Cambridge (CIE) A Level Chemistry

Your notes

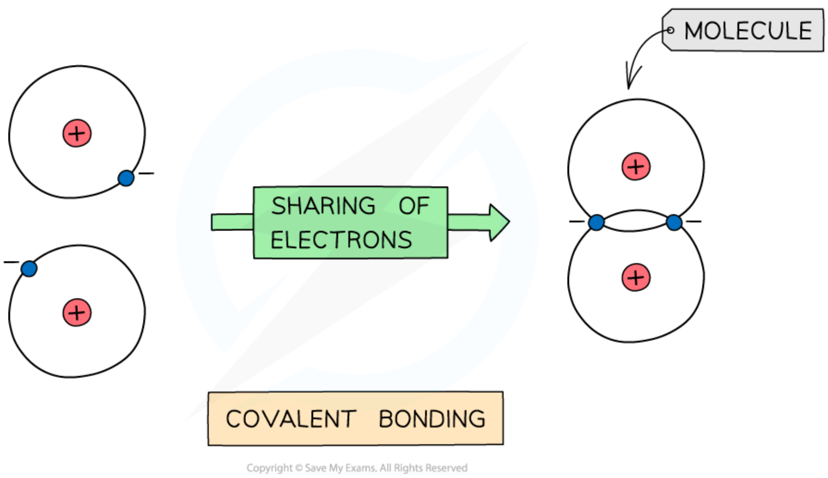
Covalent Bonding & Coordinate (Dative Covalent) Bonding

Contents

Your notes

Defining Covalent Bonding

- **Covalent** bonding occurs between two **non-metals**
- A covalent bond involves the **electrostatic attraction** between nuclei of two atoms and the bonding electrons of their outer shells
- **No electrons** are **transferred** but only **shared** in this type of bonding



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

- **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

Covalent bonds & shared electrons table

- Single / C-C bond
  - **2** electrons shared
- Double / C=C bond
  - **4** electrons shared
- Triple / C ≡ C bond
  - **6** electrons shared

Examples of Covalent Bonding

Your notes

Dot & cross diagrams

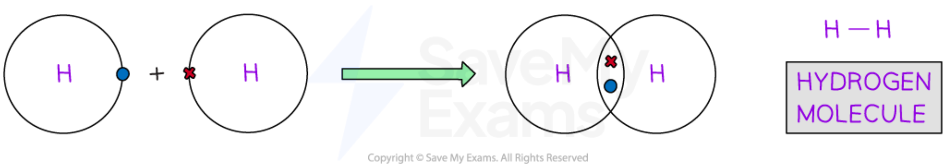
- **Dot and cross diagrams** are used to represent covalent bonding
- They show just the **outer shell** of the atoms involved
- To differentiate between the two atoms involved, **dots** for electrons of one atom and **crosses** for electrons of the other atom are used
- Electrons are shown in **pairs** on dot-and-cross diagrams

Single covalent bonding

Hydrogen, H_2

- Each hydrogen atom has one outer electron
- By sharing their outer electrons, the two hydrogen atoms are able to form a hydrogen molecule
  - The molecule contains a single covalent bond due to one shared pair of electrons

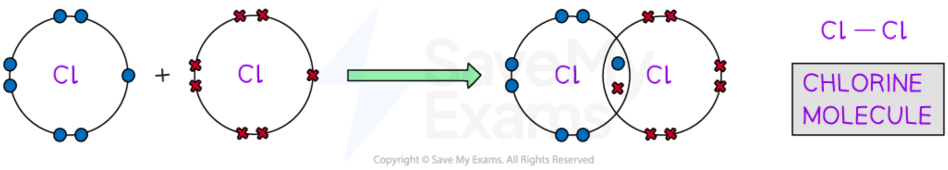
Covalent bonding in hydrogen, H_2



Chlorine, Cl_2

- Each chlorine atom has seven outer electrons
  - Six electrons are paired and one electron is unpaired
- By sharing their unpaired outer electrons, the two chlorine atoms are able to form a chlorine molecule
  - The molecule contains a single covalent bond due to one shared pair of electrons

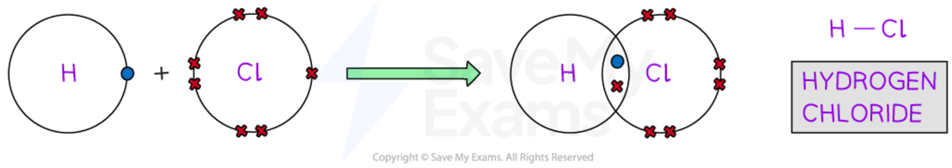
Covalent bonding in chlorine, Cl_2



Hydrogen chloride, HCl

- The hydrogen atom has one outer electron and the chlorine atom has seven outer electrons
  - The chlorine atom has six paired electrons and one unpaired electron
- When the hydrogen atom pairs its outer electron with the unpaired electron from chlorine, the two atoms are able to form a hydrogen chloride molecule
  - The molecule contains a single covalent bond due to one shared pair of electrons

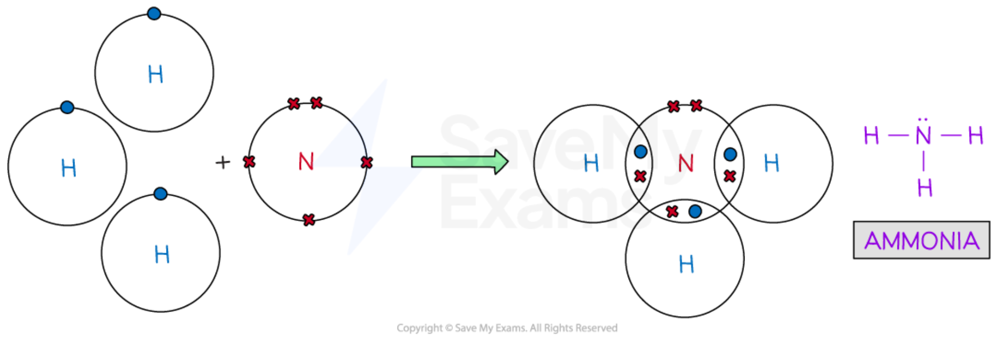
Covalent bonding in hydrogen chloride, HCl



Ammonia, NH_3

- The hydrogen atoms have one outer electron and the nitrogen atom has five outer electrons
  - The nitrogen atom has one lone pair of electrons and three unpaired electrons
- When each hydrogen atom pairs its outer electron with each of the unpaired electrons from nitrogen, the nitrogen and hydrogen atoms are able to form an ammonia molecule
  - The molecule contains three single covalent bonds due to three shared pairs of electrons

Covalent bonding in ammonia, NH_3



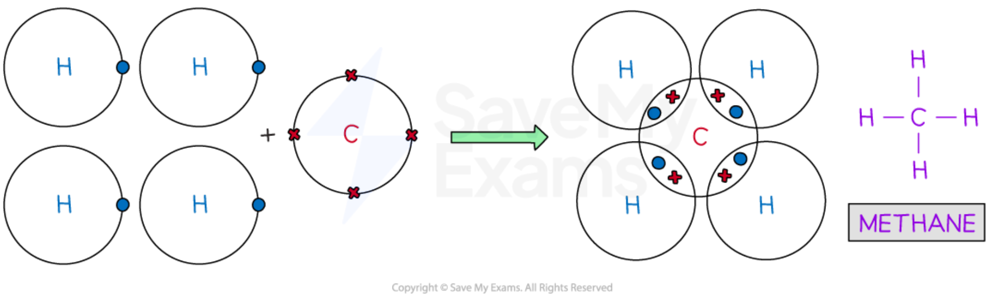
Methane, CH_4

- The hydrogen atoms have one outer electron and the carbon atom has four outer electrons
  - The carbon atom has four unpaired electrons

Your notes

- When each hydrogen atom pairs its outer electron with each of the unpaired electrons from carbon, the carbon and hydrogen atoms are able to form a methane molecule
  - The molecule contains four single covalent bonds due to four shared pairs of electrons

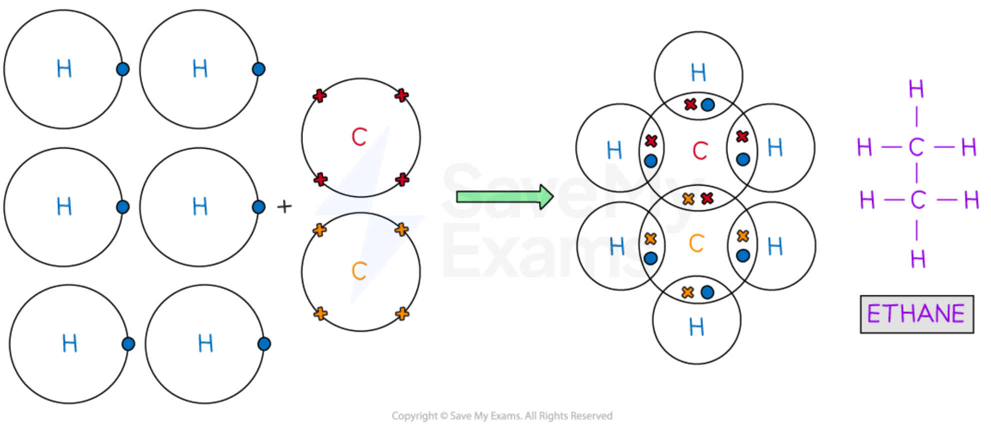
Covalent bonding in methane, CH_4



Ethane, C_2H_6

- The hydrogen atoms have one outer electron and the carbon atoms have four outer electrons
  - The carbon atom has four unpaired electrons
- Each carbon atom shares one of its unpaired electrons with the other carbon atom
  - This results in the formation of a single covalent bond between the two carbon atoms
- When each hydrogen atom pairs its outer electron with the remaining unpaired electrons from carbon, the carbon and hydrogen atoms form six single covalent C-H bonds
  - This results in a methane molecule, which contains six single covalent C-H bonds and one single covalent C-C bond

Covalent bonding in ethane, C_2H_6



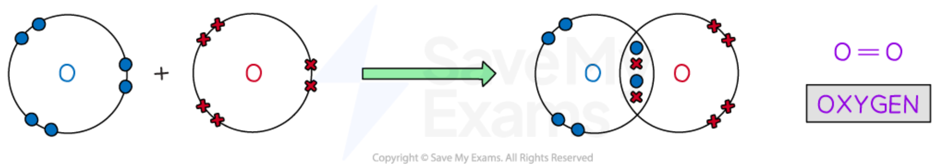
Your notes

Double covalent bonding

Oxygen, O_2

- Each oxygen atom has six outer electrons
- By sharing two of their outer electrons, the two oxygen atoms are able to form an oxygen molecule
  - The molecule contains a double covalent bond due to two shared pair of electrons

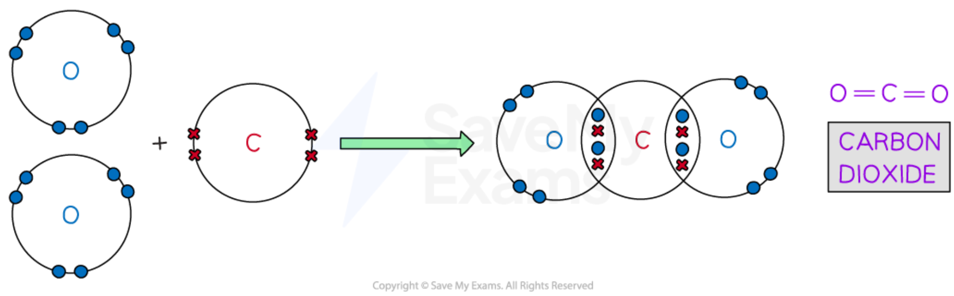
Covalent bonding in oxygen, O_2



Carbon dioxide, CO_2

- Each oxygen atom has six outer electrons and the carbon atom has four outer electrons
- Each oxygen atom shares two of its outer electrons with the carbon atom, which forms a carbon dioxide molecule
  - The molecule contains two double covalent bonds due to two sets of two shared pairs of electrons

Covalent bonding in carbon dioxide, CO_2



Ethene, C_2H_4

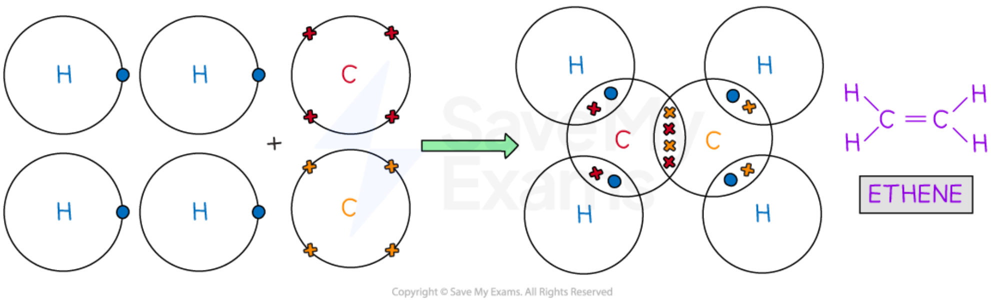
- Each hydrogen atom has one outer electron and the carbon atoms have four outer electrons
- Each carbon atom shares two of its outer electrons with the other carbon atom
  - This results in the formation of a double covalent bond between the two carbon atoms

Your notes

Your notes

- When each hydrogen atom pairs its outer electron with the remaining unpaired electrons from carbon, the carbon and hydrogen atoms form four single covalent C-H bonds
  - This results in an ethene molecule, which contains four single covalent C-H bonds and one double covalent C=C bond

Covalent bonding in ethene, C_2H_4

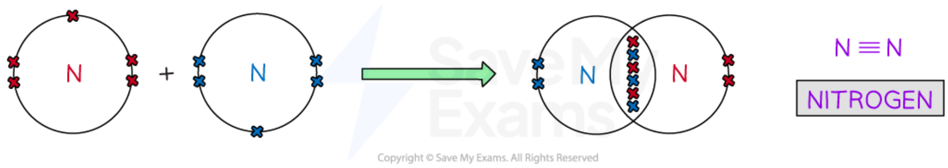


Triple covalent bonding

Nitrogen, N_2

- Each nitrogen atom has five outer electrons
- By sharing three of their outer electrons, the two nitrogen atoms are able to form a nitrogen molecule
  - The molecule contains a triple covalent bond due to three shared pairs of electrons

Covalent bonding in nitrogen, N_2



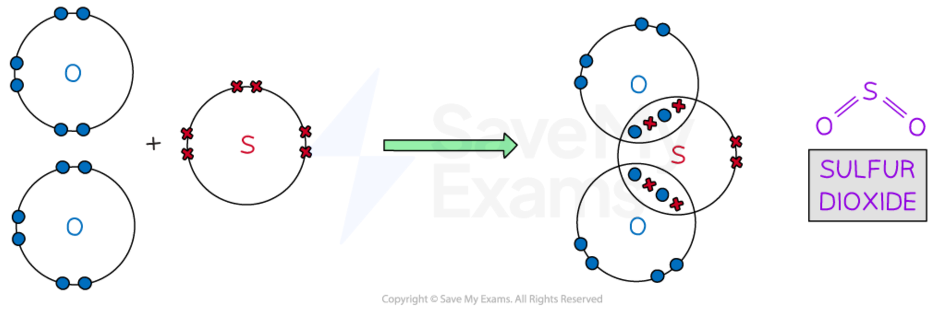
- In some instances, the central atom of a covalently bonded molecule can accommodate **more** or **less** than 8 electrons in its outer shell
- Being able to accommodate **more** than 8 electrons in the outer shell is known as **'expanding the octet rule'**
- Accommodating **less** than 8 electrons in the outer shell means than the central atom is **'electron deficient'**
- Some examples of this occurring can be seen with Period 3 elements

Sulfur dioxide, SO_2

- Each oxygen atom has six outer electrons and the sulfur atom, also, has six outer electrons

- Each oxygen atom shares two of its outer electrons with the sulfur atom, which forms a sulfur dioxide molecule
  - The molecule contains two double covalent bonds due to two sets of two shared pairs of electrons
- Sulfur now has an expanded octet as it has a share of 10 electrons

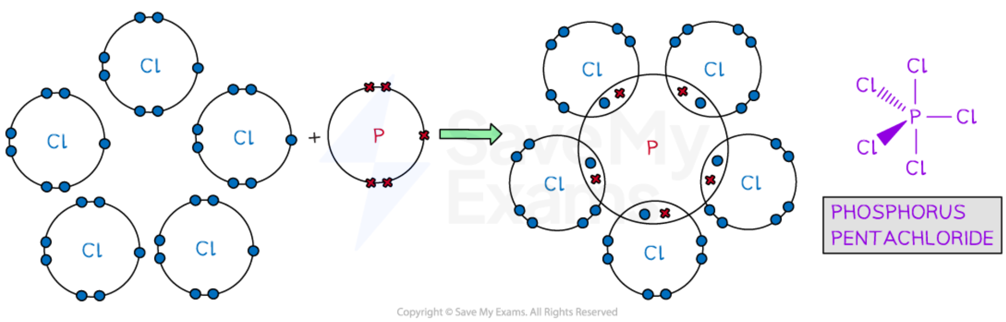
Sulfur dioxide, SO_2 – dot and cross diagram



Phosphorus pentachloride, PCl_5

- Each chlorine atom has seven outer electrons and the phosphorous atom has five outer electrons
  - The chlorine atom has six paired electrons and one unpaired electron
- When each chlorine atom pairs its unpaired outer electron with one outer electron from phosphorous, a single covalent P-Cl bond forms
  - The overall phosphorous pentachloride molecule contains five single covalent bonds
- Phosphorous now has an expanded octet as it has a share of 10 electrons

Phosphorus pentachloride, PCl_5 – dot and cross diagram

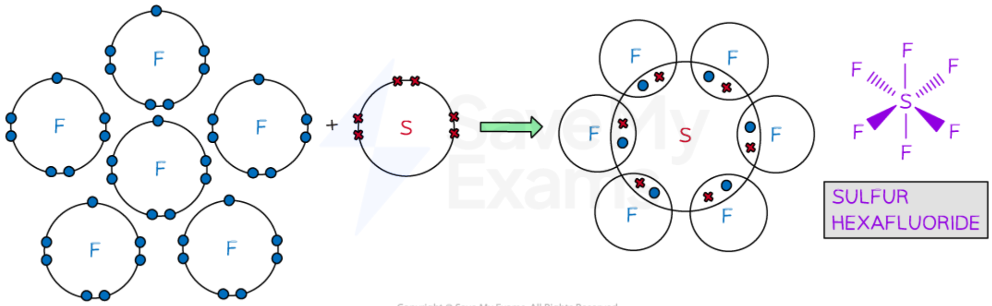


Sulfur hexafluoride, SF_6

- Each fluorine atom has seven outer electrons and the sulfur atom has six outer electrons
  - The fluorine atom has six paired electrons and one unpaired electron

- When each fluorine atom pairs its unpaired outer electron with one outer electron from sulfur, a single covalent S-F bond forms
  - The overall sulfur hexafluoride molecule contains six single covalent bonds
- Sulfur now has an expanded octet as it has a share of 12 electrons

Sulfur hexafluoride, SF_6 – dot and cross diagram



Examiner Tips and Tricks

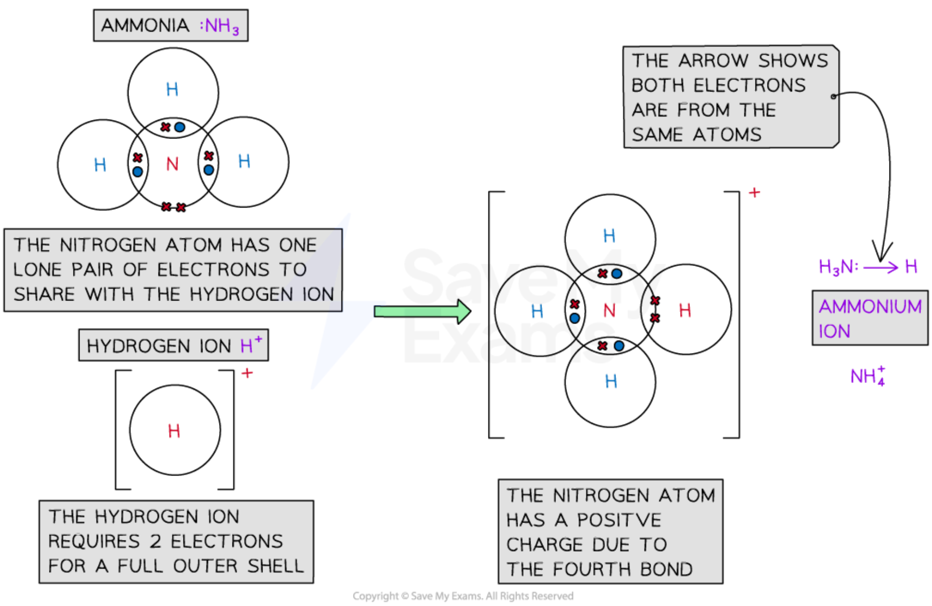
- Covalent bonding takes place between non-metal atoms.
- Remember to use the Periodic Table to decide how many electrons are in the outer shell of a non-metal atom.

Your notes

Examples of Coordinate 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 bond**
- An example of 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

Coordinate bonding in the ammonium ion

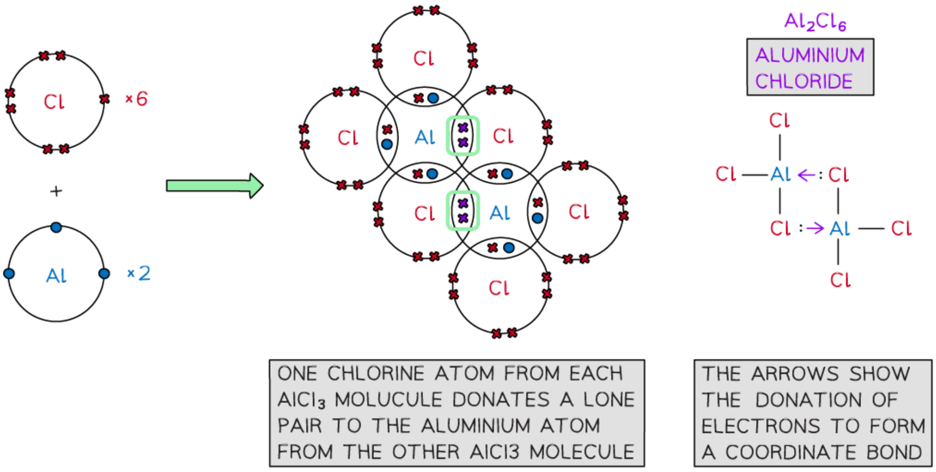


Ammonia (NH_3) can donate a lone pair to an electron-deficient proton (H^+) to form a charged ammonium ion (NH_4^+)

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

Coordinate bonding in aluminium chloride



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

- In dative covalent bonding, both electrons in the covalent bond are shared by one atom.
- A dative covalent bond uses an arrow from the donated pair of electrons to the electron-deficient atom.

Your notes

Your notes

Orbitals & Hybridisation in Covalent Bonding

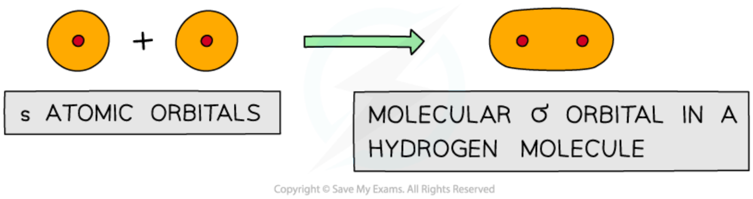
Bond overlap in covalent bonds

- A single **covalent bond** is formed when two nonmetals combine
- Each atom that combines has an **atomic orbital** containing a single unpaired electron
- When a covalent bond is formed, the **atomic orbitals** overlap to form a **combined orbital** containing two electrons
  - This new orbital is called the **molecular orbital**
- The **greater** the atomic orbital overlap, the **stronger** the bond
- **Sigma** (σ) bonds are formed by **direct overlap** of orbitals between the bonding atoms
- **Pi** (π) bonds are formed by the **sideways overlap** of **adjacent above and below** the σ bond

σ bonds

- **Sigma** (σ) bonds are formed from the **end-on overlap** of atomic orbitals
- S orbitals overlap this way as well as p orbitals

Forming sigma bonds



Sigma orbitals can be formed from the end-on overlap of s orbitals

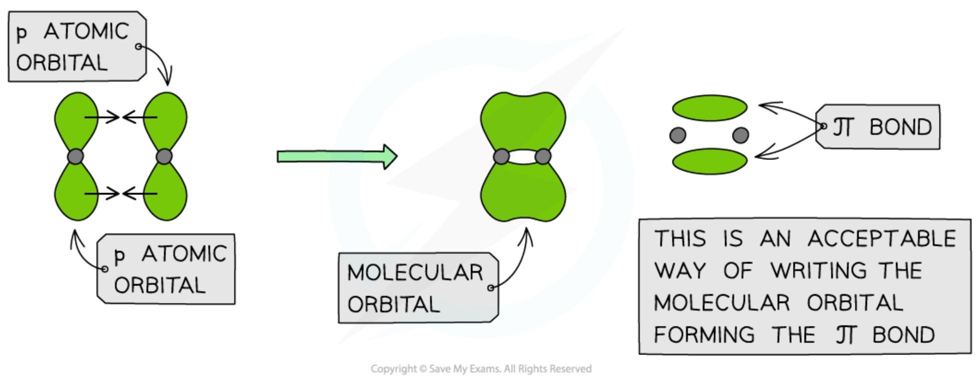
- The electron density in a σ bond is symmetrical about a line joining the nuclei of the atoms forming the bond
- The pair of electrons is found between the nuclei of the two atoms
- There is an electrostatic force of attraction between the electrons and nuclei which bonds the atoms to each other

π bonds

- **Pi** (π) bonds are formed from the **sideways overlap** of **adjacent** p orbitals

- The two lobes that make up the π bond lie **above and below the plane** of the σ bond
- This maximises the overlap of the p orbitals
- A single π bond is drawn as **two electron clouds** one arising from each lobe of the p orbitals
- The two clouds of electrons in a π bond represent **one** bond containing **two electrons**

Forming pi bonds

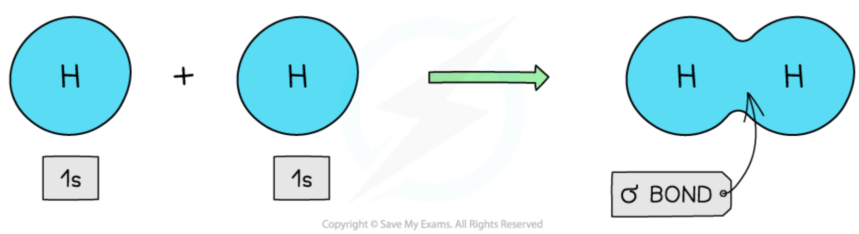


π orbitals can be formed from the end-on overlap of p orbitals

Examples of sigma & pi bonds

- **Hydrogen**
  - The hydrogen atom has only one s orbital
  - The s orbitals of the two hydrogen atoms will overlap to form a σ bond

Sigma bonding in hydrogen



Direct overlap of the 1s orbitals of the hydrogen atoms results in the formation of a σ bond

- **Ethene**
  - Each carbon atom uses **three** of its **four** electrons to form σ bonds
  - Two σ bonds are formed with the hydrogen atoms
  - One σ bond is formed with the other carbon atom
  - The fourth electron from each carbon atom occupies a p orbital which overlaps **sideways** with another p orbital on the other carbon atom to form a π bond

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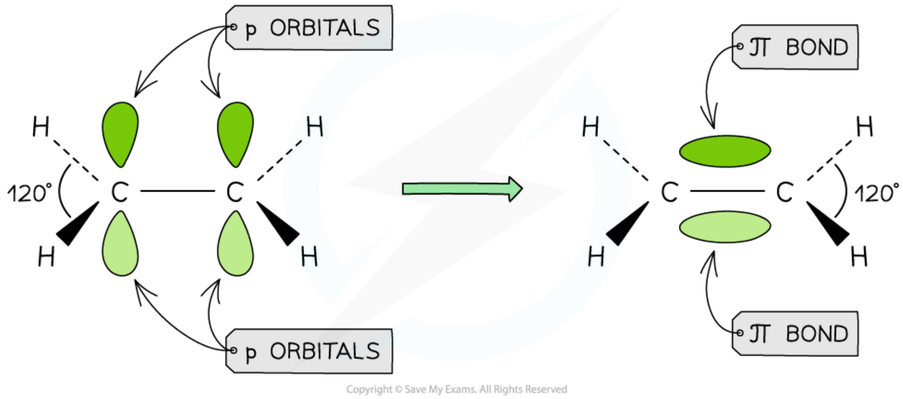
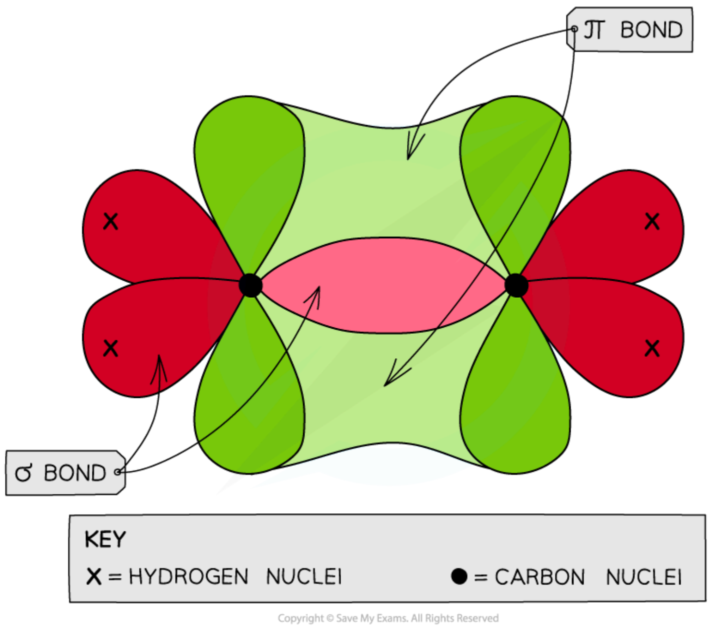
- This means that the C-C is a **double bond**: one σ and one π bond

Pi bonding in ethene



Overlap of the p orbitals results in the forming of a π bond in ethene

Sigma and pi bonding in ethene



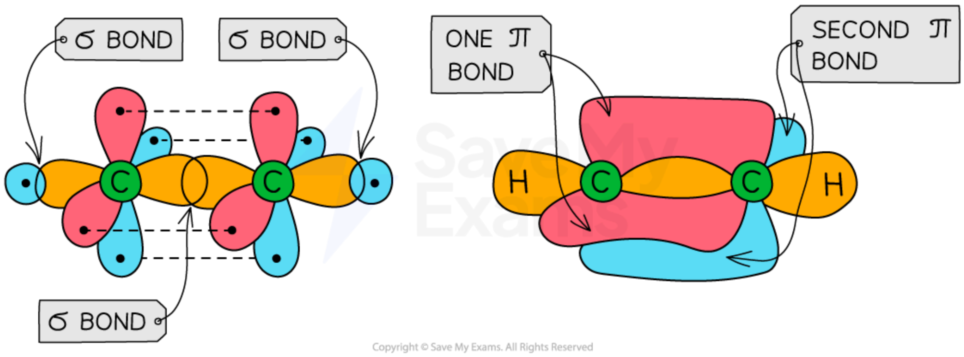
Each carbon atom in ethene forms two sigma bonds with hydrogen atoms and one σ bond with another carbon atom. The fourth electron is used to form a π bond between the two carbon atoms

- **Ethyne**
  - This molecule contains a **triple bond** formed from **two π bonds** (at right angles to each other) **and one σ bond**
  - Each carbon atom uses **two** of its **four** electrons to form σ bonds
  - One σ bond is formed with the hydrogen atom

Your notes

- One σ bond is formed with the other carbon atom
- Two electrons are used to form two π bonds with the other carbon atom

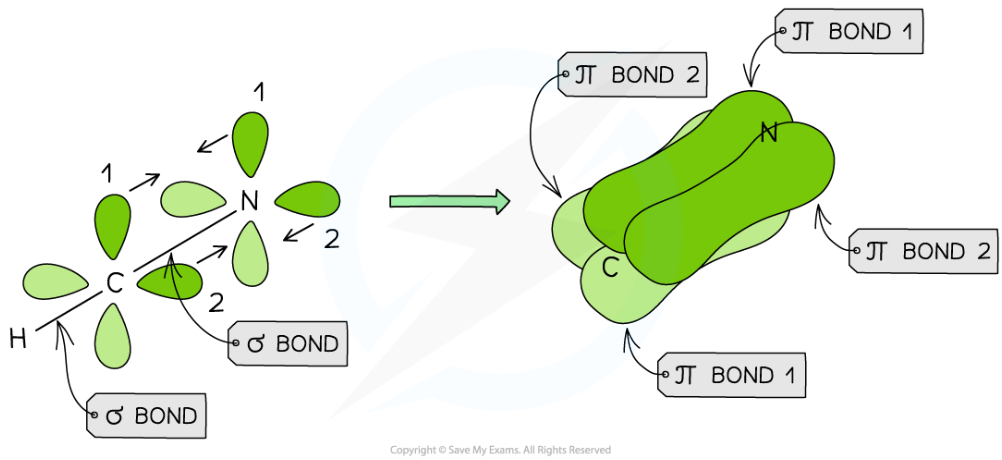
Sigma and pi bonding in ethyne



Ethyne has a triple bond formed from two π bonds and one σ bond between the two carbon atoms

- **Hydrogen cyanide**
  - Hydrogen cyanide contains a **triple bond**
  - One σ bond is formed between the H and C atom (**overlap of an sp C hybridised orbital with the 1s H orbital)**
  - A second σ bond is formed between the C and N atom (**overlap of an sp C hybridised orbital with an sp orbital of N)**
  - The remaining **two sets** of p orbitals of **nitrogen and carbon** will overlap to form **two π bonds** at right angles to each other

Sigma and pi bonding in hydrogen cyanide



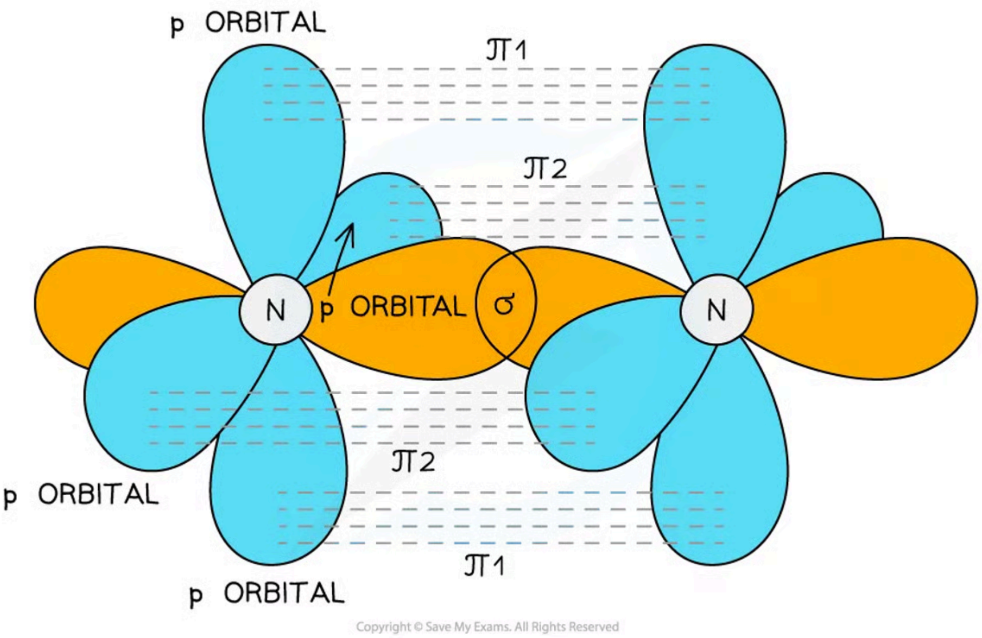
Hydrogen cyanide has a triple bond formed from the overlap of two sets of p orbitals of nitrogen and carbon and the overlap of an sp hybridised carbon orbital and a p orbital on the nitrogen

Your notes

Your notes

- **Nitrogen**
  - Nitrogen too contains a **triple bond**
  - The triple bond is formed from the overlap of the sp orbitals on each N to form a **σ bond** and the overlap of **two sets** of p orbitals on the nitrogen atoms to form **two π bonds**
  - These π bonds are at **right angles to each other**

Sigma and pi bonding in nitrogen molecules



The triple bond is formed from two π bonds and one σ bond

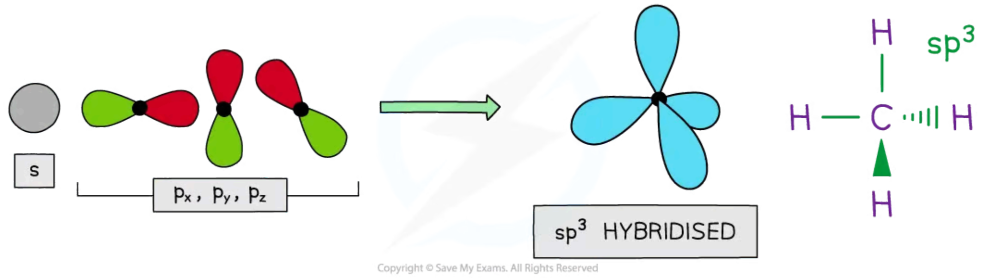
Hybridisation

- The **p atomic orbitals** can also overlap **end-on** to form σ bonds
- In order for them to do this, they first need to become **modified** in order to gain **s orbital character**
- The orbitals are therefore slightly changed in shape to make one of the p orbital **lobes bigger**
- This mixing of atomic orbitals to form covalent bonds is called **hybridisation**

What is sp^3 hybridisation?

- One s orbital and three p orbitals from the same shell mix to form **four sp^3 hybrid orbitals**
- These hybrid orbitals have **¼ s character and ¾ p character**
  - These orbitals are asymmetric, with a larger lobe similar in shape to a p orbital

- The four sp^3 orbitals arrange themselves with **tetrahedral geometry**



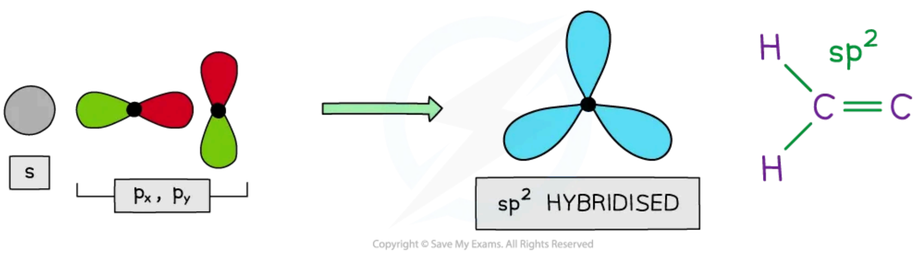
4 x sp^3 hybrid orbitals are formed from one s orbital and three p orbitals

- This hybridisation explains the bonding and shape in molecules like methane and ammonia
- **Methane, CH_4:**
  - The carbon atom forms four single covalent bonds
  - Each carbon sp^3 hybrid orbital overlaps head-on with a hydrogen 1s orbital
  - This results in:
    - Four identical sigma bonds
    - Tetrahedral electron domain geometry
    - Tetrahedral molecular geometry
    - A 109.5° bond angle
- Hybrid orbitals can accommodate both bonding pairs and lone pairs of electrons
- **Ammonia, NH_3:**
  - The nitrogen atom forms three single covalent bonds
  - Each nitrogen has three bonding pairs and one lone pair in sp^3 hybrid orbitals
  - This results in:
    - Three identical sigma bonds and one lone pair
    - Tetrahedral electron domain geometry
    - Trigonal pyramidal molecular geometry
    - A 107° bond angle

What is sp^2 hybridisation?

- One s orbital and two p orbitals from the same shell mix to form **three sp^2 hybrid orbitals**
- These hybrid orbitals have **⅓ s character and ⅔ p character**
  - These orbitals are asymmetric, with a larger lobe similar in shape to a p orbital
- The three sp^2 orbitals arrange themselves with **trigonal planar geometry**

Your notes

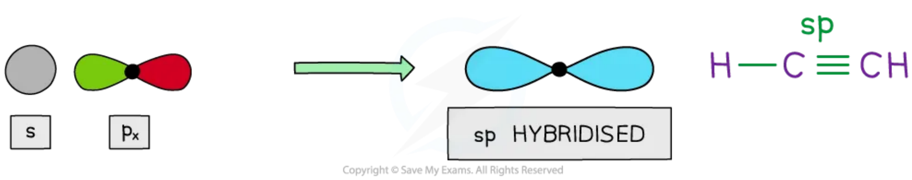


3 x sp2 hybrid orbitals are formed from one s orbital and two p orbitals

- This explains the bonding and geometry seen when carbon forms a double bond, such as in alkenes
- **Ethene:**
  - Each carbon atom forms three sigma bonds and one pi bond
  - The carbon atoms are **sp² hybridised**
  - Each carbon uses three sp² orbitals to form σ bonds:
    - Two with hydrogen atoms
    - One with the other carbon
  - One unhybridised p orbital to form a π bond with the other carbon
  - This results in:
    - One C=C double bond containing 1 σ and 1 π bond
    - Trigonal planar electron domain geometry
    - Trigonal planar molecular geometry
    - A 120° bond angle around each carbon
- This bonding arrangement also occurs in carbonyl groups, where both carbon and oxygen use sp^2 hybrid orbitals to form the double bond

What is sp hybridisation?

- One s orbital and one p orbital from the same shell mix to form **two sp hybrid orbitals**
- These hybrid orbitals have ½ **s character and** ½ **p character**
  - These orbitals are asymmetric, with a larger lobe similar in shape to a p orbital
- The two sp orbitals arrange themselves with **linear geometry**



2 sp hybrid orbitals are formed from one s orbital and one p orbital

- This explains the bonding and geometry seen when carbon forms a triple bond, such as in alkynes
- **Ethyne:**
  - Each carbon atom forms two sigma bonds and two pi bonds
  - The carbon atoms are **sp hybridised**
  - Each carbon uses two sp orbitals to form σ bonds:
    - One with hydrogen
    - One with the other carbon
  - Two unhybridised p orbitals form two π bonds with the other carbon
  - This results in:
    - One C ≡ C triple bond containing 1 σ and 2 perpendicular π bonds
    - Linear electron domain geometry
    - Linear molecular geometry
    - A 180° bond angle around each carbon

Examiner Tips and Tricks

Carbon forms four bonds. The type of bond depends on how many p orbitals are used in hybridisation:

- **sp^3**
  - 4 - 3 = 1
  - So, the carbon atom forms **single** bonds
- **sp^2**
  - 4 - 2 = 2
  - So, the carbon atom forms a **double** bond
- **sp**
  - 4 - 1 = 3
  - So, the carbon atom forms a **triple** bond

This page focuses on carbon (a second-period element), but hybridisation also occurs in third-period elements like phosphorus and sulfur.

- These atoms use 3s and 3p orbitals
- They may also use 3d orbitals when forming expanded octets

Your notes

Energy & Length of Covalent Bonds

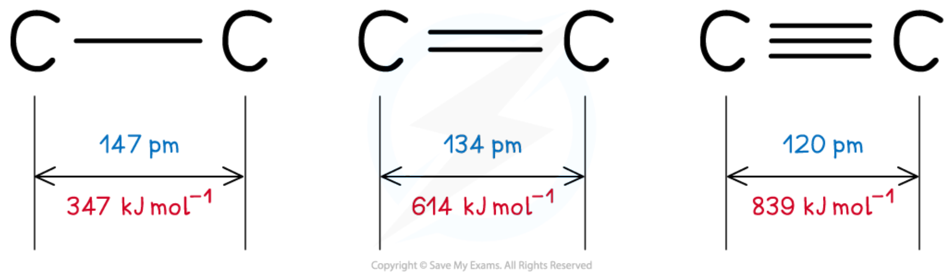
Bond energy

- The **bond energy** is the energy required to **break** one mole of a particular covalent bond in the gaseous states
  - Bond energy has units of kJ mol^{-1}
- The **larger** the bond energy, the **stronger** the covalent bond is

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 increases 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 mean that the covalent bond is **stronger**

Comparing the length of carbon-carbon covalent bonds



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

Reactivity of covalent molecules

- The **reactivity** of a covalent bond is greatly influenced by:
  - The bond **polarity**

- The bond **strength**
- The bond **type** (σ/π)

Your notes

Worked Example

Bond lengths & bond energies

Bond lengths and bond energy for various hydrogen halides is shown in the table below.

Hydrogen halide	Bond length (nm)	Bond energy ($kJ\ mol^{-1}$)
HCl	0.127	431
HBr	0.141	366
HI	0.161	299

1. Suggest why the bond energy values of hydrogen halides decrease in the order HCl > HBr > HI.
2. Suggest a value for the bond length in HF.
3. Suggest which hydrogen halide is the most reactive.

Answer 1:

- Going down the halogen group, the atoms are bigger
- This means that the attractive force between the bonding electrons and the nucleus gets smaller
- So, less energy is needed to break the atom

Answer 2:

- Going down the group the increase in bond length is approximately 0.14 - 0.20 nm
- Fluorine is smaller than HCl, so a value between 0.09 and 0.11 nm is acceptable for the bond length

Answer 3:

- The hydrogen halide with the longest bond length and therefore smallest bond energy is the most reactive as it takes the least energy to break apart the hydrogen and halide atoms apart
- Therefore, HI is the most reactive hydrogen halide