lattices** have low **melting** and **boiling points**
    - These compounds have weak intermolecular forces between the molecules
    - Only little energy is required to break the lattice
- Most compounds are insoluble with water
    - Unless they are polar and can form hydrogen bonds (such as sucrose)
- They do not **conduct electricity** in the **solid** or **liquid** state as there are no charged particles
    - Some simple covalent compounds do conduct electricity in solution, but this is because their interaction with water produces ions, for example, HCl which forms H^+ and Cl^- ions when in aqueous solution
- Buckminsterfullere, C_{60}, is an exception to some of these general points about simple molecules
    - Buckminsterfullerene and other fullerenes are spherical networks of carbon atoms
    - They are made up of large molecules but they are **not classed as giant covalent structures**

Your notes

- Compared to other simple covalent molecules, buckminsterfullerene has a higher melting and boiling point
    - Fullerenes are generally larger molecules so will have larger intermolecular forces because of the number of electrons within the molecule which require more energy to overcome
- Fullerenes are good insulators as, despite having delocalised electrons within their structure, these cannot pass between molecules and therefore cannot conduct electricity

Your notes

Covalent bonding & giant covalent lattice structures

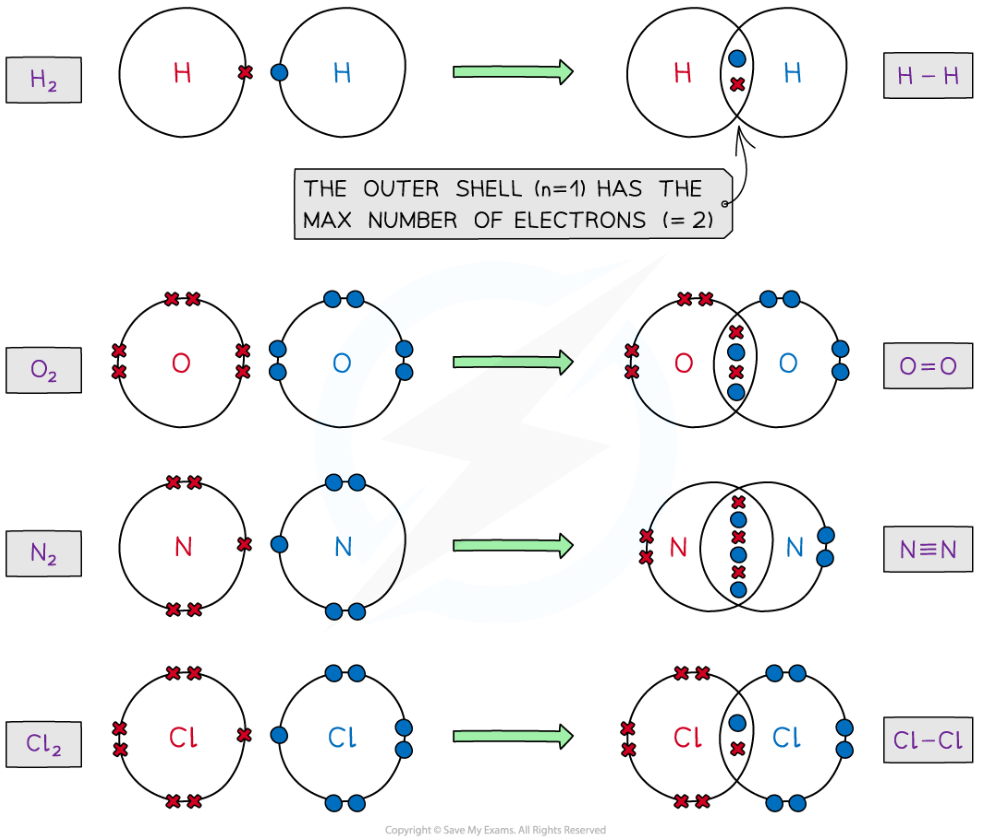
- Giant covalent structures have a **huge number** of non-metal atoms bonded to other non-metal atoms via strong covalent bonds
- These structures can also be called **giant lattices** and have a **fixed ratio** of atoms in the overall structure
- Some of the common macromolecules you should know about include diamond and graphite
- **Giant covalent lattices** have **very high melting** and **boiling points**
    - These compounds have a large number of **covalent bonds** linking the whole structure
    - A lot of energy is required to break the lattice
- The compounds can be **hard** or **soft**
    - Graphite is **soft** as the forces between the carbon layers are weak
    - Diamond and silicon(IV) oxide are **hard** as it is difficult to break their 3D network of strong covalent bonds
- Most compounds are insoluble with water
- Most compounds do not **conduct electricity** however some do
    - In graphite, each carbon atom has three outer electrons that are involved in bonding to other carbon atoms, leaving one electron which becomes **delocalised** between the carbon layers and can move along the layers when a voltage is applied
    - Diamond and silicon(IV) oxide do not conduct electricity as all four outer electrons on every carbon atom are involved in a **covalent bond** so there are no freely moving electrons available

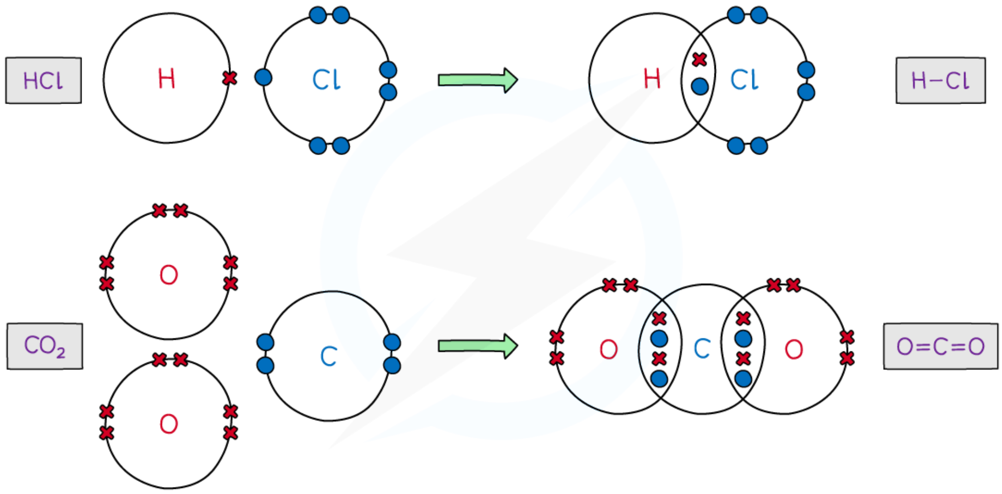
Your notes

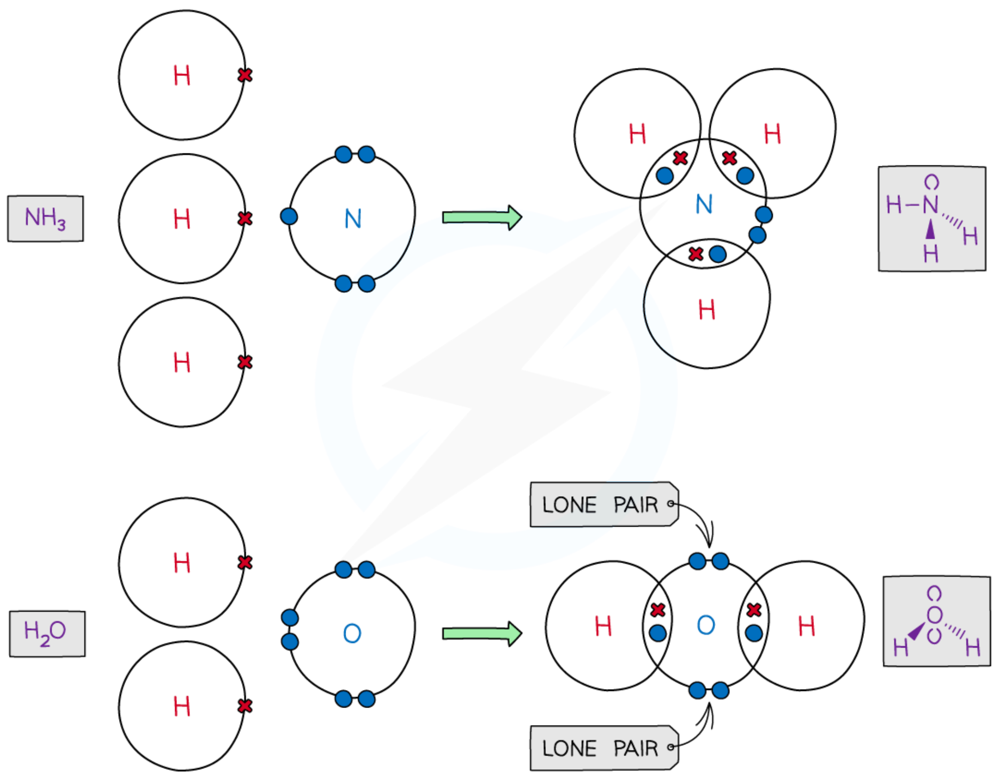
Covalent Dot & Cross Diagrams

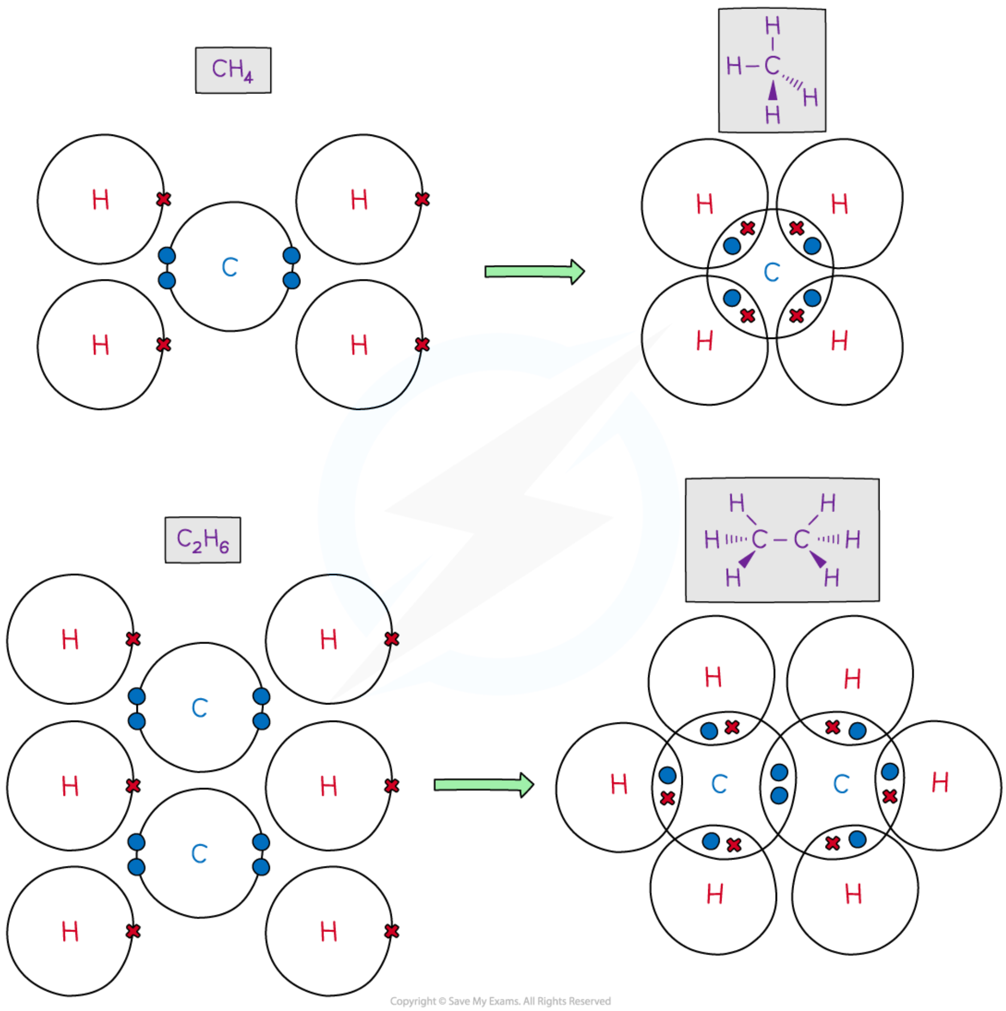
Covalent compounds

- The atoms in covalent compounds will **share** their outer valence electrons to achieve a **noble gas** configuration




HCl
H
Cl
H
Cl
H–Cl
CO$_2$
O
O
C
O
C
O
O=C=O


NH$_3$
H
H
H
N
H
H
N
H
H$_2$O
H
H
O
LONE PAIR
H
O
H
LONE PAIR

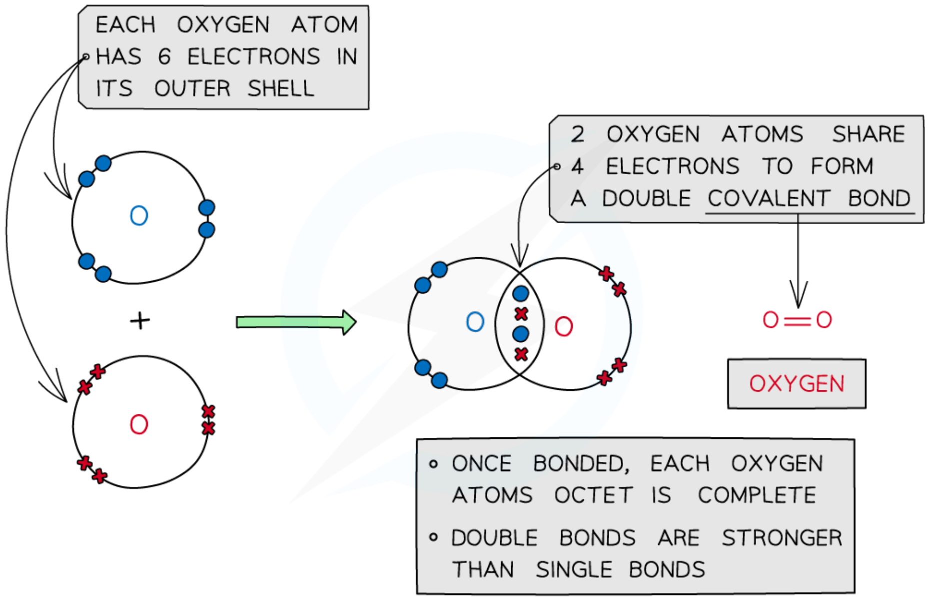


Dot-and-cross diagrams of covalent compounds in which the atoms share their valence electrons

Double covalent bonding

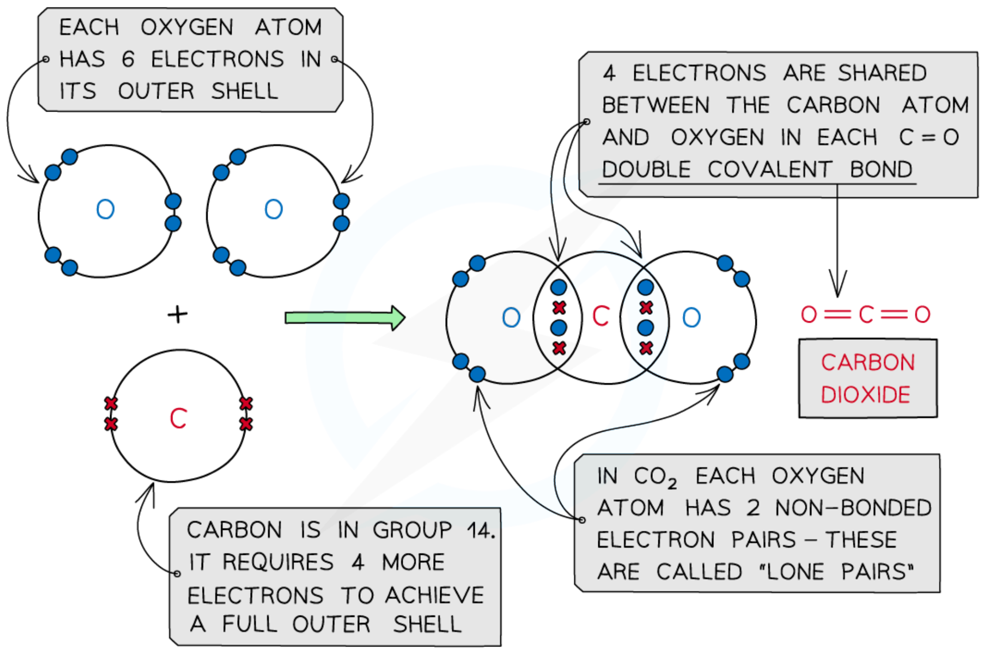
Oxygen, O_2

Your notes



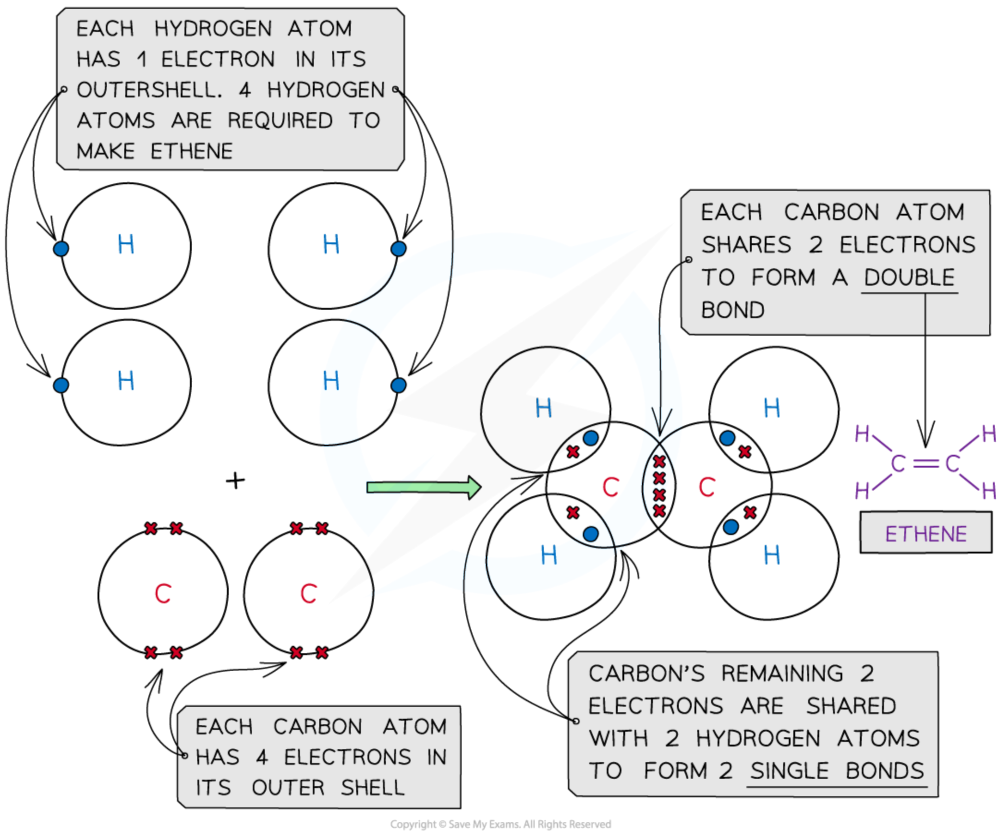
Covalent bonding in oxygen

Carbon dioxide, CO_2



Covalent bonding in carbon dioxide

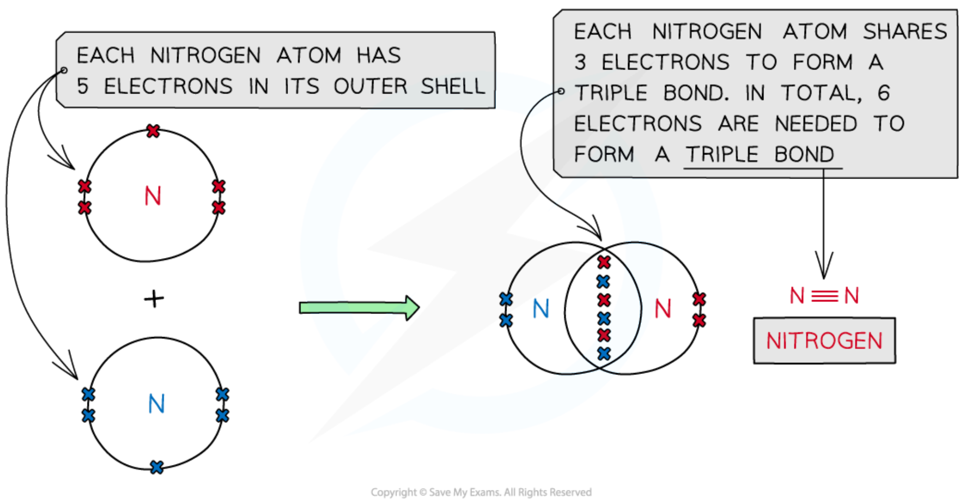
Ethene, C_2H_4



Covalent bonding in ethene

Triple covalent bonding

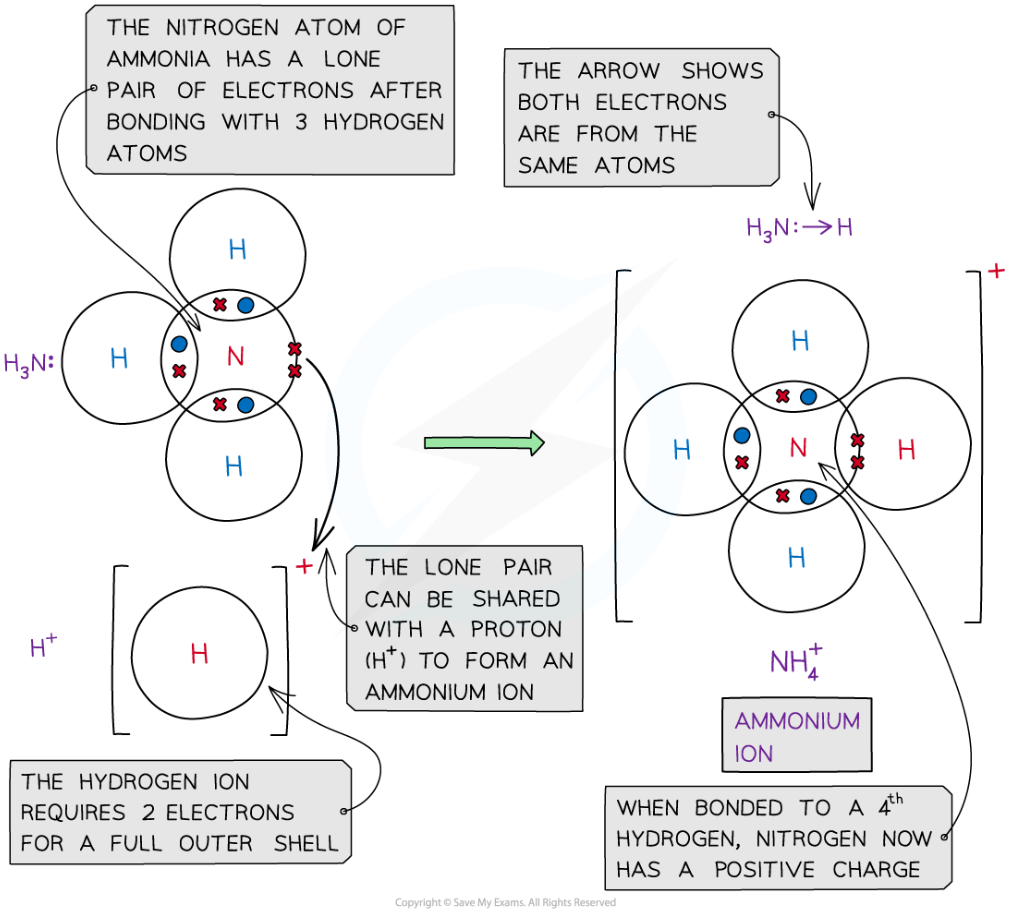
Nitrogen, N_2



Covalent bonding in nitrogen

Dative covalent bonding

- In **simple covalent bonds**, the two atoms involved share electrons
- Some molecules have a **lone** pair of electrons that can be donated to form a bond with an **electron-deficient** atom
  - An electron-deficient atom is an atom that has an **unfilled outer orbital**
- So **both electrons** are from the **same atom**
- This type of bonding is called **dative covalent bonding** or **coordinate bonding**
- An example with a dative bond is in an **ammonium ion**
  - The hydrogen ion, H^+ is **electron-deficient** and has space for two electrons in its shell
  - The nitrogen atom in ammonia has a lone pair of electrons which it can donate to the hydrogen ion to form a dative covalent bond



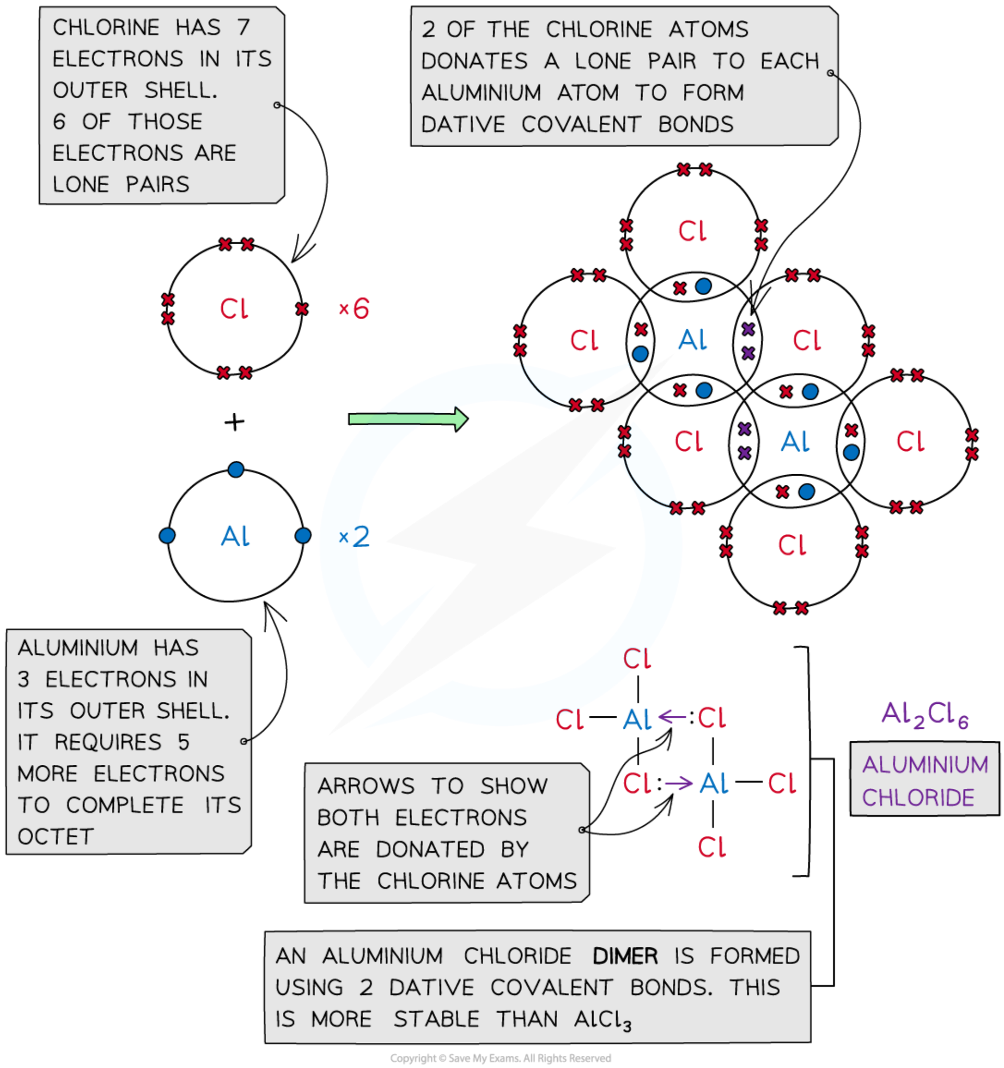
Ammonia (NH_3) can donate a lone pair to an electron-deficient proton (H^+) to form a charged ammonium ion (NH_4^+)

Aluminium chloride

- **Aluminium chloride** is also formed using dative covalent bonding

Your notes

- At **high temperatures** aluminium chloride can exist as a **monomer** ($AlCl_3$)
  - The molecule is electron-deficient and needs two electrons to complete the aluminium atom's outer shell
- At **lower temperatures** the two molecules of $AlCl_3$ join together to form a dimer (Al_2Cl_6)
  - The molecules combine because lone pairs of electrons on two of the chlorine atoms form **two coordinate bonds** with the aluminium atoms



Aluminium chloride is also formed with a dative covalent bond in which two of the chlorine atoms donate their lone pairs to each of the aluminium atoms to form a dimer

Examiner Tips and Tricks

Covalent bonding takes place between nonmetal atoms.

Remember: Use the Periodic Table to decide how many electrons are in the outer shell of a nonmetal atom.

Your notes

Carbon Allotropes

Covalent bonding & giant covalent lattice structures

- **Allotropes** of carbon are substances that only contain carbon atoms but due to the differences in bonding arrangements they are physically completely different
- **Giant covalent lattices** have **very high melting** and **boiling points**
  - These compounds have a large number of **covalent bonds** linking the whole structure
  - A lot of energy is required to break the lattice
- The compounds can be **hard** or **soft**
  - Graphite is **soft** as the forces between the carbon layers are weak
  - Diamond and silicon(IV) oxide are **hard** as it is difficult to break their 3D network of strong covalent bonds
- Most compounds are insoluble with water
- Most compounds do not **conduct electricity** however some do
  - Graphite has **delocalised** electrons between the carbon layers which can move along the layers when a voltage is applied
  - Diamond and silicon(IV) oxide do not conduct electricity as all four outer electrons on every carbon atom are involved in a **covalent bond** so there are no freely moving electrons available

Graphite

- Each carbon atom in graphite is bonded to **three** others forming **layers** of **hexagons**, leaving one free electron per carbon atom
- These free electrons migrate along the layers and are free to move and carry charge, hence graphite can **conduct electricity**
- The covalent bonds within the layers are very strong
  - But, the layers are held together by weak van der Waals' forces of attraction, which are easily overcome
  - This allows the layers to **slide** over each other, making graphite **soft** and **slippery**

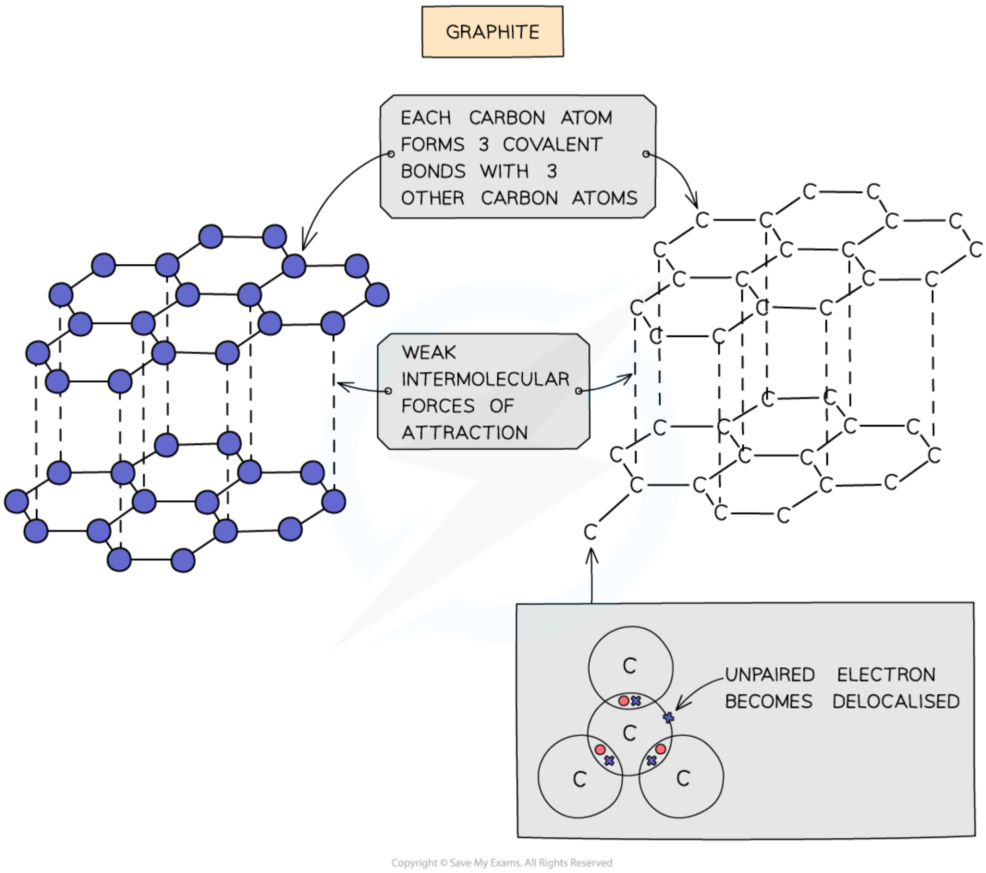


Diagram showing the structure and bonding arrangement in graphite

Diamond

- In diamond, each carbon atom bonds with four other carbons, forming a **tetrahedron**
- All the covalent bonds are identical, very strong and there are no **intermolecular forces**

Your notes

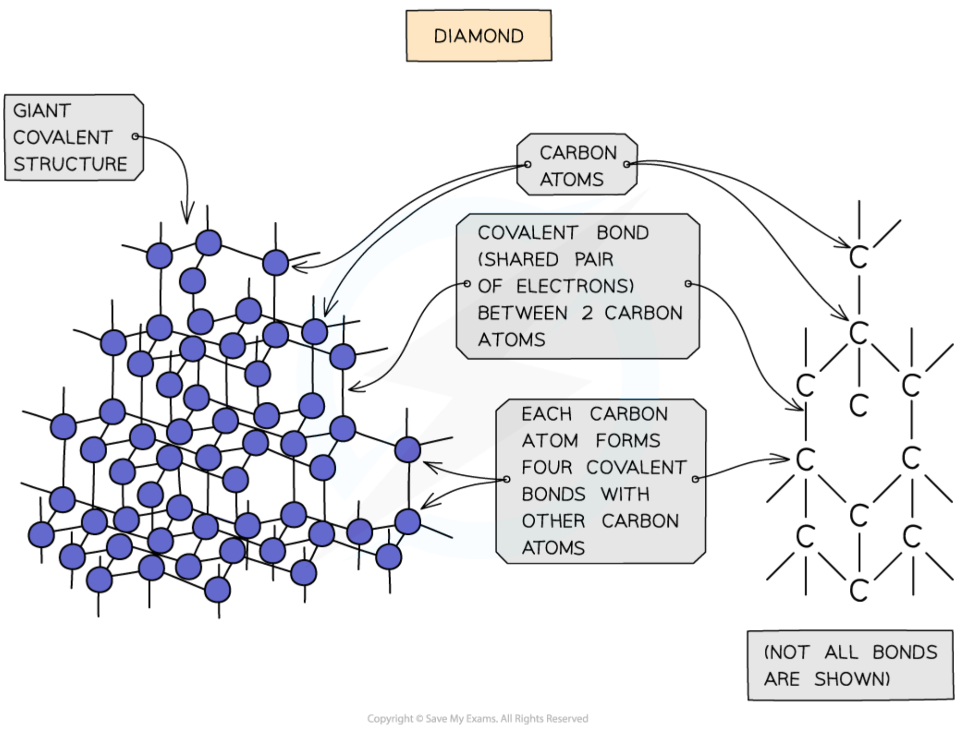
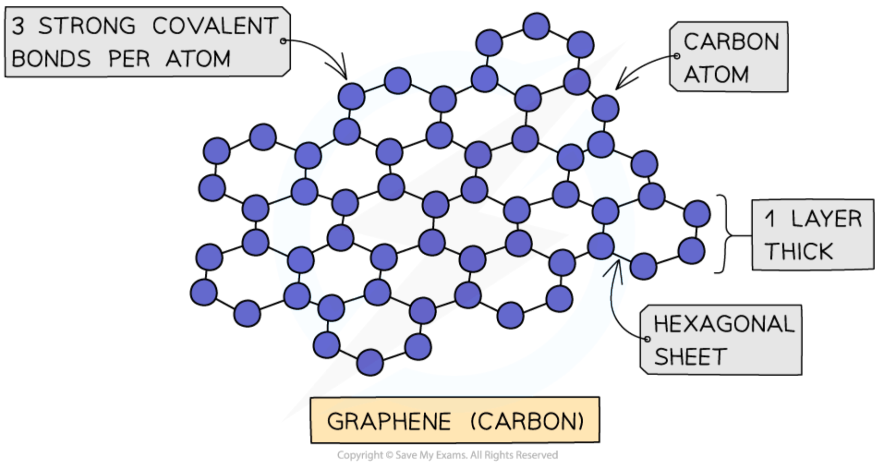


Diagram showing the structure and bonding arrangement in diamond

Graphene

- Graphene consists of a single layer of graphite which is a sheet of carbon atoms covalently bonded forming a continuous hexagonal layer
- It is essentially a 2D molecule since it is only one atom thick
- It has very unusual properties make it useful in fabricating **composite** materials and in **electronics**

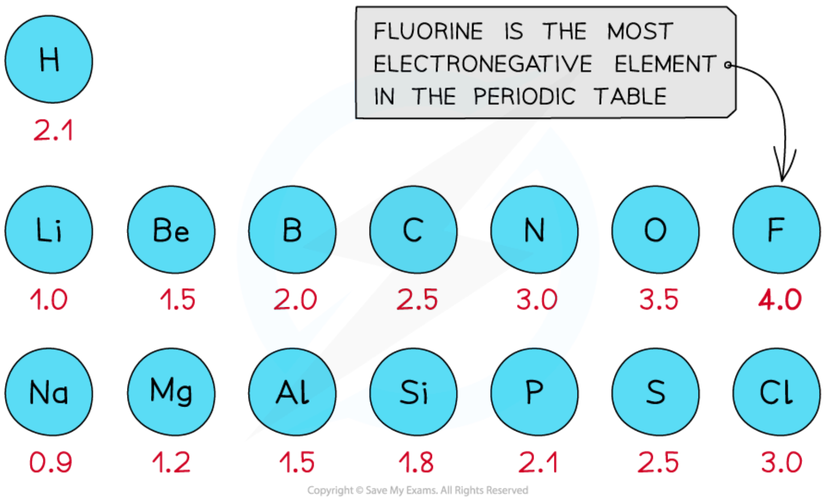


Graphene is a truly remarkable material that has some unexpected properties

Your notes

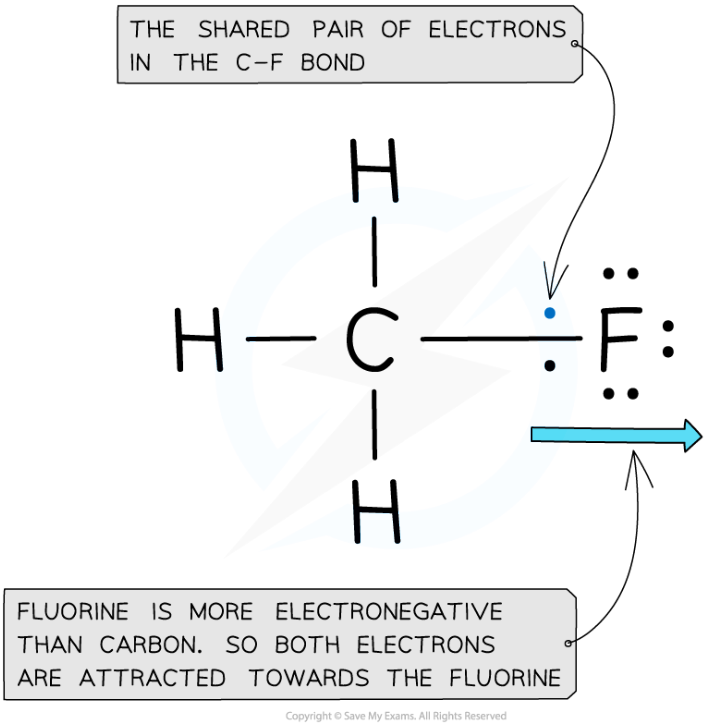
Electronegativity & Bonding

- Electronegativity is the power of an atom to attract the pair of electrons in a covalent bond towards itself
- The electron distribution in a covalent bond between elements with different electronegativities will be unsymmetrical
- This phenomenon arises from the ability of the positive nucleus to attract the negatively charged electrons, in the outer shells, towards itself
- The **Pauling scale** is used to assign a value of electronegativity for each atom



First three rows of the periodic table showing electronegativity values

- Fluorine is the most electronegative atom on the Periodic Table, with a value of 4.0 on the Pauling Scale
- It is best at attracting electrons towards itself when covalently bonded to another atom



Electron distribution in the C–F bond of fluoromethane

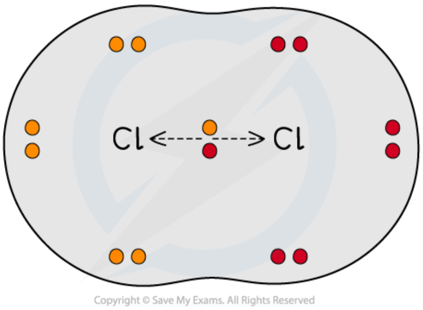
Ionic and covalent bonding

- Elements with large differences in electronegativity tend to form ionic bonds
- Atoms of elements with similar electronegativity tend to form covalent bonds
- Intermediate differences in electronegativity between covalently bonded atoms lead to polarity in the bond
  - As a rule, an electronegativity difference of 2 or more on the Pauling scale between atoms leads to the formation of an ionic bond
  - A difference of less than 2 between atoms leads to covalent bond formation

Polar Bonds & Polar Molecules

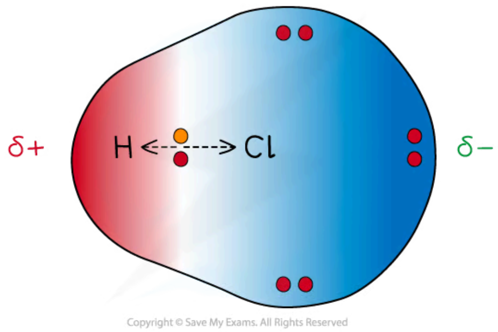
- When two atoms in a covalent bond have the **same electronegativity** the covalent bond is **nonpolar**

Your notes



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

- The difference in electronegativities will dictate the type of bond that is formed
- When the electronegativities are very different (difference of more than 1.7) then ions will be formed and the bond will be ionic
- When two atoms in a covalent bond have a difference in electronegativities of 0.3 to 1.7 a covalent bond is formed and the bond will be polar
  - 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



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

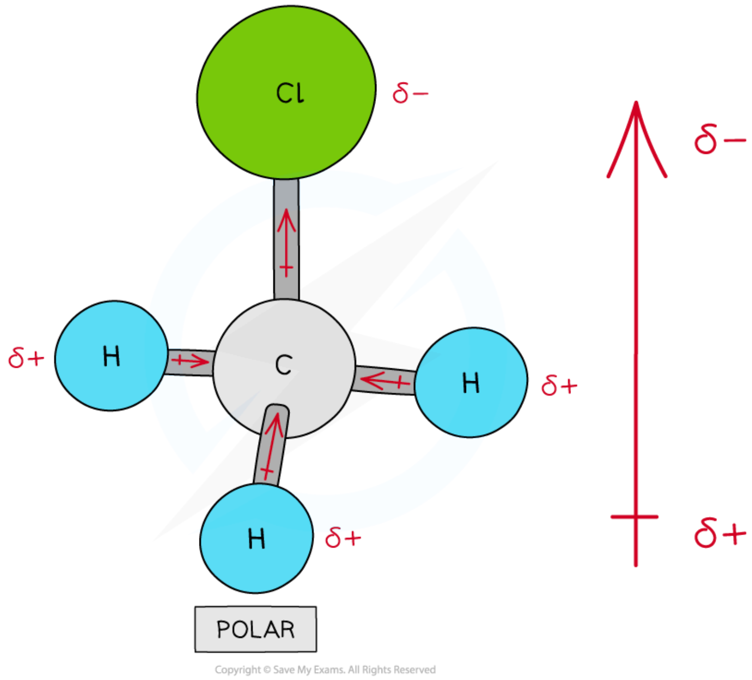
Your notes

- 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:

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

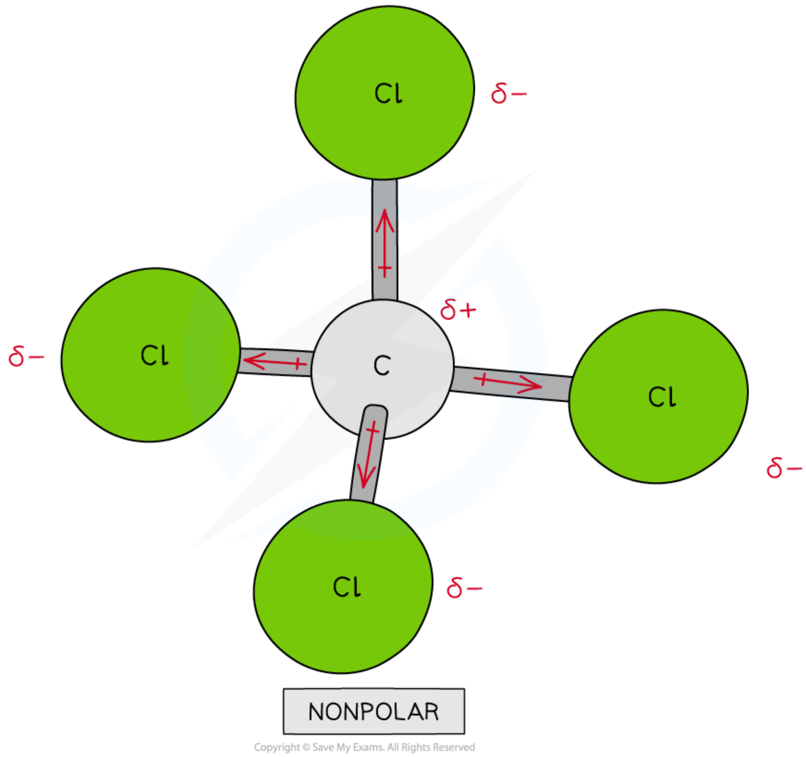
Assigning polarity to molecules

- To determine whether a molecule with more than two different 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 way that the individual dipole moments **cancel each other out**



There are four polar covalent bonds in CH_3Cl which do not cancel each other out causing CH_3Cl to be a polar molecule; the overall dipole is towards the electronegative chlorine atom

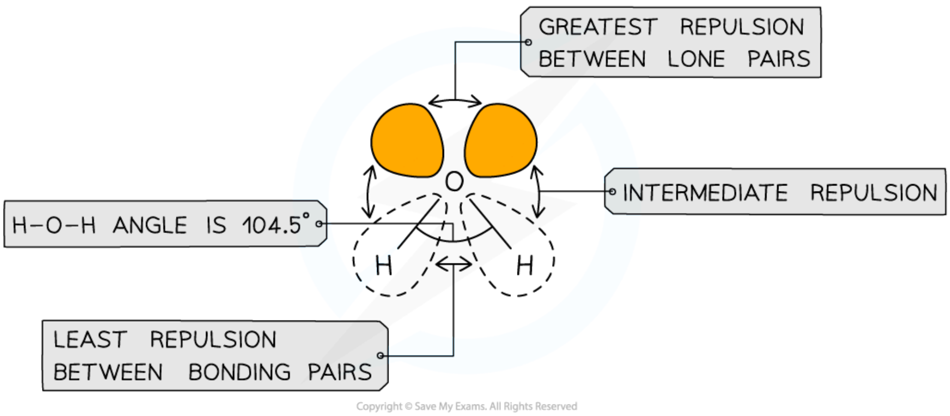
Your notes



Though CCl_4 has four polar covalent bonds, the individual dipole moments cancel each other out causing CCl_4 to be a nonpolar molecule

Shapes & Angles

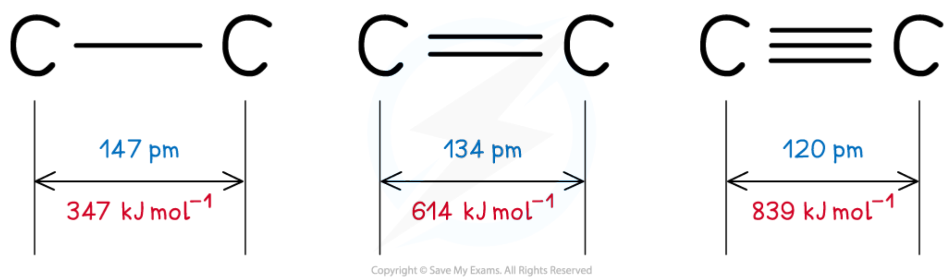
- The **valence shell electron pair repulsion theory** (VSEPR) predicts the shape and bond angles of molecules
- Electrons are **negatively charged** and will repel other electrons when close to each other
- In a molecule, the **bonding pairs of electrons** will repel other electrons around the **central atom** forcing the molecule to adopt a shape in which these **repulsive forces** are minimised
- When determining the **shape** and **bond** angles of a molecule, the following VSEPR rules should be considered:
  - Valence shell electrons are those electrons that are found in the outer shell
  - Electron pairs repel each other as they have the same charge
  - Lone pair electrons repel each other more than bonded pairs
  - Repulsion between multiple and single bonds is treated the same as for repulsion between single bonds
  - Repulsion between pairs of double bonds are greater
  - The most stable shape is adopted to minimize the repulsion forces
- Different types of electron pairs have different repulsive forces
  - Lone pairs of electrons have a more concentrated electron charge cloud than bonding pairs of electrons
  - The cloud charges are wider and closer to the central atom's nucleus
  - The order of repulsion is therefore: lone pair – lone pair > lone pair – bond pair > bond pair – bond pair



Different types of electron pairs have different repulsive forces

Bond length

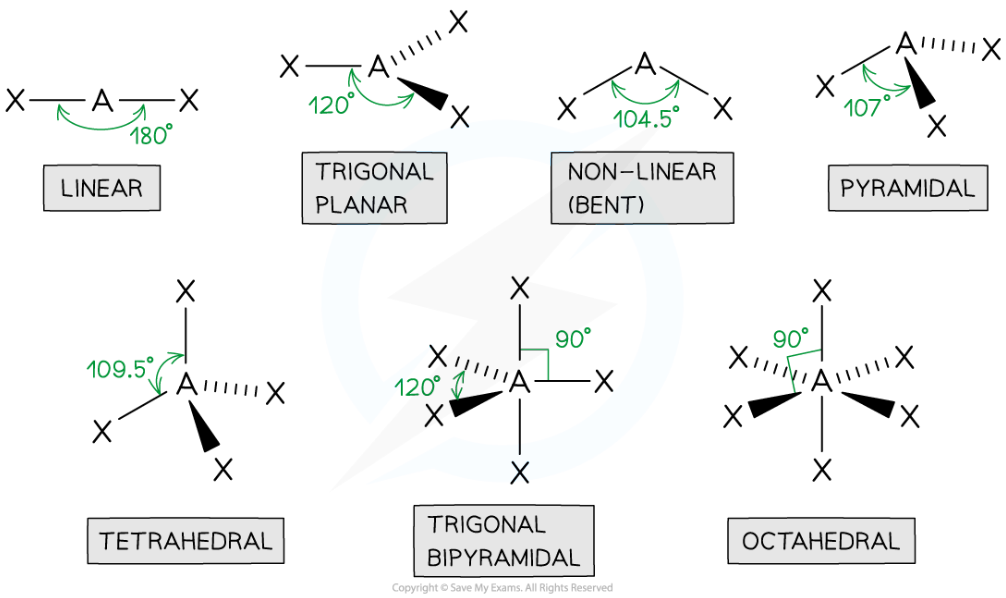
- The **bond length** is **internuclear distance of two covalently bonded atoms**
  - It is the distance from the nucleus of one atom to another atom which forms the covalent bond
- The **greater** the forces of attraction between electrons and nuclei, the more the atoms are pulled closer to each other
- This **decreases** the **bond length** of a molecule and **increases** the **strength** of the covalent bond
- **Triple bonds** are the **shortest** and **strongest** covalent bonds due to the large electron density between the nuclei of the two atoms
- This increase the forces of attraction between the electrons and nuclei of the atoms
- As a result of this, the atoms are pulled closer together causing a shorter bond length
- The increased forces of attraction also means that the covalent bond is **stronger**



Triple bonds are the shortest covalent bonds and therefore the strongest ones

Bond Angle

- Molecules can adapt the following shapes and bond angles:



Molecules of different shapes can adapt with their corresponding bond angles

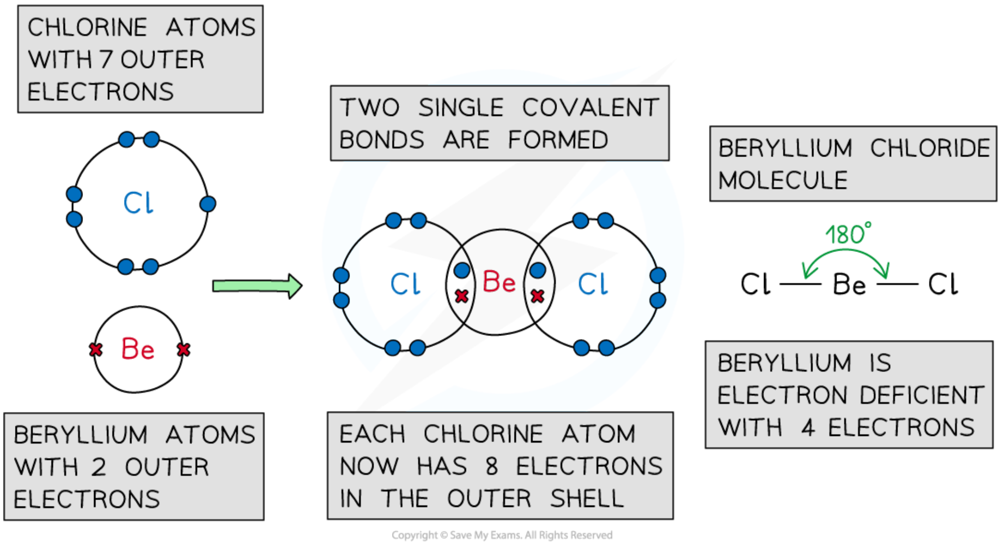
Your notes

Predicting Shapes & Angles

- You will need to know and explain the shapes of the following molecules:
  - $BeCl_2$
  - BCl_3
  - CH_4
  - NH_3
  - NH_4^+
  - H_2O
  - CO_2
  - PCl_5 (g)
  - SF_6
  - C_2H_4
- In order to write the correct shapes and structures of the molecules listed we need to consider the number of valence electrons

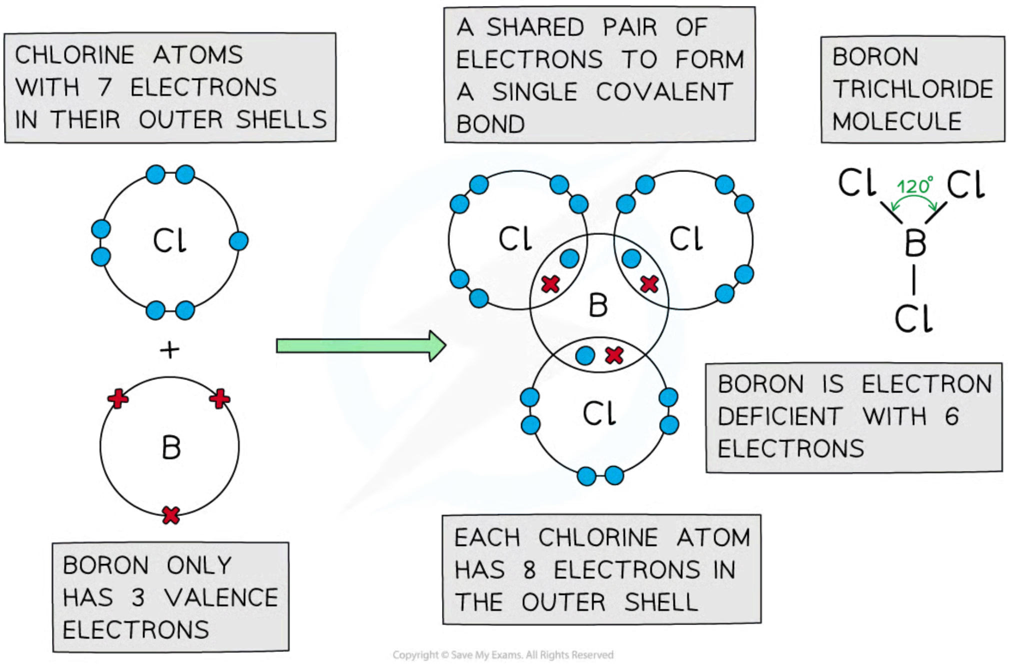
$BeCl_2$

- Beryllium is in group 2, so has 2 valence electrons; Cl is in group 17, so has 7 valence electrons
- Both electrons are used to form covalent bonds with Cl and there are no lone pairs
- Accommodating **less** than 8 electrons in the outer shell means than the central atom is **'electron deficient'**
- This gives a **linear** shape with bond angles of 180°



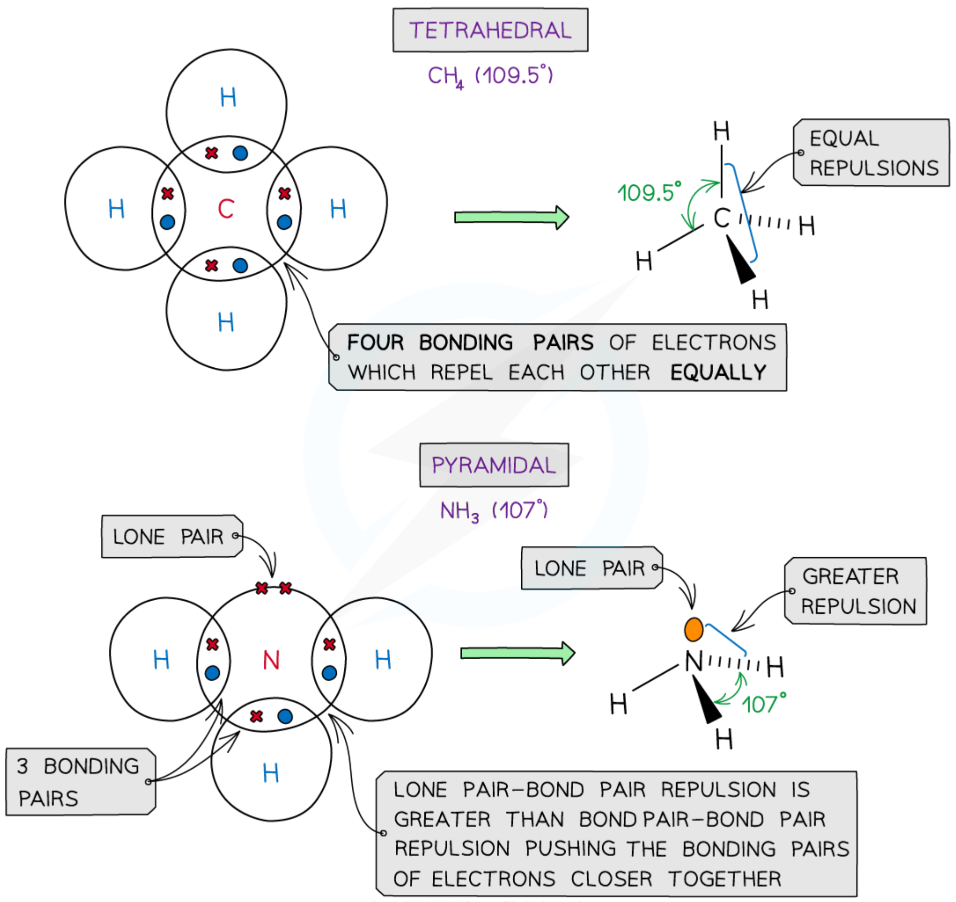
BCl_3

- Boron is in group 13, so has 3 valence electrons; Cl is in group 17, so has 7 valence electrons
- All 3 electrons are used to form covalent bonds with Cl and there are no lone pairs
- Accommodating **less** than 8 electrons in the outer shell means than the central atom is '**electron deficient**'
- This gives a **trigonal planar** shape with bond angles of 120°



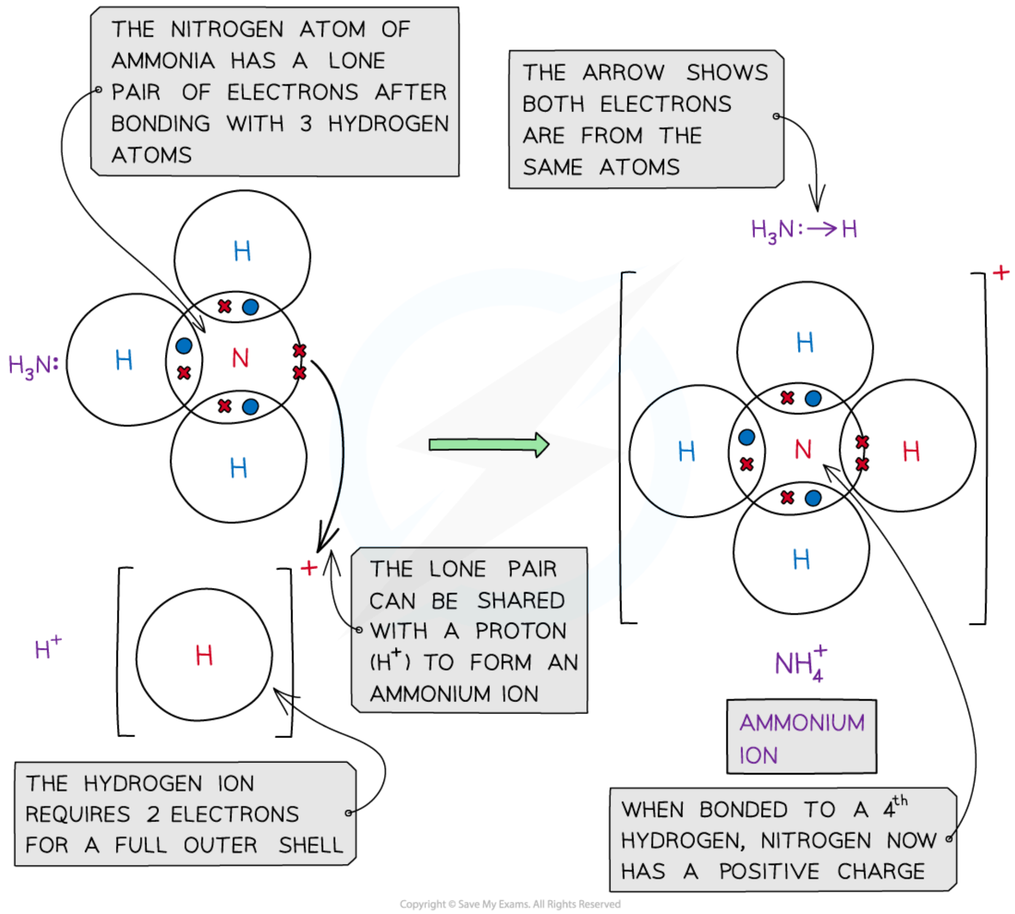
CH_4 & NH_3

- Carbon is in group 14, so has 4 valence electrons; H is in group 1, so has 1 valence electron
- All 4 electrons are used to form covalent bonds with H
- This gives a **tetrahedral** arrangement with a bond angle of 109.5°
- Nitrogen is in group 15, so has 5 valence electrons
- Only 3 electrons are used to form covalent bonds with H and 2 are unbonded as a lone pair
- This gives a **trigonal pyramid** arrangement with a bond angle of 107°



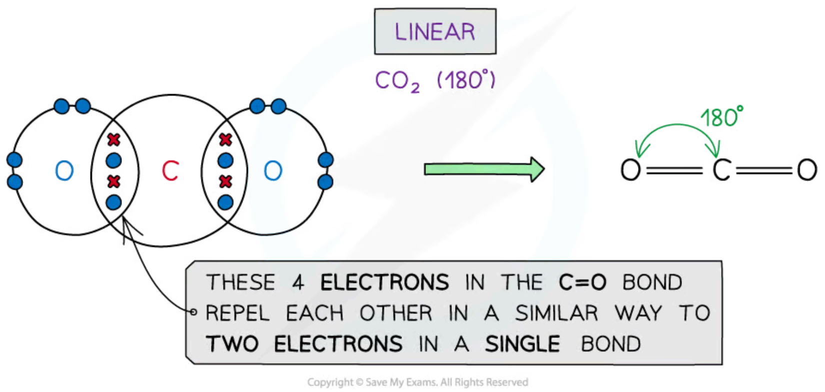
NH_4^+

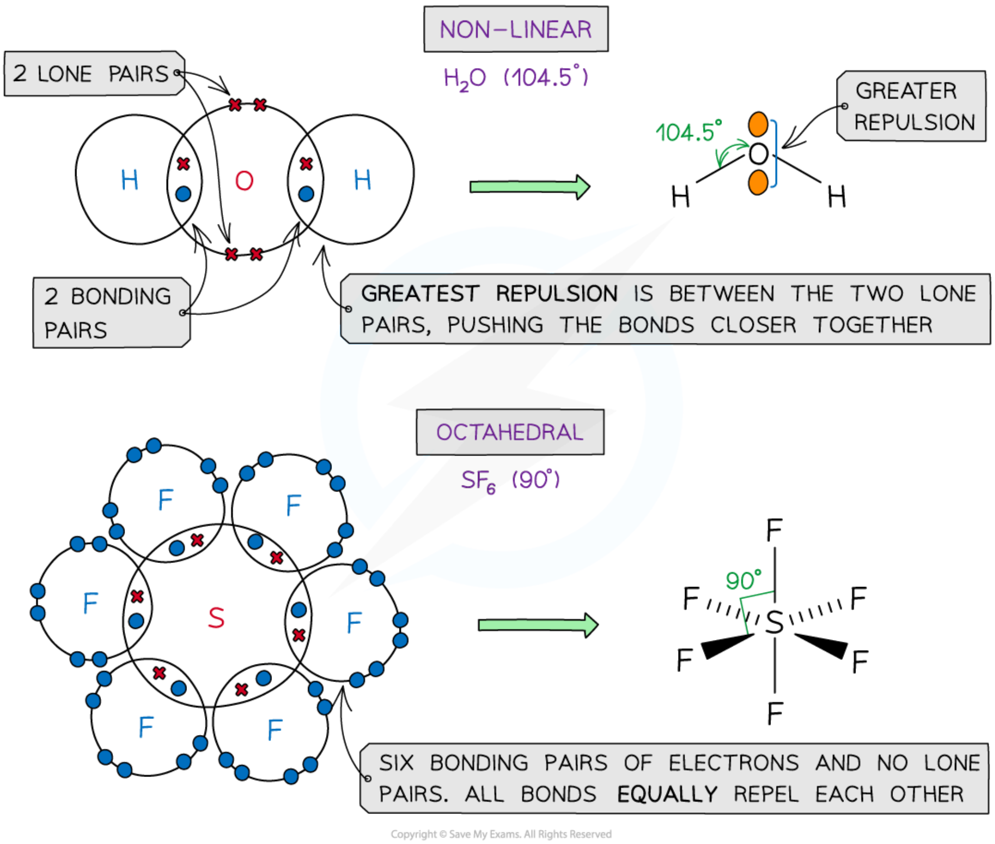
- Nitrogen is in group 15, so has 5 valence electrons; H is in group 1, so has 1 valence electron
- Only 3 electrons are used to form covalent bonds with H and 2 are used to form a dative covalent bond
- This gives a **tetrahedral** arrangement
- With a bond angle of 109.5° (similar to CH_4)



The NH_4^+ ion

Other examples

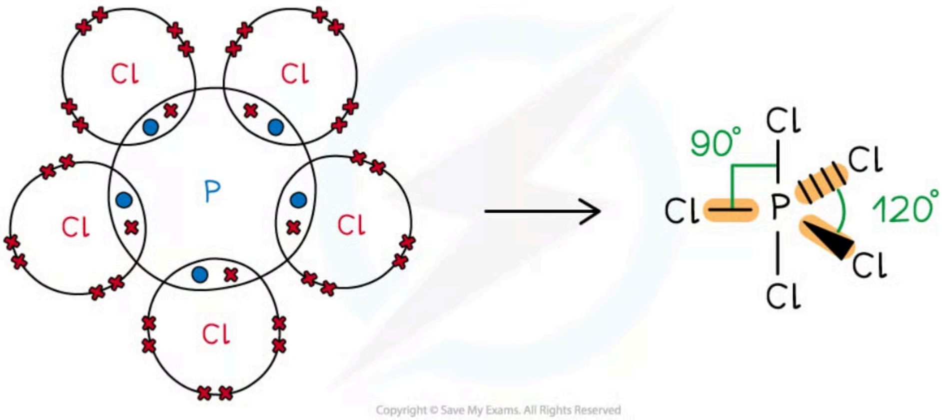




Your notes

PCl_5 (g)

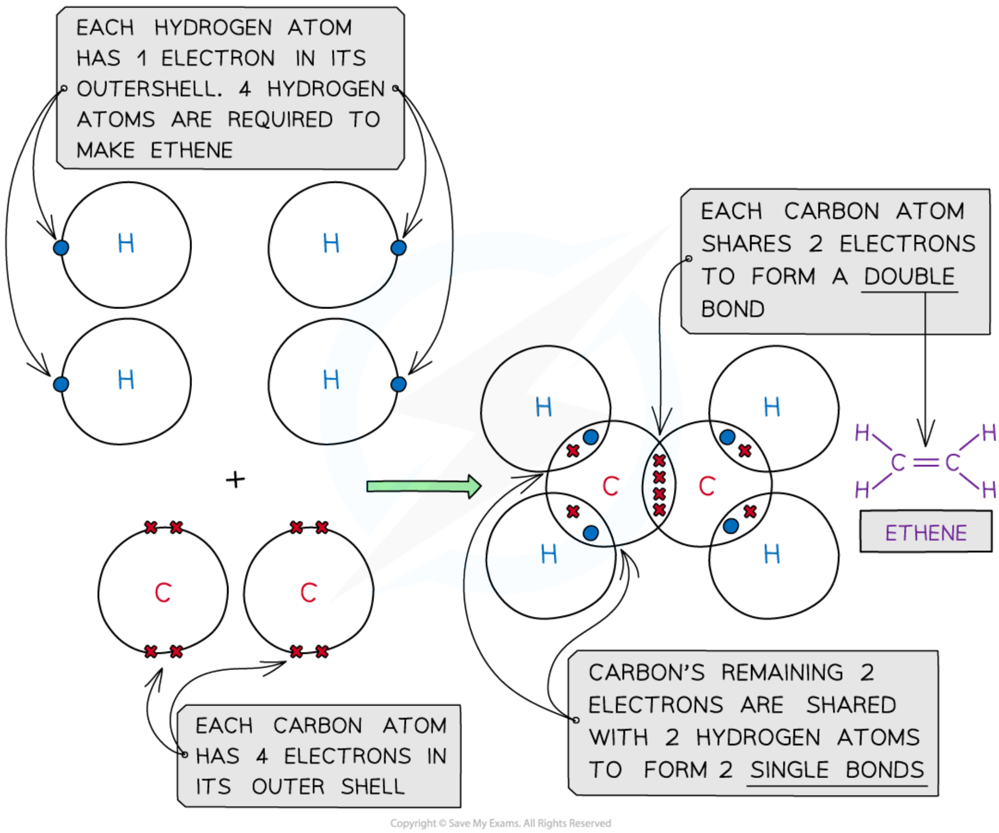
- Phosphorus is in group 15, so has 5 valence electrons; Cl is in group 17, so has 7 valence electrons
  - All 5 electrons are used to form covalent bonds with Cl and there are no lone pairs
  - This gives a **trigonal** (or **triangular**) **bipyramidal** shape
  - With bond angles of 120° and 90°



Phosphorus pentachloride molecule

C_2H_4

- Each carbon atom is in group 14, so has 4 valence electrons, each hydrogen atom is in group 1 so has 1 valence electron
- This gives a total of 12 electrons
- There are 4 C-H bonds which use 8 electrons
- This leaves 4 electrons which are involved in the C=C
- Therefore the overall shape is trigonal planar as there are three regions of electron density for each carbon atom



Ethene molecule

Your notes