A Level Chemistry AQA

YOUR NOTES
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1. Physical Chemistry

CONTENTS

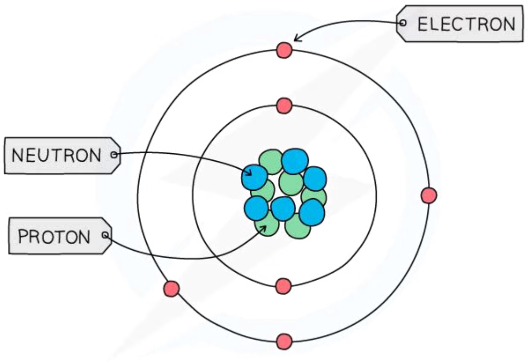
YOUR NOTES
⬇

1.1 Atomic Structure

1.1.1 Fundamental Particles

Structure of an Atom

- All matter is composed of **atoms**, which are the smallest parts of an element that can take place in **chemical reactions**
- Atoms are mostly made up of **empty space** around a very small, dense **nucleus** that contains **protons** and **neutrons**
- The nucleus has an overall **positive charge**
  - The protons have a positive charge and the neutrons have a neutral charge
- **Negatively charged** electrons are found in orbitals in the empty space around the nucleus

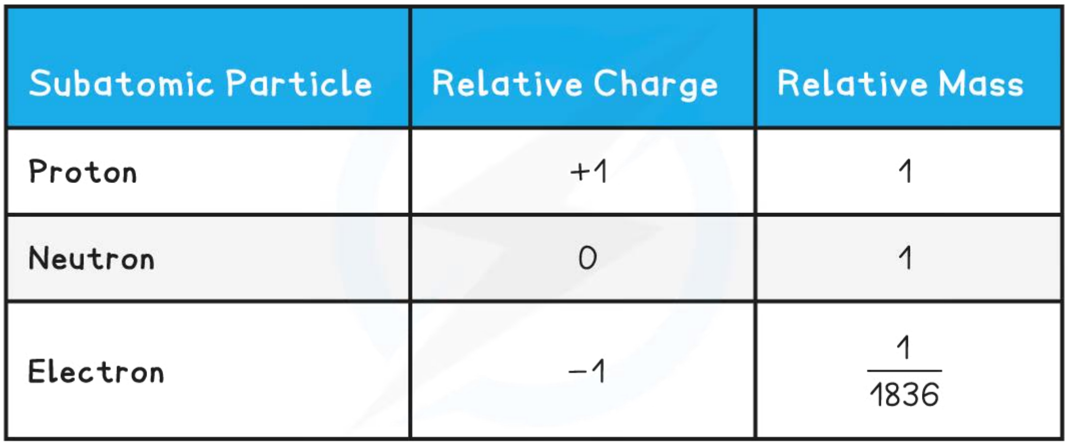


The basic structure of an atom (not to scale)

Subatomic Particles

- **Subatomic particles** are the particles an element is made up of and include **protons**, **neutrons** and **electrons**
- These subatomic particles are so small that it is not possible to measure their masses and charges using **conventional units** (such as grams and coulombs)
- Instead, their masses and charges are compared to each other using **'relative atomic masses'** and '**relative atomic charges**'
- These are not actual charges and masses but they are charges and masses of particles relative to each other
    - Protons and neutrons have a very similar mass so each is assigned a relative mass of 1 whereas electrons are 1836 times smaller than a proton and neutron
    - Protons are **positively** charged, electrons **negatively** charged and neutrons are **neutral**
- The relative mass and charge of the subatomic particles are:

Relative mass & charge of subatomic particles table



Subatomic Particle	Relative Charge	Relative Mass
Proton	+1	1
Neutron	0	1
Electron	−1	$\frac{1}{1836}$

Exam Tip

The **relative mass** of an electron is **almost negligible.**The **charge** of a single **electron** is -1.602×10^{-19} coulombs whereas the charge of a **proton** is $+1.602 \times 10^{-19}$ coulombs, however, relative to each other, their charges are −1 and +1 respectively.

Atoms: Key Terms

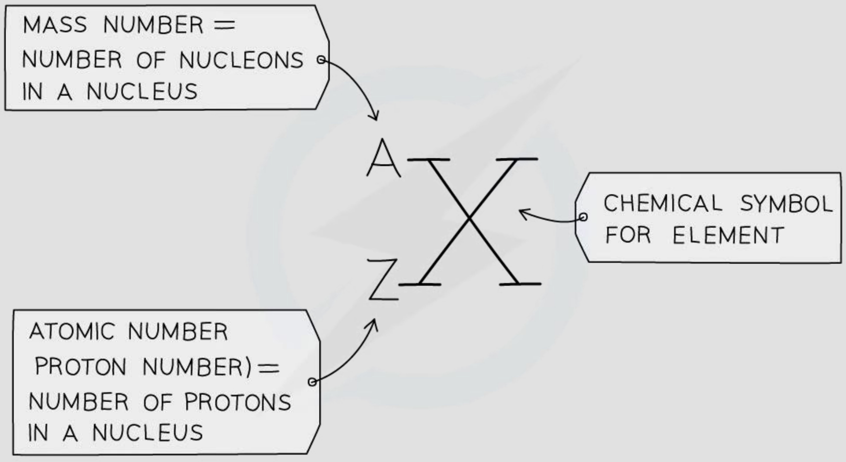
- The **atomic number** (or **proton number**) is the number of protons in the nucleus of an atom and has **symbol *Z***
    - The atomic number is equal to the number of electrons present in a **neutral** atom of an element
    - Eg. the atomic number of lithium is 3 which indicates that the neutral lithium atom has 3 protons and 3 electrons

- The **mass number** (or **nucleon number**) is the total number of **protons** and **neutrons** in the nucleus of an atom and has **symbol *A***
- The number of **neutrons** can be calculated by:

Number of neutrons = mass number - atomic number

- Protons and neutrons are also called **nucleons**

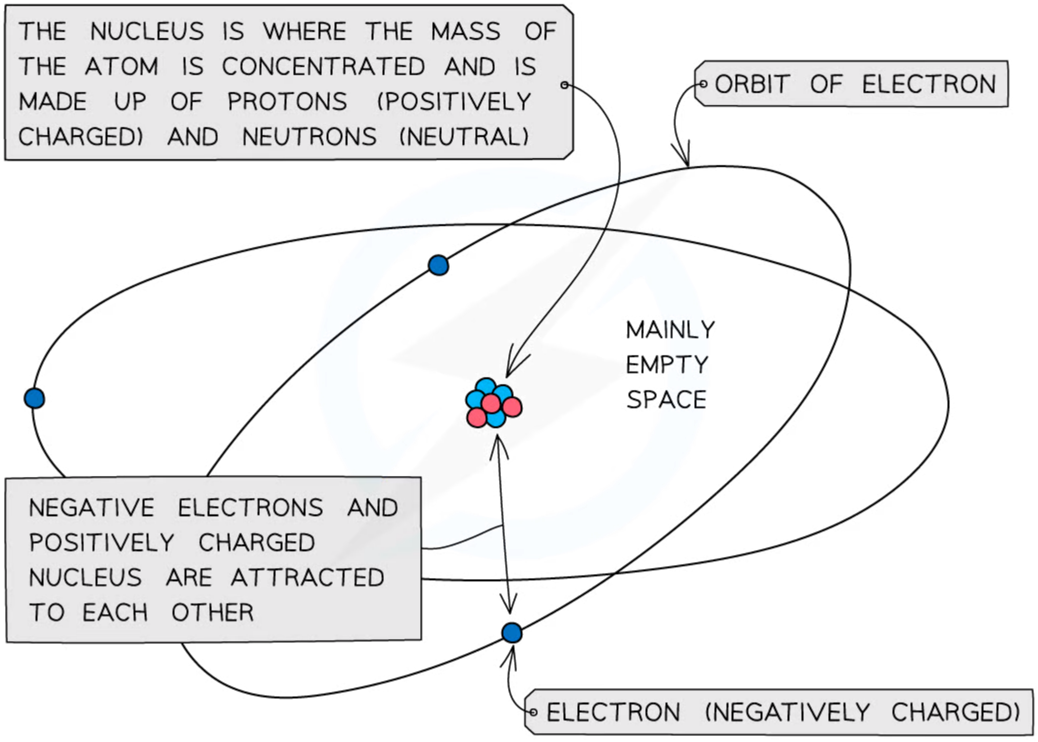
Exam Tip



The mass (nucleon) and atomic (proton) number are given for each element in the Periodic Table

Subatomic Structure of Atoms & Ions

- The mass of an atom is **concentrated** in the nucleus, because the nucleus contains the heaviest subatomic particles (the neutrons and protons)
    - The mass of the electron is negligible
- The nucleus is also **positively charged** due to the protons
- Electrons orbit the nucleus of the atom, contributing very little to its overall mass, but creating a **'cloud'** of negative charge
- The **electrostatic attraction** between the **positive nucleus** and **negatively charged electrons** orbiting around it is what holds an atom together



The mass of the atom is concentrated in the positively charged nucleus which is attracted to the negatively charged electrons orbiting around it

- An atom is **neutral** and has no overall charge
- Ions on the other hand are formed when atoms either **gain** or **lose** electrons, causing them to become **charged**
- The number of **subatomic particles** in atoms and ions can be determined given their atomic (proton) number, mass (nucleon) number and charge

Protons

- The atomic number of an atom and ion determines which element it is

- Therefore, all atoms and ions of the **same element** have the same number of protons (atomic number) in the nucleus
    - E.g. lithium has an atomic number of 3 (three protons) whereas beryllium has atomic number of 4 (4 protons)

- The number of protons equals the **atomic (proton) number**
- The number of protons of an **unknown** element can be calculated by using its mass number and number of neutrons:

Mass number = number of protons + number of neutrons

Number of protons = mass number - number of neutrons

Worked Example

Determine the number of protons of the following ions and atoms:

1. Mg^{2+} ion
2. Carbon atom
3. An unknown atom of element X with mass number 63 and 34 neutrons

Answers

Answer 1: The atomic number of a magnesium atom is 12 indicating that the number of protons in the magnesium element is 12

- Therefore the number of protons in a **Mg^{2+} ion** is also 12

Answer 2: The atomic number of a carbon atom is 6 indicating that a **carbon atom** has 6 protons in its nucleus

Answer 3: Use the formula to calculate the number of protons

Number of protons = mass number - number of neutrons

Number of protons = 63 - 34

Number of protons = 29

- **Element X** is therefore copper

Electrons

- An atom is **neutral** and therefore has the **same** number of **protons** and **electrons**
- Ions have a different number of electrons to their atomic number depending on their charge
    - A positively charged ion has **lost** electrons and therefore has **fewer** electrons than protons
    - A negatively charged ion has **gained** electrons and therefore has **more** electrons than protons

Worked Example

Determine the number of electrons of the following ions and atoms:

1. Mg^{2+} ion
2. Carbon atom
3. An unknown atom of element X with mass number 63 and 34 neutrons

Answers

Answer 1: The atomic number of a magnesium atom is 12 suggesting that the number of protons in the **neutral** magnesium **atom** is 12

- However, the 2+ charge in Mg^{2+} ion suggests it has **lost** two electrons
- It only has 10 electrons left now

Answer 2: The atomic number of a carbon atom is 6 suggesting that the **neutral** carbon **atom** has 6 electrons orbiting around the nucleus

Answer 3: The number of protons of element **X** can be calculated by:

Number of protons = mass number - number of neutrons

Number of protons = 63 - 34

Number of protons = 29

- The **neutral atom** of element **X** therefore also has 29 electrons

Neutrons

- The **mass** and **atomic numbers** can be used to find the number of **neutrons** in **ions** and **atoms:**

Number of neutrons = mass number (A) - number of protons (Z)

Worked Example

Determine the number of neutrons of the following ions and atoms:

1. Mg^{2+} ion
2. Carbon atom
3. An unknown atom of element X with mass number 63 and 29 protons

Answers

Answer 1: The atomic number of a magnesium atom is 12 and its mass number is 24

Number of neutrons = mass number (A) - number of protons (Z)

Number of neutrons = 24 - 12

Number of neutrons = 12

- The **Mg^{2+} ion** has 12 neutrons in its nucleus

Answer 2: The atomic number of a carbon atom is 6 and its mass number is 12

Number of neutrons = mass number (A) - number of protons (Z)

Number of neutrons = 12 - 6

Number of neutrons = 6

- The **carbon atom** has 6 neutrons in its nucleus

Answer 3: The atomic number of an element **X** atom is 29 and its mass number is 63

Number of neutrons = mass number (A) - number of protons (Z)

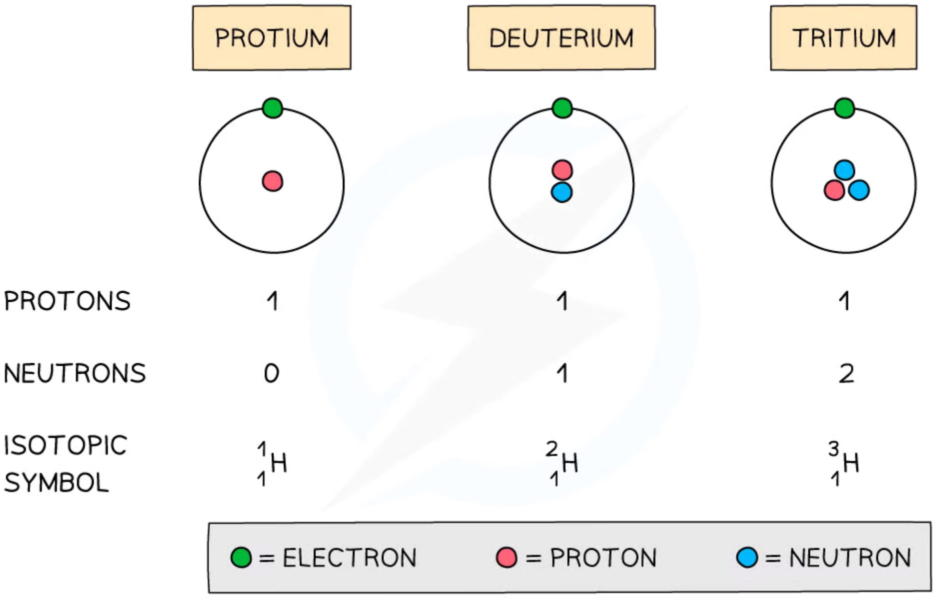
Number of neutrons = 63 - 29

Number of neutrons = 34

- The **neutral atom** of element **X** has 34 neutrons in its nucleus

Isotopes

- Isotopes are atoms of the **same element** that contain the same number of **protons** and electrons but a different number of **neutrons**
- The symbol for an isotope is the **chemical symbol** (or **word**) followed by a **dash** and then the **mass number**
  - E.g. carbon-12 and carbon-14 are isotopes of carbon containing 6 and 8 neutrons respectively



The atomic structure and symbols of the three isotopes of hydrogen

RAM from Mass Spectra

- Isotopes have the **same chemical properties** but **different physical properties**

Chemical properties

- Isotopes of the same element display the **same chemical characteristics**
- This is because they have the same number of electrons in their **outer shells**
- Electrons take part in **chemical reactions** and therefore determine the **chemistry** of an atom

Physical properties

- The only difference between isotopes is the number of **neutrons**
- Since these are neutral subatomic particles, they only add **mass** to the atom
- As a result of this, isotopes have different **physical properties** such as small differences in their **mass** and **density**

- **Isotopes** are different atoms of the **same element** that contain the same number of **protons** and electrons but a different number of **neutrons**.
  - These are atoms of the same **elements** but with different mass numbers

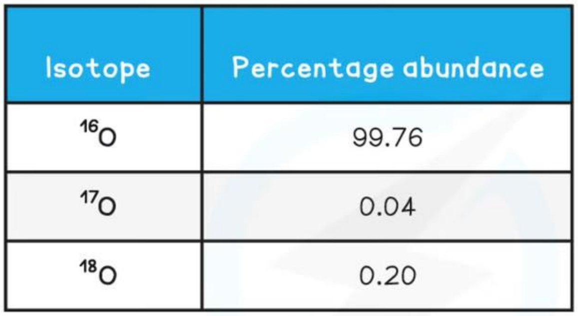
- Because of this, the mass of an element is given as **relative atomic mass (A_r)** by using the average mass of the isotopes
- The relative atomic mass of an element can be calculated by using the **relative abundance** values
  - The relative abundance of an isotope is either given or can be read off the mass spectrum
  - A_r =

$$\frac{(\text{relative abundance}_{\text{isotope 1}} \times \text{mass}_{\text{isotope 1}}) + (\text{relative abundance}_{\text{isotope 2}} \times \text{mass}_{\text{isotope 2}})\ \text{etc}}{100}$$

Worked Example

Calculating relative atomic mass of oxygen

A sample of oxygen contains the following isotopes:



Isotope	Percentage abundance
^{16}O	99.76
^{17}O	0.04
^{18}O	0.20

What is the relative atomic mass of oxygen in this sample, to 2dp?

1. 16.00
2. 17.18
3. 16.09
4. 17.00

Answer

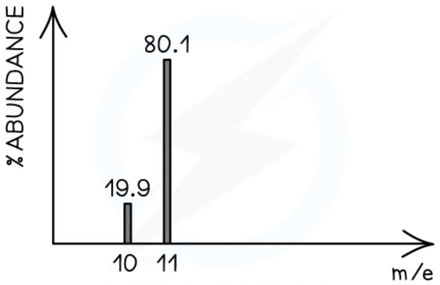
The correct answer option is 1

- $A_r = \dfrac{(99.76 \times 16) + (0.04 \times 17) + (0.20 \times 18)}{100}$
- $A_r = 16.0044$
- $A_r = 16.00$

Worked Example

Calculating relative atomic mass of boron

Calculate the relative atomic mass of boron using its mass spectrum, to 1dp:



Answer

- $A_r = \dfrac{(19.9 \times 10) + (80.1 \times 11)}{100} = 10.801 = 10.8$

YOUR NOTES
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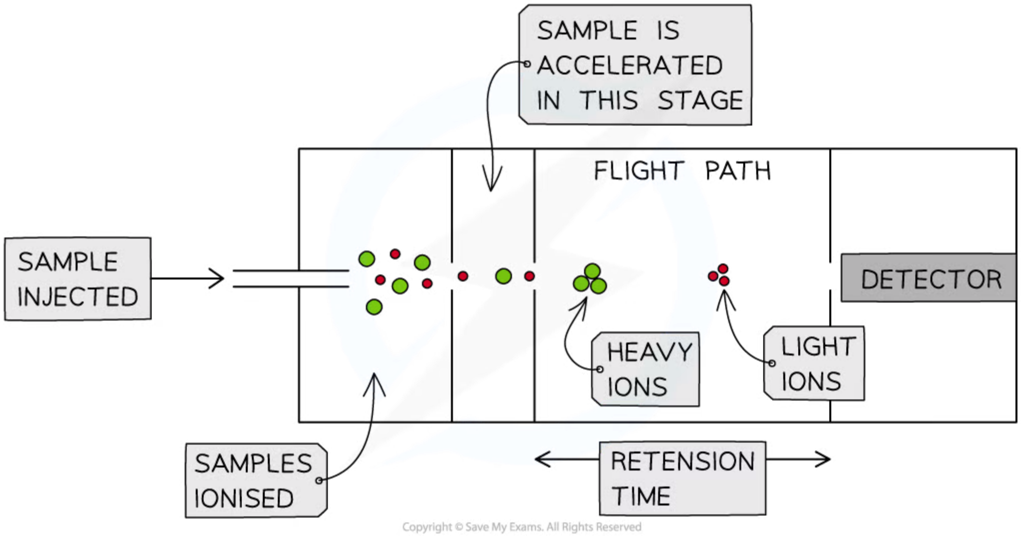
Time of Flight Mass Spectrometry

- Mass Spectrometry is a powerful analytical technique
  - It is the most useful instrument for accurate determination of the relative atomic mass of an element, based on the abundance and mass of each of its isotopes
  - It is also used to find the relative molecular mass of molecules

- As a sample passes through the mass spectrometer, a spectrum is produced of mass / charge ratio against abundance
- The spectrum can be used to find the relative isotopic abundance, atomic and molecular mass and the structure of a compound
- The peak with the highest mass is the **molecular ion peak, M+**, and the peak which has the largest abundance (tallest peak) is called the **base peak**
- There are several types of mass spectrometer, but all of them are based on an ionised sample being accelerated through the mass spectrum, and being separated based on the ratio of their charge to their mass

Time of Flight Mass Spectrometry

- This is a common form of mass spectrometry, where all particles of the sample to be analysed are ionised to form 1+ ions
- These 1+ ions are then accelerated to high speeds, deflected through the spectrometer and then arrive at the detector
- As they hit the detector, the mass spectrum graph is produced
- The whole of the apparatus is kept under a high vacuum to prevent any ions that are produced from colliding with molecules in the air



Inside the time of flight mass spectrometer

- There are 4 key stages in time of flight mass spectrometry:
  - Ionisation

  - Acceleration
  - Ion drift
  - Detection

Stage 1: Ionisation

- There are two key ways in which the sample could be ionised:
  - Electron Impact (or electron ionisation)
  - Electrospray Ionisation

Electron Impact Ionisation

- This method of ionisation is used for elements and substances which have a lower molecular mass
- The sample is vaporised and then bombarded with high energy electrons
- The electrons are 'fired' from an electron gun
  - The electron gun is a hot wire filament which emits electrons as a current runs through it
- As the sample is bombarded by these electrons, an electron is knocked off each particle, forming a 1+ ion

$$X\ (g) \rightarrow X^{+}\ (g) + e^{-}$$

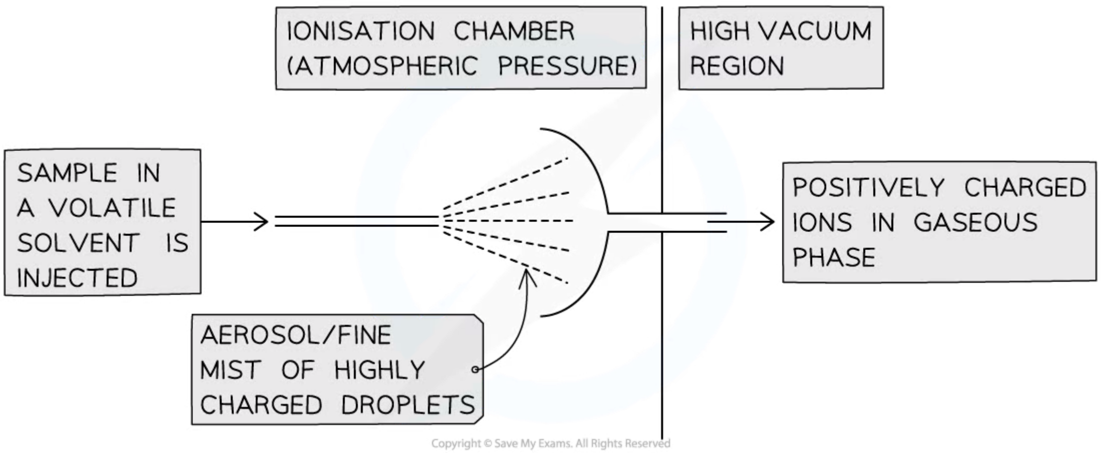
- The 1+ ions which have been formed are called molecular ions, or M+ ions
- These are then attracted towards a negatively charged plate
- This accelerates them through the mass spectrometer
- The molecular ion can be broken down further, or fragmented
  - The fragments are also accelerated through the sample and hit the detector, causing different peaks to show on the mass spectrum which is produced

Electrospray Ionisation

- This method is used for substances which have a higher molecular mass
- Unlike with electron impact ionisation, fragmentation is unlikely to happen
  - This is often called a soft ionisation technique
- For this method, the sample is dissolved in a volatile solvent
- The solvent is injected into the mass spectrometer using a hypodermic needle
  - This produces a fine mist or aerosol
- The needle is attached to a high voltage power supply, so as the sample is injected, the particles are ionised by gaining a proton from the solvent

$$X\ (g) + H^{+} \rightarrow XH^{+}\ (g)$$

- The solvent evaporates and the XH^{+} ions are attracted towards a negatively charged plate
- This accelerates them through the mass spectrometer



Time of Flight Mass Spectrometer

Stage 2: Acceleration

- The 1+ ions formed from either ionisation method are accelerated using an electric field
- They are all accelerated to have the **same kinetic energy**
    - This is important for you to remember when completing calculations
- Since all 1+ ions will have the same kinetic energy, their velocity will depend on their mass
    - Lighter ions will move faster and heavier ions will move slower

Stage 3: Ion Drift (in the flight tube)

- The 1+ ions will pass through a hole in the negatively charged plate and move into a flight tube
    - This is where the name 'Time of Flight' comes from
    - The time of flight of each 1+ ion in this tube depends on their velocity
    - Again, this is important to remember when completing calculations

Stage 4: Detection

- Once they have pass through the mass spectrometer, the 1+ ions will hit a negatively charged 'detector' plate
- As they hit this electric plate, they gain an electron
- This gaining of an electron discharges the ion, and causes a current to be produced
    - This **size of the current** is **proportional to the abundance** of those ions hitting the plate and gaining an electron
- The detector plate is connected to a computer, which produces the mass spectrum

$$KE = \frac{1}{2}mv^2$$

$$\therefore v = \sqrt{\frac{2KE}{m}}$$

$$t = \frac{d}{v} \qquad \therefore t = d\sqrt{\frac{m}{2KE}}$$

Key Equations for Time of Flight Mass Spectrometry

where

KE = kinetic energy of the particles (J)

m = mass of the particles (kg)

v = velocity of the particles (ms^{-1})

t = time of flight of the particles (s)

d = the length of the flight tube (m)

Exam Tip

Remember: all particles in the mass spectrometer are accelerated to the **same kinetic energy.** The time of flight is proportional to the square root of the mass of the ions, showing that the lighter the ion the faster it will pass through and the quicker it will hit the detector. The heavier the ion, the slower it will travel and the longer it will take to hit the detector.

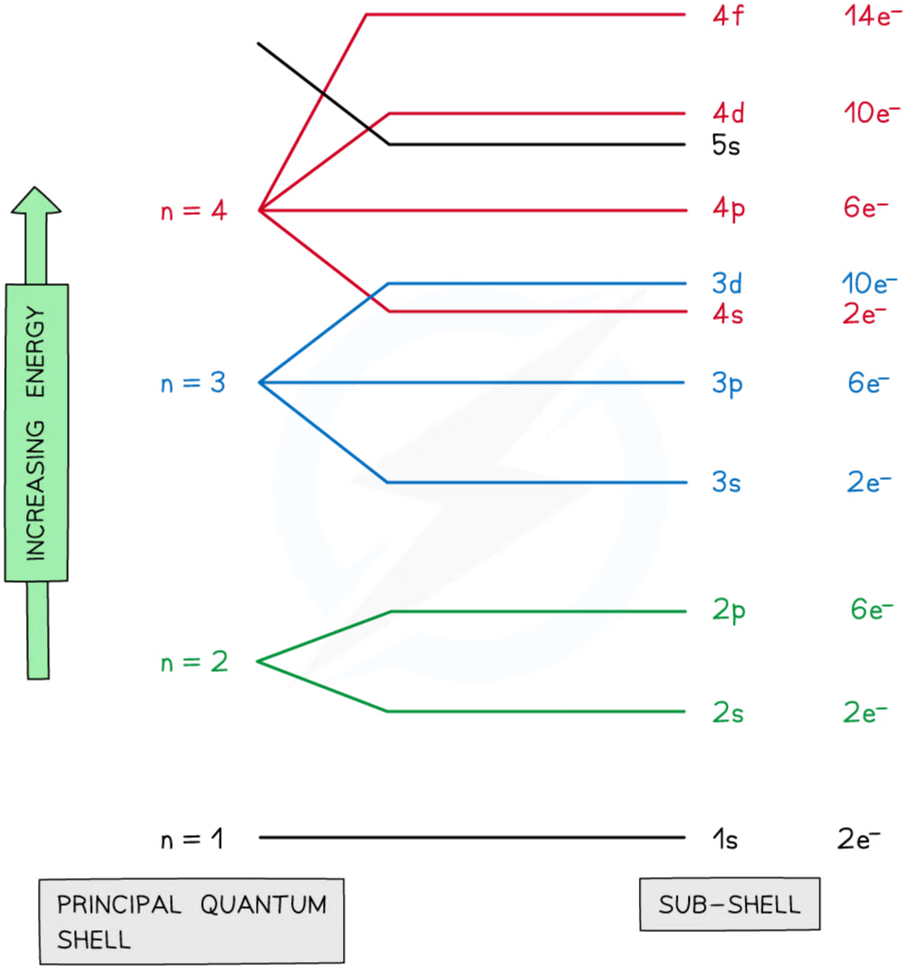
Electron Shells

Shells

- The arrangement of electrons in an atom is called the **electron configuration**
- Electrons are arranged around the nucleus in **principal energy levels** or **principal quantum shells**
- **Principal quantum numbers** (**n**) are used to number the energy levels or quantum shells
    - The **lower** the principal quantum number, the closer the shell is to the nucleus
        - So, the first shell which is the closest to the nucleus is n = 1
    - The **higher** the principal quantum number, the greater the energy of the shell and the further away from the nucleus
- Each principal quantum number has a **fixed** number of electrons it can hold
    - n = 1 : up to 2 electrons
    - n = 2 : up to 8 electrons
    - n = 3 : up to 18 electrons
    - n = 4 : up to 32 electrons

Subshells

- The principal quantum shells are split into **subshells** which are given the letters **s**, **p** and **d**
    - Elements with more than 57 electrons also have an **f** shell
    - The energy of the electrons in the subshells increases in the order s < p < d
- The order of subshells appear to overlap for the higher principal quantum shells as seen in the diagram below:



Electrons are arranged in principal quantum shells, which are numbered by principal quantum numbers

Orbitals

- Subshells contain one or more **atomic orbitals**
- Orbitals exist at **specific** energy levels and electrons can only be found at these specific levels, **not** in between them
    - Each atomic orbital can be occupied by a maximum of two electrons
- This means that the number of orbitals in each subshell is as follows:
    - **s** : one orbital (1 x 2 = total of 2 electrons)
    - **p** : three orbitals (3 x 2 = total of 6 electrons)
    - **d** : five orbitals (5 x 2 = total of 10 electrons)
    - **f** : seven orbitals (7 x 2 = total of 14 electrons)
- The orbitals have specific 3-D shapes

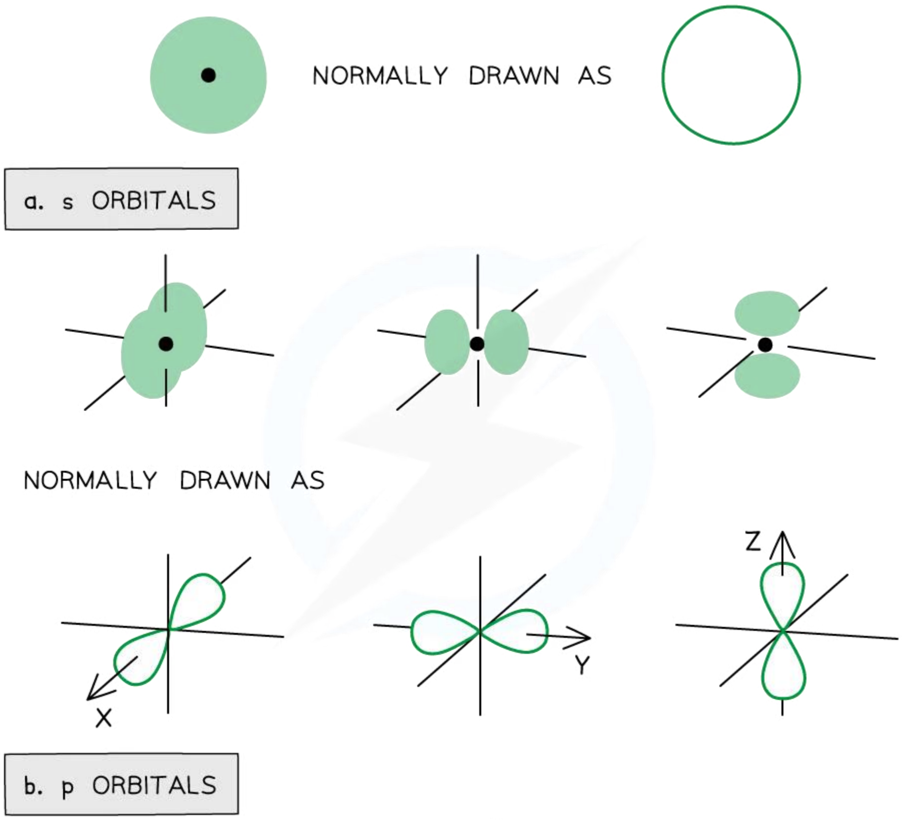
s orbital shape

- The s orbitals are **spherical** in shape

- The **size** of the s orbitals increases with increasing shell number
    - E.g. the s orbital of the **third** quantum shell ($n = 3$) is bigger than the s orbital of the **first** quantum shell ($n = 1$)

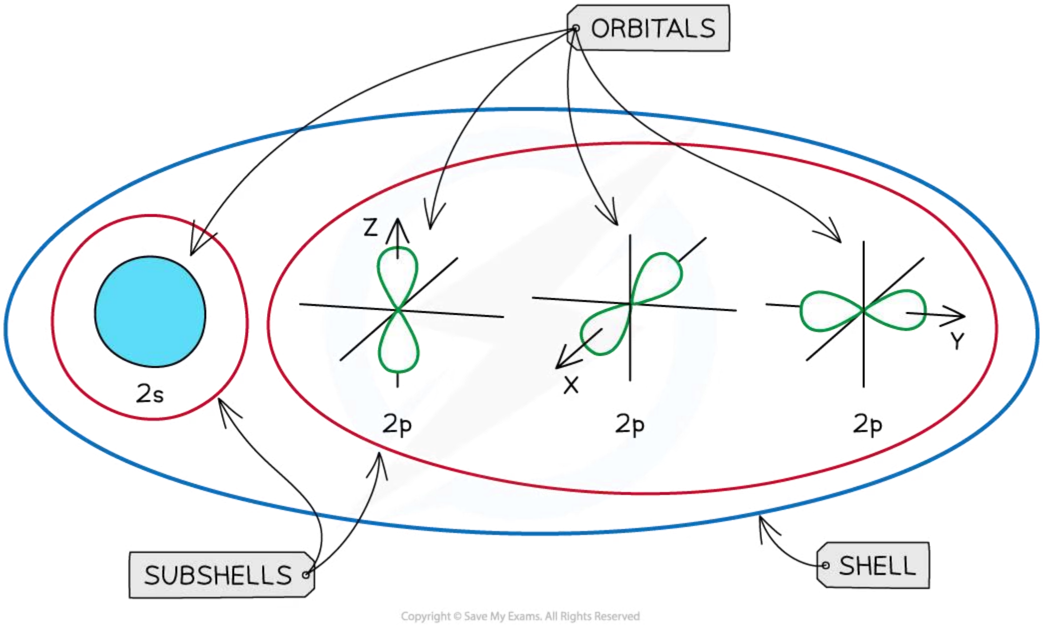
p orbital shape

- The p orbitals have a **dumbbell shape**
- Every shell has three p orbitals except for the first one ($n = 1$)
- The p orbitals occupy the x, y and z axes and point at right angles to each other, so are oriented **perpendicular** to one another
- The lobes of the p orbitals become **larger** and **longer** with increasing shell number



Representation of orbitals (the dot represents the nucleus of the atom) showing spherical s orbitals (a), p orbitals containing 'lobes' along the x, y and z axis

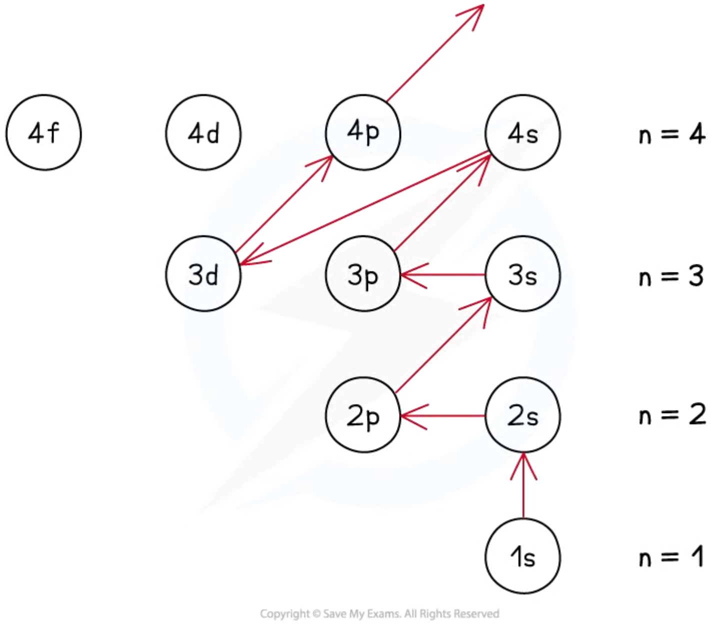
- Note that the shape of the d orbitals is **not** required



An overview of the shells, subshells and orbitals in an atom

Ground state

- The **ground state** is the **most stable electronic configuration** of an atom which has the **lowest amount of energy**
- This is achieved by filling the subshells of energy with the lowest energy first (1s)
- The order of the subshells in terms of increasing energy does **not** follow a regular pattern at n = 3 and higher



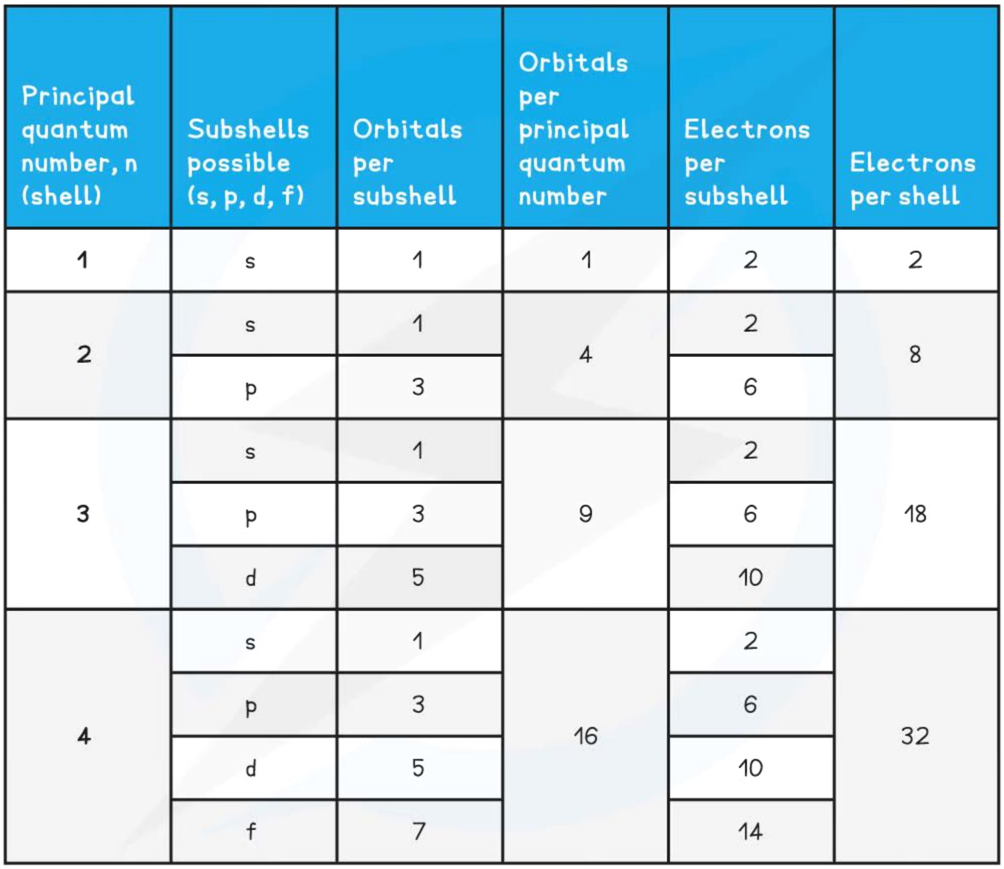
The ground state of an atom is achieved by filling the lowest energy subshells first

Electron Arrangement Summary

- Each shell can be divided further into **subshells, labelled s, p, d and f**
- Each subshell can hold a specific number of orbitals:
  - s subshell : 1 orbital
  - p subshell : 3 orbitals
  - d subshell : 5 orbitals
  - f subshell : 7 orbitals

- Each orbital can hold a maximum number of 2 electrons so the maximum number of electrons in each subshell are as follows:
  - s : 1 x 2 = total of 2 electrons
  - p : 3 x 2 = total of 6 electrons
  - d : 5 x 2 = total of 10 electrons
  - f : 7 x 2 = total of 14 electrons

Summary of the Arrangement of Electrons in Atoms Table



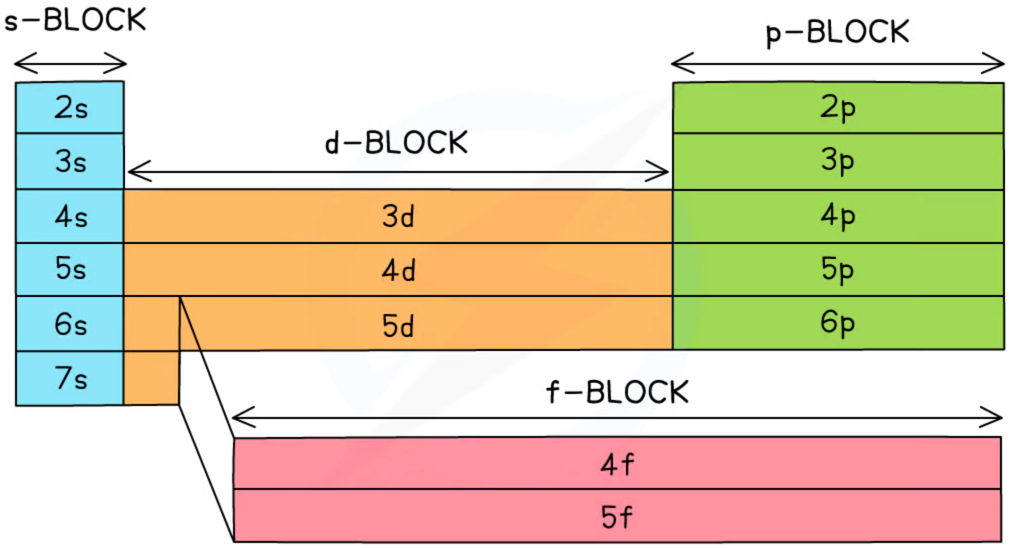
Principal quantum number, n (shell)	Subshells possible (s, p, d, f)	Orbitals per subshell	Orbitals per principal quantum number	Electrons per subshell	Electrons per shell
1	s	1	1	2	2
2	s	1	4	2	8
	p	3		6	
3	s	1	9	2	18
	p	3		6	
	d	5		10	
4	s	1	16	2	32
	p	3		6	
	d	5		10	
	f	7		14	

Exam Tip

The three p orbitals are labelled p_x, p_y and p_z, but you do not need to include this in your electron configurations!

Deducing the Electron Configuration

- The Periodic Table is split up into four main blocks depending on their electron configuration
- Elements can be classified as an s-block element, p-block element and so on, based on the position of the outermost electron:
    - s block elements
        - Have their valence electron(s) in an s orbital
    - p block elements
        - Have their valence electron(s) in a p orbital
    - d block elements
        - Have their valence electron(s) in a d orbital
    - f block elements
        - Have their valence electron(s) in an f orbital



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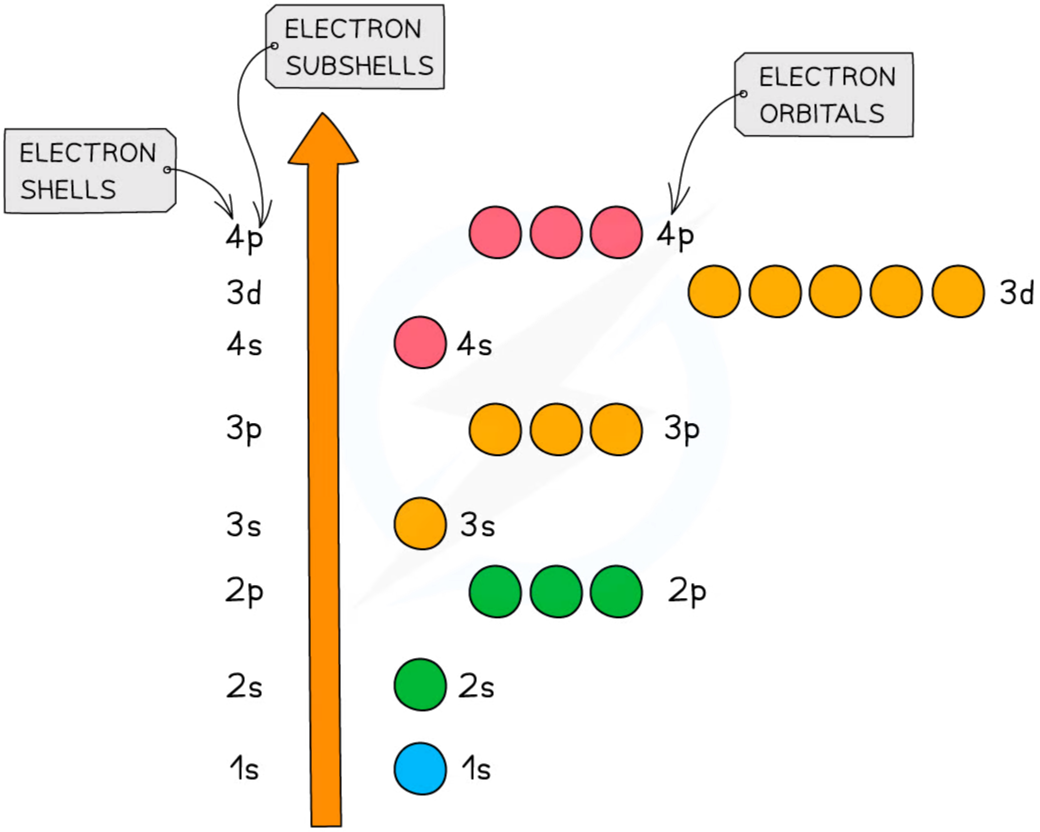
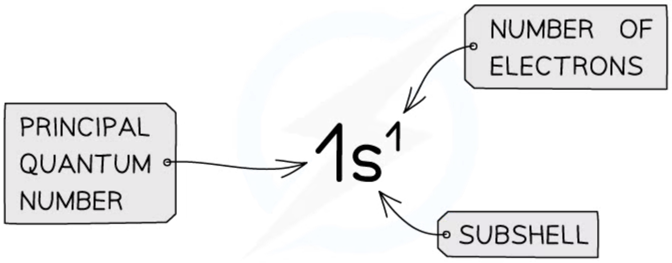
- The **principal quantum shells** increase in energy with increasing **principal quantum number**
    - E.g. $n = 4$ is higher in energy than $n = 2$
- The **subshells** increase in energy as follows: s < p < d < f
    - The only exception to these rules is the 3d orbital which has slightly higher energy than the 4s orbital
    - Because of this, the 4s orbital is filled before the 3d orbital
- All the orbitals in the **same** subshell have the same energy and are said to be **degenerate**
    - E.g. p_x, p_y and p_z are all equal in energy



Relative energies of the shells and subshells

- The **electron configuration** gives information about the number of electrons in each **shell, subshell** and **orbital** of an atom
- The subshells are filled in order of increasing energy



The electron configuration shows the number of electrons occupying a subshell in a specific shell

- Writing out the **electron configuration** tells us how the electrons in an atom or ion are arranged in their shells, subshells and orbitals
- This can be done using the **full** electron configuration or the **shorthand** version
  - The **full** electron configuration describes the arrangement of all electrons from the 1s subshell up

  - The **shorthand** electron configuration includes using the symbol of the **nearest preceding noble gas** to account for however many electrons are in that noble gas

- **Ions** are formed when atoms **lose** or **gain** electrons
  - Negative ions are formed by **adding** electrons to the outer subshell
  - Positive ions are formed by **removing** electrons from the outer subshell
  - The transition metals **fill** the 4s subshell before the 3d subshell but **lose** electrons from the 4s first and not from the 3d subshell (the 4s subshell is lower in energy

Full Electron Configurations

- Hydrogen has 1 single electron
  - The electron is in the s orbital of the first shell
  - Its electron configuration is $1s^1$

- Potassium has 19 electrons
  - The first 2 electrons fill the s orbital of the first shell
  - They then continue to fill subsequent orbitals and subshells in order of increasing energy
  - The 4s orbital is lower in energy than the 3d subshell, so it is therefore filled first
  - The full electron configuration of potassium is **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$**

Shorthand Electron Configurations

- Using potassium as an example again:
  - The nearest preceding noble gas to potassium is **argon**
  - This accounts for 18 electrons of the 19 electrons that potassium has
  - The shorthand electron configuration of potassium is **[Ar] $4s^1$**

Worked Example

Write down the full and shorthand electron configuration of the following elements:

1. Calcium
2. Gallium
3. Ca^{2+}

Answer

Answer 1:

  - Calcium has 20 electrons so the **full electronic configuration** is:

    $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

  - The 4s orbital is lower in energy than the 3d subshell and is therefore filled first

- The **shorthand** version is [Ar] $4s^2$ since argon is the nearest preceding noble gas to calcium which accounts for 18 electrons

Answer 2:

- Gallium has 31 electrons so the **full electronic configuration** is:

  $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p1$

  [Ar] $3d^{10}\ 4s^2\ 4p^1$

- Even though the 4s is filled first, the full electron configuration is often written in numerical order. So, if there are electrons in the 3d sub-shell, then these will be written before the 4s

Answer 3:

- What this means is that if you ionise calcium and remove two of its outer electrons, the electronic configuration of the Ca^{2+} ion is identical to that of argon

  Ca^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

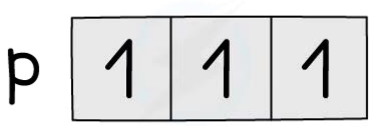
  Ar is also $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Exceptions

- Chromium and copper have the following electron configurations, which are different to what you may expect:
  - Cr is [Ar] $3d^5\ 4s^1$ **not** [Ar] $3d^4\ 4s^2$
  - Cu is [Ar] $3d^{10}\ 4s^1$ **not** [Ar] $3d^9\ 4s^2$
- This is because the [Ar] $3d^5\ 4s^1$ and [Ar] $3d^{10}\ 4s^1$ configurations are **energetically stable**

Presenting the Electron Configuration

- Electrons can be imagined as small **spinning charges** which rotate around their own axis in either a **clockwise** or **anticlockwise direction**
-
  - The spin of the electron is represented by its direction
- Electrons with similar **spin** repel each other which is also called **spin-pair repulsion**
- Electrons will therefore occupy separate orbitals in the same subshell where possible, to minimize this repulsion and have their **spin** in the same direction
  - E.g. if there are three electrons in a **p subshell**, one electron will go into each p_x, p_y and p_z orbital



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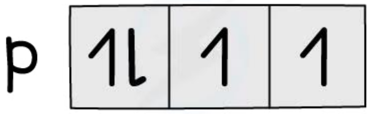
Electron configuration: three electrons in a p subshell

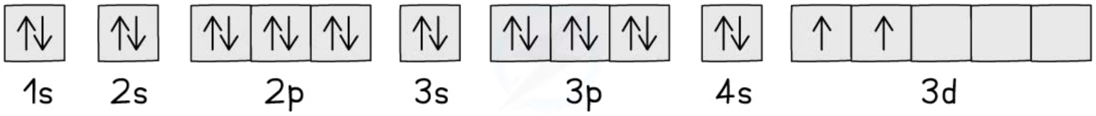
- Electrons are only paired when there are no more empty orbitals available within a subshell, in which case the spins are the **opposite** spins to minimize repulsion
    - E.g. if there are four electrons in a p subshell, one p orbital contains 2 electrons with opposite spin and two orbitals contain one electron only
    - The first 3 electrons fill up the empty p orbitals one at a time, and then the 4th one pairs up in the p_x orbital



Electron configuration: four electrons in a p subshell

Box Notation

- The **electron configuration** can be represented using the **electrons in boxes** notation
- Each box represents an **atomic orbital**
- The boxes are arranged in order of **increasing** energy from bottom to top
- The electrons are represented by opposite arrows to show the **spin** of the electrons
    - E.g. the box notation for titanium is shown below
    - Note that since the 3d subshell cannot be either full or half full, the second 4s electron is not promoted to the 3d level and stays in the 4s orbital



The electrons in titanium are arranged in their orbitals as shown. Electrons occupy the lowest energy levels first before filling those with higher energy

Exam Tip

You can use full headed arrows or half headed arrows to represent electrons in your box notations.

Ionisation Energies

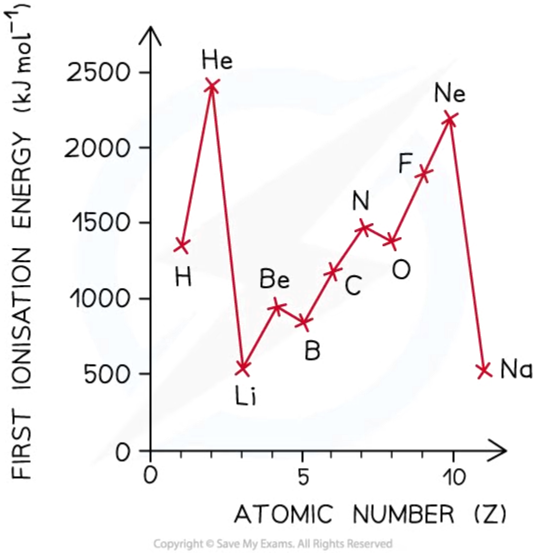
- The **Ionisation Energy** (**IE**) of an element is the amount of energy required to remove **one mole** of electrons from **one mole** of gaseous atoms of an element to form **one mole** of gaseous ions
- Ionisation energies are measured under **standard conditions** which are 298 K and 101 kPa
- The units of IE are **kilojoules per mole** (kJ mol^{-1})
- The **first ionisation energy** (IE_1) is the energy required to remove **one mole of electrons** from one mole of atoms of an element to form one mole of 1+ ions
    - E.g. the first ionisation energy of gaseous calcium:

$$Ca(g) \rightarrow Ca^{+}(g) + e^{-} \qquad IE_1 = +590 \text{ kJ mol}^{-1}$$

Trends in Ionisation Energies

- Ionisation energies show **periodicity** – a trend across a period of the Periodic Table
- As could be expected from their electron configuration, the group 1 metals have a relatively low ionisation energy, whereas the noble gases have very high ionisation energies
- The size of the first ionisation energy is affected by four factors:
    - **Size of the nuclear charge**
    - **Distance of outer electrons from the nucleus**
    - **Shielding effect of inner electrons**
    - **Spin–pair repulsion**

- First ionisation energy **increases** across a period and **decreases** down a group



A graph showing the ionisation energies of the elements hydrogen to sodium

Ionisation energy across a period

- The ionisation energy across a period generally **increases** due to the following factors:
    - Across a period the **nuclear charge increases**
    - This causes the **atomic radius** of the atoms to **decrease**, as the outer shell is pulled closer to the nucleus, so the distance between the nucleus and the outer electrons **decreases**
    - The **shielding** by inner shell electrons remain reasonably constant as electrons are being added to the same shell
    - It becomes **harder to remove an electron** as you move across a period; **more energy** is needed
    - So, the ionisation energy increases

Dips in the trend

- There is a slight **decrease** in IE_1 between **beryllium** and **boron** as the fifth electron in boron is in the 2p subshell, which is further away from the nucleus than the 2s subshell of beryllium
    - **Beryllium** has a first ionisation energy of **900 kJ mol^{-1}** as its electron configuration is **$1s^2\ 2s^2$**
    - **Boron** has a first ionisation energy of **800 kJ mol^{-1}** as its electron configuration is **$1s^2\ 2s^2\ 2p_x^1$**

- There is a slight **decrease** in IE_1 between **nitrogen** and **oxygen** due to **spin-pair repulsion** in the $2p_x$ orbital of oxygen
    - **Nitrogen** has a first ionisation energy of **1400 kJ mol^{-1}** as its electron configuration is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$
    - **Oxygen** has a first ionisation energy of **1310 kJ mol^{-1}** as its electron configuration is $1s^2\ 2s^2\ \mathbf{2p_x^2}\ 2p_y^1\ 2p_z^1$
    - In oxygen, there are 2 electrons in the $2p_x$ orbital, so the repulsion between those electrons makes it slightly easier for one of those electrons to be removed

From one period to the next

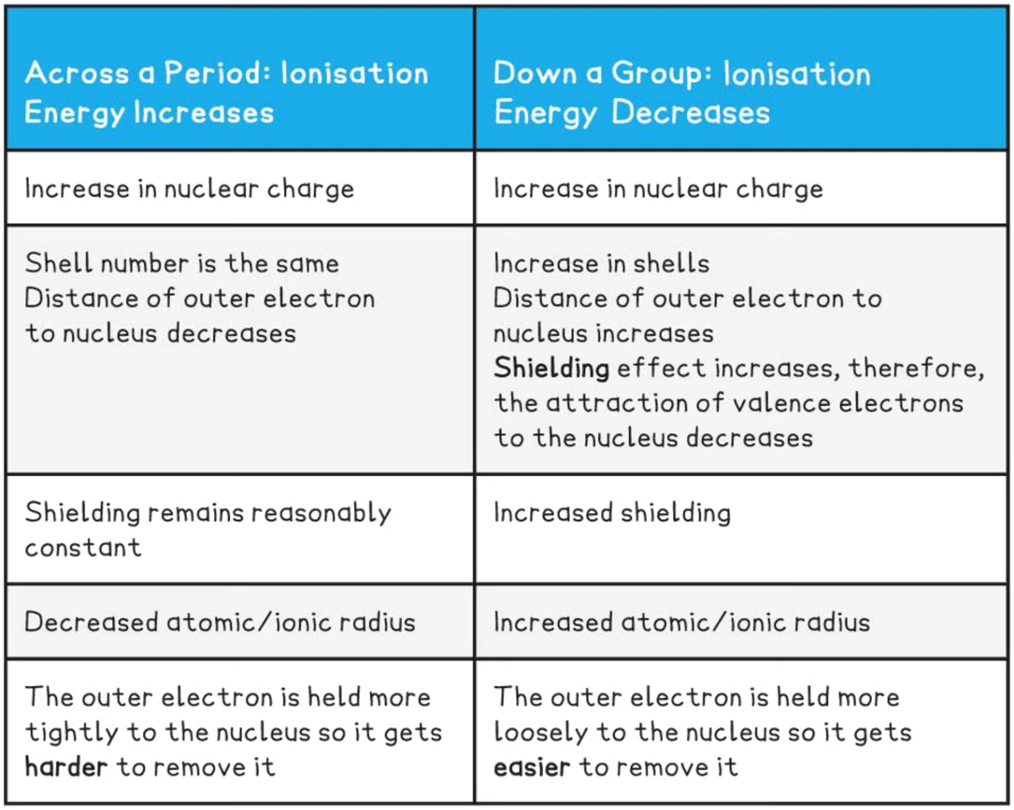
- There is a large **decrease** in ionisation energy between the **last** element in one period, and the **first** element in the next period
- This is because:
    - There is increased **distance** between the nucleus and the outer electrons as you have added a new shell
    - There is increased **shielding** by inner electrons because of the added shell
    - These two factors outweigh the increased **nuclear charge**

Ionisation energy down a group

- The ionisation energy down a group **decreases** due to the following factors:
    - The number of protons in the atom is increased, so the **nuclear charge** increases
    - But, the atomic radius of the atoms increases as you are adding more shells of electrons, making the atoms bigger

- So, the **distance** between the nucleus and outer electron **increases** as you descend the group
- The **shielding** by inner shell electrons **increases** as there are more shells of electrons
- These factors outweigh the increased nuclear charge, meaning it becomes **easier to remove the outer electron** as you descend a group
- So, the ionisation energy decreases

Ionisation Energy Trends across a Period & going down a Group Table

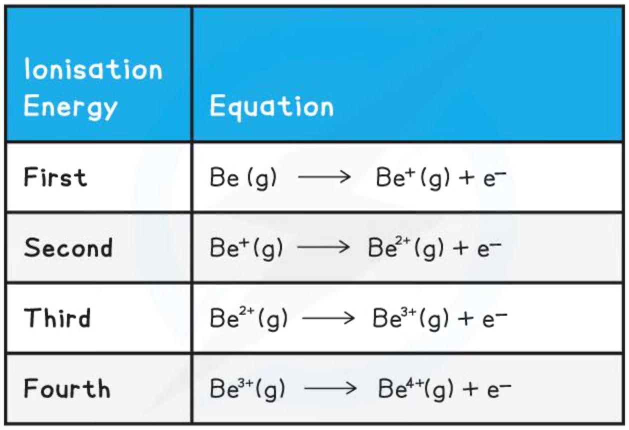


Across a Period: Ionisation Energy Increases	Down a Group: Ionisation Energy Decreases
Increase in nuclear charge	Increase in nuclear charge
Shell number is the same Distance of outer electron to nucleus decreases	Increase in shells Distance of outer electron to nucleus increases **Shielding** effect increases, therefore, the attraction of valence electrons to the nucleus decreases
Shielding remains reasonably constant	Increased shielding
Decreased atomic/ionic radius	Increased atomic/ionic radius
The outer electron is held more tightly to the nucleus so it gets **harder** to remove it	The outer electron is held more loosely to the nucleus so it gets **easier** to remove it

Ionisation Energies: Equations

- The **second ionisation energy** (**IE$_2$**) is the energy required to remove the second mole of electrons from each +1 ion in a mole of gaseous +1 ions, to form one mole of +2 ions
- The **third ionisation energy** (**IE$_3$**) is the energy required to remove the third mole of electrons from each +2 ion in a mole of gaseous +2 ions, to form one mole of +3 ions
- And so on...
- The electrons from an atom can be continued to be removed until only the **nucleus** is left
- This sequence of ionisation energies is called **successive ionisation energies**

Successive Ionisation Energies of Beryllium Table



Ionisation Energy	Equation
First	$Be(g) \longrightarrow Be^{+}(g) + e^{-}$
Second	$Be^{+}(g) \longrightarrow Be^{2+}(g) + e^{-}$
Third	$Be^{2+}(g) \longrightarrow Be^{3+}(g) + e^{-}$
Fourth	$Be^{3+}(g) \longrightarrow Be^{4+}(g) + e^{-}$

Exam Tip

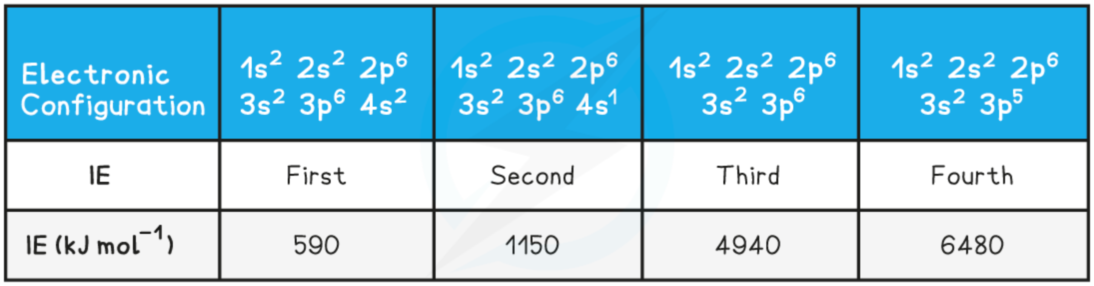
Remember that equations to represent ionisation energies must have **gaseous** (g) state symbols for the **atoms** and **ions** but **not** for the electrons.You will lose the mark in your exam if you do not include the state symbols, even if the question does not specify for you to include them.

Successive Ionisation Energies

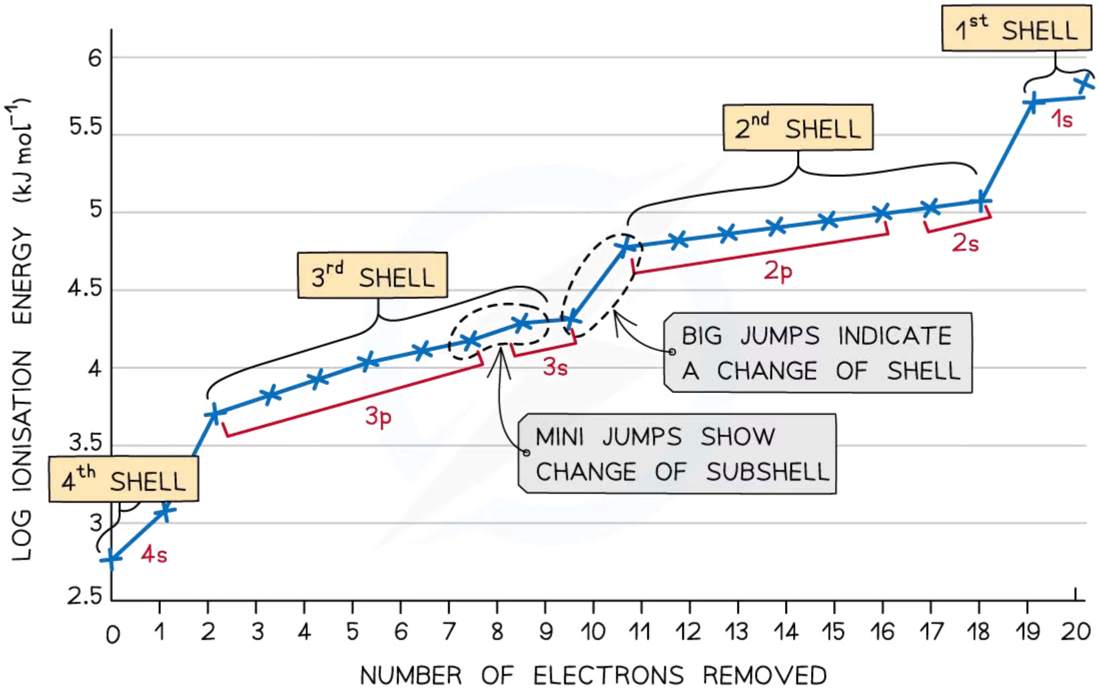
Successive ionisation energies of an element

- The **successive** ionisation energies of an element **increase**
- This is because once you have removed the outer electron from an atom, you have formed a **positive ion**
- Removing an electron from a positive ion is **more difficult** than from a neutral atom
- As more electrons are removed, the **attractive forces increase** due to decreasing shielding and an increase in the proton to electron ratio
- The increase in ionisation energy, however, is not constant and is dependent on the atom's electronic configuration
- Taking calcium as an example:

Ionisation Energies of Calcium Table



Electronic Configuration	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
IE	First	Second	Third	Fourth
IE (kJ mol^{-1})	590	1150	4940	6480



- The **first** electron removed has a low IE$_1$ as it is easily removed from the atom due to the spin-pair repulsion of the electrons in the 4s orbital

- The **second** electron is more difficult to remove than the first electron as there is no **spin-pair repulsion**
- The **third** electron is much more difficult to remove than the second one corresponding to the fact that the third electron is in a **principal quantum** shell which is closer to the nucleus (3p)
- Removal of the **fourth** electron is more difficult as the orbital is no longer full, and there is less **spin-pair repulsion**
- The graph shows there is a large increase in successive ionisation energy as the electrons are being removed from an increasingly positive ion
- The big jumps on the graph show the change of **shell** and the small jumps are the change of **subshell**

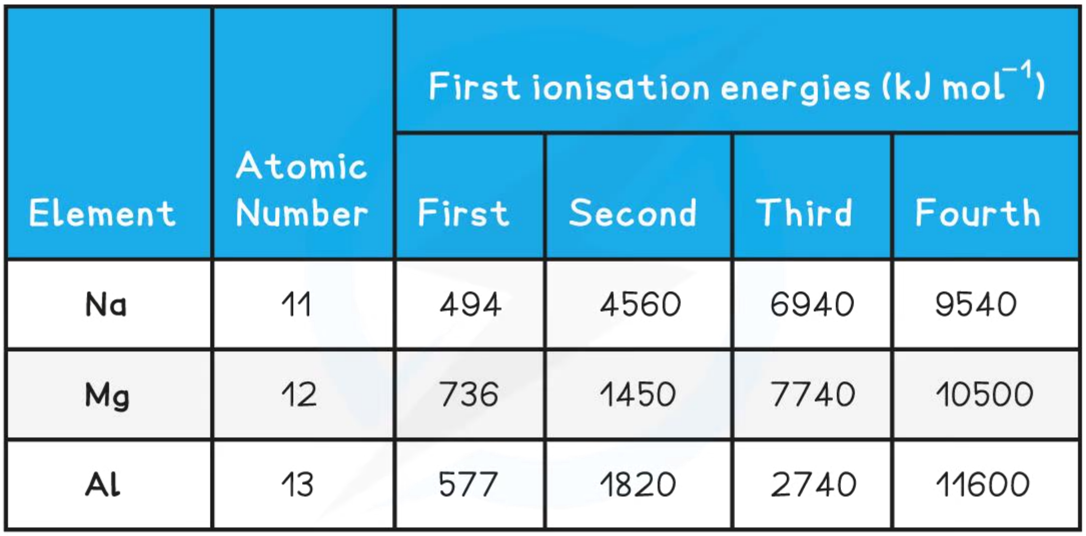
Exam Tip

It gets more difficult to remove electrons from **principal quantum shells** that get closer to the nucleus, as there is less **shielding** and an increase in **attractive forces** between the electrons and nuclear charge.Be careful with how you interpret successive ionisation energy graphs, especially if you are not given every successive ionisation energy and are just shown part of the graph – you should count the electrons from left to right!It is a good idea to label the shells and subshells on ionisation energy graphs in an exam, so that you do not make the mistake of reading the graph backwards.

- **Successive ionisation data** can be used to:
    - Predict or confirm the simple electronic configuration of elements
    - Confirm the number of electrons in the outer shell of an element
    - Deduce the Group an element belongs to in the Periodic Table

- By analyzing where the large jumps appear and the number of electrons removed when these large jumps occur, the **electron configuration** of an atom can be determined
- Na, Mg and Al will be used as examples to deduce the electronic configuration and positions of elements in the Periodic Table using their successive ionisation energies

Successive Ionisation Energies Table



Element	Atomic Number	First ionisation energies ($kJ\ mol^{-1}$)			
		First	Second	Third	Fourth
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
Al	13	577	1820	2740	11600

Sodium

- For sodium, there is a huge **jump** from the **first** to the **second** ionisation energy, indicating that it is much easier to remove the first electron than the second
- Therefore, the first electron to be removed must be the last electron in the **valence shell** thus Na belongs to group I
- The large jump corresponds to moving from the 3s to the full 2p subshell
  Na $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^1}$

Magnesium

- There is a huge increase from the **second** to the **third** ionisation energy, indicating that it is far easier to remove the first two electrons than the third
- Therefore the **valence shell** must contain only two electrons indicating that magnesium belongs to group II
- The large jump corresponds to moving from the 3s to the full 2p subshell
  Mg $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2}$

Aluminium

- There is a huge increase from the **third** to the **fourth** ionisation energy, indicating that it is far easier to remove the first three electrons than the fourth
- The 3p electron and 3s electrons are relatively easy to remove compared with the 2p electrons which are located closer to the nucleus and experience greater **nuclear charge**
- The large jump corresponds to moving from the **third shell** to the **second shell**
  Al $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^1}$

1.2 Formulae, Equations & Calculations

1.2.1 Relative Atomic Mass & Relative Molecular Mass

Relative Masses

Atomic Mass Unit

- The mass of a single atom is so small that it is impossible to weigh it directly
- Atomic masses are therefore defined in terms of a **standard** atom which is called the **unified atomic mass unit**
- This unified atomic mass is defined as **one-twelfth** of the mass of a carbon-12 isotope
- The symbol for the unified atomic mass is ***u*** (often *Da*, Dalton, is used as well)
- 1 u = 1.66 x 10^{-27} kg

Relative atomic mass, A_r

- The **relative atomic mass** (A_r) of an element is the **ratio** of the average mass of the atoms of an element to the **unified atomic mass unit**
- The relative atomic mass is determined by using the **average** mass of the **isotopes** of a particular element
- The A_r has **no units** as it is a ratio and the units cancel each other out

$$\textit{Relative atomic mass of an element X} = \frac{\textit{average mass of one atom of X}}{1/12 \textit{ of the mass of one carbon}-12 \textit{ atom}}$$

Relative isotopic mass

- The **relative isotopic mass** is the mass of a particular atom of an **isotope** compared to the value of the **unified atomic mass unit**
- Atoms of the same element with a different number of neutrons are called **isotopes**
- **Isotopes** are represented by writing the **mass number** as ^{20}Ne, or neon-20 or Ne-20
  - To calculate the average atomic mass of an element the **percentage abundance** is taken into account
  - Multiply the atomic mass by the percentage abundance for each isotope and add them all together
  - Divide by 100 to get average relative atomic mass
  - This is known as the **weighted average** of the masses of the isotopes

$$\text{RELATIVE ATOMIC MASS} = \frac{\Sigma(\text{ISOTOPE ABUNDANCE} \times \text{ISOTOPE MASS NUMBER})}{100}$$

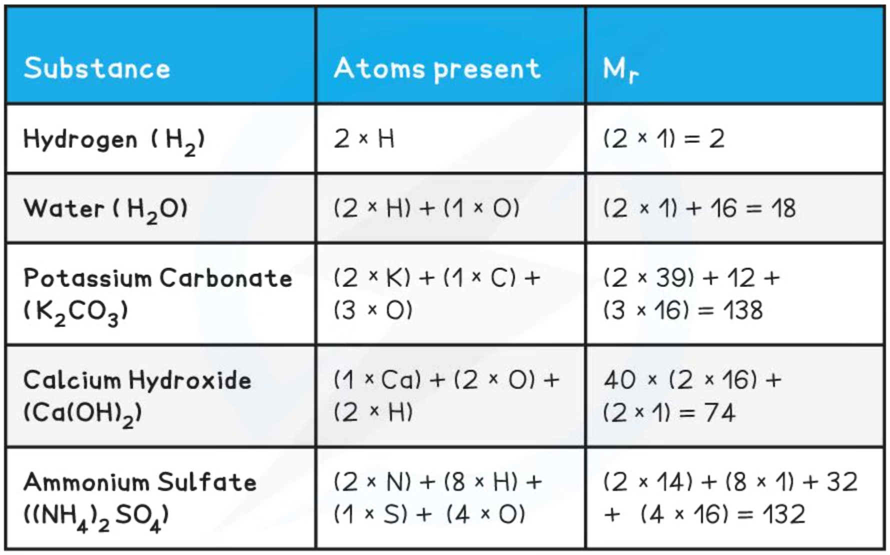
(WHERE Σ = SUM OF)

Relative molecular mass, M_r

- The **relative molecular mass** (M_r) is the **ratio** of weighted average mass of a molecule of a molecular compound to the **unified atomic mass unit**
- The M_r has **no units**

$$M_r = \frac{\textit{weighted average mass of molecules in a given sample of a molecular compound}}{\textit{unified atomic mass unit}}$$

- The M_r can be found by adding up the **relative atomic masses** of all atoms present in one molecule
- When calculating the M_r the **simplest formula** for the compound is used, also known as the **formula unit**
  - Eg. silicon dioxide has a giant covalent structure, however the simplest formula (the **formula unit**) is SiO_2



Substance	Atoms present	M_r
Hydrogen (H_2)	2 × H	(2 × 1) = 2
Water (H_2O)	(2 × H) + (1 × O)	(2 × 1) + 16 = 18
Potassium Carbonate (K_2CO_3)	(2 × K) + (1 × C) + (3 × O)	(2 × 39) + 12 + (3 × 16) = 138
Calcium Hydroxide ($Ca(OH)_2$)	(1 × Ca) + (2 × O) + (2 × H)	40 × (2 × 16) + (2 × 1) = 74
Ammonium Sulfate ($(NH_4)_2SO_4$)	(2 × N) + (8 × H) + (1 × S) + (4 × O)	(2 × 14) + (8 × 1) + 32 + (4 × 16) = 132

Relative formula mass, M_r

- The **relative formula mass** (M_r) is used for compounds containing **ions**
- It has the same units and is calculated in the same way as the **relative molecular mass**
- In the table above, the M_r for potassium carbonate, calcium hydroxide and ammonium sulfates are relative formula masses

Empirical & Molecular Formulae

- The **molecular formula** is the formula that shows the **number** and **type** of each atom in a molecule
  - E.g. the molecular formula of ethanoic acid is $C_2H_4O_2$
- The **empirical formula** is the simplest whole number ratio of atoms of each element present in one molecule or formula unit of a compound
  - E.g. the empirical formula of ethanoic acid is CH_2O

Empirical & Molecular Formulae Calculations

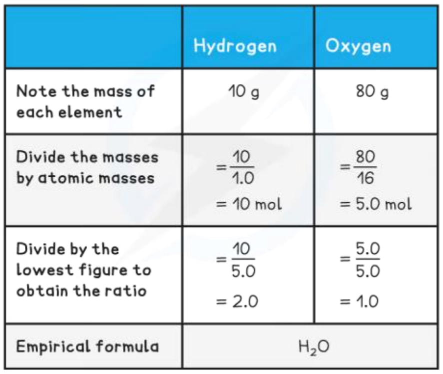
Empirical formula

- **Empirical formula** is the **simplest whole number ratio** of the elements present in one molecule or formula unit of the compound
- It is calculated from knowledge of the ratio of masses of each element in the compound
- The empirical formula can be found by determining the **mass** of each element present in a sample of the compound
- It can also be deduced from data that gives the **percentage compositions by mass** of the elements in a compound

Worked Example

Empirical formula from mass

Determine the empirical formula of a compound that contains 10 g of hydrogen and 80 g of oxygen.



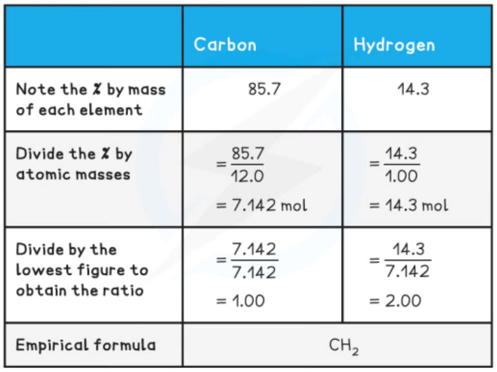
	Hydrogen	Oxygen
Note the mass of each element	10 g	80 g
Divide the masses by atomic masses	$= \frac{10}{1.0}$ $= 10$ mol	$= \frac{80}{16}$ $= 5.0$ mol
Divide by the lowest figure to obtain the ratio	$= \frac{10}{5.0}$ $= 2.0$	$= \frac{5.0}{5.0}$ $= 1.0$
Empirical formula	H_2O	

- The above example shows how to calculate empirical formula from the mass of each element present in the compound
- The example below shows how to calculate the empirical formula from percentage composition

Worked Example

Empirical formula from %

Determine the empirical formula of a compound that contains 85.7% carbon and 14.3% hydrogen.



	Carbon	Hydrogen
Note the % by mass of each element	85.7	14.3
Divide the % by atomic masses	$= \frac{85.7}{12.0}$ = 7.142 mol	$= \frac{14.3}{1.00}$ = 14.3 mol
Divide by the lowest figure to obtain the ratio	$= \frac{7.142}{7.142}$ = 1.00	$= \frac{14.3}{7.142}$ = 2.00
Empirical formula	CH_2	

Molecular formula

- The **molecular formula** gives the exact numbers of atoms of each element present in the formula of the compound
- The molecular formula can be found by dividing the **relative formula mass** of the **molecular formula** by the **relative formula mass** of the **empirical formula**
- **Multiply** the number of each element present in the empirical formula by this number to find the molecular formula

Worked Example

Calculating molecular formula

The empirical formula of X is $C_4H_{10}S$ and the relative molecular mass of X is 180

What is the molecular formula of X?

(A_r data: C = 12, H = 1, S = 32)

Answer

Step 1: Calculate relative mass of the empirical formula

- Relative empirical mass = (C x 4) + (H x 10) + (S x 1)
- Relative empirical mass = (12 x 4) + (1 x 10) + (32 x 1)
- Relative empirical mass = 90

Step 2: Divide relative formula mass of **X** by relative empirical mass

- Ratio between M_r of X and the M_r of the empirical formula = 180/90
- Ratio between M_r of X and the M_r of the empirical formula = 2

Step 3: Multiply each number of elements by 2

- $(C_4 \times 2) + (H_{10} \times 2) + (S \times 2) = (C_8) + (H_{20}) + (S_2)$
- Molecular Formula of **X** is $C_8H_{20}S_2$

Deducing Formulae of Compounds

- **Ionic compounds** are formed from a **metal** and a **non-metal** bonded together
- Ionic compounds are electrically neutral; the positive charges equal the negative charges

Charges on positive ions

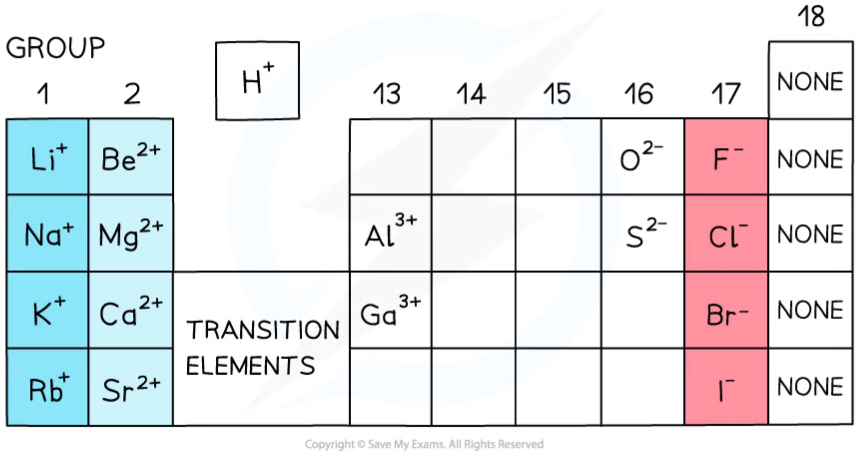
- All metals form **positive** ions
  - There are also some non-metal positive ions, such as ammonium, NH_4^+, and hydrogen, H^+

- The **metals** in Group 1, Group 2 and Group 3 (13) have a charge of 1+ and 2+ and 3+ respectively
- The charge on the ions of the **transition elements can vary** which is why **Roman numerals** are often used to indicate their charge
- **Roman numerals** are used in some compounds formed from transition elements to show the **charge** (or **oxidation state**) of metal ions
  - E.g. in copper (II) oxide, the copper ion has a charge of 2+ whereas in copper (I) nitrate, the copper has a charge of 1+

Non-metal ions

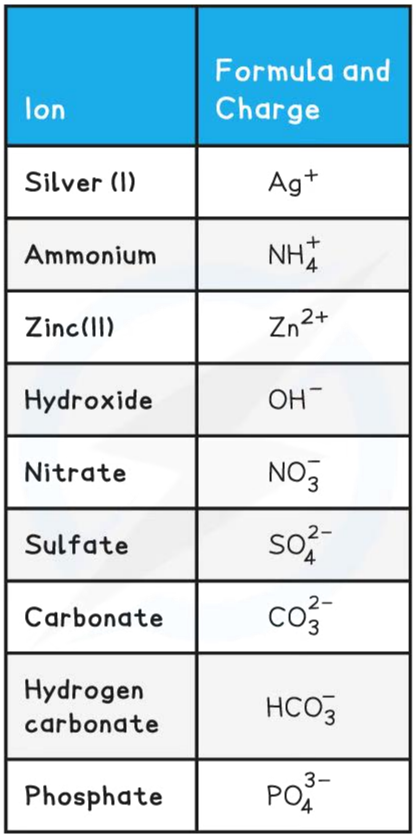
- The **non-metals** in group 15 to 17 have a negative charge and have the suffix **'ide'**
  - E.g. nitride, chloride, bromide, iodide

- Elements in group 17 gain 1 electron so have a 1– charge, eg. Br^-
- Elements in group 16 gain 2 electrons so have a 2– charge, eg. O^{2-}
- Elements in group 15 gain 3 electrons so have a 3– charge, eg. N^{3-}
- There are also **polyatomic** negative ions, which are negative ions made up of more than one type of atom



The charges of simple ions depend on their position in the Periodic Table

Formulae of Ionic Compounds Table



Ion	Formula and Charge
Silver (I)	Ag^+
Ammonium	NH_4^+
Zinc(II)	Zn^{2+}
Hydroxide	OH^-
Nitrate	NO_3^-
Sulfate	SO_4^{2-}
Carbonate	CO_3^{2-}
Hydrogen carbonate	HCO_3^-
Phosphate	PO_4^{3-}

Worked Example

Formulae

Determine the formulae of the following ionic compounds

1. Magnesium chloride
2. Iron(III) oxide
3. Aluminium nitrate

Answer

Answer 1: Magnesium chloride

- Magnesium is in Group 2 so has a charge of 2+
- Chlorine is in group 17 so has a charge of 1−
- Magnesium needs two chloride ions for each magnesium ion to be balanced so the formula is $\mathbf{MgCl_2}$

Answer 2: Iron (III) oxide

- The Roman numeral states that iron has a charge of 3+
- Oxygen is in group 16 so has a charge of 2−

  - The charges need to be equal so 2 iron ions to 3 oxide ions will balance electrically, so the formula is **Fe_2O_3**

Answer 3: Aluminum nitrate

  - Aluminium is in group 13 so has a charge of 3+
  - Nitrate is a **polyatomic ion** and has a charge of 1−
  - The **polyatomic ion** needs to be placed in a bracket if more than 1 is needed
  - The formula of aluminium nitrate is **$Al(NO_3)_3$**

Exam Tip

Remember: **Polyatomic ions** are ions that contain more than one type of element, such as OH^-

Balancing Equations

- A **symbol** equation is a shorthand way of describing a chemical reaction using **chemical symbols** to show the number and type of each atom in the reactants and products
- A **word** equation is a longer way of describing a chemical reaction using only **words** to show the reactants and products

Balancing equations

- During chemical reactions, atoms cannot be **created** or **destroyed**
- The number of each atom on each side of the reaction must therefore be the **same**
  - E.g. the reaction needs to be **balanced**

- When balancing equations remember:
  - Not to change any of the formulae
  - To put the numbers used to balance the equation **in front** of the formulae
  - To balance firstly the carbon, then the hydrogen and finally the oxygen in **combustion reactions** of organic compounds

- When balancing equations follow the following the steps:
  - Write the formulae of the reactants and products
  - Count the numbers of atoms in each reactant and product
  - Balance the atoms one at a time until all the atoms are balanced
  - Use appropriate state symbols in the equation

- The **physical state** of reactants and products in a chemical reaction is specified by using **state symbols**
  - **(s)** solid
  - **(l)** liquid
  - **(g)** gas
  - **(aq)** aqueous

Ionic Equations

Ionic equations

- In aqueous solutions ionic compounds **dissociate** into their ions
- Many chemical reactions in aqueous solutions involve ionic compounds, however only some of the ions in solution take part in the reactions
- The ions that do **not** take part in the reaction are called **spectator ions**
- An **ionic equation** shows **only** the ions or other particles taking part in a reaction, and not the spectator ions

Worked Example

Balance the following equation:

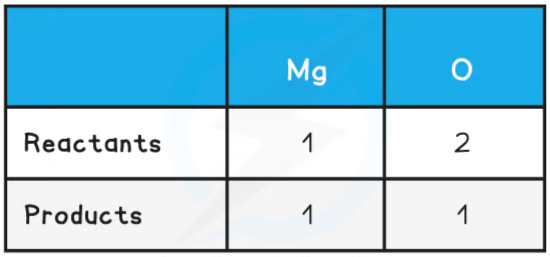
magnesium + oxygen → magnesium oxide

Answer:

Step 1: Write out the symbol equation showing reactants and products

$$\mathbf{Mg + O_2 \rightarrow MgO}$$

Step 2: Count the numbers of atoms in each reactant and product



	Mg	O
Reactants	1	2
Products	1	1

Step 3: Balance the atoms one at a time until all the atoms are balanced

$$\mathbf{2Mg + O_2 \rightarrow 2MgO}$$

This is now showing that 2 moles of magnesium react with 1 mole of oxygen to form 2 moles of magnesium oxide

Step 4: Use appropriate **state symbols** in the fully balanced equation

$$\mathbf{2Mg\ (s) + O_2\ (g) \rightarrow 2MgO\ (s)}$$

Worked Example

1. Balance the following equation

zinc + copper(II) sulfate → zinc sulfate + copper

2. Write down the ionic equation for the above reaction

Answer 1:

Step 1: To balance the equation, write out the symbol equation showing reactants and products

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

Step 2: Count the numbers of atoms in each reactant and product. The equation is already balanced

	Zn	Cu	S	O
Reactants	1	1	1	4
Products	1	1	1	4

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Step 3: Use appropriate **state symbols** in the equation

$$Zn\,(s) + CuSO_4\,(aq) \rightarrow ZnSO_4\,(aq) + Cu\,(s)$$

Answer 2:

Step 1: The full chemical equation for the reaction is

$$Zn\,(s) + CuSO_4\,(aq) \rightarrow ZnSO_4\,(aq) + Cu\,(s)$$

Step 2: Break down reactants into their respective ions

$$Zn\,(s) + Cu^{2+} + SO_4^{2-}\,(aq) \rightarrow Zn^{2+} + SO_4^{2-}\,(aq) + Cu\,(s)$$

Step 3: Cancel the spectator ions on both sides to give the ionic equation

$$Zn\,(s) + Cu^{2+} + \cancel{SO_4}^{2-}\,(aq) \rightarrow Zn^{2+} + \cancel{SO_4}^{2-}\,(aq) + Cu\,(s)$$

$$Zn\,(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

YOUR NOTES
↓

Percentage Yield

- In a lot of reactions, not all reactants react to form products which can be due to several factors:
  - Other reactions take place simultaneously
  - The reaction does not go to **completion**
  - Reactants or products are **lost** to the atmosphere
- The **percentage yield** shows how much of a particular product you get from the reactants compared to the maximum theoretical amount that you can get:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{predicted yield (theoretical yield)}} \times 100$$

- The **actual yield** is the number of moles or mass of product obtained **experimentally**
- The **predicted yield** is the number of moles or mass obtained by calculation
- You will often have to use the following equation to work out the reacting masses, to calculate the predicted yield

$$\text{number of mol} = \frac{\text{mass of a substance in grams (g)}}{\text{molar mass (g mol}^{-1})}$$

- It is important to be clear about the type of particle you are referring to when dealing with moles
  - Eg. 1 mole of CaF_2 contains one mole of CaF_2 formula units, but one mole of Ca^{2+} and two moles of F^- **ions**

Worked Example

Calculate % yield using moles In an experiment to displace copper from copper sulfate, 6.5 g of zinc was added to an excess of copper (II) sulfate solution.The copper was filtered off, washed and dried.The mass of copper obtained was 4.8 g.Calculate the percentage yield of copper

Answer

Step 1: The symbol equation is:

$$Zn\ (s) + CuSO_4\ (aq) \rightarrow ZnSO_4\ (aq) + Cu\ (s)$$

Step 2: Calculate the amount of zinc reacted in moles

$$\text{number of mol} = \frac{6.5\ g}{65\ g\ mol^{-1}} = \underline{\mathbf{0.10\ moles}}$$

Step 3: Calculate the maximum amount of copper that could be formed from the molar ratio:

Since the ratio of Zn(s) to Cu(s) is 1:1 a maximum of 0.10 moles can be produced

Step 4: Calculate the maximum mass of copper that could be formed (**theoretical yield**)

$$\text{mass} = \text{mol} \times M_r$$

mass = 0.10 mol x 64 g mol^{-1}

mass = 6.4 g

Step 5: Calculate the percentage yield of copper

$$\text{Percentage yield} = \frac{4.8\ g}{6.4\ g} \times 100 = \underline{\mathbf{75\ \%}}$$

Limiting & Excess Reagents

Limiting & Excess reagents

- Sometimes, there is an **excess** of one or more of the reactants (**excess reagent**)
- The reactant which is not in excess is called the **limiting reagent**
- To determine which reactant is limiting:
  - The number of moles of each reactant should be calculated
  - The ratio of the reactants shown in the equation should be taken into account e.g.

$$\mathbf{2Na + S \rightarrow Na_2S}$$

- Here, the ratio of Na : S is 2 : 1, and this should be taken into account when doing calculations
- Once all of one reactant has been used up, the reaction will stop, even if there are moles of the other reactant(s) leftover
  - The reactant leftover is in excess, the reactant which causes the reaction to stop once it is used up is the limiting reagent

Worked Example

Excess & limiting reagent9.2 g of sodium is reacted with 8.0 g of sulfur to produce sodium sulfide, Na_2S.Which reactant is in excess and which is the limiting reactant?

Answer

Step 1: Calculate the moles of each reactant

$$\textit{number of mol (Na)} = \frac{9.2\ g}{23\ g\ mol^{-1}} = 0.40 \text{ mol}$$

$$\textit{number of mol (S)} = \frac{8.0\ g}{32\ g\ mol^{-1}} = 0.25 \text{ mol}$$

Step 2: Write the balanced equation and determine the molar ratio

$$\mathbf{2Na + S \rightarrow Na_2S}$$

The molar ratio of Na: Na_2S is 2:1

Step 3: Compare the moles and determine the limiting reagent

So to react completely 0.40 moles of Na require 0.20 moles of S and since there are 0.25 moles of S, then S is in excess. Na is therefore the limiting reactant.

Once all of the S has been used up, the reaction will stop, even though there is Na left.

1.2.5 Atom Economy

Atom Economy

- The atom economy of a reaction shows how many of the atoms used in the reaction become the desired product
    - The rest of the atoms or mass is wasted
- It is found directly from the balanced equation by calculating the Mr of the desired product

$$\text{ATOM ECONOMY} = \frac{\text{MOLECULAR MASS OF DESIRED PRODUCT}}{\text{SUM OF MOLECULAR MASSES OF ALL REACTANTS}} \times 100$$

- In addition reactions, the atom economy will always be 100%, because all of the atoms are used to make the desired product
    - Whenever there is only one product, the atom economy will always be 100%
- For example, in the reaction between ethene and bromine:

$$\mathbf{CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br}$$

Exam Tip

Careful: sometimes a question may ask you to show your working when calculating atom economy. In this case, even if it is an addition reaction and it is obvious that the atom economy is 100%, you will still need to show your working.

- The atom economy could also be calculated using mass, instead or Mr
- In this case, you would divide the mass of the desired product formed by the total mass of all reactants, and then multiply by 100

Water of Crystallisation

- **Water of crystallisation** is when some compounds can form **crystals** which have **water** as part of their structure
- A compound that contains water of crystallisation is called a **hydrated compound**
- The water of crystallisation is separated from the main formula by a **dot** when writing the chemical formula of hydrated compounds
  - Eg. hydrated copper(II) sulfate is $CuSO_4 \cdot 5H_2O$
- A compound which doesn't contain water of crystallisation is called an **anhydrous compound**
  - Eg. anhydrous copper(II) sulfate is $CuSO_4$
- A compound can be hydrated to **different degrees**
  - Eg. cobalt(II) chloride can be hydrated by **six** or **two** water molecules
  - $CoCl_2 \cdot 6H_2O$ or $CoCl_2 \cdot 2H_2O$
- The conversion of anhydrous compounds to hydrated compounds is **reversible** by heating the hydrated salt

Anhydrous to hydrated salt:

$$\mathbf{CuSO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O}$$

Hydrated to anhydrous salt (by heating):

$$\mathbf{CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 + 5H_2O}$$

Exam Tip

To calculate the M_r of hydrated salts, the M_r of the salt and water should be calculated **separately** and then added together.

1.3 The Mole, Avogadro & The Ideal Gas Equation

1.3.1 The Mole & the Avogadro Constant

Mole & Avogadro Constant

- The **Avogadro constant** (N_A or L) is the number of particles equivalent to the relative **atomic mass** or **molecular mass** of a substance
    - The Avogadro constant applies to atoms, molecules, ions and electrons

- The value of N_A is **6.02 x 10^{23} g mol^{-1}**
- The mass of a substance with this number of particles is called a **mole** (mol)
    - The **mass** of a substance containing the same number of fundamental units as there are atoms in exactly 12.00 g of ^{12}C

- One mole of any element is equal to the relative atomic mass of that element in grams
    - If you had one mole of carbon in your hand, that is 6.02 x 10^{23} atoms of carbon, you would have a mass of 12.00 g
    - One mole of water would have a mass of (2 x 1 + 16) = 18 g

Worked Example

MolesDetermine the number of atoms, molecules and the relative mass of 1 mole of:

1. Na
2. H_2
3. NaCl

Answer 1:

- The relative atomic mass of Na is 22.99
- Therefore, 1 mol of Na has a mass of 22.99 g mol^{-1}
- 1 mol of Na will contain 6.02 x 10^{23} atoms of Na (Avogadro's constant)

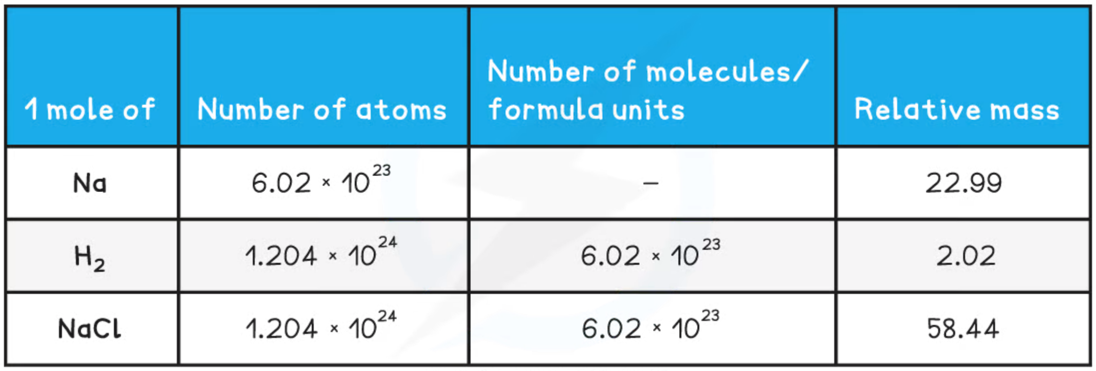
Answer 2

- The relative atomic mass of H is 1.005
- Since there are 2 H atoms in H_2, the mass of 1 mol of H_2 is (2 x 1.005) 2.01 g mol^{-1}
- 1 mol of H_2 will contain 6.02 x 10^{23} molecules of H_2
- Since there are 2 H atoms in H_2, 1 mol of H_2 will contain 1.204 x 10^{24} H atoms

Answer 3

- The relative atomic mass of Na and Cl is 22.99 and 35.45 respectively
- Therefore, 1 mol of NaCl has a mass of (22.99 + 35.45) 58.44 g mol^{-1}
- 1 mol of NaCl will contain 6.02 x 10^{23} formula units of NaCl

  - Since there are Na and Cl ions in NaCl, 1 mol of NaCl will contain 1.204 x 10^{24} ions in total



1 mole of	Number of atoms	Number of molecules/ formula units	Relative mass
Na	6.02×10^{23}	–	22.99
H_2	1.204×10^{24}	6.02×10^{23}	2.02
NaCl	1.204×10^{24}	6.02×10^{23}	58.44

Reacting Masses

- The number of moles of a substance can be found by using the following equation:

$$\text{number of mol} = \frac{\textit{mass of a substance in grams (g)}}{\textit{molar mass } (g\ mol^{-1})}$$

- It is important to be clear about the type of particle you are referring to when dealing with moles
    - E.g. 1 mole of CaF_2 contains one mole of CaF_2 formula units, but one mole of Ca^{2+} and two moles of F^- ions

Reacting masses

- The masses of reactants are useful to determine how much of the reactants **exactly** react with each other to prevent waste
- To calculate the reacting masses, the chemical equation is required
- This equation shows the ratio of moles of all the reactants and products, also called the **stoichiometry,** of the equation
- To find the mass of products formed in a reaction the following pieces of information are needed:
    - The mass of the reactants
    - The molar mass of the reactants
    - The balanced equation

Worked Example

Mass calculation using moles Calculate the mass of magnesium oxide that can be made by completely burning 6 g of magnesium in oxygen.

magnesium (s) + oxygen (g) → magnesium oxide (s)

Answer

Step 1: The symbol equation is:

$$2Mg\ (s) \quad + \quad O_2\ (g) \quad \rightarrow \quad 2MgO\ (s)$$

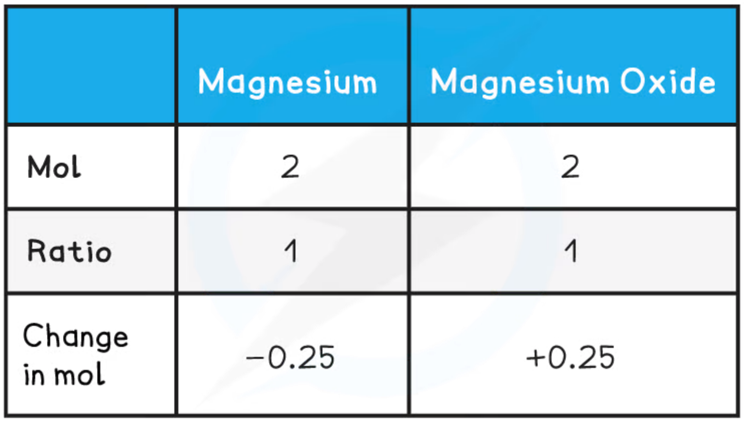
Step 2: The relative formula masses are:

Magnesium : 24 **Oxygen : 32** **Magnesium Oxide : 40**

Step 3: Calculate the moles of magnesium used in reaction

$$\text{number of mol} = \frac{6.0\ g}{24\ g\ mol^{-1}} = \underline{\mathbf{0.25\ mol}}$$

Step 4: Find the ratio of magnesium to magnesium oxide using the balanced chemical equation



	Magnesium	Magnesium Oxide
Mol	2	2
Ratio	1	1
Change in mol	−0.25	+0.25

Therefore, 0.25 mol of MgO is formed

Step 5: Find the mass of magnesium oxide

$$\textbf{mass} = \textbf{\textit{mol}} \times \textbf{\textit{M}}_r$$

mass **= 0.25** ***mol*** **x 40** ***g mol***$^{-1}$
mass **= 10 g**

Therefore, **mass of magnesium oxide produced is 10 g**

Stoichiometric relationships

- The stoichiometry of a reaction can be found if the **exact amounts** of reactants and products formed are known
- The **amounts** can be found by using the following equation:

$$\textit{number of mol} = \frac{\textit{mass of a substance in grams (g)}}{\textit{molar mass (g mol}^{-1}\textit{)}}$$

- The gas volumes can be used to deduce the **stoichiometry** of a reaction
  - E.g. in the **combustion** of 50 cm^3 of propane reacting with 250 cm^3 of oxygen, 150 cm^3 of carbon dioxide is formed suggesting that the ratio of propane:oxygen:carbon dioxide is 1:5:3

$$\mathbf{C_3H_8\ (g) + 5O_2\ (g) \longrightarrow 3CO_2\ (g) + 4H_2O\ (l)}$$

Volumes & Concentrations of Solutions

- The **concentration** of a solution is the amount of **solute** dissolved in a **solvent** to make 1 dm^3 of **solution**
  - The solute is the substance that dissolves in a solvent to form a solution
  - The solvent is often water

$$\text{concentration (mol dm}^{-3}) = \frac{\text{number of moles of solute (mol)}}{\text{volume of solution (dm}^3)}$$

- A **concentrated** solution is a solution that has a **high** concentration of solute
- A **dilute** solution is a solution with a **low** concentration of solute
- When carrying out calculations involve concentrations in mol dm^{-3} the following points need to be considered:
  - Change mass in grams to **moles**
  - Change cm^3 to dm^3
- To calculate the **mass** of a substance present in solution of known **concentration and volume**:
  - Rearrange the concentration equation

$$\textbf{number of moles (mol) = concentration (mol dm}^{-3}\textbf{) x volume (dm}^3\textbf{)}$$

  - Multiply the moles of solute by its molar mass

$$\textbf{mass of solute (g) = number of moles (mol) x molar mass (g mol}^{-1}\textbf{)}$$

?

Worked Example

Calculating volume from concentration

Calculate the volume of hydrochloric acid of concentration 1.0 mol dm^{-3} that is required to react completely with 2.5 g of calcium carbonate

Answer

Step 1: Write the balanced symbol equation

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

Step 2: Calculate the amount, in moles, of calcium carbonate that reacts

$$\text{number of mol }(CaCO_3) = \frac{2.5\ g}{100\ g\ mol^{-1}} = 0.025\text{ mol}$$

Step 3: Calculate the moles of hydrochloric acid required using the reaction's stoichiometry

1 mol of $CaCO_3$ requires 2 mol of HCl

So 0.025 mol of $CaCO_3$ requires 0.05 mol of HCl

Step 4: Calculate the volume of HCl required

$$\text{volume (HCl) (dm}^3\text{)} = \frac{amount\ (mol)}{concentration\ (mol\ dm^{-3})} = \frac{0.05\ mol}{1.0\ mol\ dm^{-3}} = 0.05\ \text{dm}^3$$

Volume of hydrochloric acid = 0.05 dm³

Worked Example

Neutralisation calculation

25.0 cm^3 of 0.050 dm^{-3} sodium carbonate was completely neutralised by 20.00 cm^3 of dilute hydrochloric acid. Calculate the concentration in moldm^{-3} of the hydrochloric acid.

Answer

Step 1: Write the balanced symbol equation

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

Step 2: Calculate the amount, in moles, of sodium carbonate reacted by rearranging the equation for amount of substance (mol) and dividing the volume by 1000 to convert cm^3 to dm^3

$$\textbf{amount } (Na_2CO_3) = 0.025\ dm^3 \times 0.050\ mol\ dm^{-3} = 0.00125\ mol$$

Step 3: Calculate the moles of hydrochloric acid required using the reaction's stoichiometry

1 mol of Na_2CO_3 reacts with 2 mol of HCl, so the molar ratio is 1 : 2

Therefore 0.00125 moles of Na_2CO_3 react with 0.00250 moles of HCl

Step 4: Calculate the concentration, in mol dm^{-3}, of hydrochloric acid

$$\text{concentration (HCl) (mol dm}^{-3}\text{)} = \frac{amount\ (mol)}{volume\ (dm^3)}$$

$$\text{concentration (HCl) (mol dm}^{-3}\text{)} = \frac{0.00250}{0.0200}$$

$$\text{concentration (HCl) (mol dm}^{-3}\text{)} = 0.125\ \text{mol dm}^{-3}$$

Volumes of gases

- **Avogadro** suggested that 'equal volumes of gases contain the same number of molecules' (also called **Avogadro's hypothesis)**
- At room temperature (20 degrees Celsius) and pressure (1 atm) **one mole** of any gas has a volume of 24.0 dm^3
- This **molar gas volume** of 24.0 dm^3 mol^{-1} can be used to find:
  - The volume of a given mass or number of moles of gas:

$$\textbf{volume of gas (dm}^3\textbf{) = amount of gas (mol) x 24 dm}^3\textbf{ mol}^{-1}$$

- The mass or number of moles of a given volume of gas:

$$\text{amount of gas (mol)} = \frac{\text{volume of gas (dm}^3)}{24\ (\text{dm}^3\ \text{mol}^{-1})}$$

Worked Example

Calculation volume of gas using excess & limiting reagents

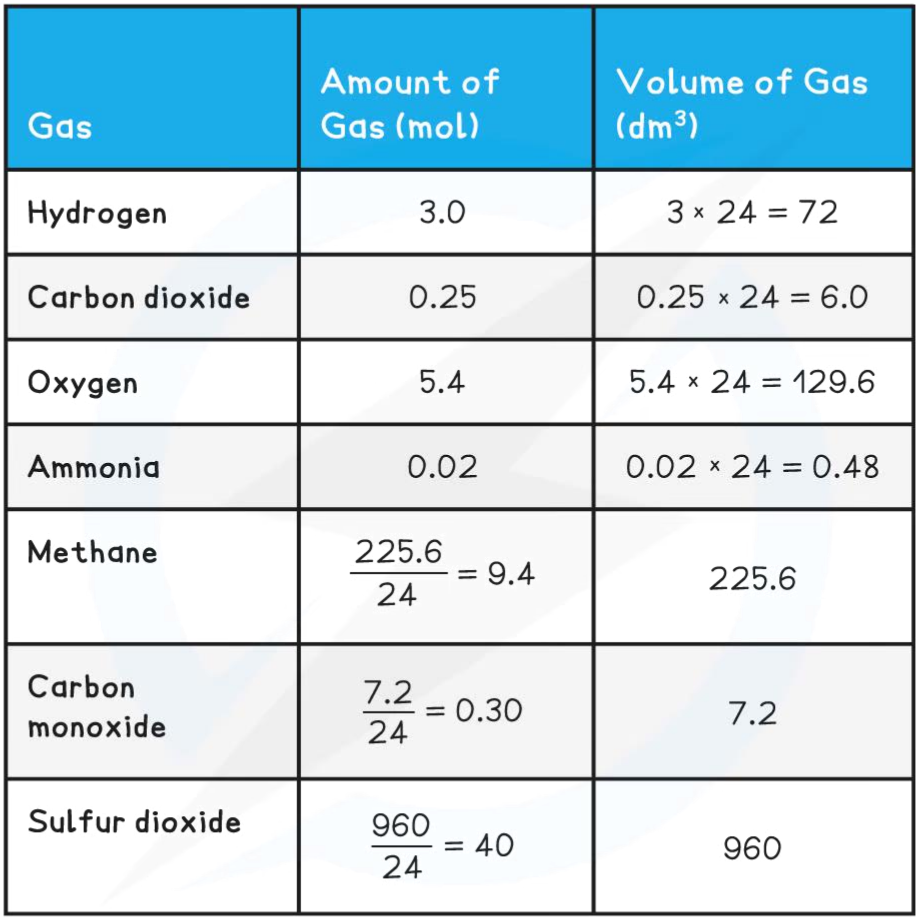
Calculate the volume the following gases occupy:

1. Hydrogen (3 mol)
2. Carbon dioxide (0.25 mol)
3. Oxygen (5.4 mol)
4. Ammonia (0.02 mol)

Calculate the moles in the following volumes of gases:

1. Methane
2. Carbon monoxide
3. Sulfur dioxide

Answer



Gas	Amount of Gas (mol)	Volume of Gas (dm^3)
Hydrogen	3.0	$3 \times 24 = 72$
Carbon dioxide	0.25	$0.25 \times 24 = 6.0$
Oxygen	5.4	$5.4 \times 24 = 129.6$
Ammonia	0.02	$0.02 \times 24 = 0.48$
Methane	$\frac{225.6}{24} = 9.4$	225.6
Carbon monoxide	$\frac{7.2}{24} = 0.30$	7.2
Sulfur dioxide	$\frac{960}{24} = 40$	960

The Ideal Gas Equation

Kinetic theory of gases

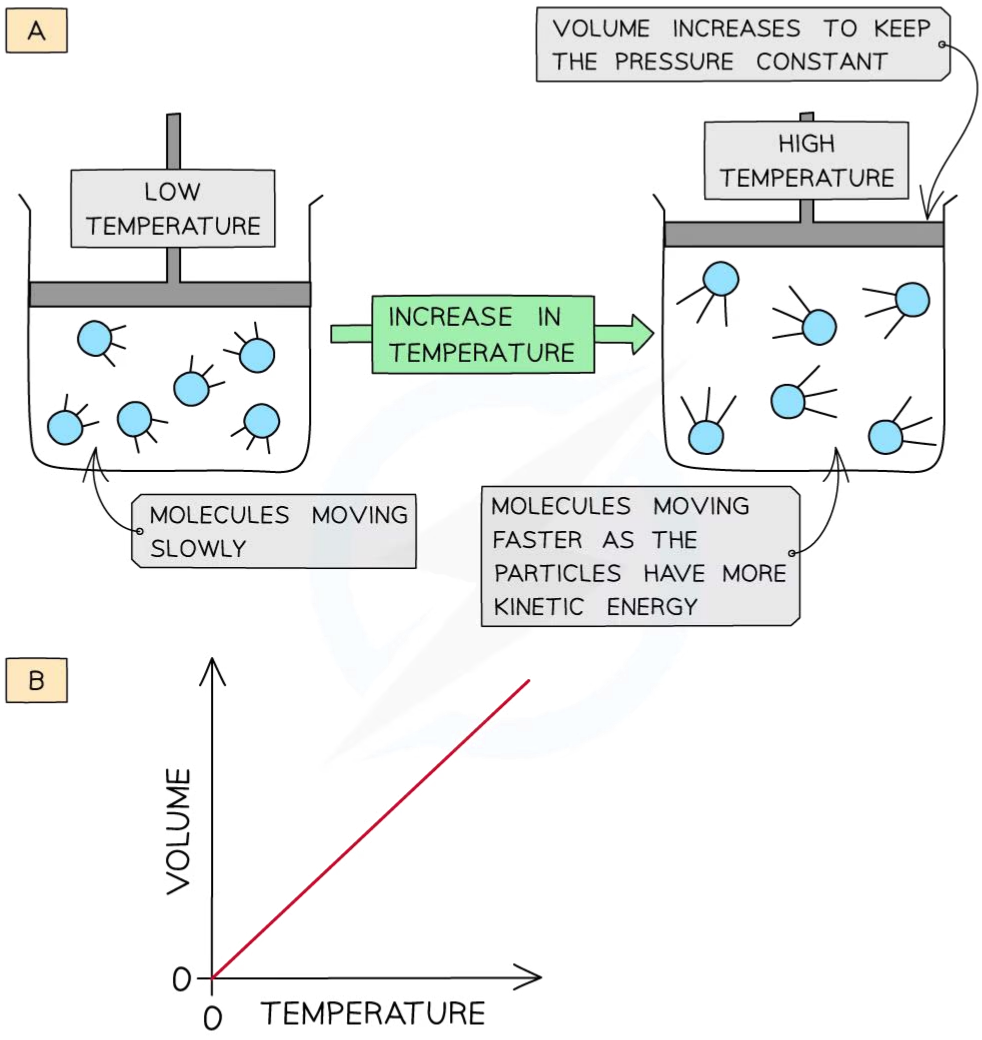
- **The kinetic theory of gases** states that molecules in gases are constantly moving
- The theory makes the following assumptions:
  - That gas molecules are moving very fast and randomly
  - That molecules hardly have any volume
  - That gas molecules do not attract or repel each other (**no intermolecular forces**)
  - No kinetic energy is lost when the gas molecules collide with each other (**elastic collisions**)
  - The temperature of the gas is related to the average kinetic energy of the molecules

- Gases that follow the kinetic theory of gases are called **ideal gases**
- However, in reality gases do not fit this description exactly **but** may come very close and are called **real gases**

Ideal gases

- The volume that an ideal gas occupies depends on:
  - Its pressure
  - Its temperature

- When a gas is **heated** (at constant pressure) the particles gain more **kinetic energy** and undergo more **frequent collisions** with the container wall
- To keep the **pressure constant**, the molecules must get further apart and therefore the **volume increases**
- The **volume** is therefore **directly proportional** to the **temperature** (at constant pressure)



The volume of a gas increases upon heating to keep a constant pressure (a); volume is directly proportional to the temperature (b)

Limitations of the ideal gas law

- At very **low temperatures** and **high pressures** real gases do not obey the kinetic theory as under these conditions:
    - Molecules are close to each other
    - There are instantaneous dipole- induced dipole or permanent dipole-permanent dipole forces between the molecules
    - These attractive forces pull the molecules away from the container wall
    - The volume of the molecules is not negligible
- Real gases therefore do not obey the following kinetic theory **assumptions** at low temperatures and high pressures:
    - There is zero attraction between molecules (due to attractive forces, the **pressure** is **lower** than expected for an ideal gas)

  - The volume of the gas molecules can be ignored (**volume** of the gas is **smaller** than expected for an ideal gas)

Ideal gas equation

- The **ideal gas equation** shows the relationship between pressure, volume, temperature and number of moles of gas of an ideal gas:

$$PV = nRT$$

P = pressure (pascals, Pa)

V = volume (m^3)

n = number of moles of gas (mol)

R = gas constant (8.31 J K^{-1} mol^{-1})

T = temperature (kelvin, K)

Worked Example

Calculating the volume of a gas

Calculate the volume occupied by 0.781 mol of oxygen at a pressure of 220 kPa and a temperature of 21 °C

Answer

Step 1: Rearrange the ideal gas equation to find volume of gas

$$V = \frac{nRT}{P}$$

Step 2: Calculate the volume the oxygen gas occupies

  - P = 220 kPa = 220 000 Pa
  - n = 0.781 mol
  - R = 8.31 J K^{-1} mol^{-1}
  - T = 21 ^{o}C = 294 K

$$V = \frac{0.781 \times 8.31 \times 294}{220000} = 0.00867 \text{ m}^3 = 8.67 \text{ dm}^3$$

Worked Example

Calculating the molar mass of a gas

A flask of volume 1000 cm^3 contains 6.39 g of a gas. The pressure in the flask was 300 kPa and the temperature was 23 °C.

Calculate the relative molecular mass of the gas.

Answer

Step 1: Rearrange the ideal gas equation to find the number of moles of gas

$$n = \frac{pV}{RT}$$

Step 2: Calculate the number of moles of gas

p = 300 kPa = 300 000 Pa

V = 1000 cm^3 = 1 dm^3 = 0.001 m^3

R = 8.31 J K^{-1} mol^{-1}

T = 23 ^oC = 296 K

$$n = \frac{300\,000\ Pa \times 0.001\ m^3}{8.31\ J\ K^{-1}\ mol^{-1} \times 296\ K} = 0.12\text{ mol}$$

Step 3: Calculate the molar mass using the number of moles of gas

$$n = \frac{mass}{molar\ mass}$$

$$\text{molar mass} = \frac{6.39\ g}{0.12\ mol} = 53.25\text{ g mol}^{-1}$$

Exam Tip

To calculate the temperature in **Kelvin**, add 273 to the Celsius temperature – e.g. 100 ^oC is 373 Kelvin.

You must be able to rearrange the ideal gas equation to work out all parts of it.

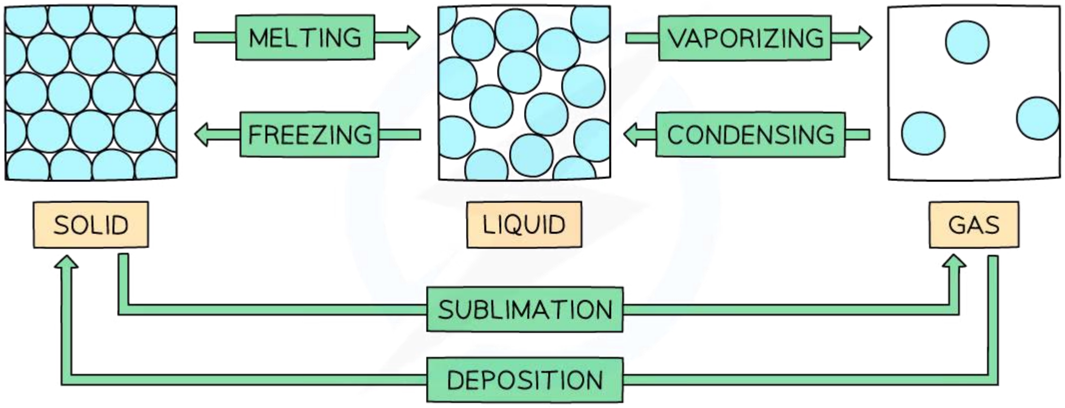
The **units** are incredibly important in this equation – make sure you know what units you should use, and do the necessary conversions when doing your calculations!

1.4 Types of Bonding & Properties

1.4.1 Changes in State: Energy Changes

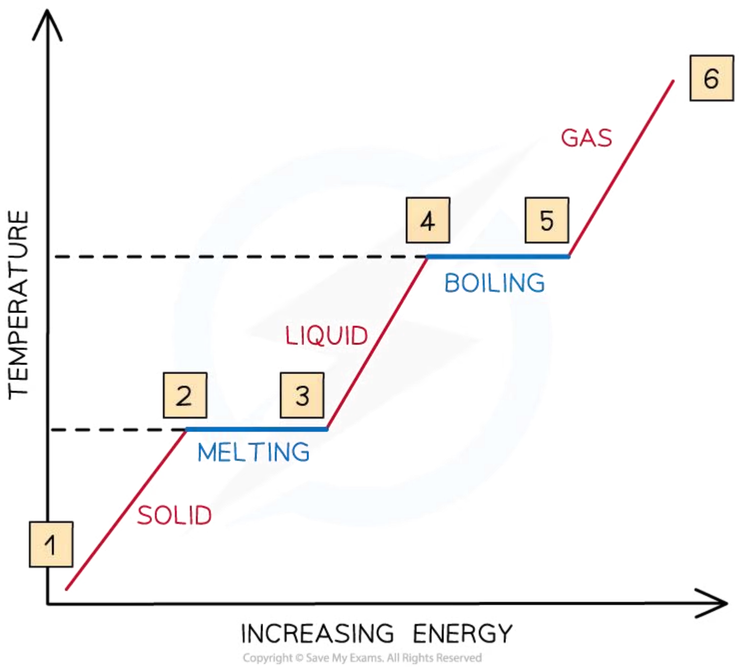
State Changes

- Changes of state are **physical changes** that are reversible
- These changes do not change the chemical properties or chemical makeup of the substances involved
- **Vaporization** includes **evaporation** and **boiling**
- **Evaporation** involves the change of liquid to gas, but unlike boiling, **evaporation** occurs only at the surface and takes place at temperatures below the **boiling point**
- **Boiling** occurs at a specific temperature and takes place when the **vapour pressure** reaches the external atmospheric pressure



State Changes

- The relationship between temperature and energy during state changes can be represented graphically



The relationship between temperature and energy during state changes

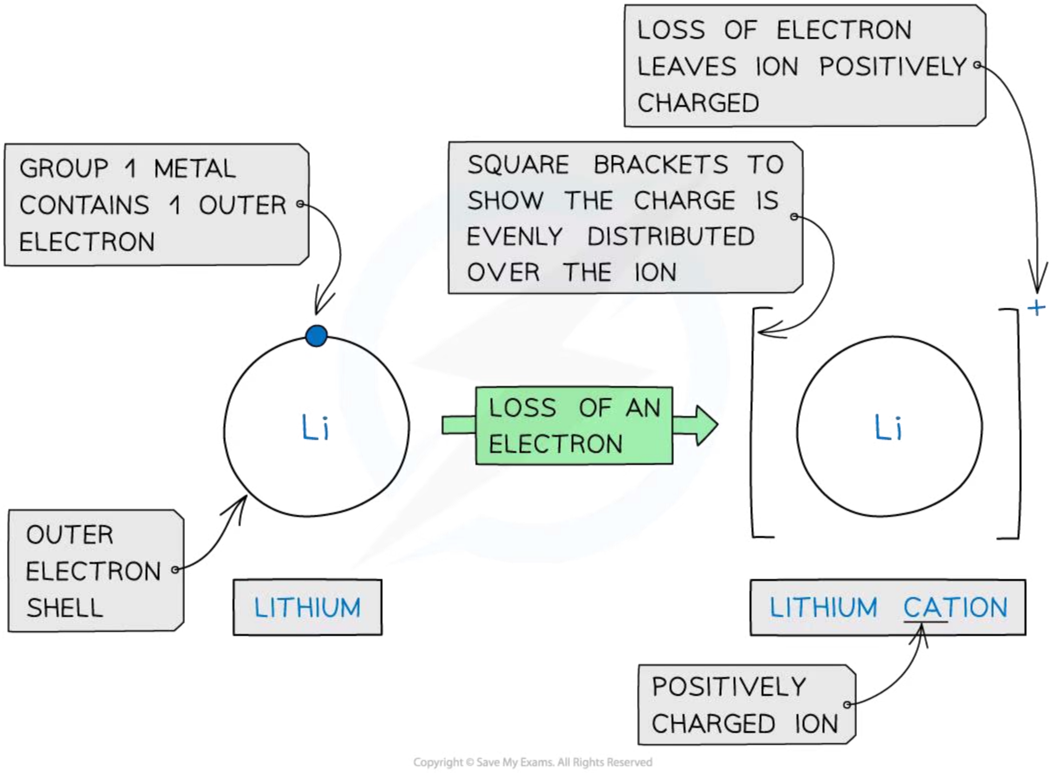
- Between 1 & 2, the particles are vibrating and gaining **kinetic energy** and the temperature rises
- Between 2 & 3, all the energy goes into breaking bonds – there is **no** increase in **kinetic energy** or **temperature**
- Between 3 & 4, the particles are moving around and gaining in **kinetic energy**
- Between 4 & 5, the substance is boiling, so bonds are breaking and there is **no** increase in **kinetic energy** or **temperature**
- From 5 & 6, the particles are moving around rapidly and increasing in **kinetic energy**

Exam Tip

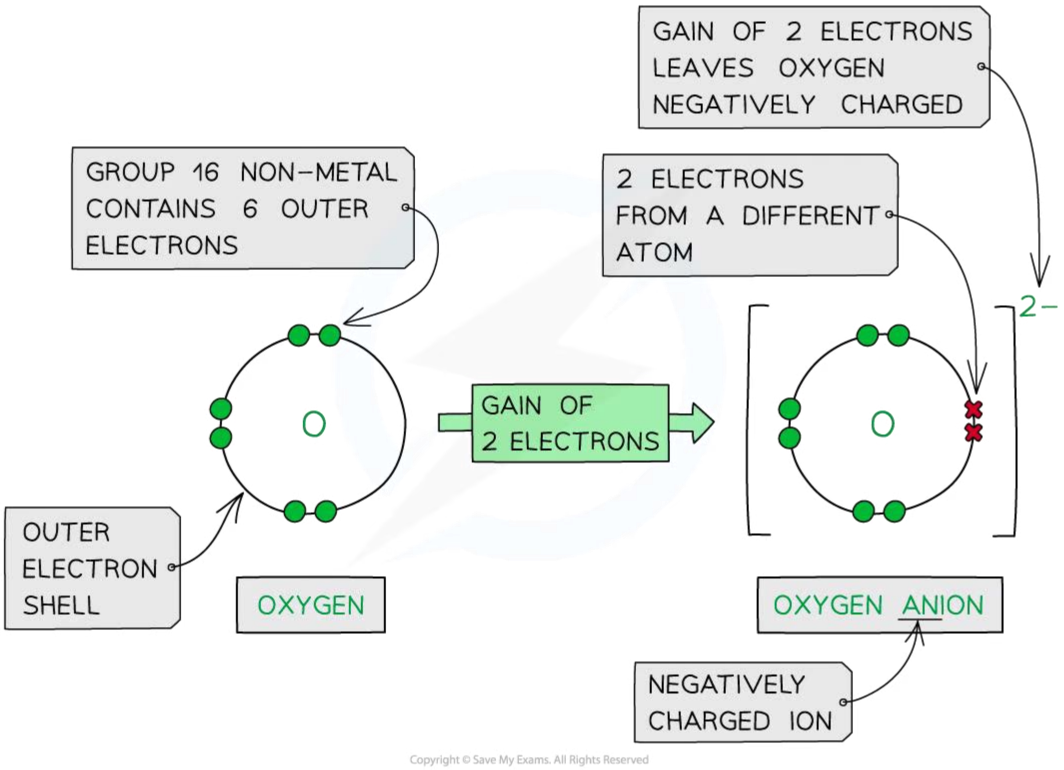
Be careful to match the bond breaking or making processes to the flow of energy during state changes. Remember that to **break** bonds, energy is always **needed** to overcome the **forces of attraction** between the particles

Ionic Bonding

- As a general rule, **metals** are on the **left** of the periodic table and **nonmetals** are on the **right-hand** side
- **Ionic bonding** involves the **transfer** of electrons from a **metallic** element to a **non-metallic** element
- Transferring electrons usually leaves the metal and the non-metal with a **full outer shell**
- Metals **lose** electrons from their valence shell forming **positively charged cations**
- Non-metal atoms **gain** electrons forming **negatively charged anions**
- Once the atoms become ions, their electronic configurations are the same as a noble gas
  - A potassium ion (K^+) has the same electronic configuration as argon: $[2,8,8]^+$
  - A chloride ion (Cl^-) also has the same electronic configuration as argon: $[2,8,8]^-$

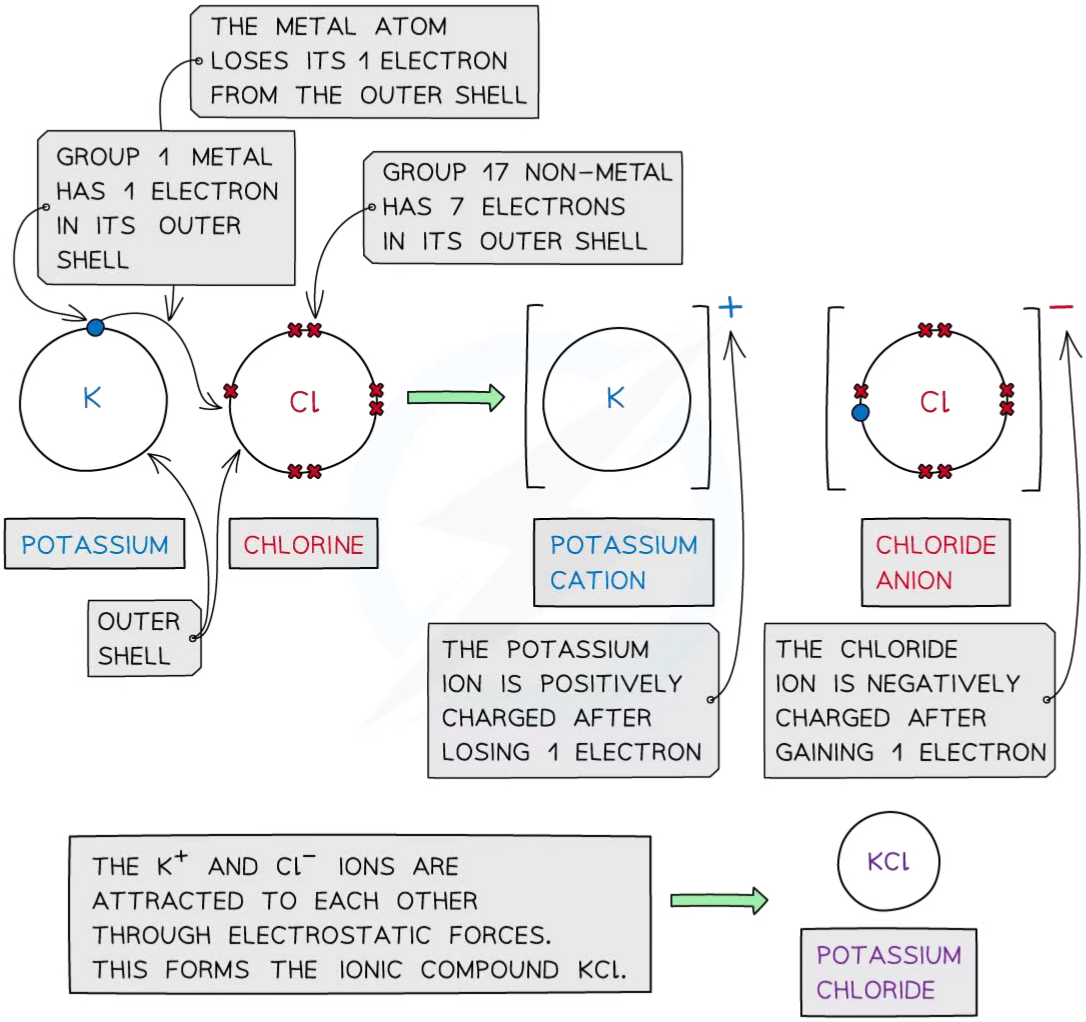


Forming cations by the removal of electrons from metals



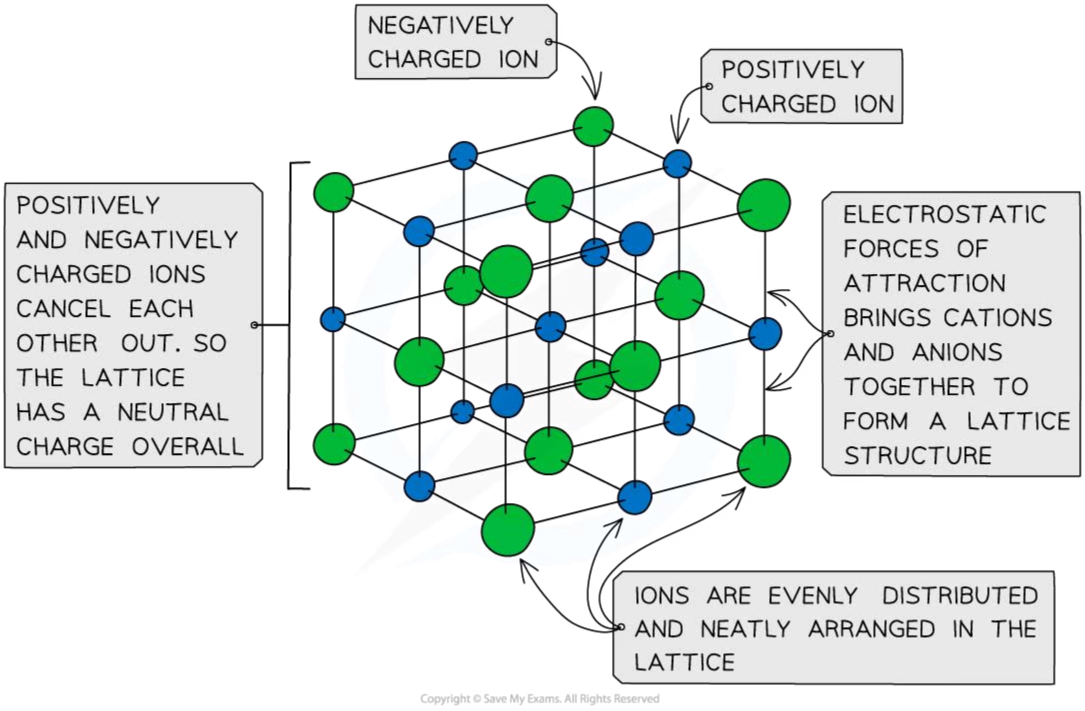
Forming anions by the addition of electrons to nonmetals

- **Cations** and **anions** are oppositely charged and therefore attracted to each other
- **Electrostatic attractions** are formed between the oppositely charged ions to form **ionic compounds**
- The **ionic bond** is the **electrostatic attraction** formed **between the oppositely charged ions**, which occurs in all directions (this called **non-directional bonding**)
- This form of attraction is **very strong** and requires a **lot of energy** to overcome
    - This causes high melting points in ionic compounds



Cations and anions bond together using strong electrostatic forces, which require a lot of energy to overcome

- The ions form a **lattice structure** which is an evenly distributed **crystalline** structure
- Ions in a lattice are arranged in a **regular repeating pattern** so that positive charges cancel out negative charges
- The attraction between the cations and anions is occurring in all directions
  - Each ion is attracted to all of the oppositely charged ions around it
- Therefore the final lattice is overall electrically **neutral**



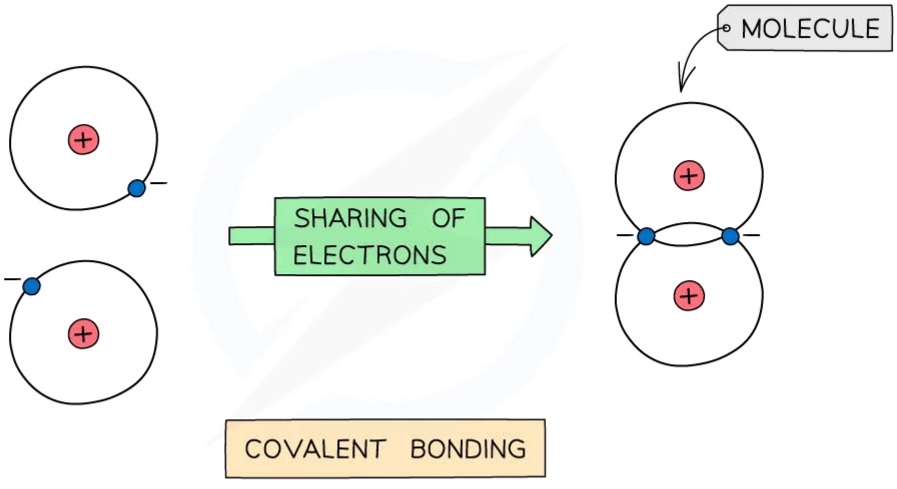
Ionic solids are arranged in lattice structures

Exam Tip

Metals usually **lose** all electrons from their outer valence shell to become **cations.**You can make use of the groups on the periodic table to work out how many electrons an atom is likely to lose or gain by looking at the **group** an atom belongs to.The electrostatic attraction between oppositely charged ions is the ionic bond.

Covalent Bonding

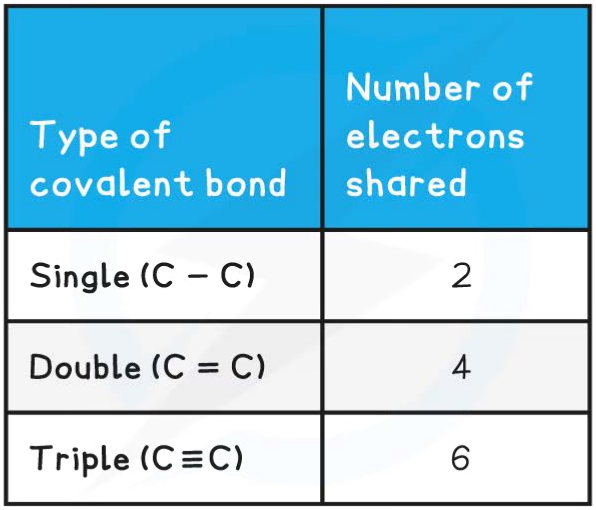
- **Covalent** bonding occurs between two **non-metals**
- A covalent bond involves the **electrostatic attraction** between nuclei of two atoms and the bonding electrons of their outer shells
- **No electrons** are **transferred** but only **shared** in this type of bonding



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



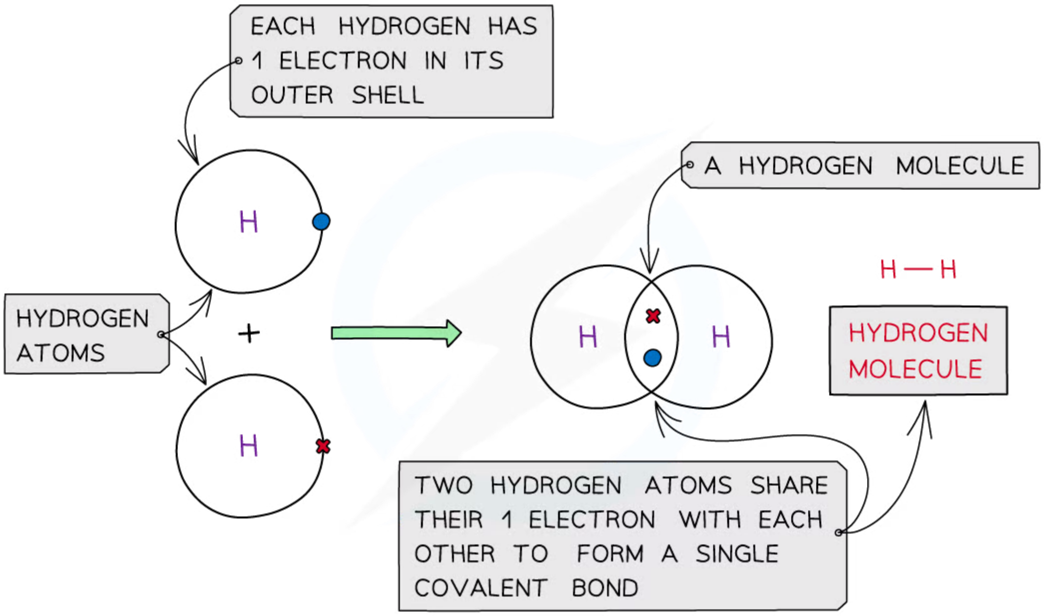
Type of covalent bond	Number of electrons shared
Single (C – C)	2
Double (C = C)	4
Triple (C≡C)	6

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

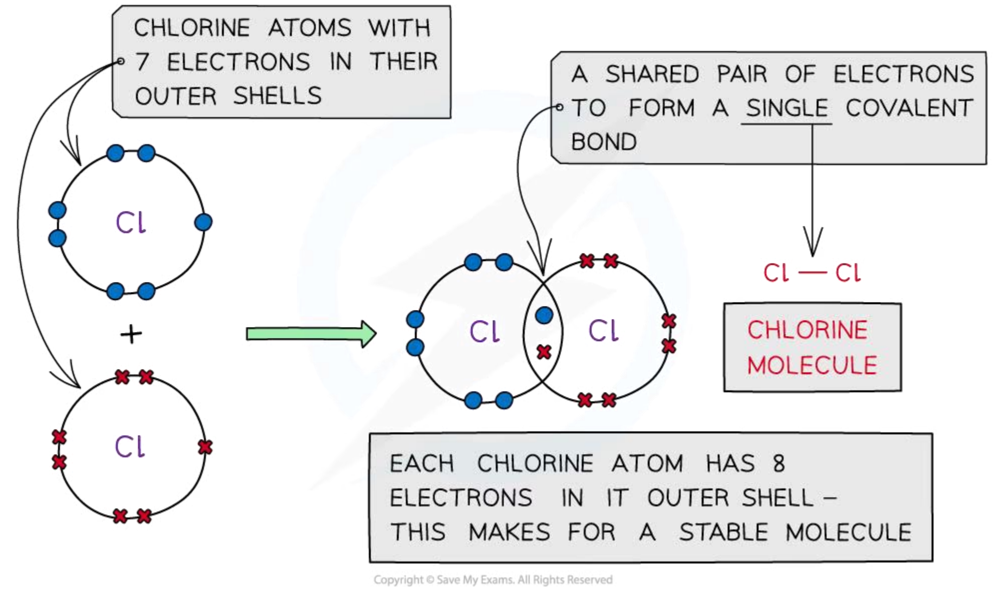
Single covalent bonding

Hydrogen, H_2



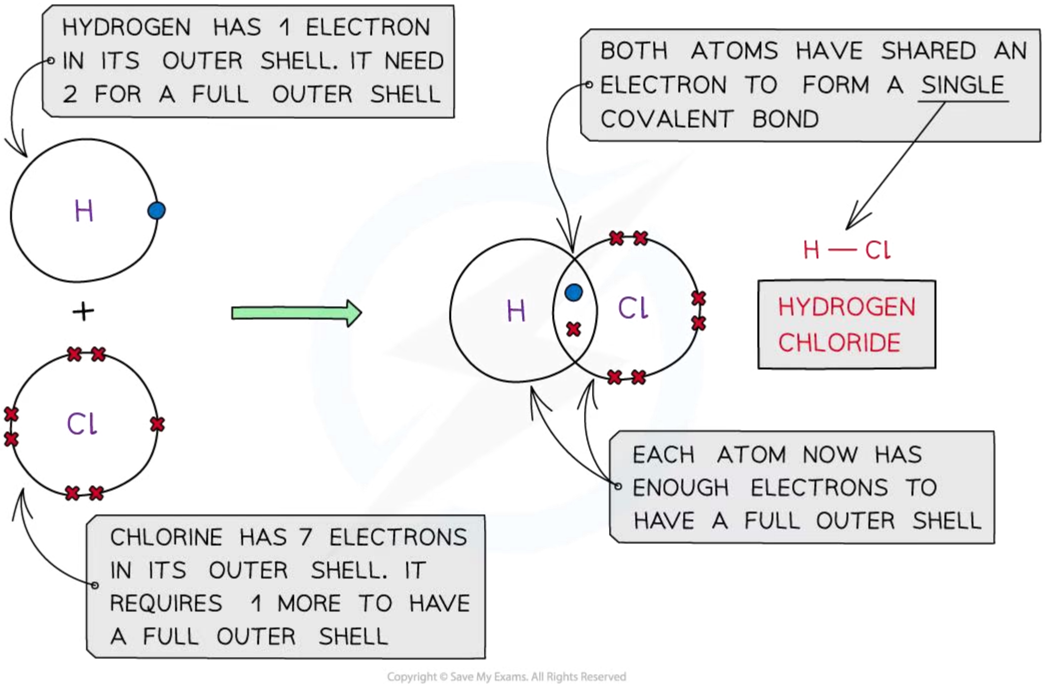
Covalent bonding in hydrogen

Chlorine, Cl_2



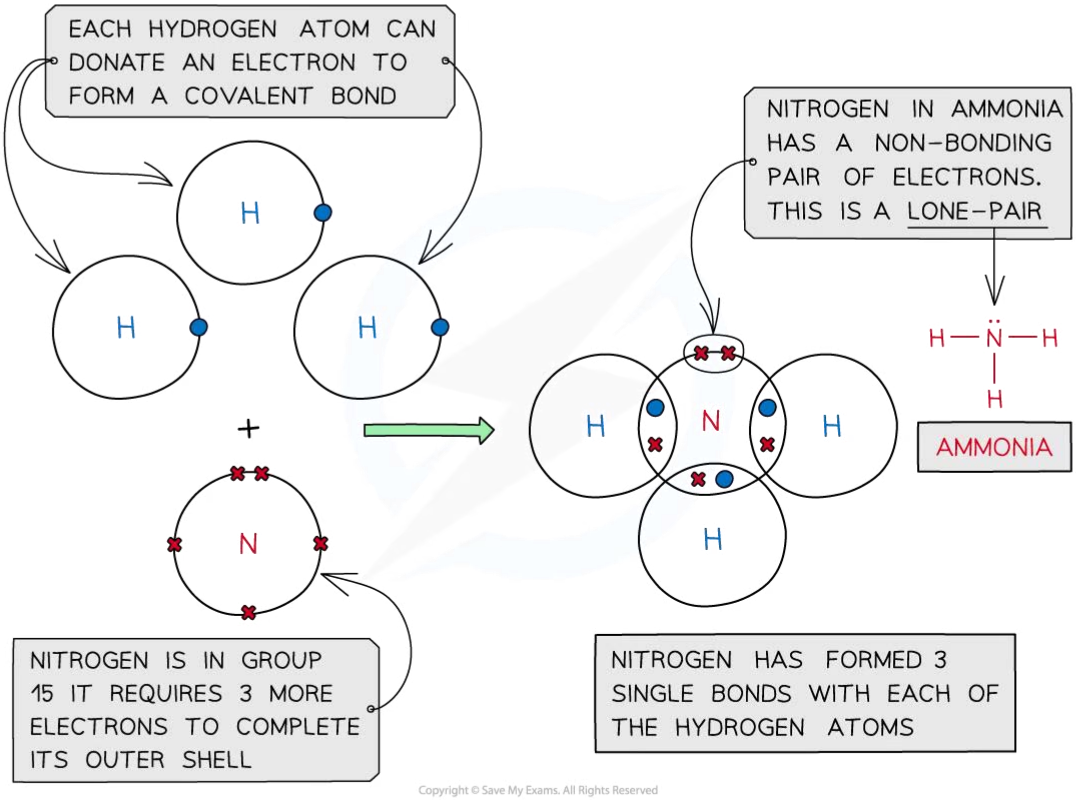
Covalent bonding in chlorine

Hydrogen Chloride, HCl



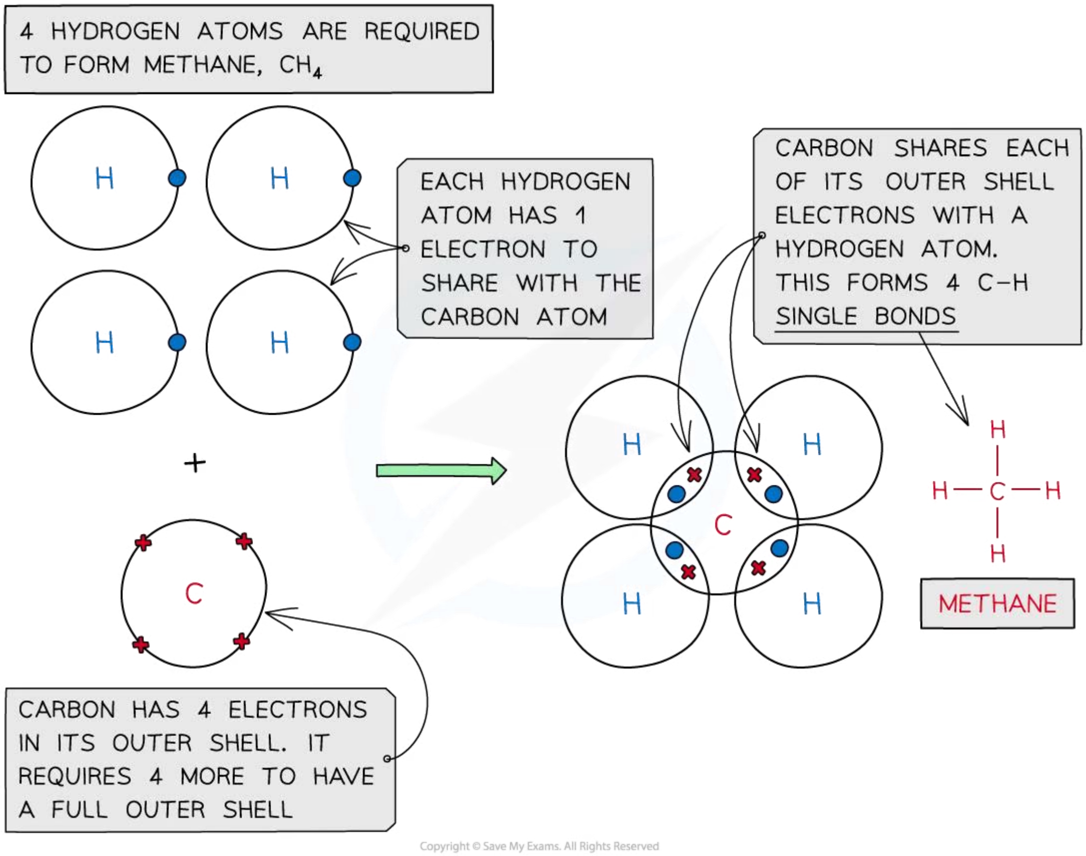
Covalent bonding in hydrogen chloride

Ammonia, NH_3



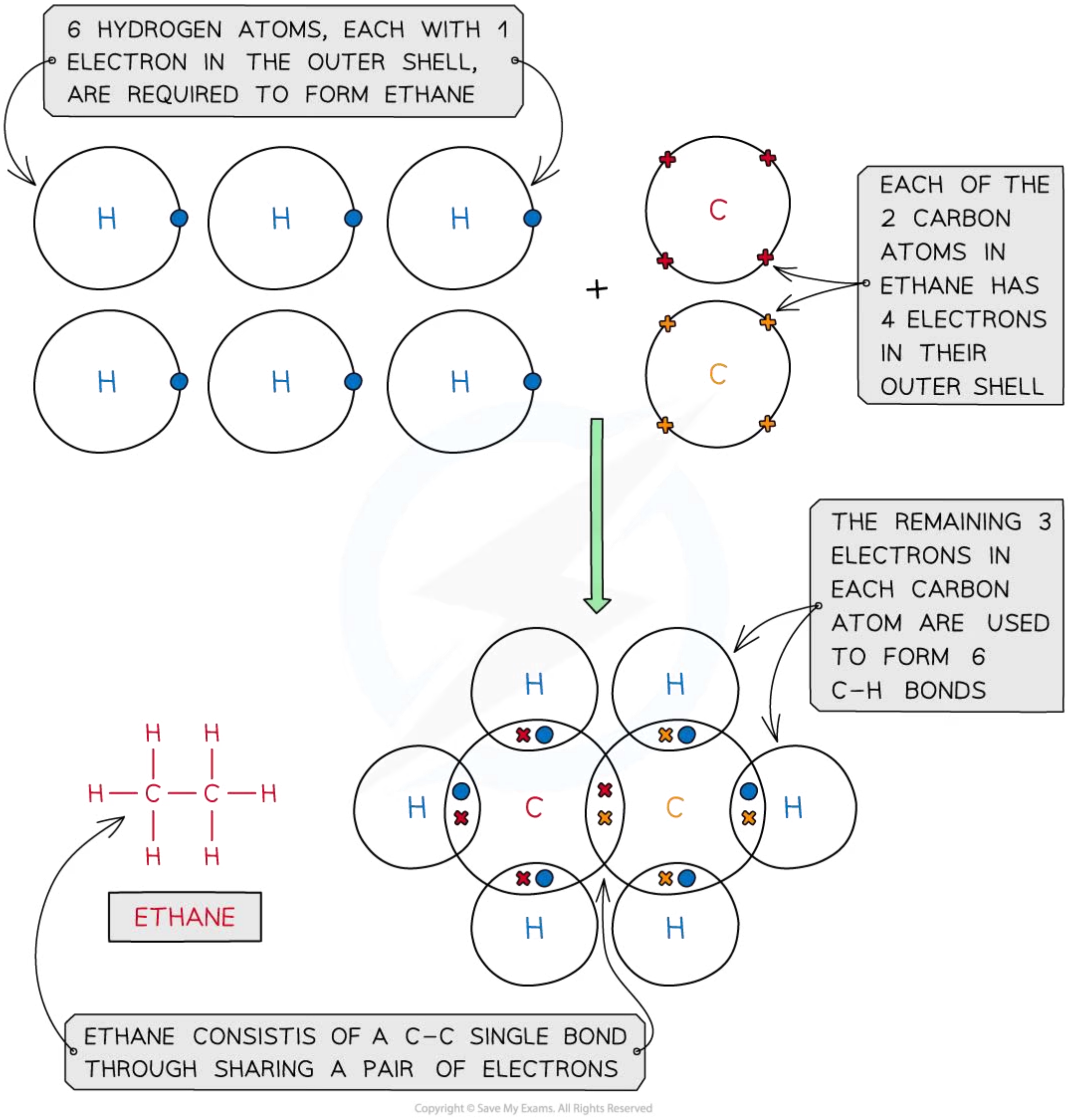
Covalent bonding in ammonia

Methane, CH_4



Covalent bonding in methane

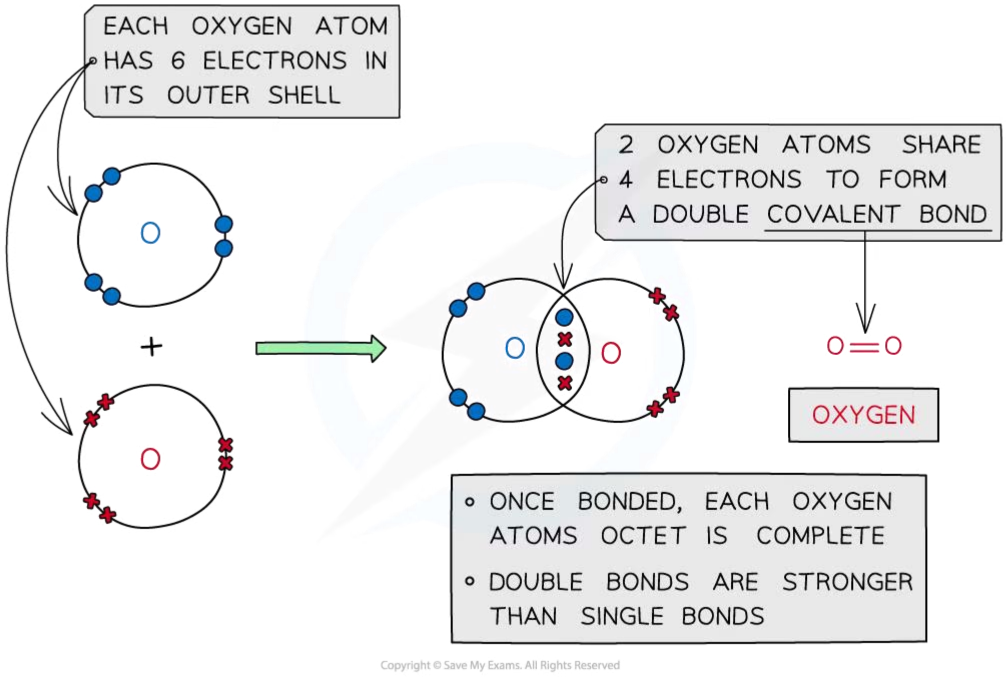
Ethane, C_2H_6



Covalent bonding in ethane

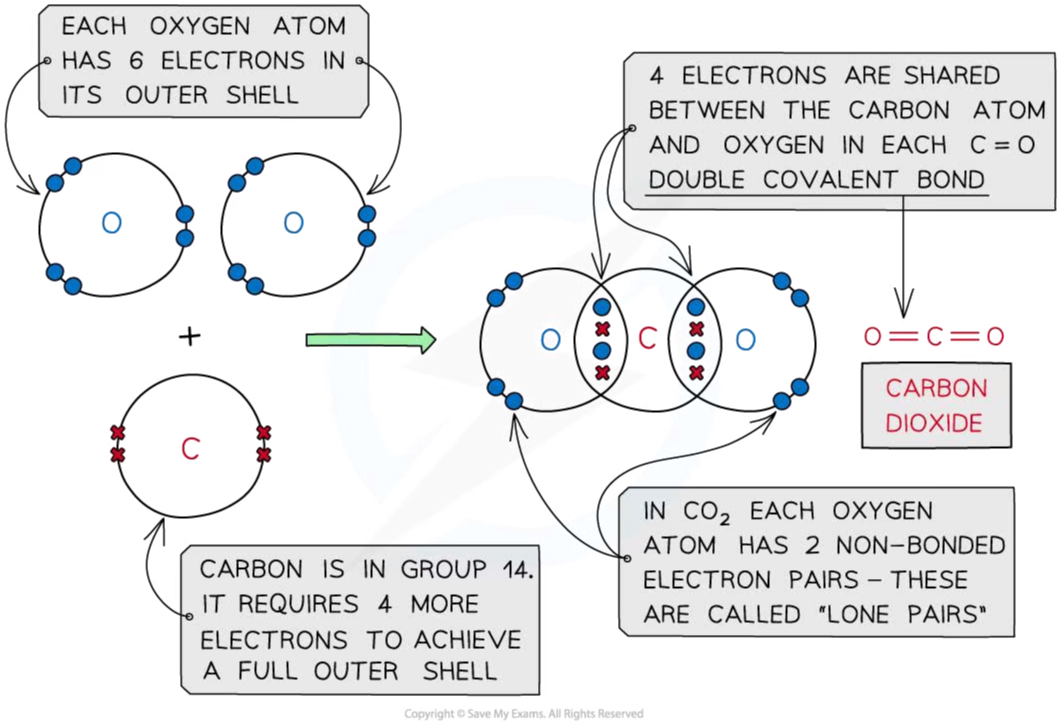
Double covalent bonding

Oxygen, O_2



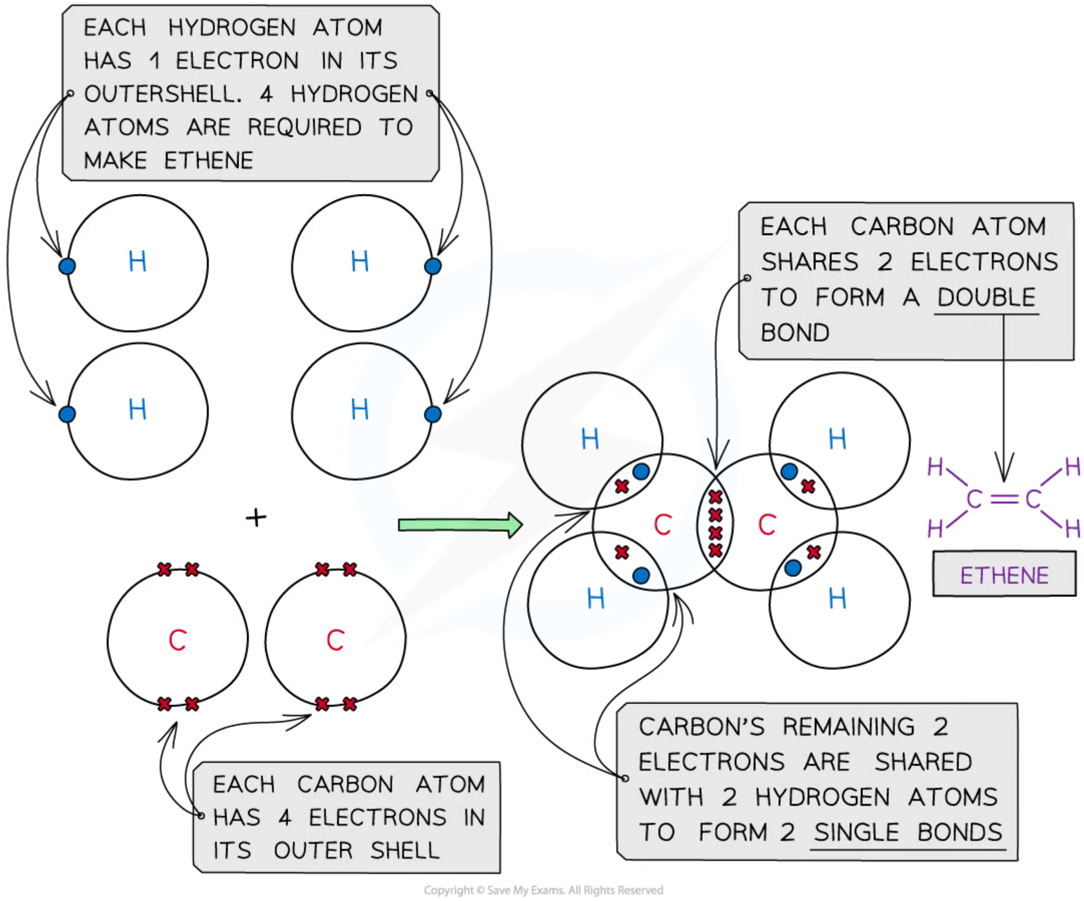
Covalent bonding in oxygen

Carbon dioxide, CO_2



Covalent bonding in carbon dioxide

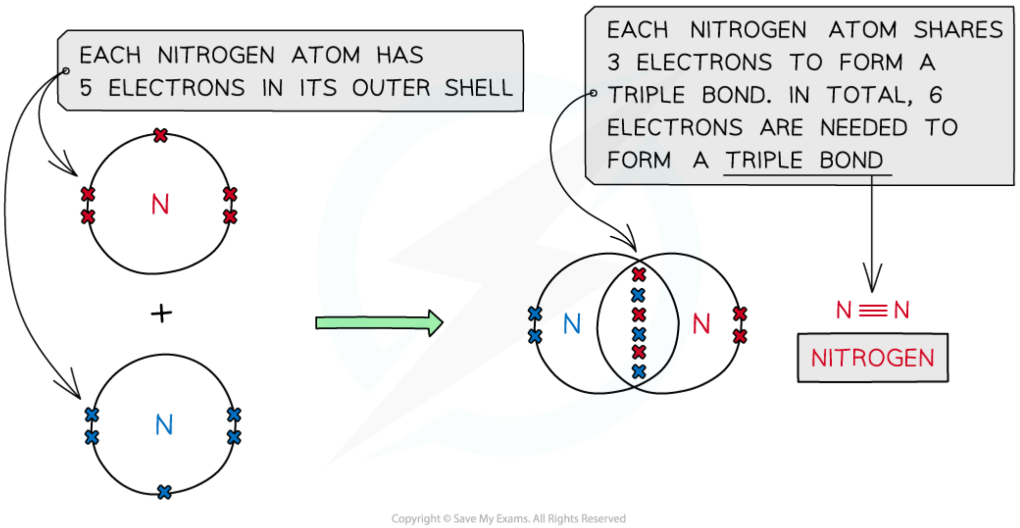
Ethene, C_2H_4



Covalent bonding in ethene

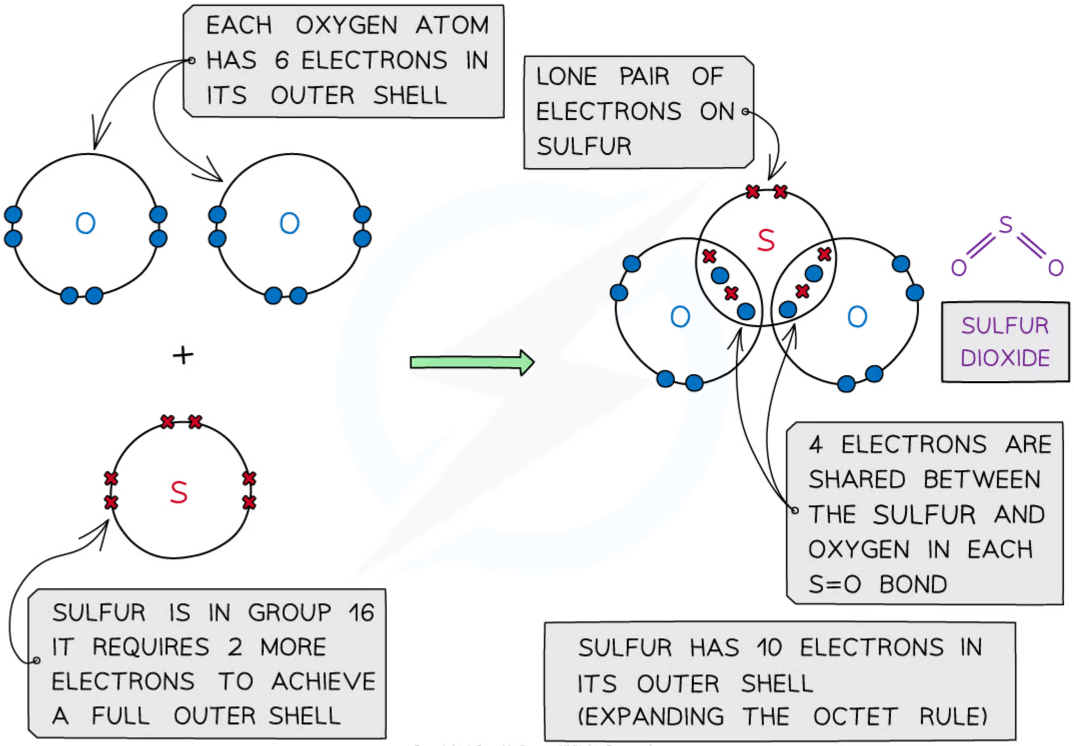
Triple covalent bonding

Nitrogen, N_2



Covalent bonding in nitrogen

- 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



EACH OXYGEN ATOM HAS 6 ELECTRONS IN ITS OUTER SHELL

LONE PAIR OF ELECTRONS ON SULFUR

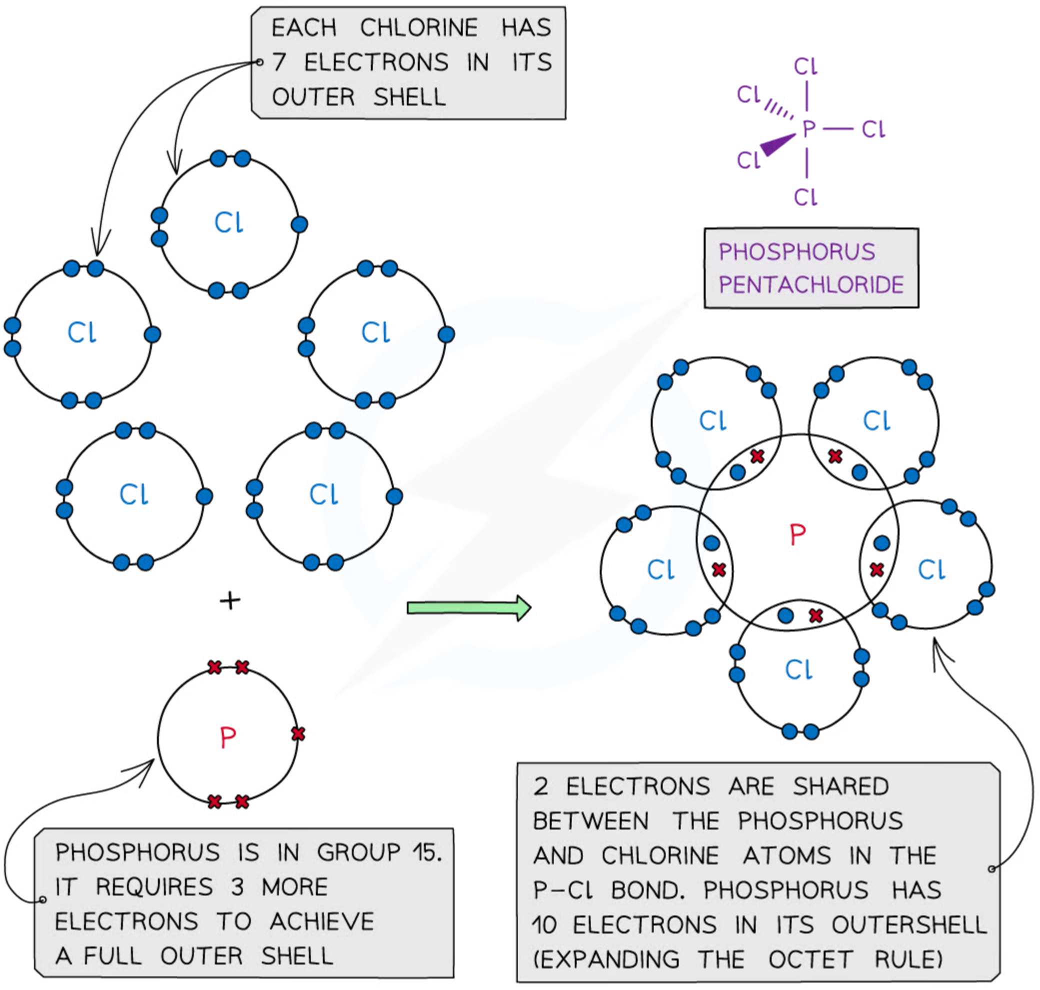
SULFUR DIOXIDE

4 ELECTRONS ARE SHARED BETWEEN THE SULFUR AND OXYGEN IN EACH S=O BOND

SULFUR IS IN GROUP 16 IT REQUIRES 2 MORE ELECTRONS TO ACHIEVE A FULL OUTER SHELL

SULFUR HAS 10 ELECTRONS IN ITS OUTER SHELL (EXPANDING THE OCTET RULE)

Sulfur dioxide, **SO_2** ***– dot and cross diagram***

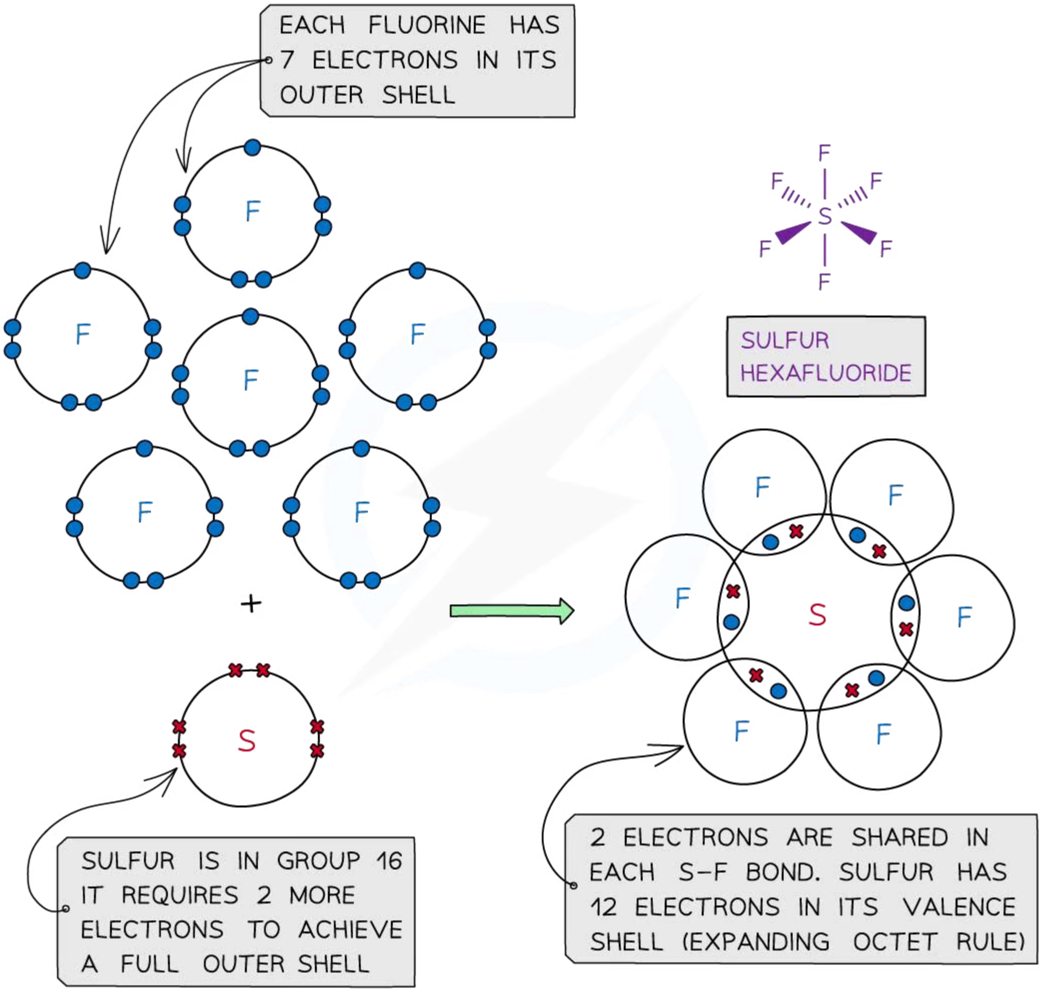


EACH CHLORINE HAS 7 ELECTRONS IN ITS OUTER SHELL

PHOSPHORUS IS IN GROUP 15. IT REQUIRES 3 MORE ELECTRONS TO ACHIEVE A FULL OUTER SHELL

2 ELECTRONS ARE SHARED BETWEEN THE PHOSPHORUS AND CHLORINE ATOMS IN THE P–Cl BOND. PHOSPHORUS HAS 10 ELECTRONS IN ITS OUTERSHELL (EXPANDING THE OCTET RULE)

Phosphorus pentachloride, PCl_5 – dot and cross diagram



EACH FLUORINE HAS 7 ELECTRONS IN ITS OUTER SHELL

SULFUR HEXAFLUORIDE

SULFUR IS IN GROUP 16 IT REQUIRES 2 MORE ELECTRONS TO ACHIEVE A FULL OUTER SHELL

2 ELECTRONS ARE SHARED IN EACH S–F BOND. SULFUR HAS 12 ELECTRONS IN ITS VALENCE SHELL (EXPANDING OCTET RULE)

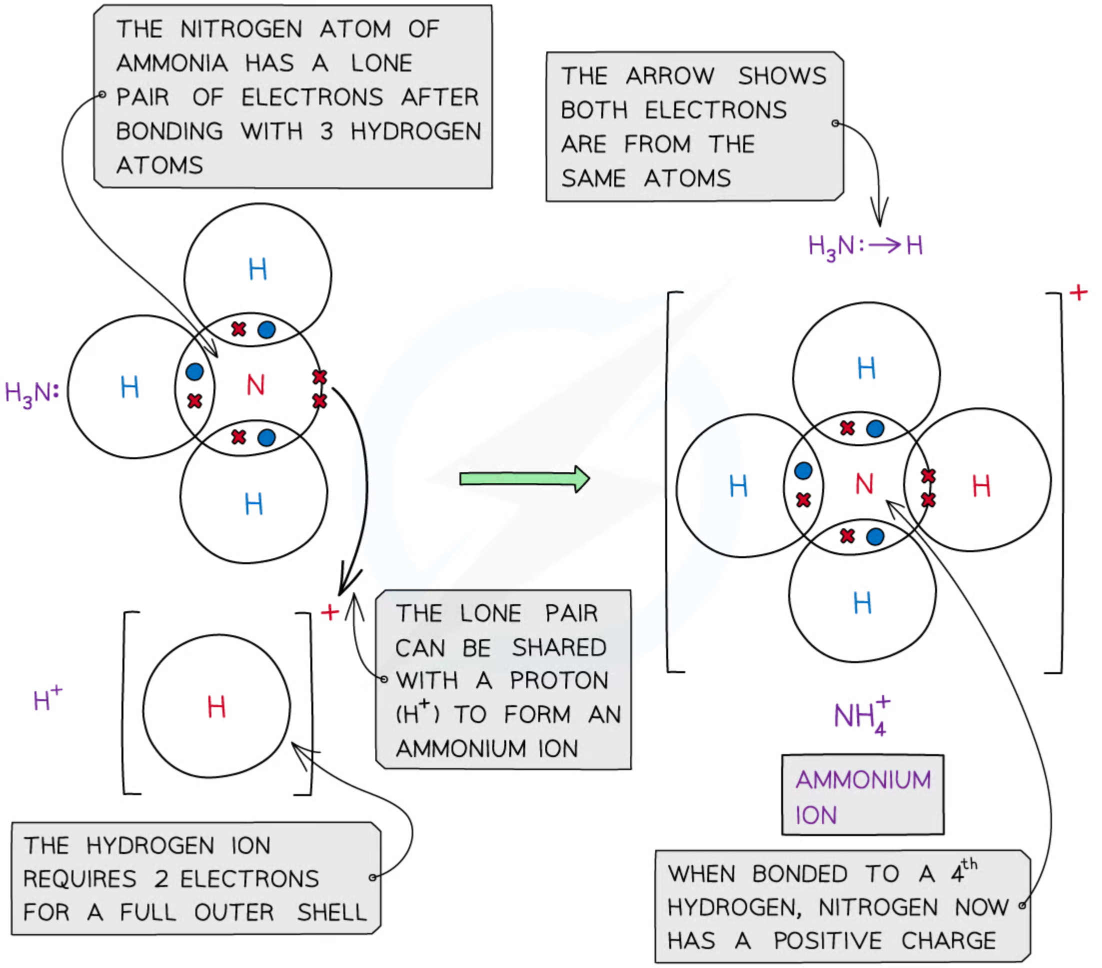
Sulfur hexafluoride, SF_6 – dot and cross diagram

Exam Tip

Covalent bonding takes place between nonmetal atoms. Remember to use the periodic table to decide how many electrons are in the outer shell of a nonmetal atom.

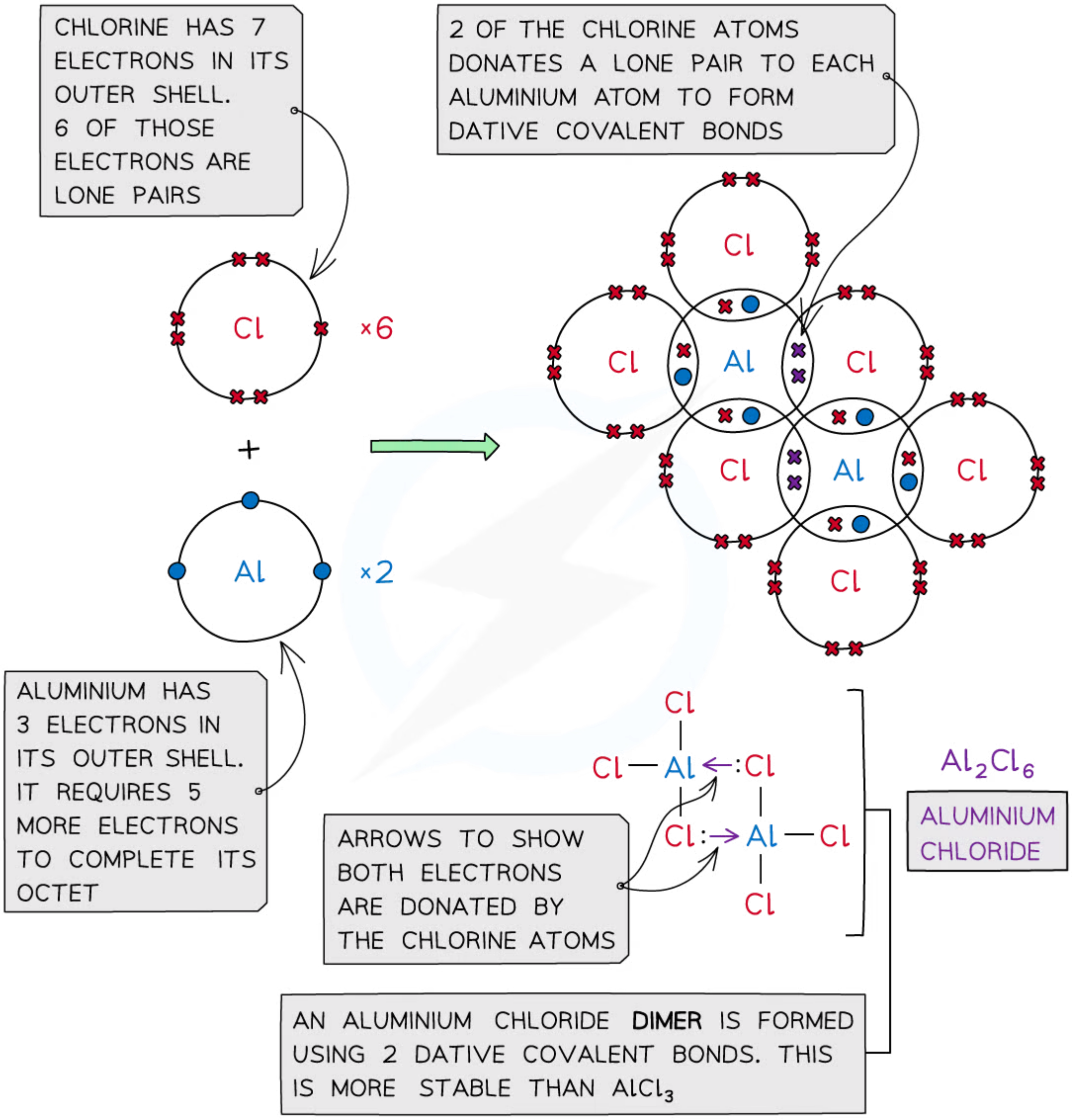
Dative Covalent Bonding

- 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** 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 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



CHLORINE HAS 7 ELECTRONS IN ITS OUTER SHELL. 6 OF THOSE ELECTRONS ARE LONE PAIRS

2 OF THE CHLORINE ATOMS DONATES A LONE PAIR TO EACH ALUMINIUM ATOM TO FORM DATIVE COVALENT BONDS

ALUMINIUM HAS 3 ELECTRONS IN ITS OUTER SHELL. IT REQUIRES 5 MORE ELECTRONS TO COMPLETE ITS OCTET

ARROWS TO SHOW BOTH ELECTRONS ARE DONATED BY THE CHLORINE ATOMS

AN ALUMINIUM CHLORIDE **DIMER** IS FORMED USING 2 DATIVE COVALENT BONDS. THIS IS MORE STABLE THAN $AlCl_3$

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

Exam Tip

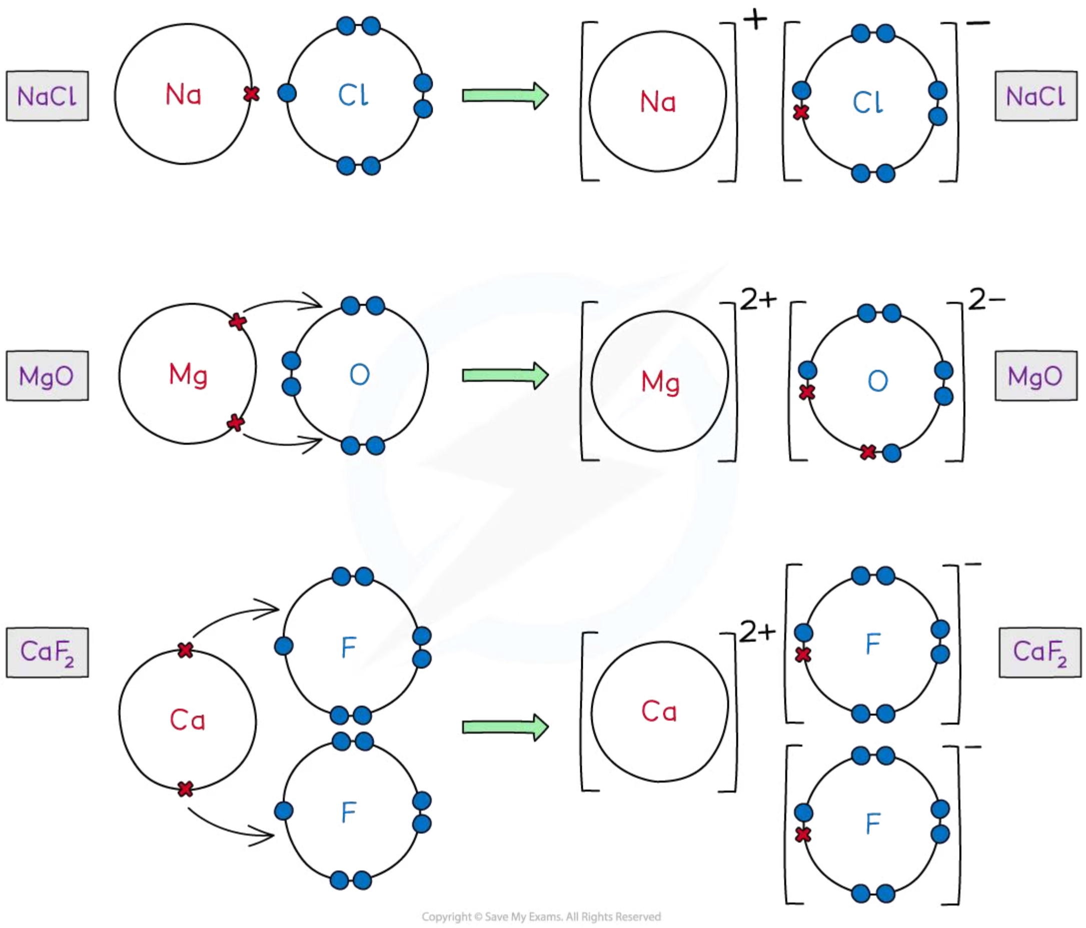
In dative covalent bonding, both electrons in the covalent bond are shared by one atom. A dative covalent bond is drawn using an arrow from the donated pair of electrons to the electron-deficient atom.

Representing Dot & Cross Diagrams

- **Dot and cross diagrams** are diagrams that show the arrangement of the outer-shell electrons in an **ionic** or **covalent** compound or element
    - The electrons are shown as dots and crosses
- In a dot and cross diagram:
    - Only the outer electrons are shown
    - The charge of the ion is spread evenly which is shown by using brackets
    - The charge on each ion is written at the top right-hand corner

Ionic compounds

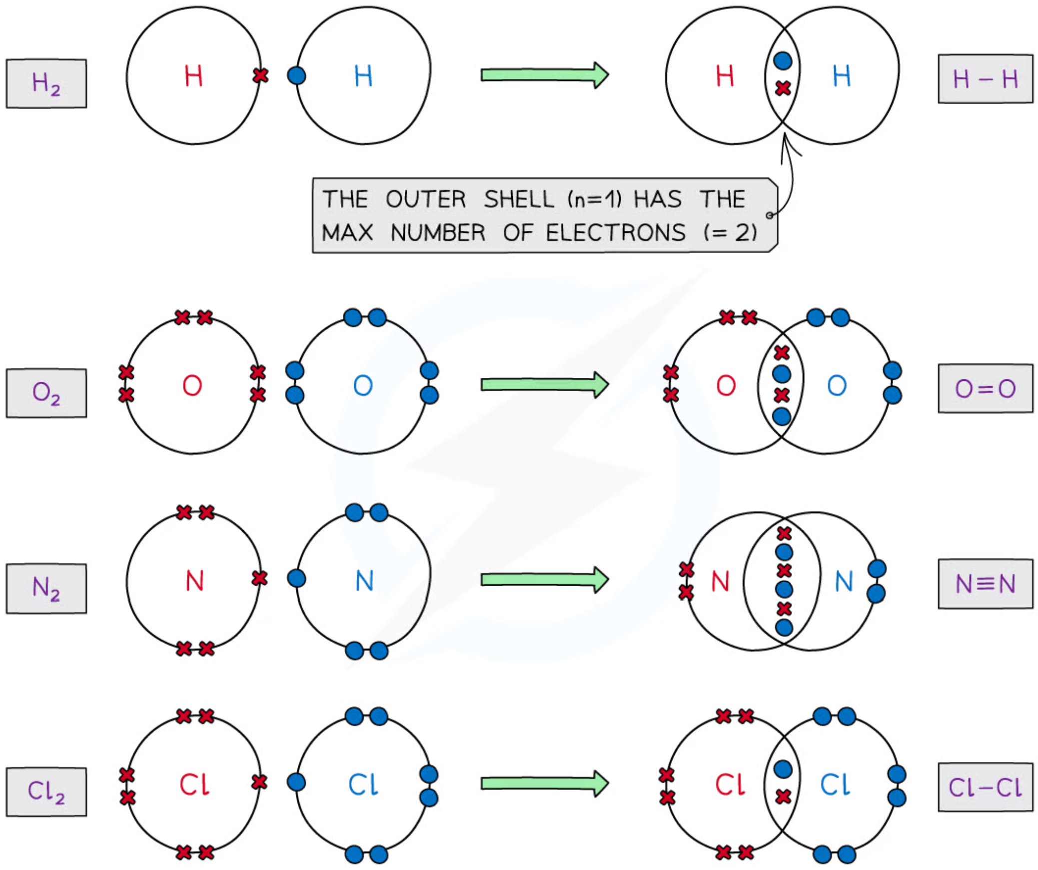
- Ionic bonds are formed when **metal atoms** transfer electrons to a **non-metal** to form a positively charged and negatively charged ion
- The atoms achieve a **noble gas** configuration

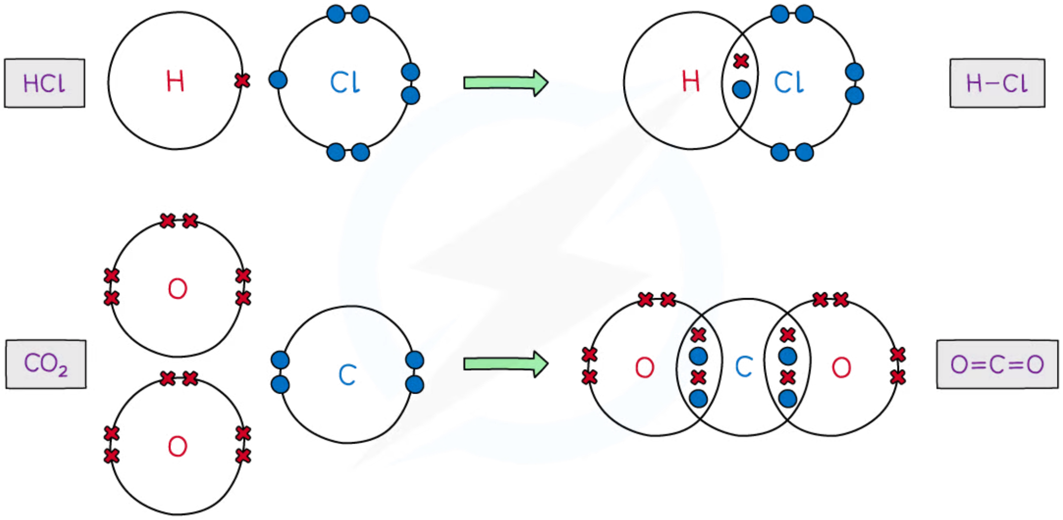


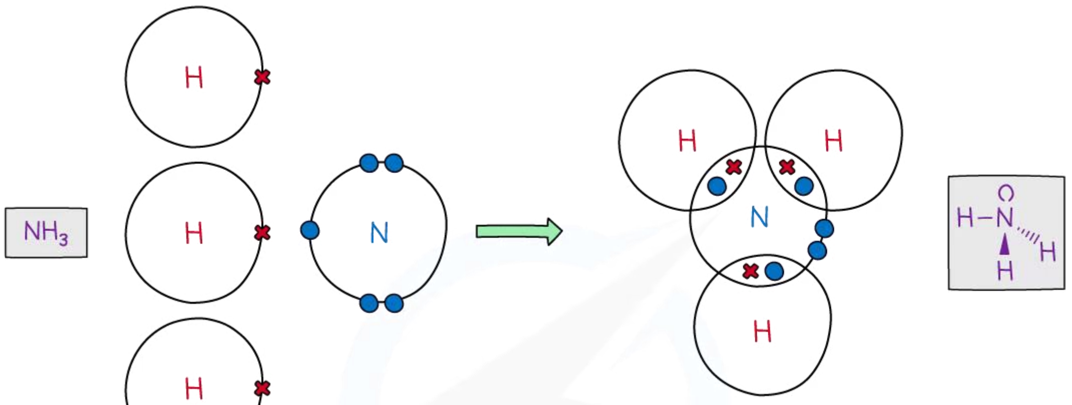
Dot-and-cross diagrams of ionic compounds in which one of the atoms transfers their valence electrons to the other

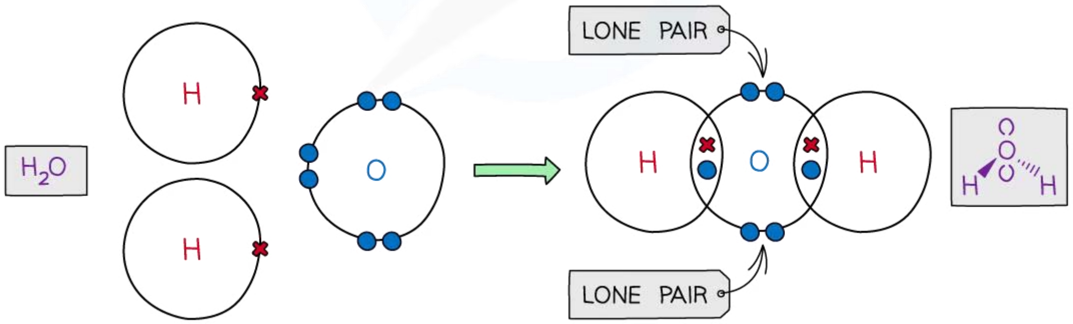
Covalent compounds

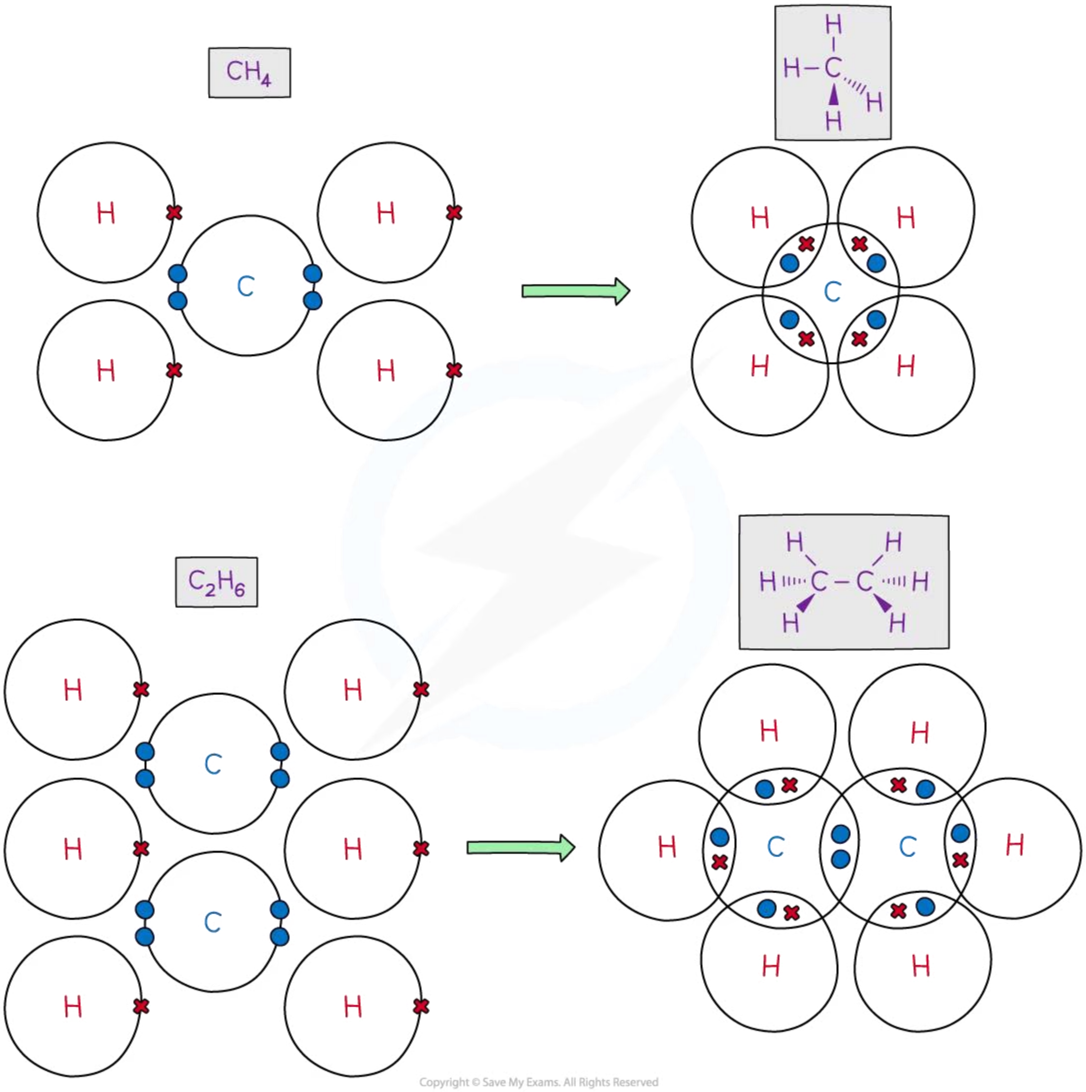
- The atoms in covalent compounds will **share** their outer valence electrons to achieve a **noble gas** configuration






NH_3
H
H
H
N
H
H
N
H
H–N–H
H


H_2O
H
H
O
LONE PAIR
H
O
H
LONE PAIR
H
O
H



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

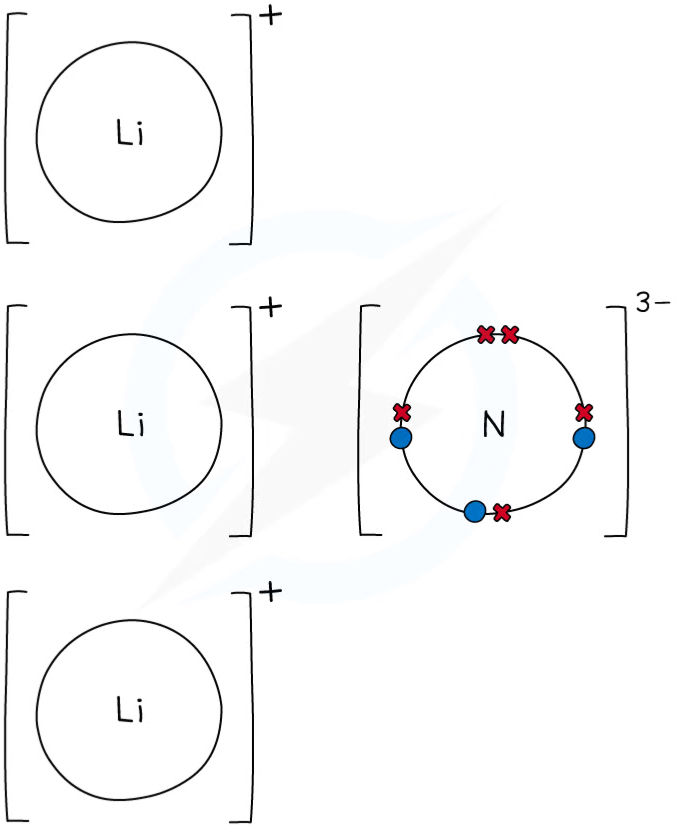
Worked Example

Draw a dot and cross diagram for lithium nitride

Answer

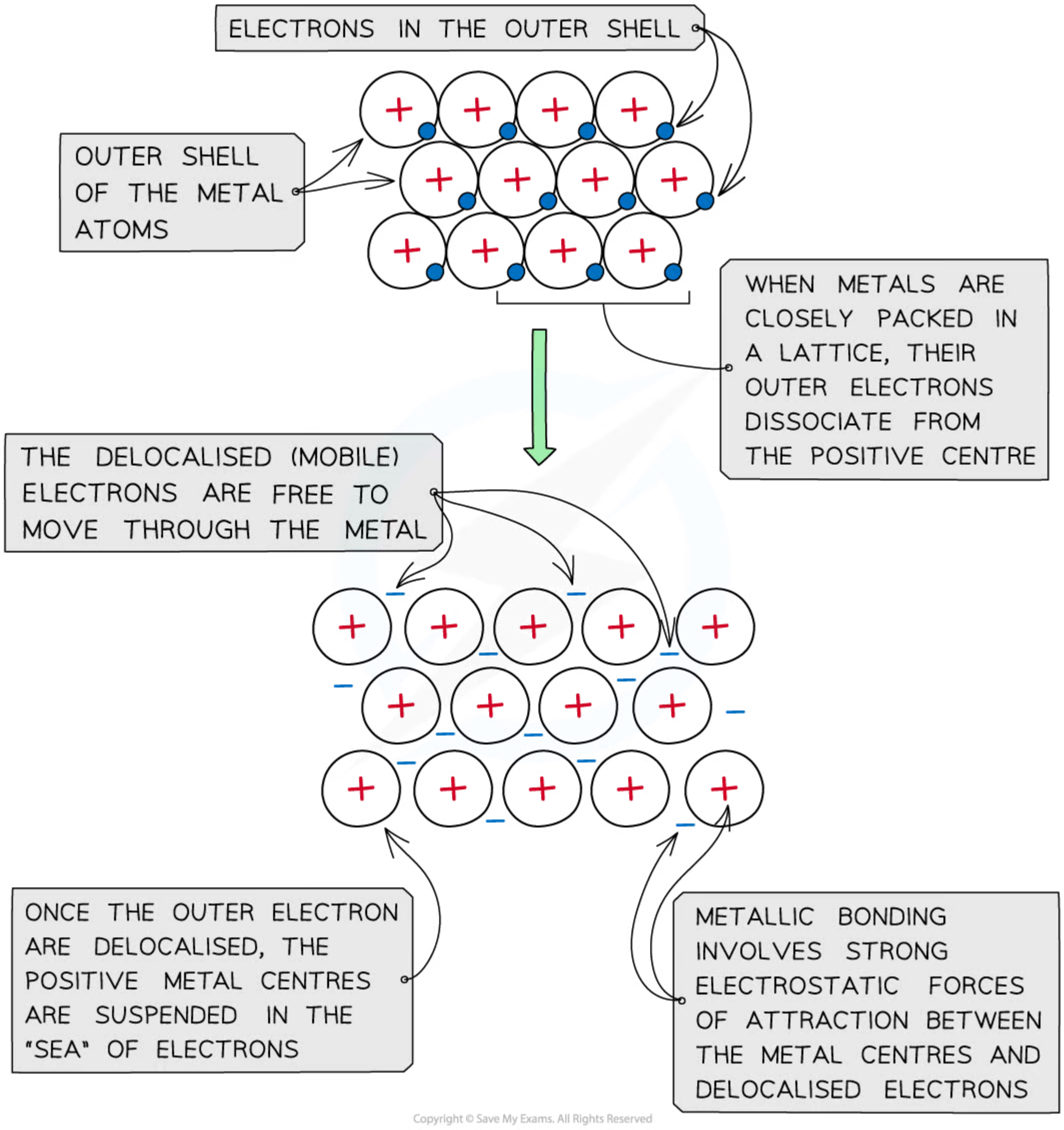
- Lithium is a Group 1 metal, so it loses its 1 electron from its outer shell
- This forms a Li^+ ion
- Nitrogen is a Group 5 non–metal, so it needs to gain 3 electrons to complete its outer shell
- This forms an N^{3-} ion

- Overall, three lithium atoms each donate an electron to one nitrogen atom, to form 3 x Li^+ ions and 1 x N^{3-}
- The overall ionic compound formed is **Li_3N**



Metallic Bonding: Definition

- **Metal** atoms are tightly packed together in **lattice** structures
- When the metal atoms are in lattice structures, the electrons in their outer shells are free to move throughout the structure
- The free-moving **electrons** are called **'delocalised electrons'** and they are not bound to their atom
- When the electrons are delocalised, the metal atoms become **positively** charged
- The positive charges **repel** each other and keep the neatly arranged lattice in place
- There are very strong **forces** between the positive metal centres and the 'sea' of delocalised electrons



The positive metal centres are suspended in a 'sea' of delocalised electrons

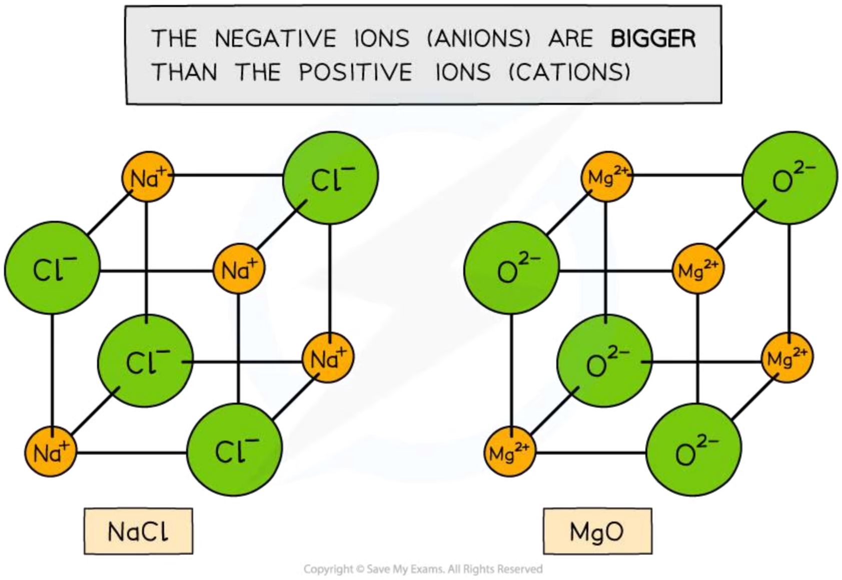
Ionic Lattice Structures

- Most ionic, metallic and covalent solids are **crystalline lattices**
- The ions, atoms or molecules are arranged in a **regular and repeating arrangement**

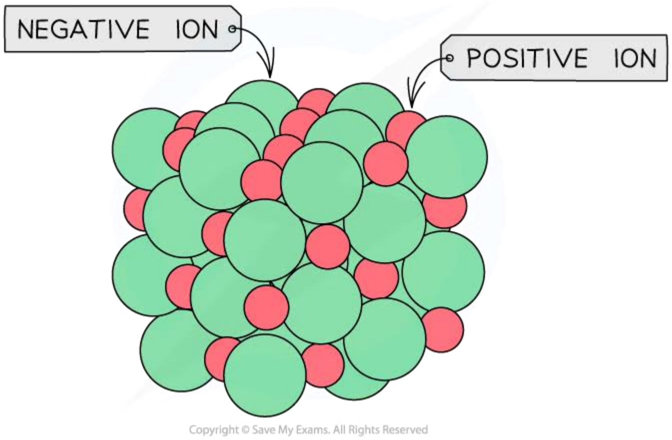
Giant ionic lattices

- An **ionic bond** is an electrostatic force of attraction between a positively charged metal (**cation**) ion and a negatively charged non-metal (**anion**) ion
  - The metal becomes positively charged as it transfers electrons to the non-metal which then becomes negatively charged
  - When an ionic compound is formed, the attraction between the ions happens in all directions

- Ionic compounds are arranged in giant **ionic lattices** (also called **giant ionic structures**)
- The type of lattice formed depends on the sizes of the **positive** and **negative** ions which are arranged in an **alternating** fashion
  - The ionic lattice of MgO and NaCl are **cubic**



Ionic lattices of the ionic compounds NaCl and MgO



General ionic lattice which shows the actual packing of the ions

Exam Tip

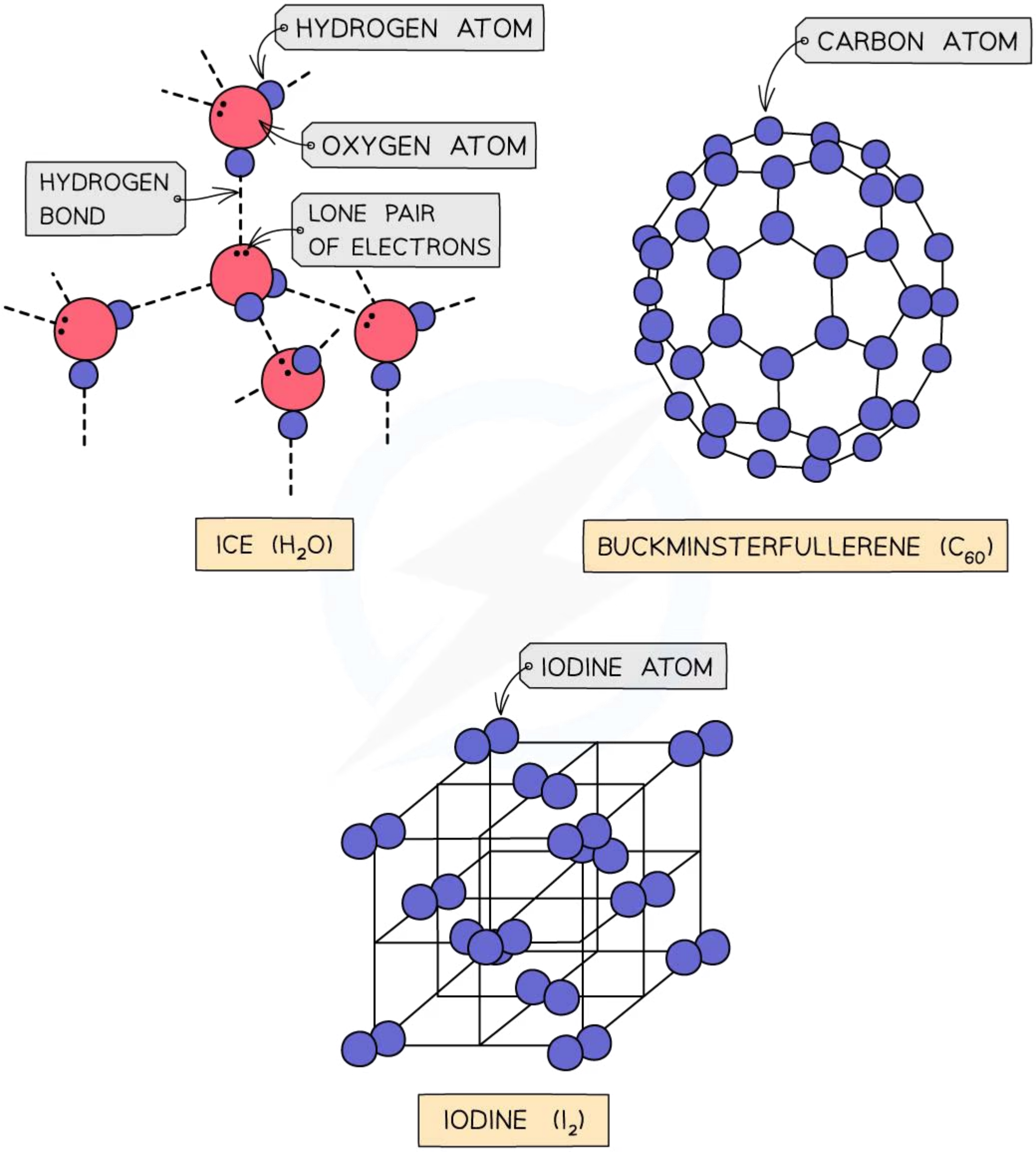
It is important that you can state and fully explain the different properties which arise based on the structure and bonding present in a substance

1.4.8 Properties of Covalent Substances

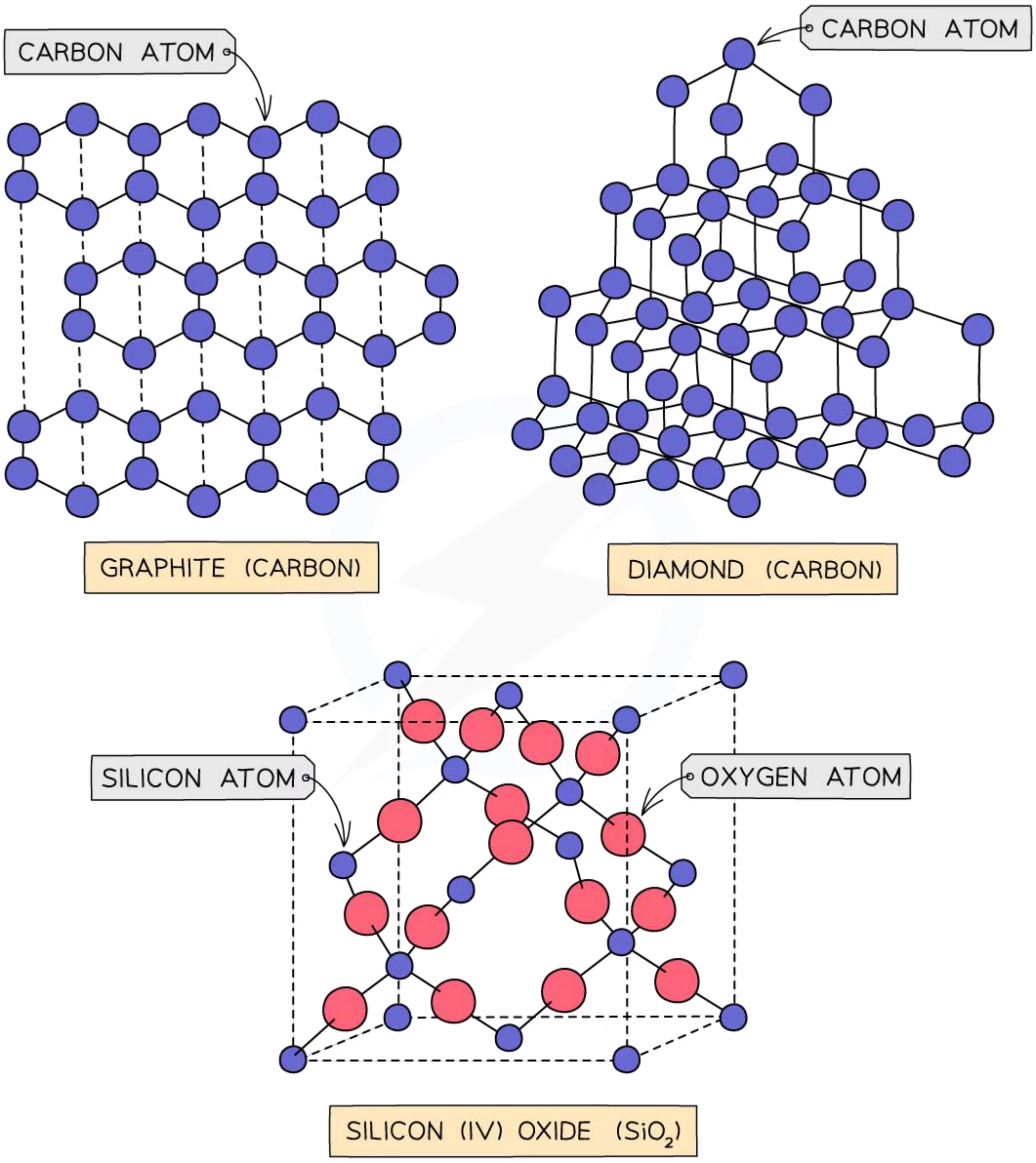
Covalent Lattice Structures

Covalent lattices

- **Covalent bonds** are bonds between nonmetals in which electrons are **shared** between the atoms
- Covalent compounds can be arranged in **simple molecular** or **giant molecular lattices**
  - Simple molecular lattices: iodine, buckminsterfullerene (C_{60}) and ice
  - Giant molecular: silicon(IV) oxide, graphite and diamond



Simple molecular lattices



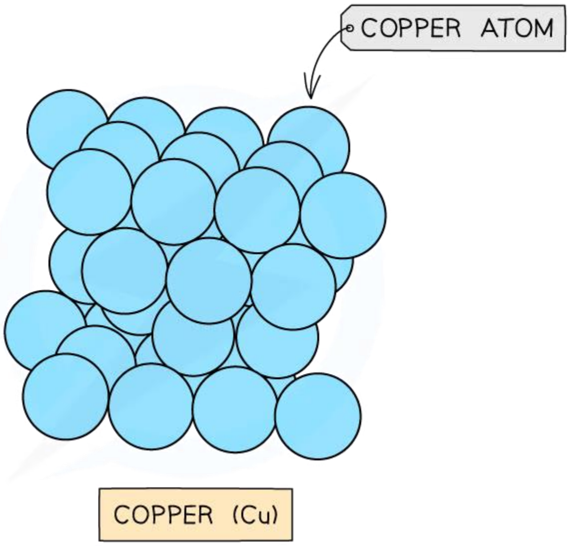
Giant molecular lattices

Exam Tip

Graphite, diamond and buckminsterfullerene are all **allotropes** of carbon; they are different **structural forms** of the same element (which is carbon).

Metallic Lattice Structures

- Metals form **giant metallic lattices** in which the metal ions are surrounded by a 'sea' of **delocalised** electrons
- The metal ions are often packed in **hexagonal layers** or in a **cubic arrangement**
- This layered structure with the delocalised electrons gives a metal its key properties



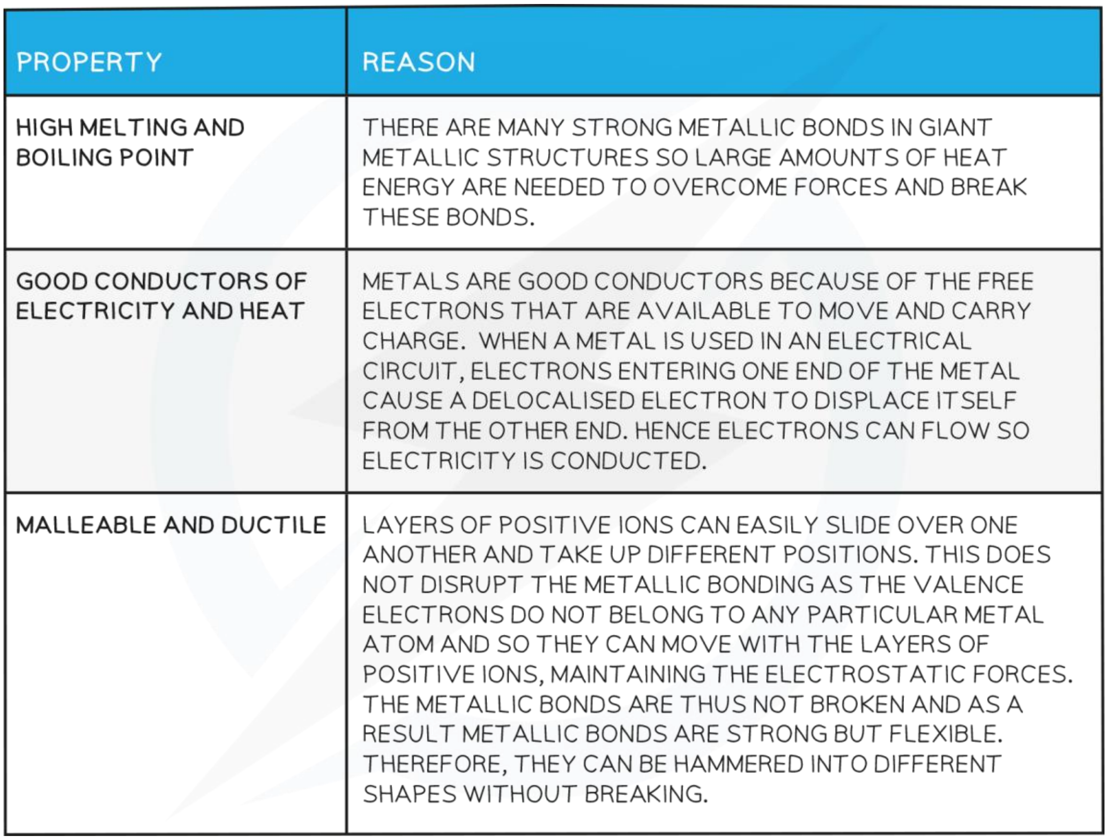
Layers of copper ions (the delocalised electrons are not shown in the diagram)

- If other atoms are added to the metal structure, such as carbon atoms, this creates an **alloy**
- Alloys are much stronger than pure metals, because the other atoms stop the layers of metal ions sliding over each other easily

- The **strength** of the metallic attraction can be increased by:
  - **Increasing** the number of **delocalised electrons** per metal atom
  - **Increasing** the **positive charges** on the metal centres in the lattice
  - **Decreasing** the **size** of the metal ions

- Due to the delocalised 'sea' of electrons, metallic structures have some **characteristic properties** shown below:

Metallic Bonding Properties Table



PROPERTY	REASON
HIGH MELTING AND BOILING POINT	THERE ARE MANY STRONG METALLIC BONDS IN GIANT METALLIC STRUCTURES SO LARGE AMOUNTS OF HEAT ENERGY ARE NEEDED TO OVERCOME FORCES AND BREAK THESE BONDS.
GOOD CONDUCTORS OF ELECTRICITY AND HEAT	METALS ARE GOOD CONDUCTORS BECAUSE OF THE FREE ELECTRONS THAT ARE AVAILABLE TO MOVE AND CARRY CHARGE. WHEN A METAL IS USED IN AN ELECTRICAL CIRCUIT, ELECTRONS ENTERING ONE END OF THE METAL CAUSE A DELOCALISED ELECTRON TO DISPLACE ITSELF FROM THE OTHER END. HENCE ELECTRONS CAN FLOW SO ELECTRICITY IS CONDUCTED.
MALLEABLE AND DUCTILE	LAYERS OF POSITIVE IONS CAN EASILY SLIDE OVER ONE ANOTHER AND TAKE UP DIFFERENT POSITIONS. THIS DOES NOT DISRUPT THE METALLIC BONDING AS THE VALENCE ELECTRONS DO NOT BELONG TO ANY PARTICULAR METAL ATOM AND SO THEY CAN MOVE WITH THE LAYERS OF POSITIVE IONS, MAINTAINING THE ELECTROSTATIC FORCES. THE METALLIC BONDS ARE THUS NOT BROKEN AND AS A RESULT METALLIC BONDS ARE STRONG BUT FLEXIBLE. THEREFORE, THEY CAN BE HAMMERED INTO DIFFERENT SHAPES WITHOUT BREAKING.

Exam Tip

You should be able to draw the structure of a metal with positive ions in layers, and the delocalised electrons surrounding the ionsIf drawing the structure of a metal in the exam, make sure to include labels for metal ion and delocalised electrons

Effects of Bonding & Structure on Physical Properties

- Different types of **structure** and **bonding** have different effects on the **physical properties** of substances such as their **melting** and **boiling points**, **electrical conductivity** and **solubility**

Ionic bonding & giant ionic lattice structures

- Ionic compounds are **strong**
    - The **strong electrostatic forces** in ionic compounds keep the ions strongly together

- They are **brittle** (meaning ionic crystals can split apart easily)
- Ionic compounds have **high melting** and **boiling** points
    - The strong electrostatic forces between the ions in the lattice act in all directions and keep them strongly together
    - Melting and boiling points increase with charge density of the ions due to the greater **electrostatic attraction** of charges
    - For example, $Mg^{2+}O^{2-}$ has a higher melting point than $Na^{+}Cl^{-}$

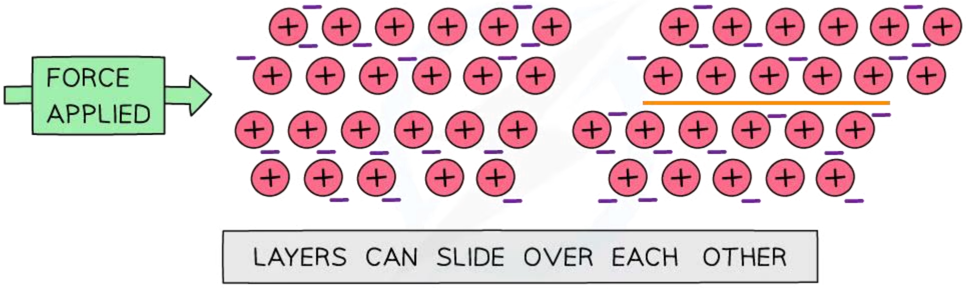
- Ionic compounds are **soluble** in water as they can form **ion - dipole bonds**
- Ionic compounds only **conduct electricity** when **molten** or in **solution**
    - When molten or in solution, the ions can freely move around and conduct electricity
    - In the solid state they're in a fixed position and unable to move around

Metallic bonding & giant metallic lattice structures

- Metallic structures are **malleable**
    - When a force is applied, the metal layers can slide
    - The **attractive forces** between the metal ions and electrons act in all directions
    - So when the layers slide, the metallic bonds are re-formed
    - The lattice is not broken and has changed shape

- Metallic lattices are **strong** and **hard**
    - Due to the strong attractive forces between the metal ions and delocalised electrons

- Metals have **high melting** and **boiling points**
- **Pure metals** are **insoluble** in water
- Metals can **conduct electricity** when in the **solid** or **liquid** state
    - As both in the solid and liquid state there are **mobile electrons** which can freely move around and conduct electricity



Metals are malleable as the layers can slide over each without breaking the attraction

Covalent bonding & simple covalent lattice structures

- **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 a reaction with the water than produces ions such as HCl which forms H^+ and Cl^- ions

Covalent bonding & giant covalent lattice structures

- **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

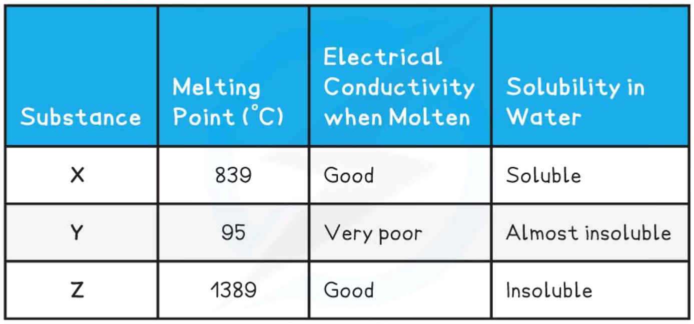
- Most compounds are insoluble with water
- Most compounds do not **conduct electricity** however some do
  - Graphite has **delocalised** electrons between the carbon layers which can move along the layers when a voltage is applied
  - Diamond and silicon(IV) oxide do not conduct electricity as all four outer electrons on every carbon atom are involved in a **covalent bond** so there are no freely moving electrons available

Characteristics of Different Compound Structure Types Table

	Giant Ionic	Giant Metallic	Simple Covalent	Giant Covalent
Melting and Boiling Points	High	Moderately high to high	Low	Very high
Electrical Conductivity	Only when molten or in solution	When solid or liquid	Do not conduct electricity	Do not conduct electricity (except for **graphite**)
Solubility	Soluble	Insoluble but some may react	Usually insoluble unless they are polar	Insoluble
Hardness	Hard, brittle	Hard, malleable	Soft	Very hard (**diamond** and **SiO_2**) or soft (**graphite**)
Physical State at Room Temperature	Solid	Solid	Solid, liquid or gas	Solid
Forces	Electrostatic attraction between ions	Delocalised sea of electrons attracting positive ions	Weak intermolecular forces between molecules and covalent bonds within a molecule	Electrons in covalent bonds between atoms
Particles	Ions	Positive ions in a sea of electrons	Small molecules	Atoms
Examples	NaCl	Copper	Br_2	Graphite, silicon(IV) oxide

Worked Example

Bonding & structure The table below shows the physical properties of substances X, Y and Z



Substance	Melting Point (°C)	Electrical Conductivity when Molten	Solubility in Water
X	839	Good	Soluble
Y	95	Very poor	Almost insoluble
Z	1389	Good	Insoluble

Which one of the following statements about X and Y is completely true?**Statement 1:** X has a giant ionic structure, Y has a giant molecular structure, Z is a metal**Statement 2:** X is a metal, Y has a simple molecular structure, Z has a giant molecular structure**Statement 3:** X is a metal, Y has a simple molecular structure, Z has a giant ionic structure**Statement 4:** X has a giant ionic structure, Y has a simple molecular structure, Z is a metal

Answer

The correct answer is **Statement 4**

- The relatively high melting point, solubility in water and electrical conductivity when molten suggest that **X** is a **giant ionic structure.**
- The low melting point of **Y** suggests that little energy is needed to break the lattice which corresponds to a **simple molecular structure**. This is further supported by the low electrical conductivity and its being almost insoluble in water.
- Compound **Z** has a very high melting point which is characteristic of either metallic or giant molecular lattices, however since it conducts electricity, compound Z must be a **giant metallic lattice.**

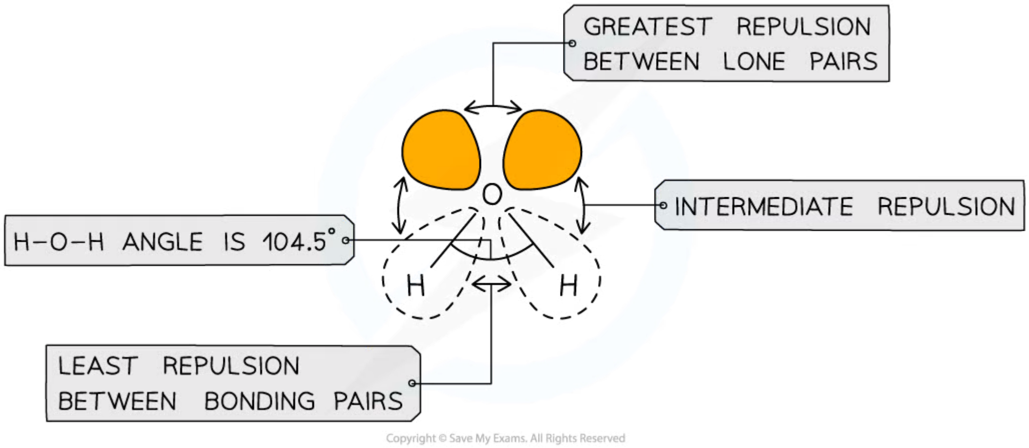
1.5 Molecules: Shapes & Forces

1.5.1 Shapes of Simple Molecules & Ions

Electron Pairs

- 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

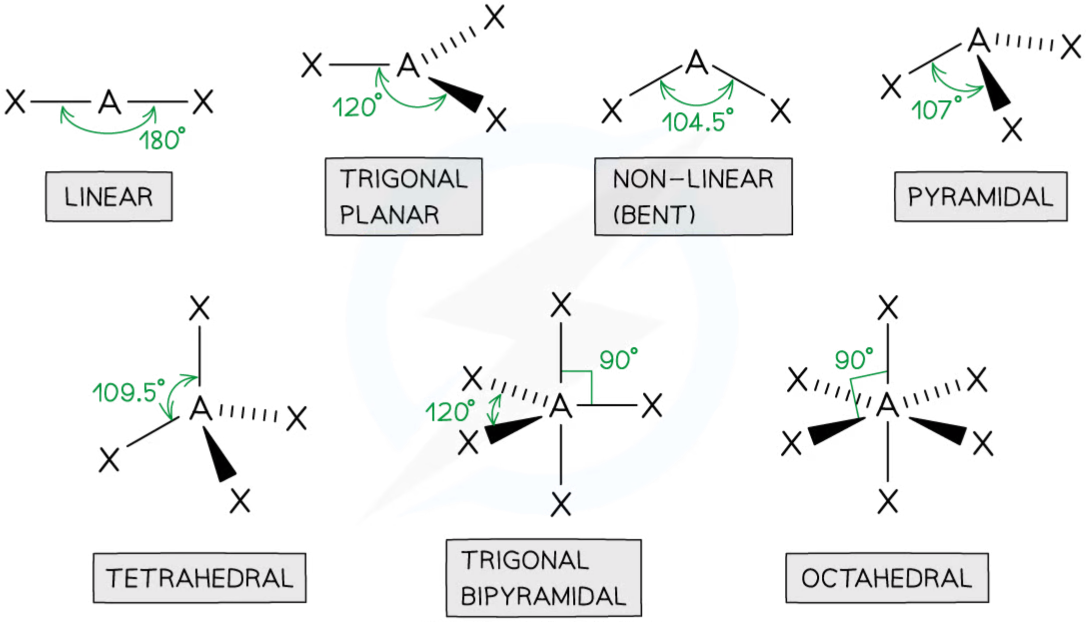
- Different types of electron pairs have different repulsive forces
    - Lone pairs of electrons have a more concentrated electron charge cloud than bonding pairs of electrons
    - The cloud charges are wider and closer to the central atom's nucleus
    - The order of repulsion is therefore: lone pair – lone pair > lone pair – bond pair > bond pair – bond pair



Different types of electron pairs have different repulsive forces

Shapes of Molecules & Ions

- Molecules can adapt the following shapes and bond angles:

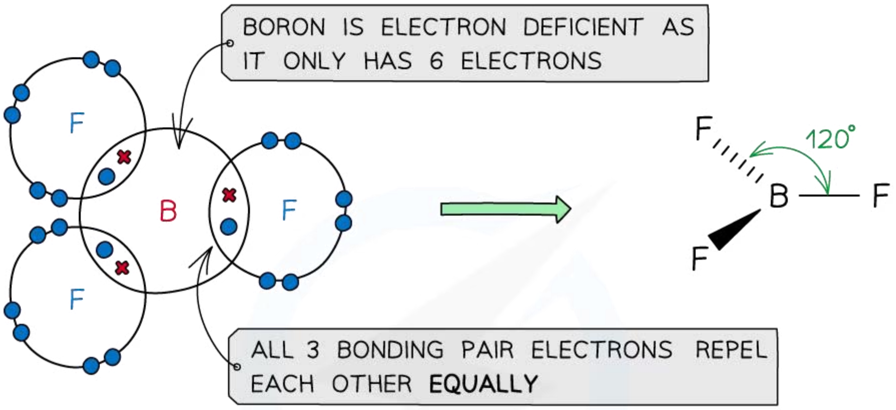


Molecules of different shapes can adapt with their corresponding bond angles

Examples

TRIGONAL PLANAR

BF_3 (120°)

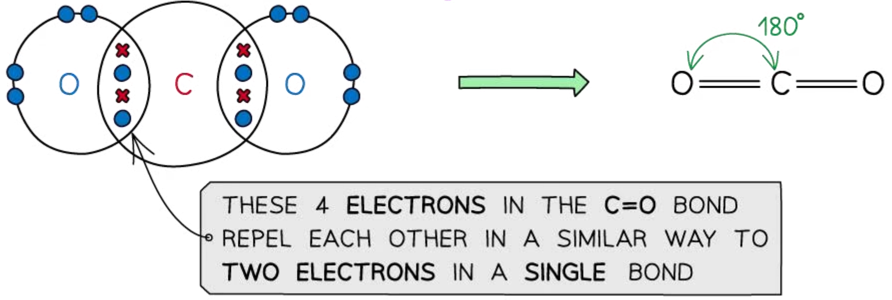


BORON IS ELECTRON DEFICIENT AS IT ONLY HAS 6 ELECTRONS

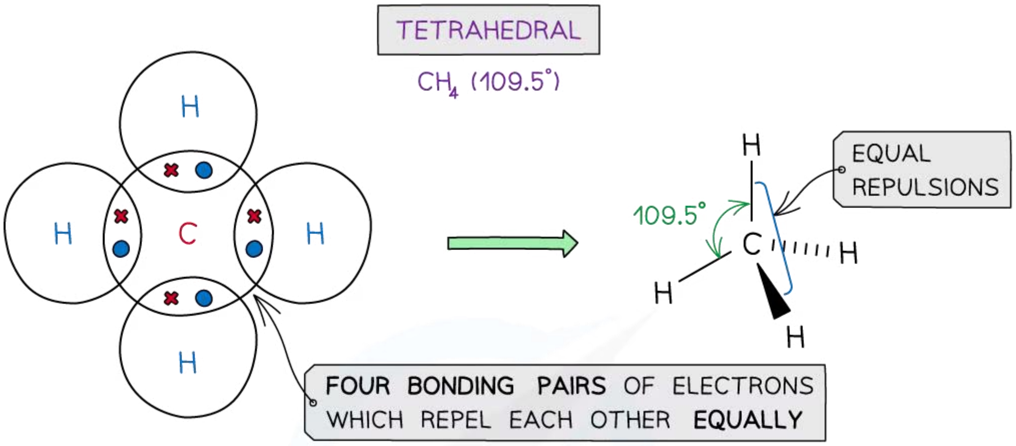
ALL 3 BONDING PAIR ELECTRONS REPEL EACH OTHER **EQUALLY**

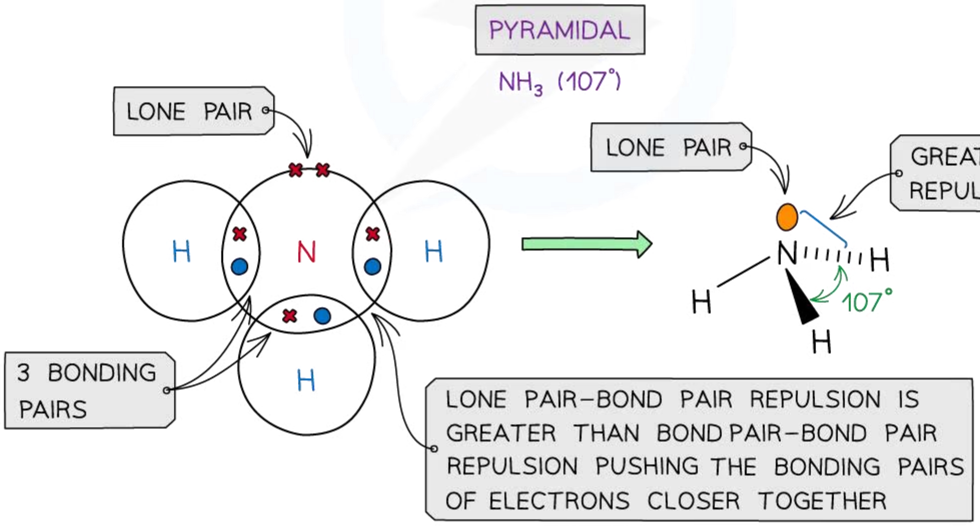
LINEAR

CO_2 (180°)

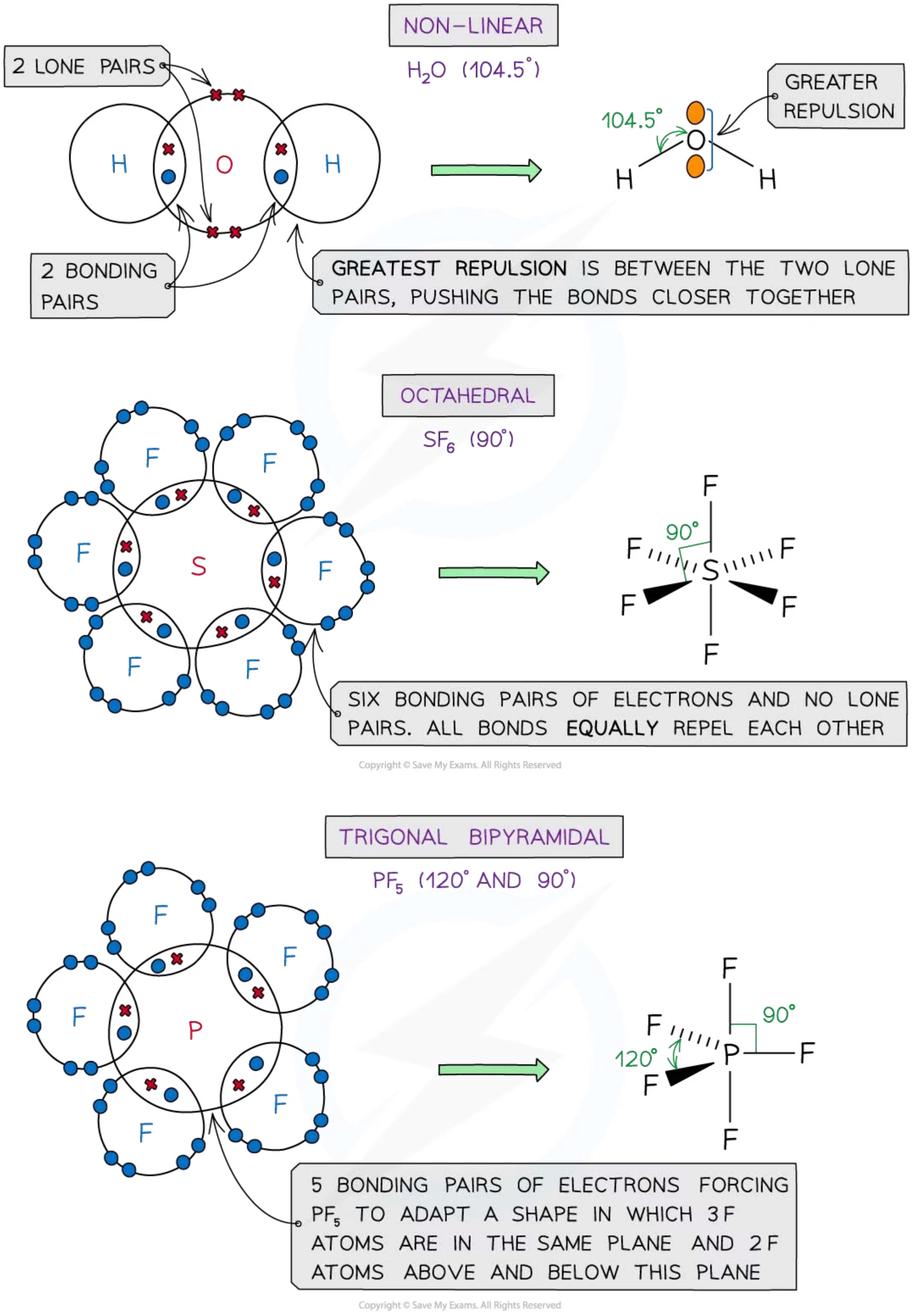


THESE 4 **ELECTRONS** IN THE **C=O** BOND REPEL EACH OTHER IN A SIMILAR WAY TO **TWO ELECTRONS** IN A **SINGLE** BOND


TETRAHEDRAL
CH4 (109.5°)
H
H
C
H
H
109.5°
EQUAL REPULSIONS
H
C
H
H
H
FOUR BONDING PAIRS OF ELECTRONS WHICH REPEL EACH OTHER EQUALLY


PYRAMIDAL
NH3 (107°)
LONE PAIR
H
N
H
H
3 BONDING PAIRS
LONE PAIR
GREATER REPULSION
N
H
H
H
107°
LONE PAIR–BOND PAIR REPULSION IS GREATER THAN BOND PAIR–BOND PAIR REPULSION PUSHING THE BONDING PAIRS OF ELECTRONS CLOSER TOGETHER

YOUR NOTES
↓



GREATEST REPULSION IS BETWEEN THE TWO LONE PAIRS, PUSHING THE BONDS CLOSER TOGETHER

SIX BONDING PAIRS OF ELECTRONS AND NO LONE PAIRS. ALL BONDS **EQUALLY** REPEL EACH OTHER

5 BONDING PAIRS OF ELECTRONS FORCING PF_5 TO ADAPT A SHAPE IN WHICH 3 F ATOMS ARE IN THE SAME PLANE AND 2 F ATOMS ABOVE AND BELOW THIS PLANE

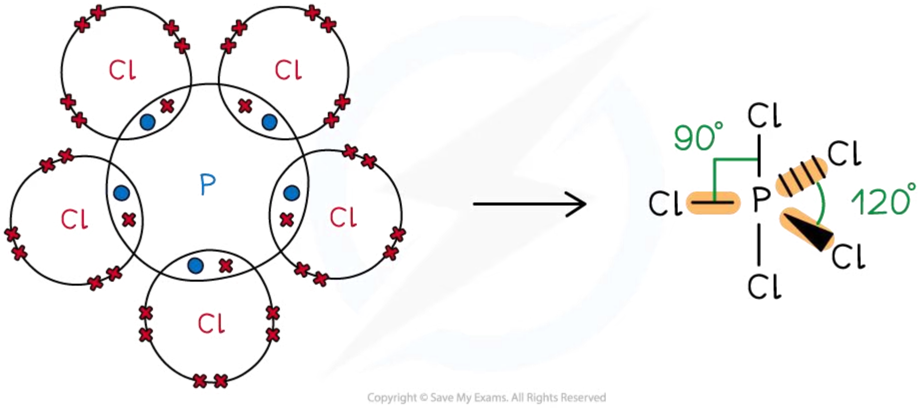
Examples of molecules with different shapes and bond angles

VSEPR & shapes of molecules Draw the shape of the following molecules:

1. Phosphorus(V) chloride
2. $N(CH_3)_3$
3. CCl_4

Answer 1:

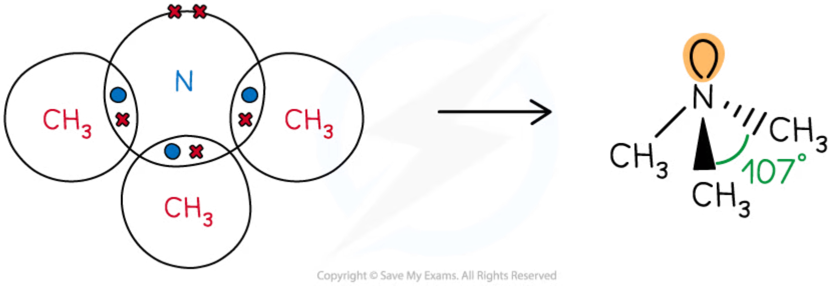
- Phosphorus is in group 15, so has 5 valence electrons; Cl is in group 17, so has 17 valence electrons
- All 5 electrons are used to form covalent bonds with Cl and there are no lone pairs
- This gives a **trigonal** (or **triangular**) **bipyramidal** shape:



Phosphorus pentachloride or phosphorus (V) chloride

Answer 2:

- Nitrogen is in group 15, so has 5 valence electrons; carbon is in group 14, so has 4 valence electrons, 3 of which are already used in the covalent bonds with hydrogen
- Three of the valence electrons in N are used to form bonding pairs, so there is one lone pair left
- $N(CH_3)_3$ has a **triangular pyramid** shape:

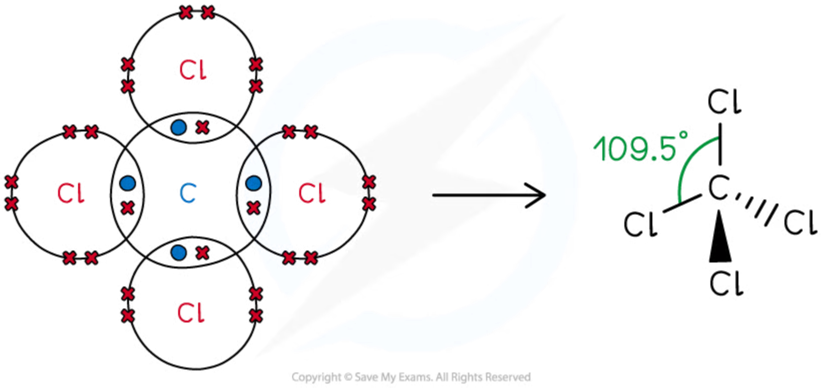


Trimethylamine

Answer 3:

- Carbon is in group 14, so has 4 valence electrons; chlorine is in group 17, so has 7 valence electrons

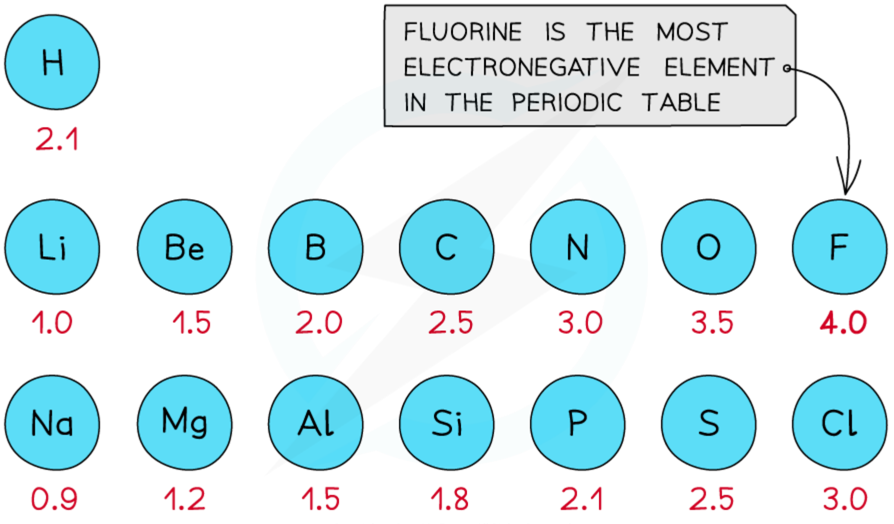
- All four valence electrons are use to bond with chlorine and there are no lone pairs
- The shape of CCl_4 is **tetrahedral**



Tetrachloromethane

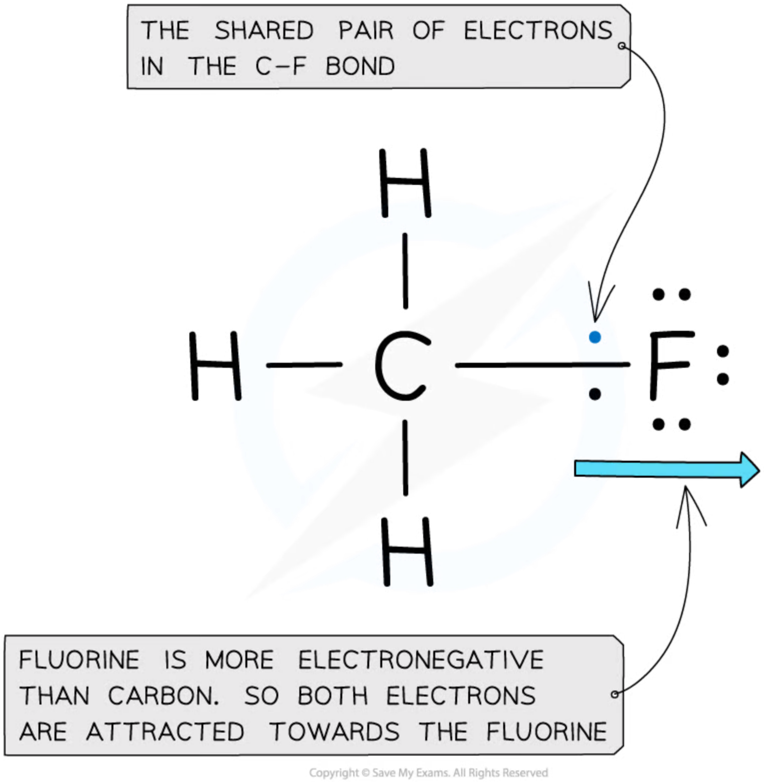
Electronegativity

- **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 **positive** nucleus's ability 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 electron density towards itself when covalently bonded to another atom



Electron distribution in the C–F bond of fluoromethane

Nuclear charge

- **Attraction** exists between the positively charged **protons** in the nucleus and negatively charged **electrons** found in the energy levels of an atom
- An **increase** in the number of **protons** leads to an **increase** in **nuclear attraction** for the electrons in the outer shells
- Therefore, an **increased nuclear charge** results in an **increased electronegativity**

Atomic radius

- The **atomic radius** is the distance between the nucleus and electrons in the **outermost shell**
- Electrons **closer** to the nucleus are more **strongly** attracted towards its positive **nucleus**
- Those electrons **further away** from the nucleus are **less strongly** attracted towards the **nucleus**
- Therefore, an **increased atomic radius** results in a **decreased electronegativity**

Shielding

- **Filled** energy levels can **shield** (mask) the effect of the nuclear charge causing the outer electrons to be **less attracted** to the nucleus
- Therefore, the addition of extra **shells and subshells** in an atom will cause the outer electrons to experience **less** of the attractive force of the nucleus
    - Sodium (period 3, group 1) has higher **electronegativity** than caesium (period 6, group 1) as it has fewer shells and therefore the outer electrons experience

less shielding than in caesium

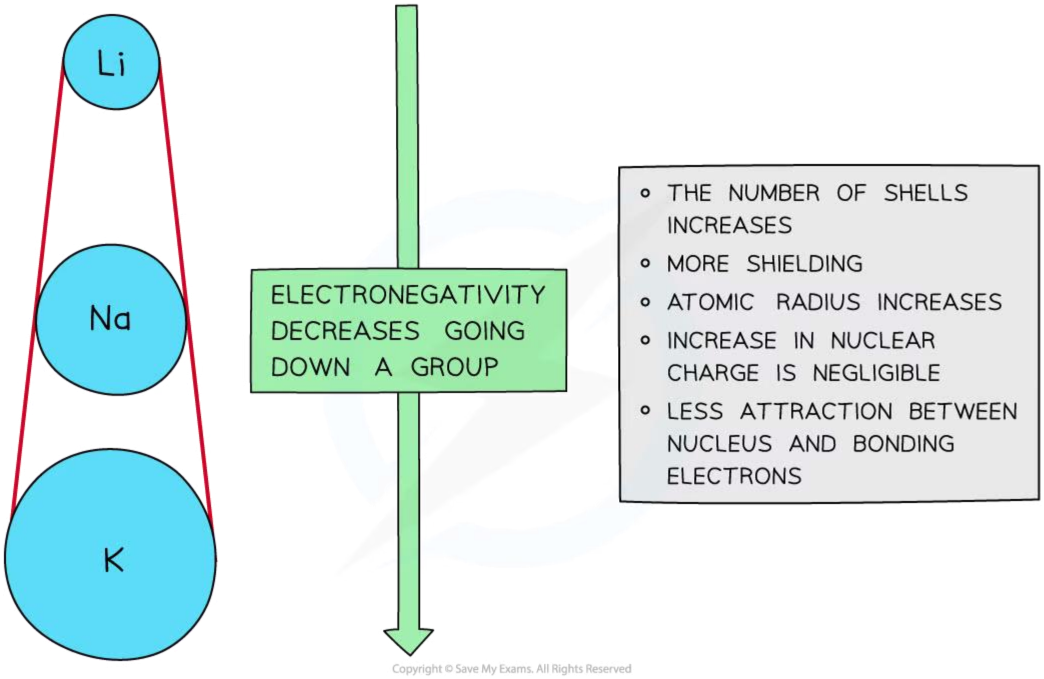
- Thus, an increased number of **inner shells and subshells** will result in a **decreased electronegativity**

Trends in Electronegativity

- **Electronegativity** varies across **periods** and down the groups of the periodic table

Down a group

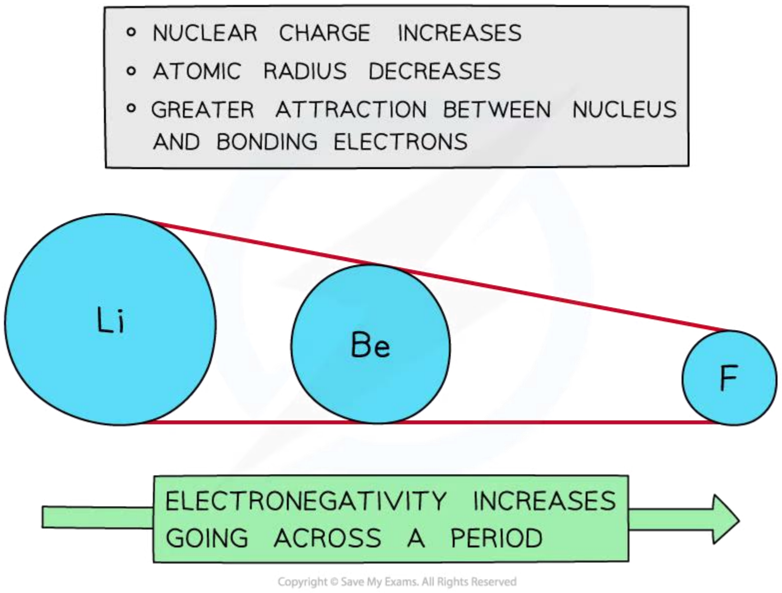
- There is a **decrease** in **electronegativity** going down the group
- The **nuclear charge increases** as more protons are being added to the nucleus
- However, each element has an extra filled electron shell, which increases **shielding**
- The addition of the extra shells increases the distance between the nucleus and the outer electrons resulting in **larger atomic radii**
- Overall, there is decrease in attraction between the nucleus and outer bonding electrons



Electronegativity decreases going down the groups of the periodic table

Across a period

- Electronegativity **increases** across a period
- The **nuclear charge increases** with the addition of protons to the nucleus
- **Shielding** remains relatively **constant** across the period as no new shells are being added to the atoms
- The nucleus has an increasingly strong attraction for the bonding pair of electrons of atoms across the period of the periodic table
- This results in **smaller atomic radii**



Electronegativity increases going across the periods of the Periodic Table

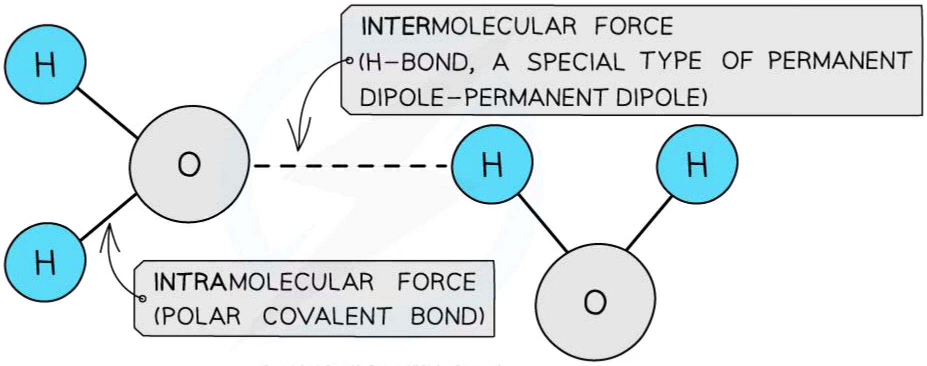
Exam Tip

Remember the general trend is an **increase** in electronegativity towards the top right of the periodic table.Fluorine is the most electronegative element in the periodic table.

Intramolecular Forces vs. Intermolecular Forces

Intramolecular forces

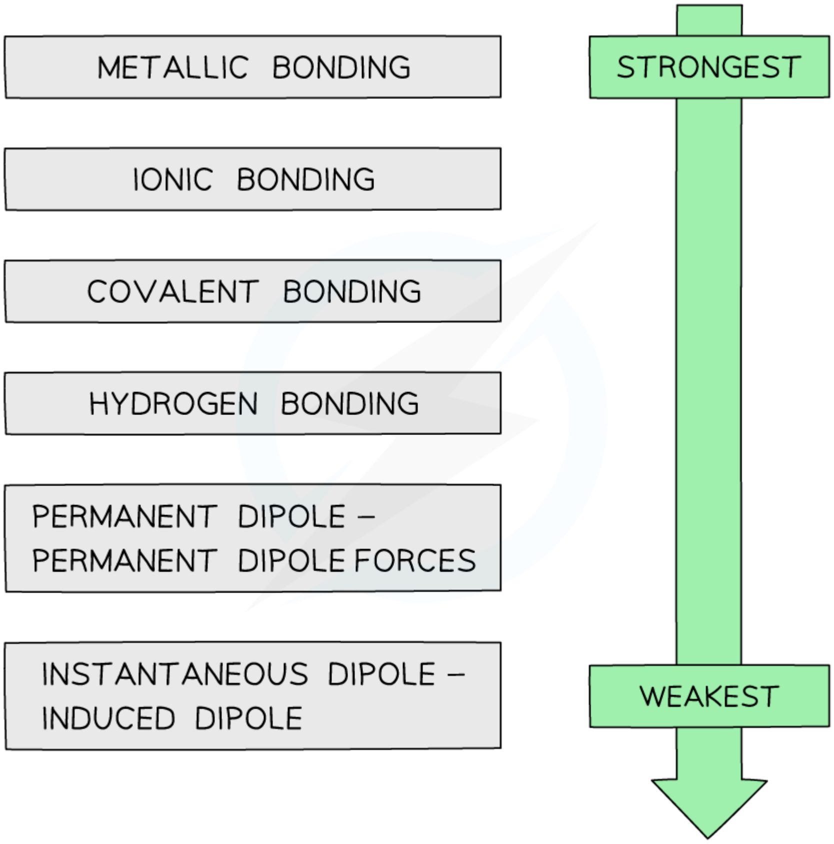
- **Intramolecular forces** are forces **within** a molecule and are usually covalent bonds
- **Covalent bonds** are formed when the outer electrons of two atoms are **shared**
- Single, double, triple and co-ordinate bonds are all types of intramolecular forces



Intermolecular forces

- Molecules also contain weaker **intermolecular forces** which are forces **between** the molecules
- There are three types of intermolecular forces:
  - **Induced dipole – dipole forces** also called **van der Waals** or **London dispersion forces**
  - **Permanent dipole – dipole forces** are the attractive forces between two neighbouring molecules with a permanent dipole
  - **Hydrogen Bonding** are a special type of **permanent dipole - permanent dipole** forces
  - **Intramolecular forces** are **stronger** than intermolecular forces
    - For example, a hydrogen bond is about one tenth the strength of a covalent bond
  - The strengths of the types of bond or force are as follows:

YOUR NOTES
↓

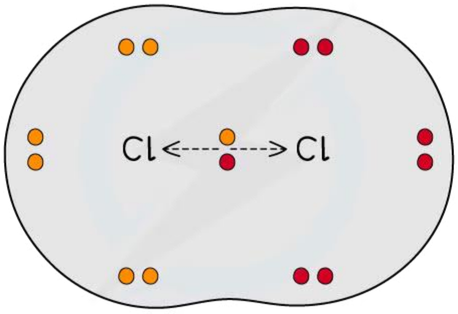


The varying strengths of different types of bonds

Polar Bonds

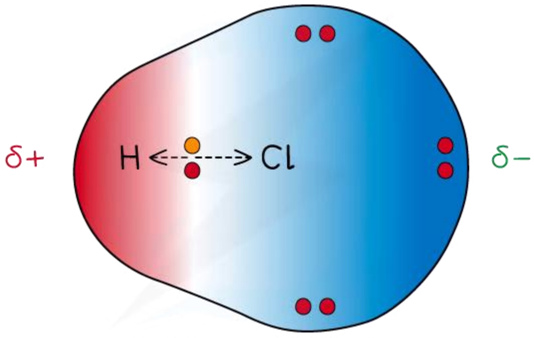
Polarity

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



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

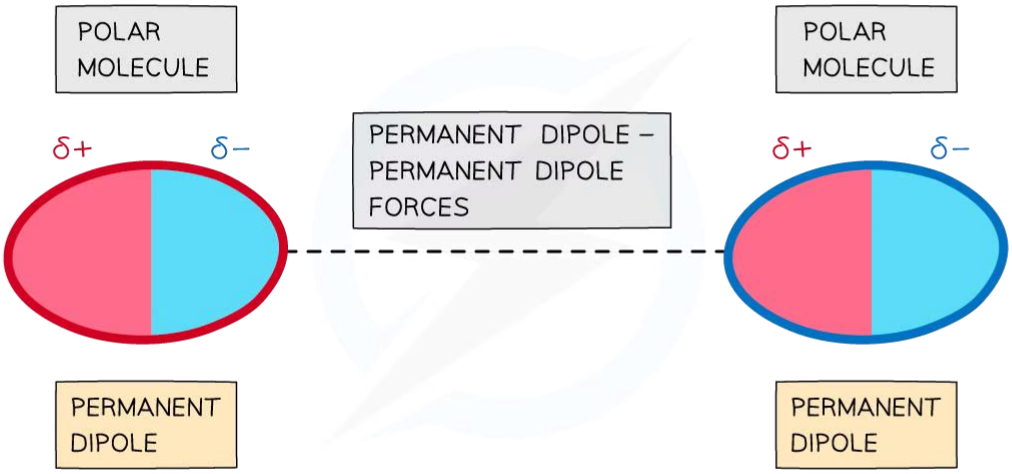
- When two atoms in a covalent bond have **different electronegativities** the covalent bond is **polar** and the electrons will be drawn towards the **more electronegative** atom
- As a result of this:
  - The negative charge centre and positive charge centre do not **coincide** with each other
  - 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



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

Permanent dipole – dipole forces:

- **Polar molecules** have **permanent dipoles**
- The molecule will always have a **negatively** and **positively charged end**

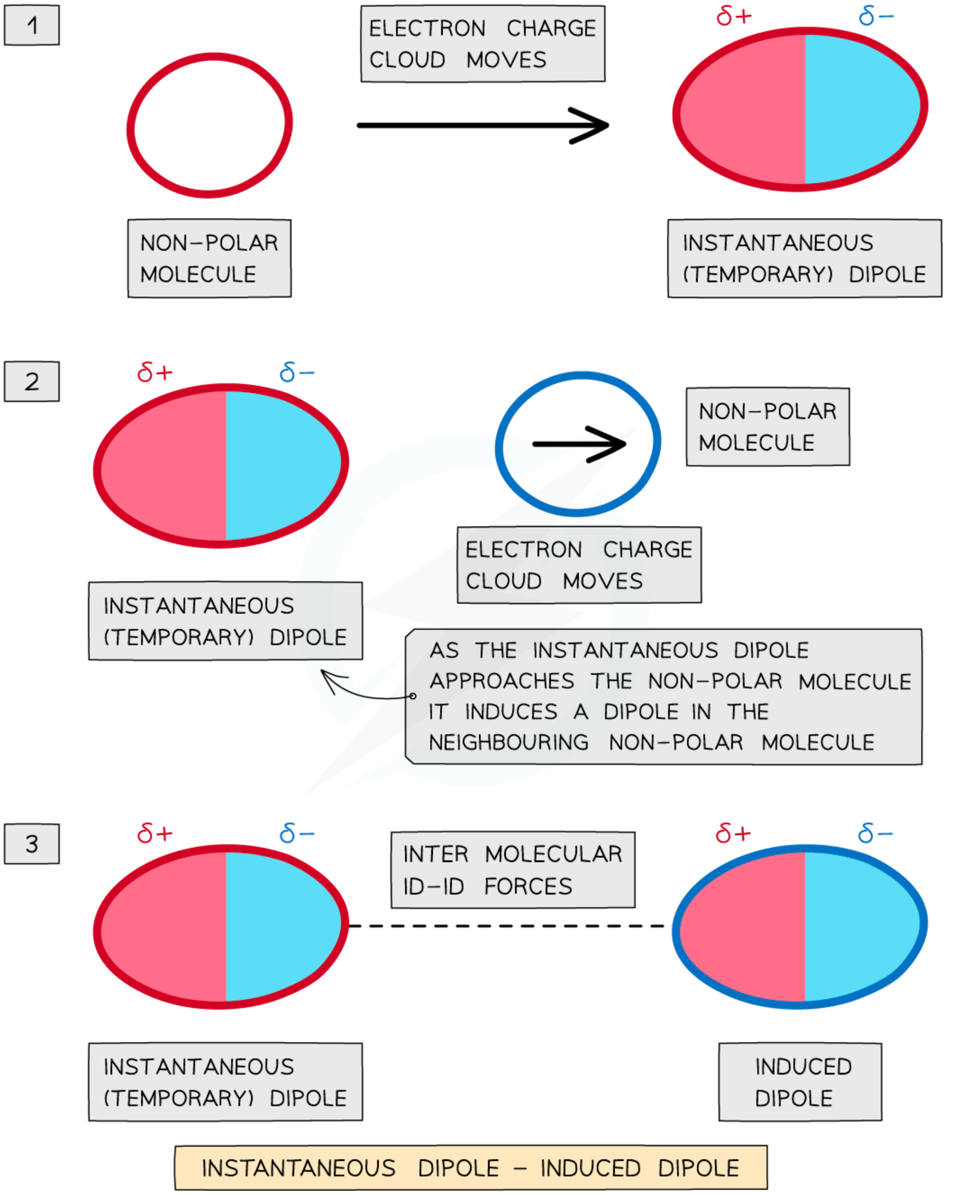


- Forces between two molecules that have permanent dipoles are called **permanent dipole – dipole forces**
- The **δ+ end of the dipole** in one molecule and the **δ- end of the dipole** in a neighbouring molecule are **attracted** towards each other

Induced Dipole-Dipole Forces

Induced dipole-dipole forces:

- **Induced dipole - dipole forces** exist between all atoms or molecules
  - They are also known as **van der Waals forces** or **London dispersion forces**

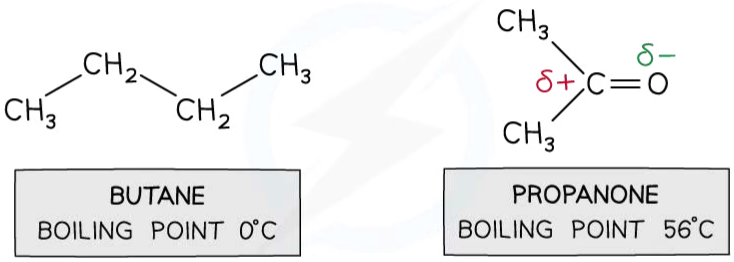


- The **electron charge cloud** in non-polar molecules or atoms are constantly moving
- During this movement, the electron charge cloud can be more on one side of the atom or molecule than the other
- This causes a **temporary dipole** to arise
- This **temporary dipole** can **induce** a dipole on neighbouring molecules
- When this happens, the **δ+ end of the dipole** in one molecule and the **δ- end of the dipole** in a neighbouring molecule are **attracted** towards each other

- Because the electron clouds are moving constantly, the dipoles are only **temporary**

Relative strength

- For small molecules with **the same number of electrons,** permanent dipoles are **stronger** than induced dipoles
    - Butane and propanone have the same number of electrons
    - Butane is a nonpolar molecule and will have induced dipole forces
    - Propanone is a polar molecule and will have permanent dipole forces
    - Therefore, more energy is required to break the intermolecular forces between propanone molecules than between butane molecules
    - So, propanone has a higher boiling point than butane



Pd–pd forces are stronger than id–id forces in smaller molecules with an equal number of electrons

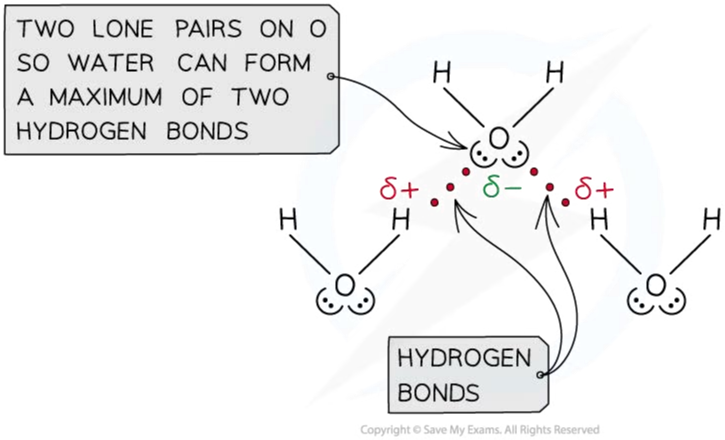
Exam Tip

Remember this difference: intramolecular forces are forces **within** a molecule, whereas intermolecular forces are forces **between** a molecule.

Hydrogen Bonds

Hydrogen bonding

- **Hydrogen bonding** is the **strongest** form of **intermolecular bonding**
  - Intermolecular bonds are bonds **between** molecules
  - Hydrogen bonding is a type of **permanent dipole – permanent dipole** bonding
- For hydrogen bonding to take place the following is needed:
  - A species which has an **O, N or F** (very **electronegative**) atom bonded to a hydrogen
- When hydrogen is covalently bonded to an **O**, **N** or **F**, the bond becomes highly **polarised**
- The H becomes so **δ$^+$** charged that it can form a bond with the **lone pair** of an **O**, **N or F** atom in another molecule
- For example, in water
  - Water can form two hydrogen bonds, because the O has two lone pairs



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Hydrogen bonding in water

Exam Tip

Make sure to use a **dashed, straight line** when drawing your intermolecular forces!Hydrogen bonds should **start at the lone pair** and go **right up to the delta positive atom** – it must be really clear where your H bond starts and ends.

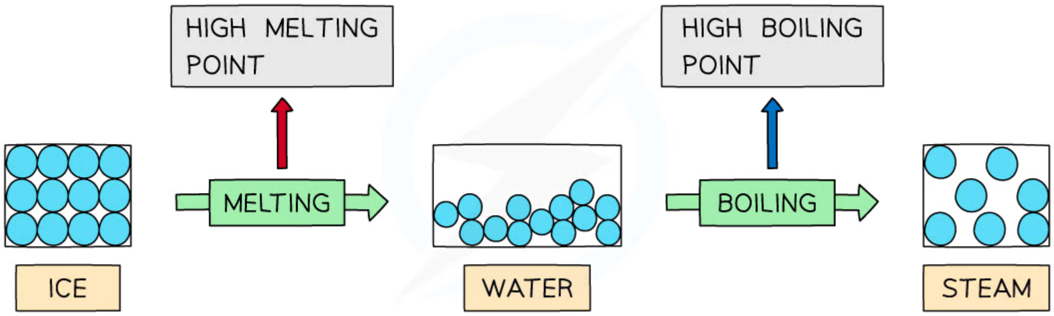
Influence of Intermolecular Forces

Properties of water

- Hydrogen bonding in water, causes it to have **anomalous properties** such as high melting and boiling points, high surface tension and a higher density in the liquid than the solid

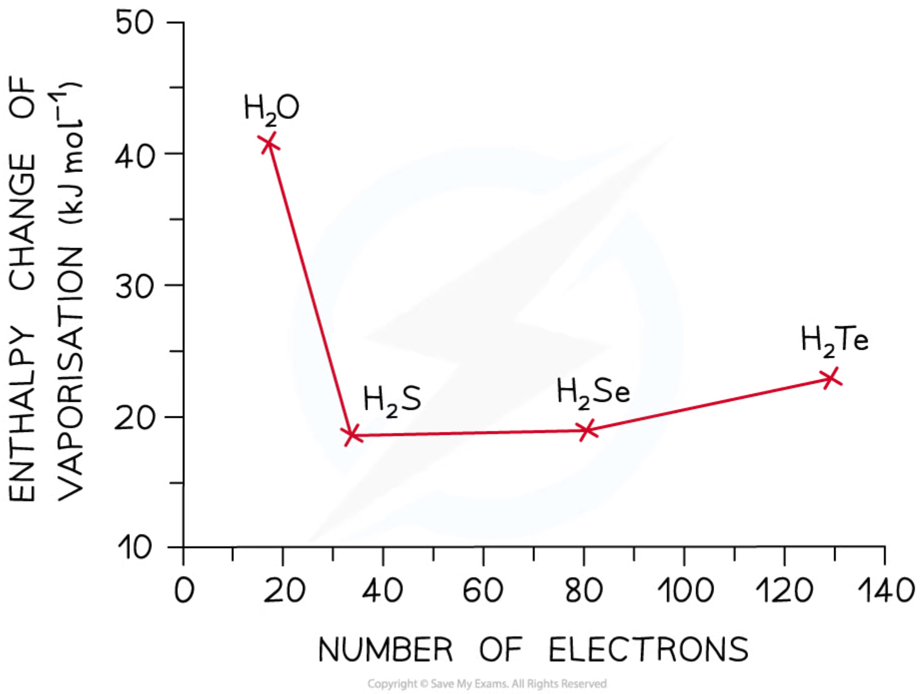
High melting & boiling points

- Water has high **melting** and **boiling points** due to the the **strong intermolecular forces** of hydrogen bonding between the molecules in both ice (solid H_2O) and water (liquid H_2O)
- A lot of energy is therefore required to separate the water molecules and melt or boil them



Hydrogen bonds are strong intermolecular forces which are harder to break causing water to have a higher melting and boiling point than would be expected for a molecule of such a small size

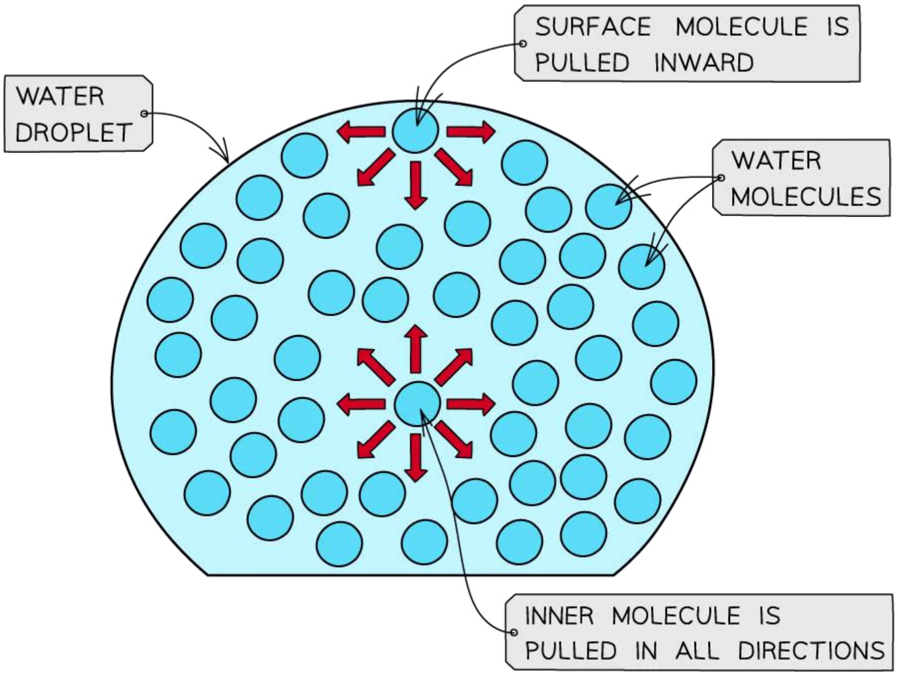
- The graph below compares the **enthalpy of vaporisation** (energy required to boil a substance) of different hydrides
- The enthalpy changes **increase** going from H_2S to H_2Te due to the increased number of electrons in the Group 16 elements
- This causes an increase in the **instantaneous dipole - induced dipole forces (dispersion forces)** as the molecules become larger
- Based on this, H_2O should have a much lower enthalpy change (around 17 kJ mol^{-1})
- However, the enthalpy change of vaporisation is almost 3 times **larger** which is caused by the **hydrogen bonds** present in water but not in the other hydrides



The high enthalpy change of evaporation of water suggests that instantaneous dipole–induced dipole forces are not the only forces present in the molecule – there are also strong hydrogen bonds, which cause the high boiling point

High surface tension

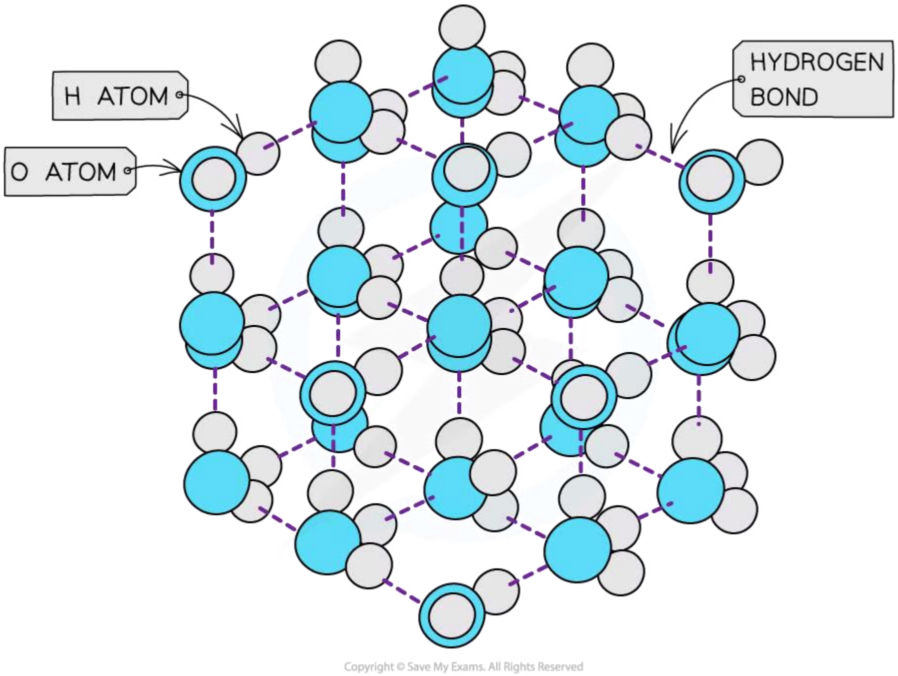
- Water has a **high surface tension**
- **Surface tension** is the ability of a **liquid surface** to resist any **external forces** (i.e. to stay unaffected by forces acting on the surface)
- The water molecules at the **surface** of liquid are bonded to other water molecules through **hydrogen bonds**
- These molecules **pull downwards** the **surface molecules** causing the surface of them to become compressed and more tightly together at the surface
- This increases water’s **surface tension**



The surface molecules are pulled downwards due to the hydrogen bonds with other molecules, whereas the inner water molecules are pulled in all directions

Density

- **Solids** are **denser** than their **liquids** as the particles in solids are more **closely packed** together than in their liquid state
- The water molecules are packed into an open lattice
- This way of packing the molecules and the relatively long **bond lengths** of the hydrogen bonds means that the water molecules are slightly further apart than in the liquid form
- Therefore, ice has a lower density than liquid water by about 9%



The 'more open' structure of molecules in ice causes it to have a lower density than liquid water

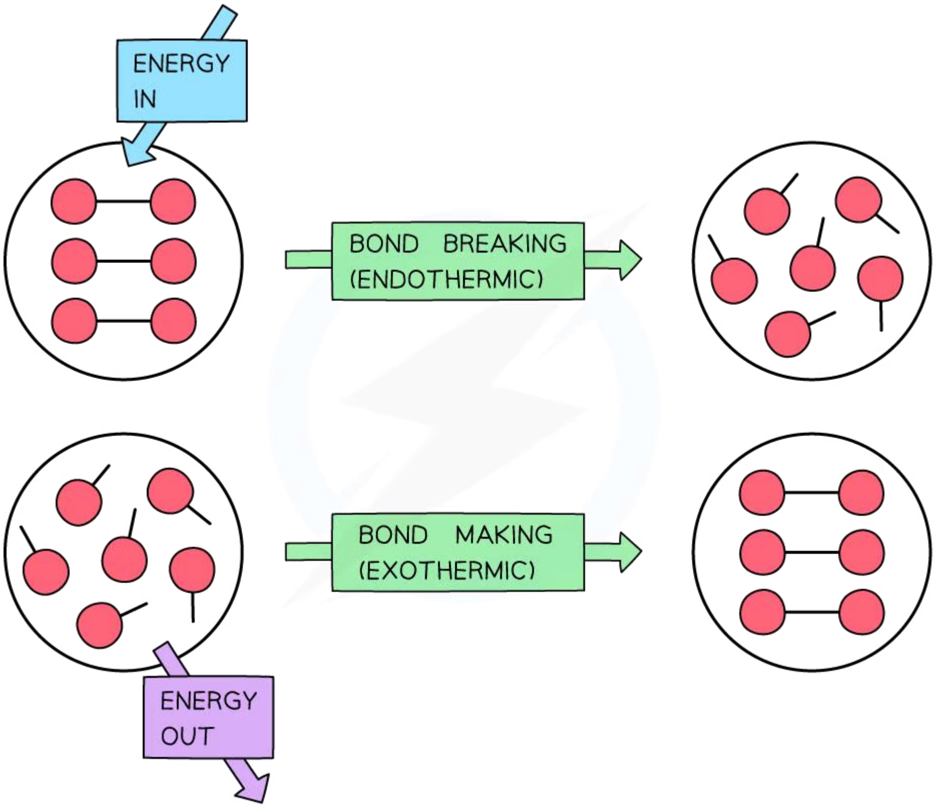
Exam Tip

Ice floats on water because of ice's lower density.

1.6.1 Bond Energy

Bond Energy

- During a reaction, enthalpy changes take place because bonds are being broken and formed
- Energy (in the form of heat) is needed to overcome attractive forces between atoms
- **Bond breaking** is therefore **endothermic**
- Energy is released from the reaction to the surroundings (in the form of heat) when new bonds are formed
- **Bond forming** is therefore **exothermic**



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To break bonds energy is required from the surroundings and to make new bonds energy is released from the reaction to the surroundings

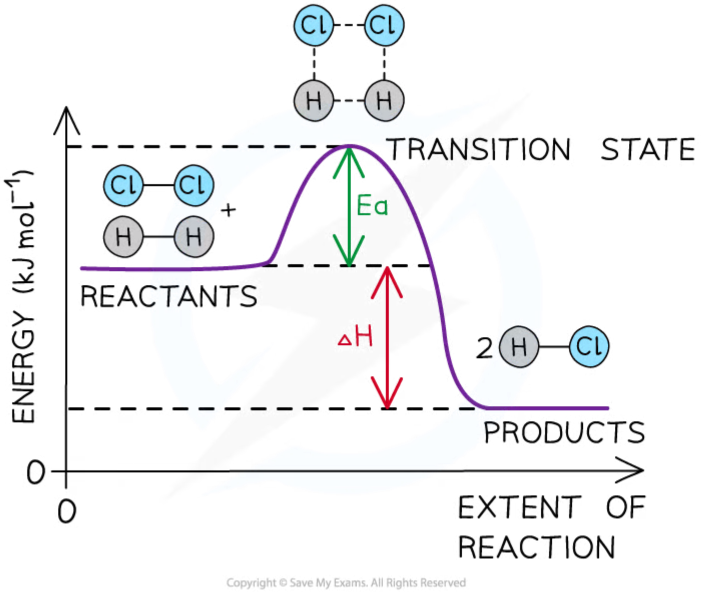
- The sum of the energy in and energy out determines whether the reaction is overall **exothermic** or **endothermic**
- If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is **endothermic**
- If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is **exothermic**

- In reality, only some bonds in the reactants are broken and then new ones are formed

YOUR NOTES
↓

Energy Level Diagrams

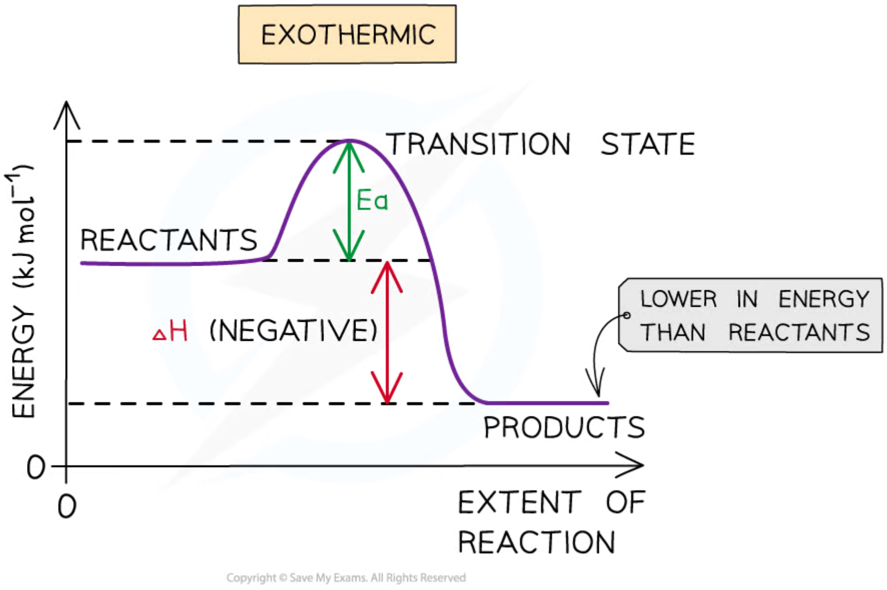
- An energy level diagram is a diagram that shows the energies of the reactants, the transition state(s) and the products of the reaction as the reaction proceeds (called 'extent of the reaction' below)
- The **transition state** is a stage during the reaction at which chemical bonds are partially broken and formed
- The transition state is very unstable – a molecule in the transition state cannot be isolated and is higher in energy than the reactants and products
- The **activation energy (E_a)** is the energy needed to reach the transition state
- We can define the **activation energy** as '*the minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction*'



The energy level diagram for the reaction of hydrogen with chlorine to form hydrogen chloride gas

Exothermic reaction

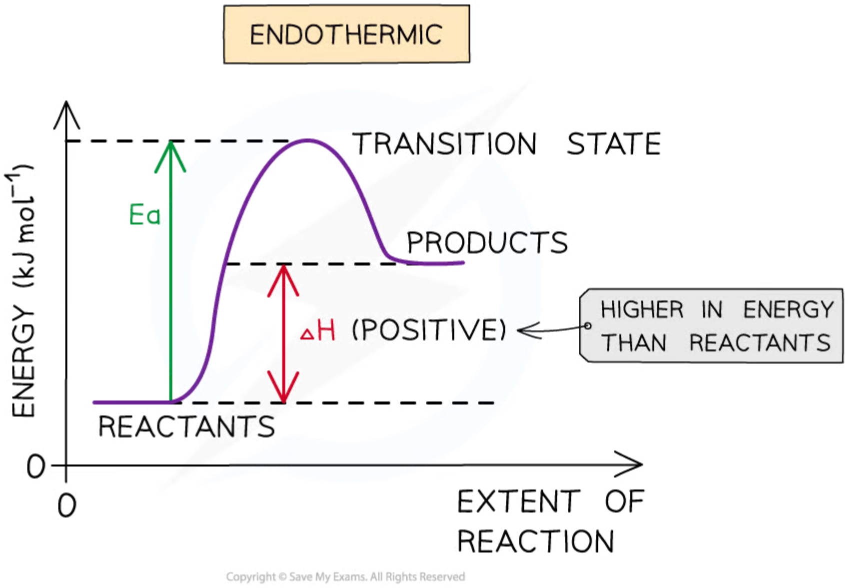
- In an exothermic reaction, the reactants are higher in energy than the products
- The reactants are therefore closer in energy to the transition state
- This means that exothermic reactions have a lower activation energy compared to endothermic reactions



***The energy level diagram for exothermic reactions. ΔH* is negative because the system (reactants) loses energy to the surroundings.**

Endothermic reaction

- In an endothermic reaction, the reactants are lower in energy than the products
- The reactants are therefore further away in energy to the transition state
- This means that endothermic reactions have a higher activation energy compared to exothermic reactions



The energy level diagram for endothermic reactions. The system (reactant substances) have gained energy so ΔH is positive.

YOUR NOTES
↓

Worked Example

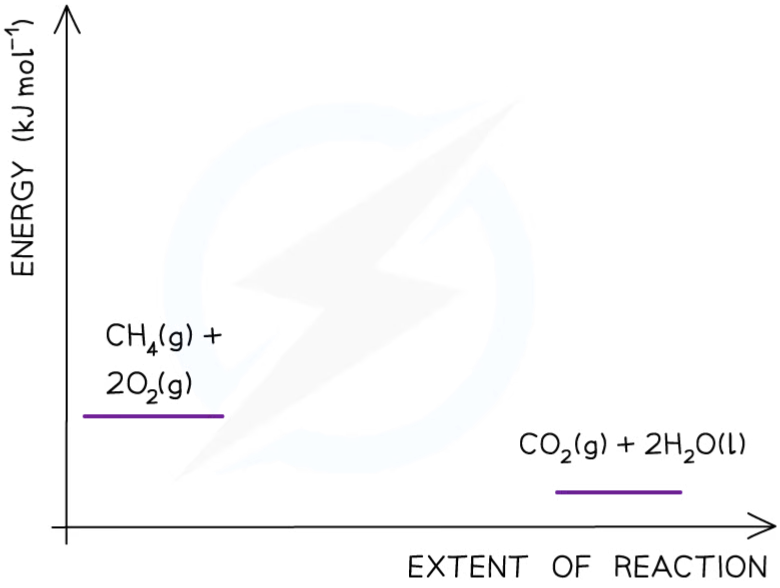
Drawing energy level diagrams of the combustion of methane The E_a and ∆H for the complete combustion of methane are +2653 kJ mol^{-1} and –890 kJ mol^{-1} respectively. Draw the energy level diagram for this reaction.

Answer

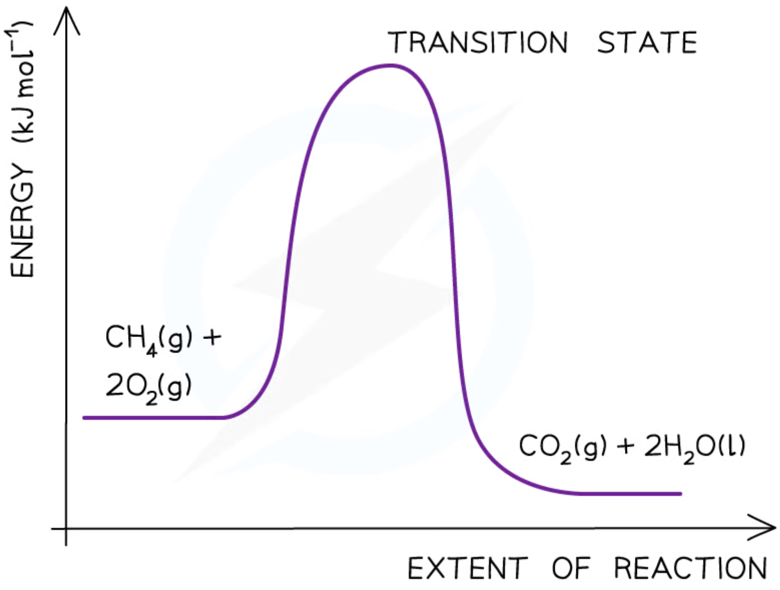
Step 1: The chemical equation for the complete combustion of methane is:

$$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$$

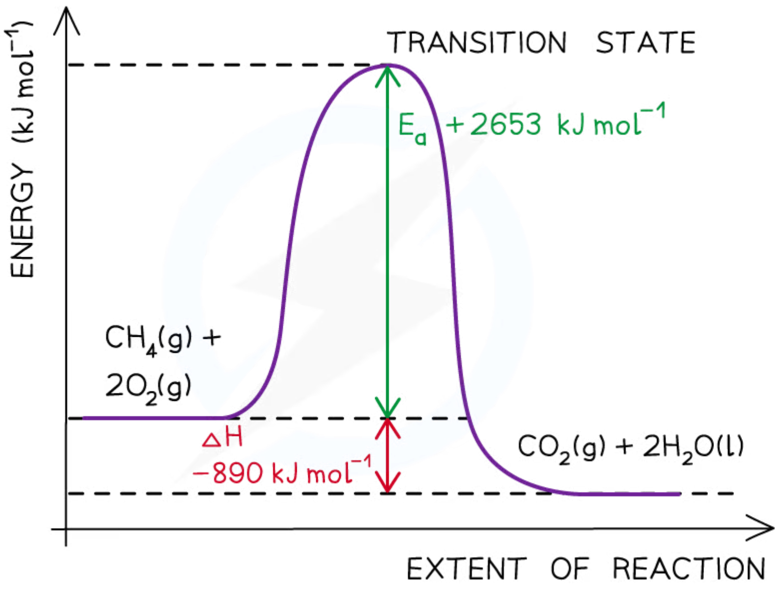
Step 2: Combustion reactions are always exothermic (∆*H* is negative) so the reactants should be drawn higher in energy than the products



Step 3: Draw the curve in the energy level diagram clearly showing the transition state



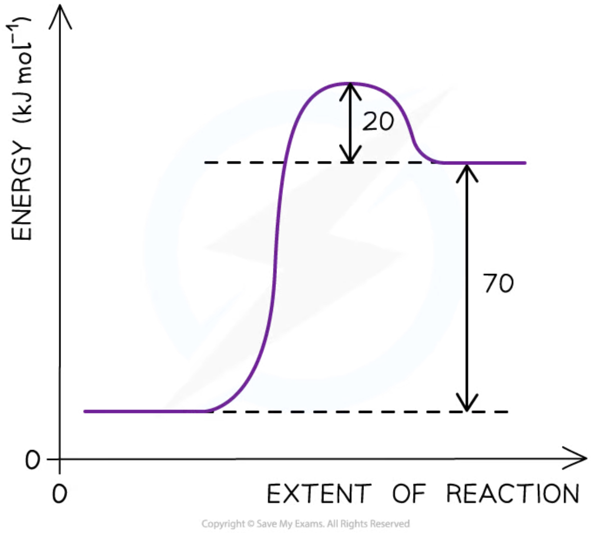
Step 4: Draw arrows to show the E_a and ΔH including their values



YOUR NOTES
↓

Worked Example

Determining the activation energyΔH for a reaction is +70 kJ mol^{-1} and E$_a$ for the reverse reaction is +20 kJmol^{-1}. Use the reaction pathway diagram below to determine the E$_a$ for the forward reaction.



The reaction pathway diagram for a reversible reaction

Answer

- The E_a is the energy difference from the energy level of the reactants to the top of the 'hump'
- E_a (forward reaction) = (+70 kJ mol^{-1}) + (+ 20 kJ mol^{-1}) = **+90 kJ mol^{-1}**

Exam Tip

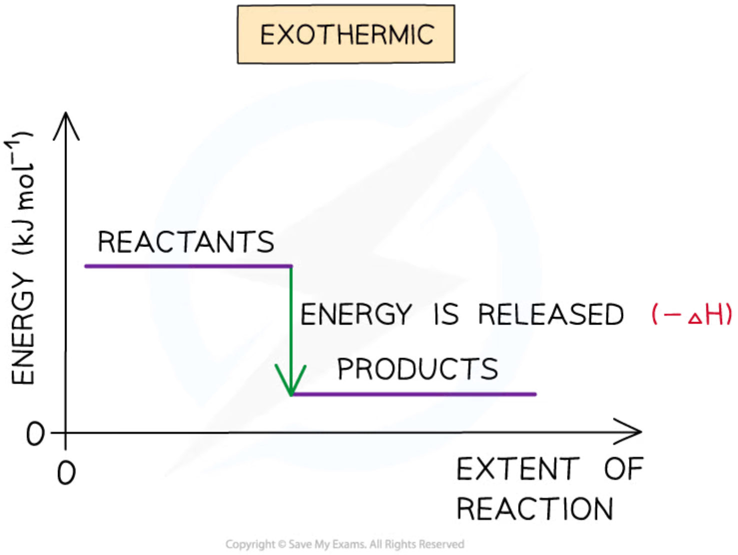
The activation energy is the energy difference from **reactants** to **transition state.** The enthalpy change of the reaction is the energy difference from **reactants** to **products.** Remember to label the axis of the energy level diagrams!

Enthalpy Changes

- The total chemical energy inside a substance is called the **enthalpy** (or heat content)
- When chemical reactions take place, changes in chemical energy take place and therefore the enthalpy changes
- An **enthalpy change** is represented by the symbol ΔH (Δ= change; H = enthalpy)
- An enthalpy change can be positive or negative

Exothermic reactions

- A reaction is exothermic when the products have less energy than the reactants
- Heat energy is **given off** by the reaction **to the surroundings**
    - The **temperature** of the **environment increases** – this can be measured with a thermometer
    - The **energy** of the **system decreases**
- There is an enthalpy decrease during the reaction so ΔH is negative
- Exothermic reactions are **thermodynamically** possible (because the enthalpy of the reactants is **higher** than that of the products)
- However, if the rate is too slow, the reaction may not occur
    - In this case the reaction is **kinetically** controlled

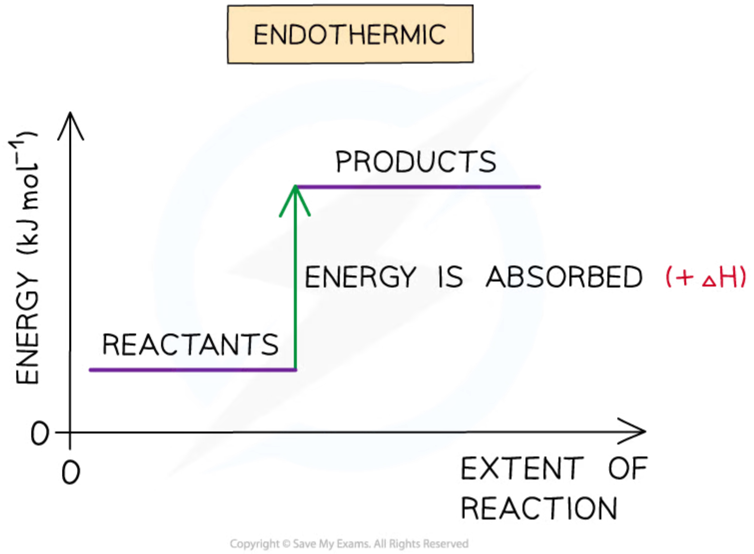


The enthalpy change during an exothermic reaction

Endothermic reactions

- A reaction is endothermic when the products have more energy than the reactants
- Heat energy is **absorbed by** the reaction **from** the **surroundings**
    - The **temperature** of the **environment decreases** – this can be measured with a thermometer

  - The **energy** of the **system increases**
- There is an enthalpy increase during the reaction so ΔH is positive



The enthalpy change during an endothermic reaction

Exam Tip

It is important to specify the physical states of each species in an equation when dealing with enthalpy changes as any changes in state can cause very large changes of enthalpy. For example:

$$\mathbf{NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)\ \Delta \mathit{H} = +4\ kJ\ mol^{-1}}$$

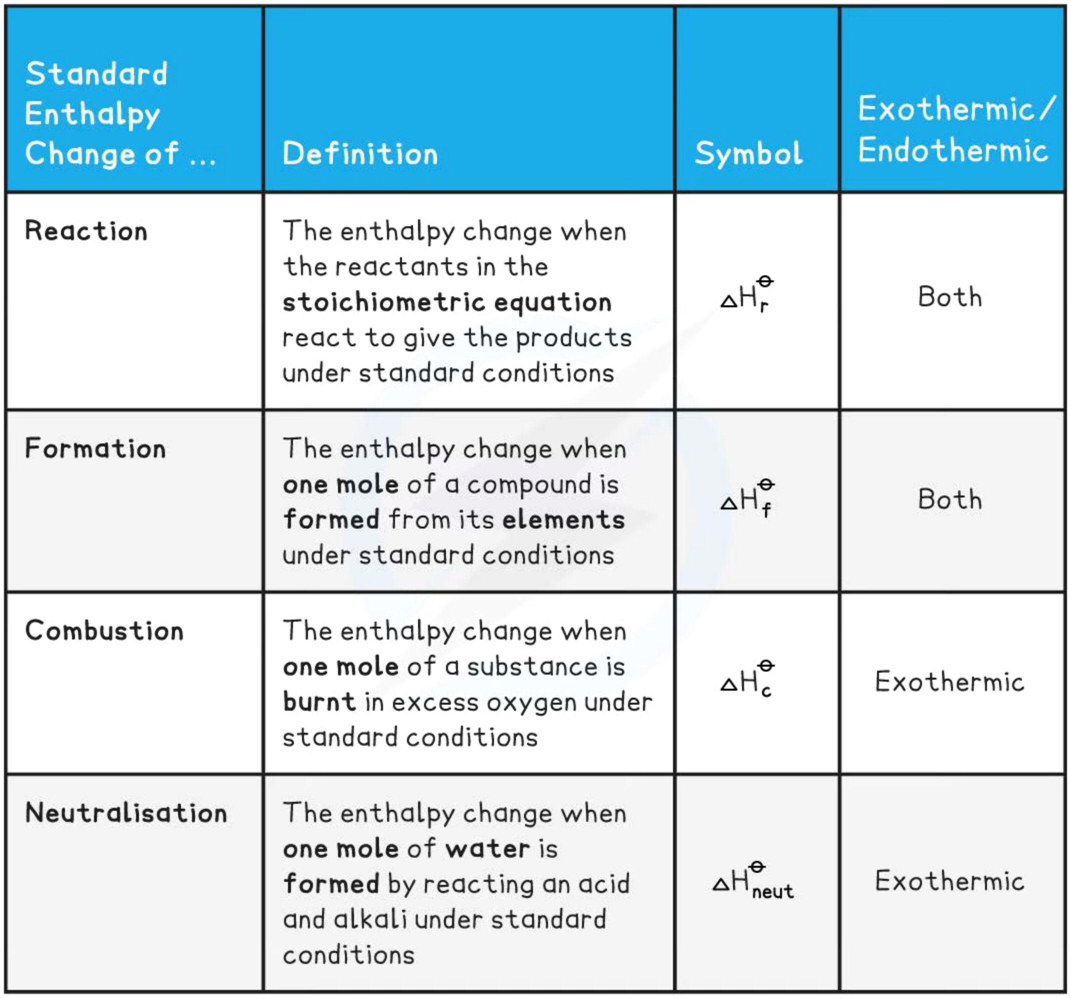
$$\mathbf{NaCl\ (g) \rightarrow Na^+\ (g) + Cl^-\ (g)\ \ \Delta \mathit{H} = +500\ kJ\ mol^{-1}}$$

Also, remember that the **system** is the substances **that are reacting** (i.e. the reaction itself) and the **surroundings is everything else** (e.g. the flask the reaction is taking place in).

Standard Enthalpy Changes

- To be able to compare the changes in enthalpy between reactions, all thermodynamic measurements are carried out under standard conditions
- These standard conditions are:
  - A **pressure** of 100 kPa (you may see some older exam questions that use a figure of 101 kPa; the exact figure is 101 325 Pa, but it has been simplified in the current syllabus for problem-solving purposes)
  - A **temperature** of 298 K (25 °C)
  - Each substance involved in the reaction is in its **standard physical state** (solid, liquid or gas)
- To show that a reaction has been carried out under standard conditions, the symbol is used
  - ΔH = the standard enthalpy change
- There are a number of key definitions relating to enthalpy changes that you need to know

Enthalpy Definitions Table



Standard Enthalpy Change of ...	Definition	Symbol	Exothermic / Endothermic
Reaction	The enthalpy change when the reactants in the **stoichiometric equation** react to give the products under standard conditions	$\Delta H_r^{\ominus}$	Both
Formation	The enthalpy change when **one mole** of a compound is **formed** from its **elements** under standard conditions	$\Delta H_f^{\ominus}$	Both
Combustion	The enthalpy change when **one mole** of a substance is **burnt** in excess oxygen under standard conditions	$\Delta H_c^{\ominus}$	Exothermic
Neutralisation	The enthalpy change when **one mole of water** is **formed** by reacting an acid and alkali under standard conditions	$\Delta H_{neut}^{\ominus}$	Exothermic

Worked Example

Calculating the enthalpy change of reaction

One mole water is formed from hydrogen and oxygen, releasing 286 kJ of energy

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H_r = -286 \text{ kJ mol}^{-1}$$

Calculate ΔH_r for the reaction below:

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$$

Answer

- Since two moles of water molecules are formed in the question above, the energy released is simply:
- $\Delta H_r = 2 \text{ mol} \times (-286 \text{ kJ mol}^{-1}) = -572 \text{ kJ mol}^{-1}$

YOUR NOTES
↓

Worked Example

Calculating the enthalpy change

Calculate ΔH_f for the reaction below, given that ΔH_f $[Fe_2O_3(s)] = -824.2$ kJ mol^{-1}

$$4Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$$

Answer

- Since two moles of Fe_2O_3 (s) are formed the total change in enthalpy for the reaction above is:
- ΔH_f = 2 x (−824.2 kJ mol^{-1}) = − 1648 kJ

Worked Example

Calculating enthalpy changes

Identify each of the following as ΔH_r , ΔH_f , ΔH_c or ΔH_{neut}

1. $MgCO_3\,(s) \rightarrow MgO\,(s) + CO_2\,(g)$
2. $C\,(graphite) + O_2\,(g) \rightarrow CO_2\,(g)$
3. $HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$

Answer

Answer 1: ΔH_r

Answer 2: ΔH_f as one mole of CO_2 is formed from its elements in standard state *and* ΔH_c as one mole of carbon is burnt in oxygen

Answer 3: ΔH_{neut} as one mole of water is formed from the reaction between an acid and an alkali

Exam Tip

The ΔH_f of an **element** in its standard state is zero.

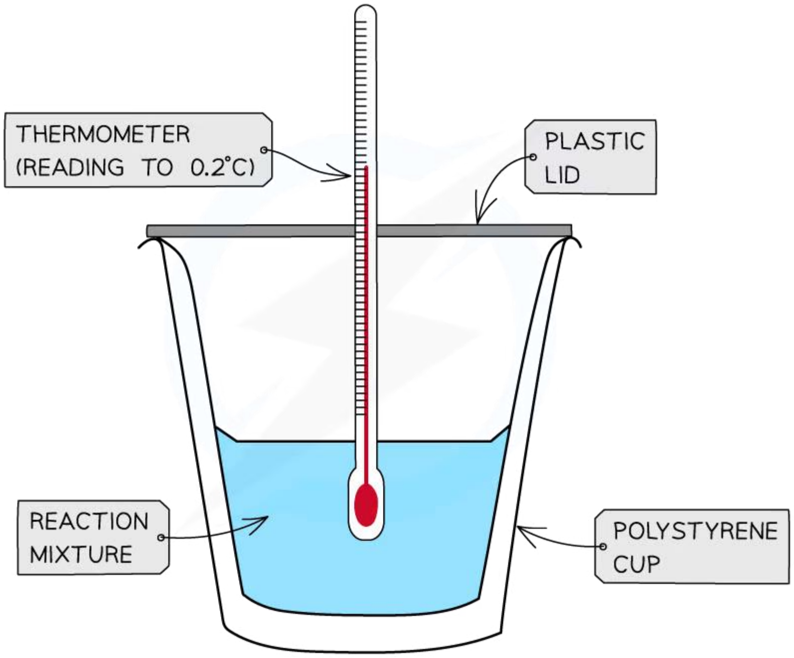
For example, ΔH_f of $O_2(g)$ is 0 kJ mol^{-1}

1.6.4 Calorimetry

Calorimetry

Measuring enthalpy changes

- **Calorimetry** is the measurement enthalpy changes in chemical reactions
- A simple **calorimeter** can be made from a **polystyrene drinking cup**, a **vacuum flask** or **metal can**



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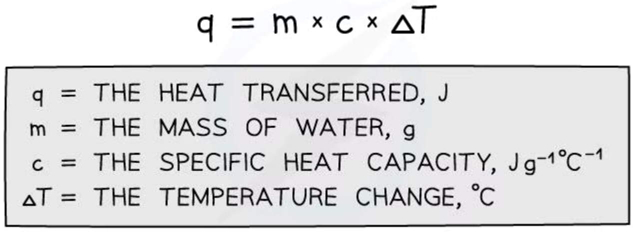
A polystyrene cup can act as a calorimeter to find enthalpy changes in a chemical reaction

- The energy needed to increase the temperature of 1 g of a substance by 1 °C is called the **specific heat capacity** (*c*) of the liquid
- The specific heat capacity of water is 4.18 J g^{-1} $^{o}C^{-1}$
- The energy transferred as heat can be calculated by:



$$q = m \times c \times \Delta T$$

q = THE HEAT TRANSFERRED, J
m = THE MASS OF WATER, g
c = THE SPECIFIC HEAT CAPACITY, $J g^{-1} {}^{\circ}C^{-1}$
ΔT = THE TEMPERATURE CHANGE, °C

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Equation for calculating energy transferred in a calorimeter

Worked Example

Specific heat capacity calculations In a calorimetry experiment 2.50 g of methane is burnt in excess oxygen. 30% of the energy released during the combustion is absorbed by 500 g of water, the temperature of which rises from 25 °C to 68 °CThe specific heat capacity of water is 4.18 J g^{-1}°C^{-1} What is the total energy released per gram of methane burnt?

Answer

Step 1: $q = m \times c \times \Delta T$

m (of water) = 500 g

c (of water) = 4.18 J g^{-1} °C^{-1}

ΔT (of water) = 68 °C – 25 °C

= 43 °C

Step 2: q = 500 x 4.18 x 43

= 89 870 J

Step 3: This is only 30% of the total energy released by methane

Total energy x 0.3 = 89 870 J

Total energy = 299 567 J

Step 4: This is released by 2.50 g of methane

Energy released by 1.00 g of methane = 299 567 ÷ 2.50

= 119 827 J = 120 000 J

= **120 kJ g^{-1}**

Exam Tip

When new bonds are formed the amount of energy released is equal to the amount of energy absorbed when the same bonds are broken.For example:**O_2 (g) → 2O (g) *E* (O=O) = +498 kJ mol^{-1}2O (g) → O_2 (g) *E* (O=O) = -498 kJ mol^{-1}** Aqueous solutions of acid, alkalis and salts are assumed to be largely water so you can just use the *m* and *c* values of water when calculating the energy transferred. To calculate any changes in enthalpy per mole of a reactant or product the following relationship can be used:

$$\Delta H = -m \times c \times \Delta T$$

When there is a rise in temperature, the value for ΔH becomes negative suggesting that the reaction is exothermic and when the temperature falls, the value for ΔH becomes positive suggesting that the reaction is endothermic.

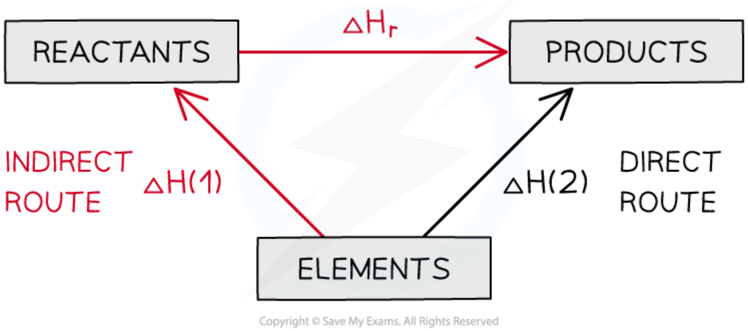
Using Hess' Law

Calculating ΔH_r from ΔH_f using Hess's Law energy cycles

- The products can be directly formed from the elements = **ΔH_2**

OR

- The products can be indirectly formed from the elements = **ΔH_1 + ΔH_r**



The enthalpy change from elements to products (direct route) is equal to the enthalpy change of elements forming reactants and then products (indirect route)

- **Equation**

$$\Delta H_2 = \Delta H_1 + \Delta H_r$$

Therefore,

$$\Delta H_r = \Delta H_2 - \Delta H_1$$

Worked Example

Calculating the enthalpy change of reaction

Calculate the ΔHf for the following reaction:

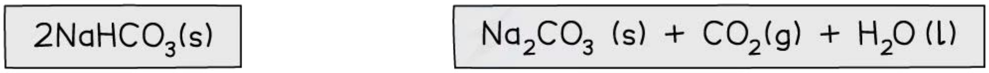
$2NaHCO_3$ (s) → Na_2CO_3 (s) + CO_2 (g) + O(l)

The table below shows the standard enthalpy of formations (ΔHf) relevant to this reaction:

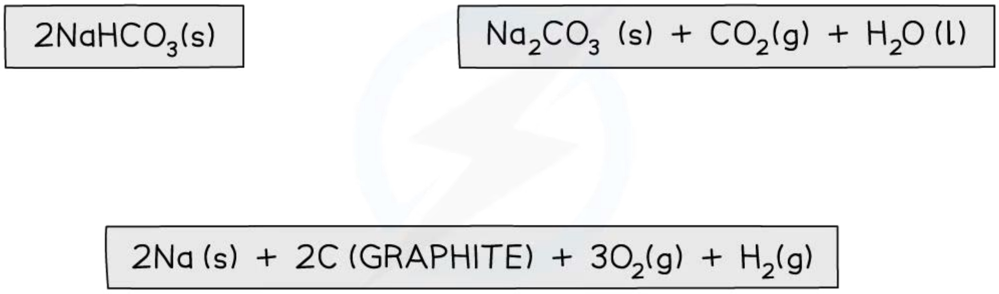
Molecule	ΔHf (kJ mol^{-1})
$NaHCO_3$(s)	−950.8
Na_2CO_3 (s)	−1130.7
CO_2(g)	−393.5
H_2O (l)	−285.8

Answer

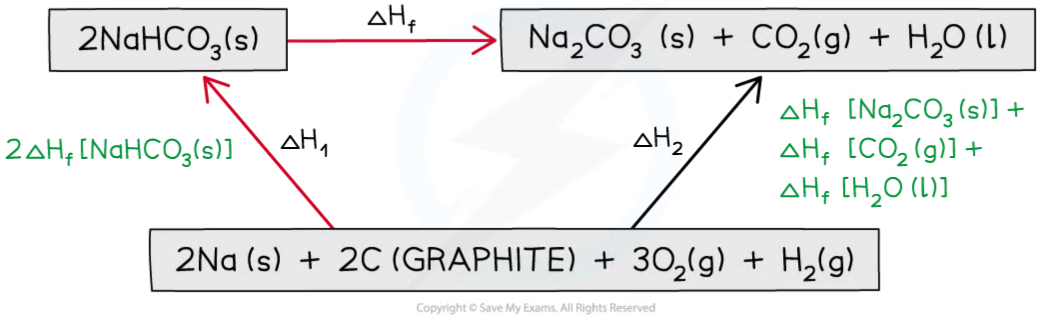
Step 1: Write the balanced equation at the top



Step 2: Draw the cycle with the elements at the bottom



Step 3: Draw in all arrows, making sure they go in the correct directions. Write the standard enthalpy of formations



Step 4: Apply Hess's Law

$\Delta H_r = \Delta H_2 - \Delta H_1$

$= (\Delta H_f\,[Na_2CO_3\,(s)] + \Delta H_f\,[CO_2\,(g)] + \Delta H_f\,[H_2O\,(l)]) - 2\Delta H_f\,[NaHCO_3\,(s)]$

$= ((-1130.7) + (-393.5) + (-285.8)) - 2(-950.8)$

$= +91.6$ kJ mol^{-1}

Calculating average bond energies using Hess's cycles

- Bond energies cannot be found directly so enthalpy cycles are used to find the **average bond energy**
- This can be done using enthalpy changes of **atomisation** and **combustion** or **formation**
- The **enthalpy change of atomisation** (ΔH_{at}) is the enthalpy change when **one mole of gaseous** atoms is **formed** from its elements under standard conditions.
  - Eg. ΔH_{at} [H_2] relates to the equation:

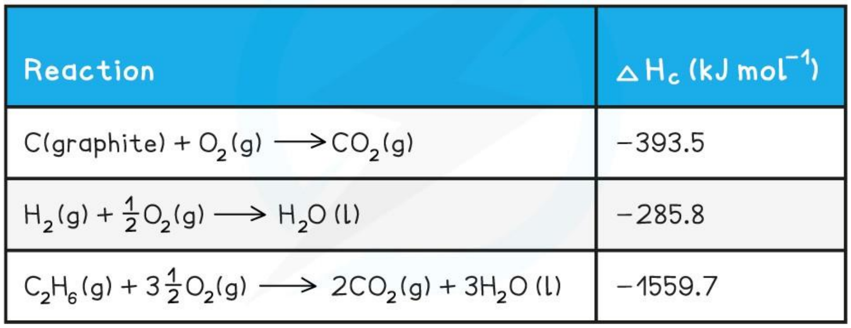
$$\frac{1}{2}\,H_2(g) \rightarrow H(g)$$

Hess' Law Calculations

- You must make sure that you can apply Hess' Law effectively and calculate enthalpy changes in different situations
- Remember – it is the data that is important
- Check whether the data you have been given is formation data or combustion data, and then complete the cycle or calculation according to that

Worked Example

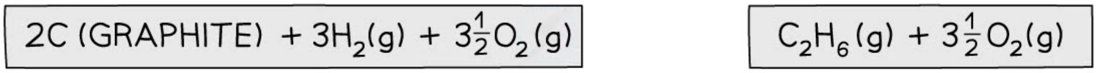
Calculating the enthalpy change of formation of ethane Calculate ∆Hf [ethane]. The relevant change in standard enthalpy of combustion (∆Hc) values are shown in the table below:



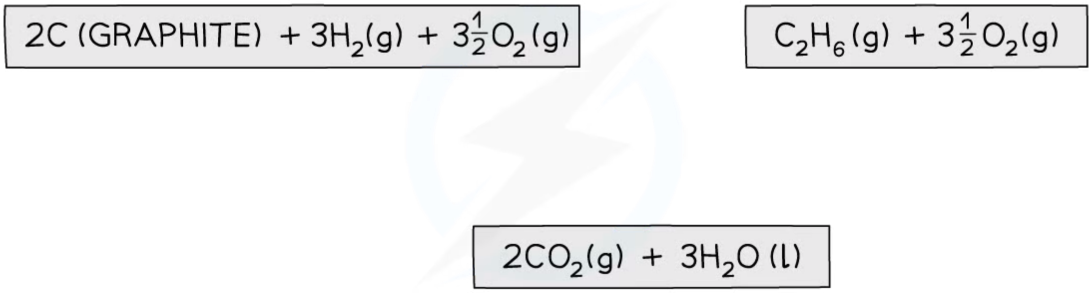
Reaction	ΔH_c (kJ mol^{-1})
$C(graphite) + O_2(g) \longrightarrow CO_2(g)$	−393.5
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
$C_2H_6(g) + 3\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1559.7

Answer

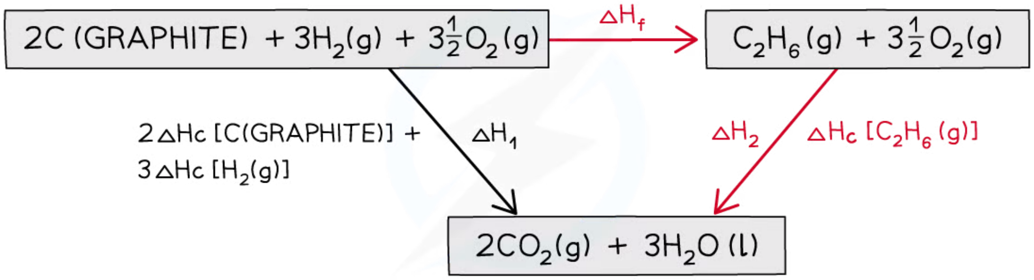
Step 1: Write the equation for enthalpy change of formation at the top and add oxygen on both sides



Step 2: Draw the cycle with the combustion products at the bottom



Step 3: Draw all arrows in the correct direction



Step 4: Apply Hess's Law

$$\Delta H_f = \Delta H_1 - \Delta H_2$$

$$= 2(-393.5) + 3(-285.8)) - (-1559.7)$$

$$= -84.7\ kJ\ mol^{-1}$$

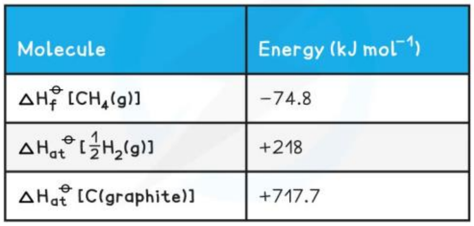
Calculating average bond energies using Hess's cycles

- Bond energies cannot be found directly so enthalpy cycles are used to find the **average bond energy**
- This can be done using enthalpy changes of **atomisation** and **combustion** or **formation**
- The **enthalpy change of atomisation** (ΔH_{at}) is the enthalpy change when **one mole of gaseous** atoms is **formed** from its elements under standard conditions.
    - Eg. ΔH_{at} [H_2] relates to the equation:

$\frac{1}{2}H_2(g) \rightarrow H(g)$

Worked Example

Calculating average C-H bond energy Calculate the average bond energy of the C–H bond using the relevant ΔH_f and ΔH_{at} values in the table below:

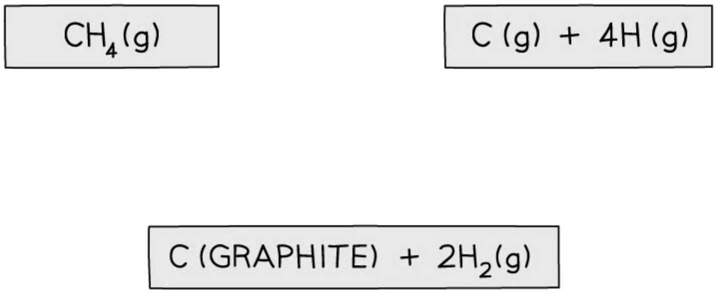


Molecule	Energy (kJ mol^{-1})
$\Delta H_f^{\ominus}[CH_4(g)]$	−74.8
$\Delta H_{at}^{\ominus}[\frac{1}{2}H_2(g)]$	+218
$\Delta H_{at}^{\ominus}[C(graphite)]$	+717.7

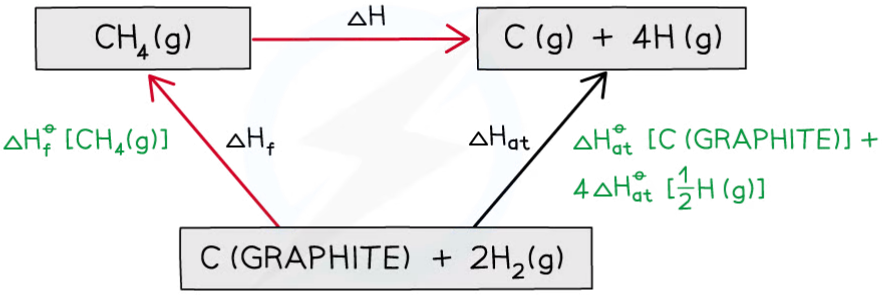
Answer

Step 1: Write down the equation for the dissociation of methane at the top

Step 2: Write down the elements at the bottom



Step 3: Draw all arrows in the correct direction



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Step 4: Apply Hess's Law

$$\mathbf{\Delta H} = \Delta H_{at}^\ominus \quad - \quad \Delta H_f^\ominus$$

$$= ((+717.7) + 4(+218) \quad - \quad (-74.8)$$

$$= +1664.5\text{kJ mol}^{-1}$$

Step 5: Since there are 4 C–H bonds in methane:

$$\text{Average bond energy (C-H)} = \frac{+1664.5}{4}$$

$$= +416.1\text{ kJ mol}^{-1}$$

Exam Tip

Remember to take into account the number of moles of each reactant and product.For example, there are two moles of $NaHCO_3(s)$ so the ΔH_f value is multiplied by 2.

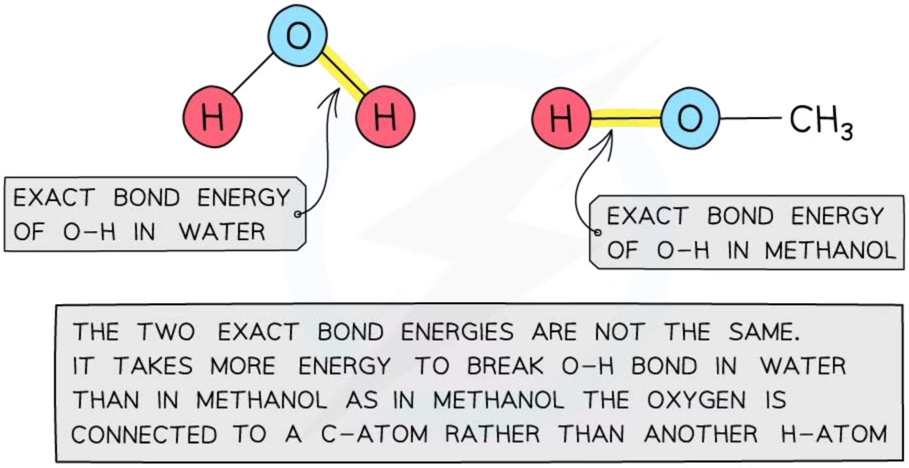
1.6.7 Bond Enthalpies

Bond Enthalpies

- The amount of energy required to break one mole of a **specific** covalent bond in the gas phase is called the bond dissociation energy
- Bond dissociation energy (*E*) is usually just simplified to **bond energy** or **bond enthalpy**
- In symbols, the type of bond broken is written in brackets after *E*
    - Eg. *E* (H–H) is the bond energy of a mole of single bonds between two hydrogen atoms

Average bond energy

- Bond energies are affected by other atoms in the molecule (the environment)
- Therefore, an average of a number of the **same type of bond** but in different environments is calculated
- This bond energy is known as the **average bond energy**
- Since bond energies cannot be determined directly, **enthalpy cycles** are used to calculate the average bond energy



THE TWO EXACT BOND ENERGIES ARE NOT THE SAME. IT TAKES MORE ENERGY TO BREAK O–H BOND IN WATER THAN IN METHANOL AS IN METHANOL THE OXYGEN IS CONNECTED TO A C-ATOM RATHER THAN ANOTHER H-ATOM

Bond energies are affected by other atoms in the molecule, so average bond enthalpies are listed in data tables

Calculating enthalpy change from bond energies

- Bond energies are used to find the ΔH_r of a reaction when this cannot be done experimentally
- The formula is:

$$\Delta H_r^{\ominus} = \text{ENTHALPY CHANGE FOR BONDS BROKEN} + \text{ENTHALPY CHANGE FOR BONDS FORMED}$$

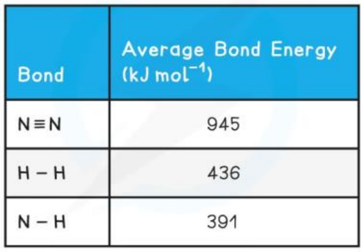
The formula for calculating the standard enthalpy change of reaction using bond energies

Worked Example

Calculating the enthalpy change in the Haber process Calculate the change in enthalpy of reaction for the Haber process, producing ammonia from hydrogen and nitrogen:

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

The relevant bond energies are given in the table below:

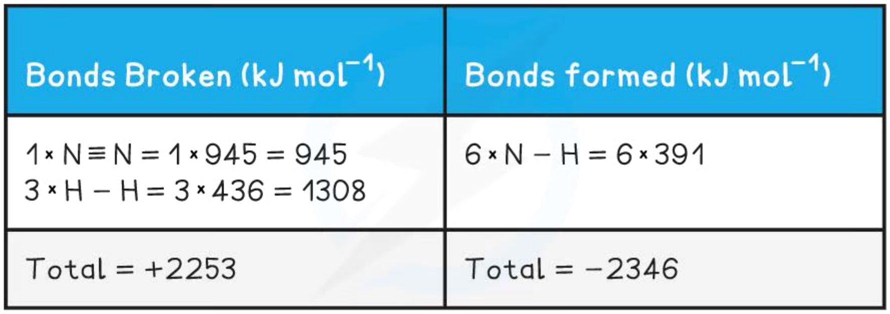


Bond	Average Bond Energy (kJ mol^{-1})
N≡N	945
H – H	436
N – H	391

Answer

Step 1: Use the equation to work out the bonds broken and formed and set out the calculation as a balance sheet as shown below:

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$



Bonds Broken (kJ mol^{-1})	Bonds formed (kJ mol^{-1})
1 × N≡N = 1 × 945 = 945 3 × H – H = 3 × 436 = 1308	6 × N – H = 6 × 391
Total = +2253	Total = –2346

Note! Values for bonds broken are positive (endothermic) and values for bonds formed are negative (exothermic)

Step 2: Calculate the standard enthalpy of reaction

$\Delta H_r^{\square}$ = enthalpy change for bonds broken + enthalpy change for bonds formed

$= (+2253\ \text{kJ mol}^{-1}) + (-2346\ \text{kJ mol}^{-1})$

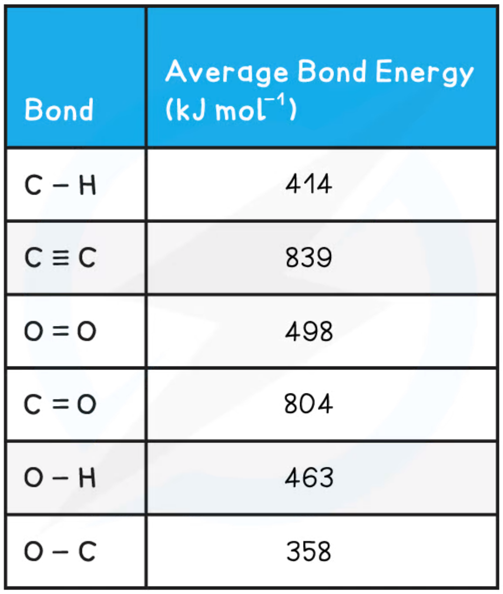
$= -93\ \text{kJ mol}^{-1}$

Worked Example

Calculating the enthalpy of combustion using bond enthalpies The complete combustion of ethyne, C_2H_2, is shown in the equation below:

2H-C≡C-H + 5O=O → 2H-O-H + 4O=C=O

Using the average bond enthalpies given in the table, what is the enthalpy of combustion of ethyne?



Bond	Average Bond Energy (kJ mol^{-1})
C – H	414
C ≡ C	839
O = O	498
C = O	804
O – H	463
O – C	358

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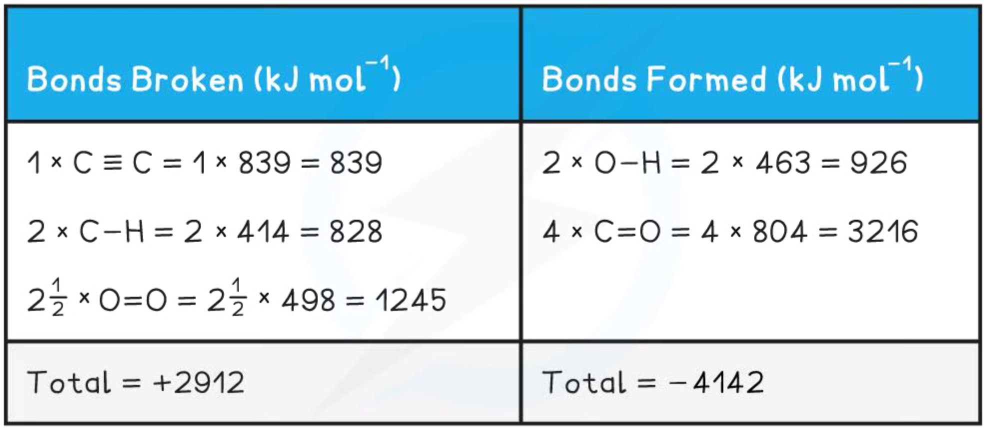
Answer

Step 1: The enthalpy of combustion is the enthalpy change when **one mole** of a substance reacts in excess oxygen to produce water and carbon dioxide

The chemical reaction should be therefore simplified such that only **one mole** of **ethyne** reacts in excess oxygen:

H-C≡C-H + 2 ½ O=O → H-O-H + 2O=C=O

Step 2: Set out the calculation as a balance sheet as shown below:



Bonds Broken (kJ mol^{-1})	Bonds Formed (kJ mol^{-1})
$1 \times C \equiv C = 1 \times 839 = 839$ $2 \times C{-}H = 2 \times 414 = 828$ $2\frac{1}{2} \times O{=}O = 2\frac{1}{2} \times 498 = 1245$	$2 \times O{-}H = 2 \times 463 = 926$ $4 \times C{=}O = 4 \times 804 = 3216$
Total = +2912	Total = −4142

$\Delta H_r^{\square}$ = enthalpy change for bonds broken + enthalpy change for bonds formed

$= (+2912 \text{ kJ mol}^{-1}) + (-4142 \text{ kJ mol}^{-1})$

$= -1230 \text{ kJ mol}^{-1}$

1.7 Kinetics

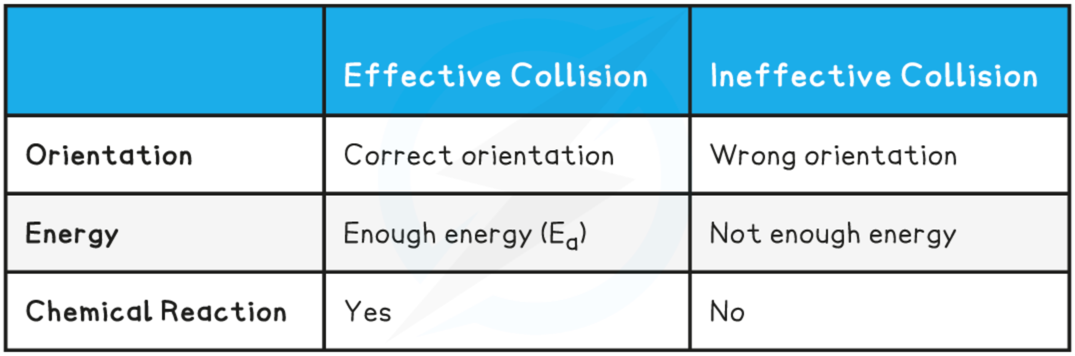
1.7.1 Collision Theory

Collision Theory

Collision theory

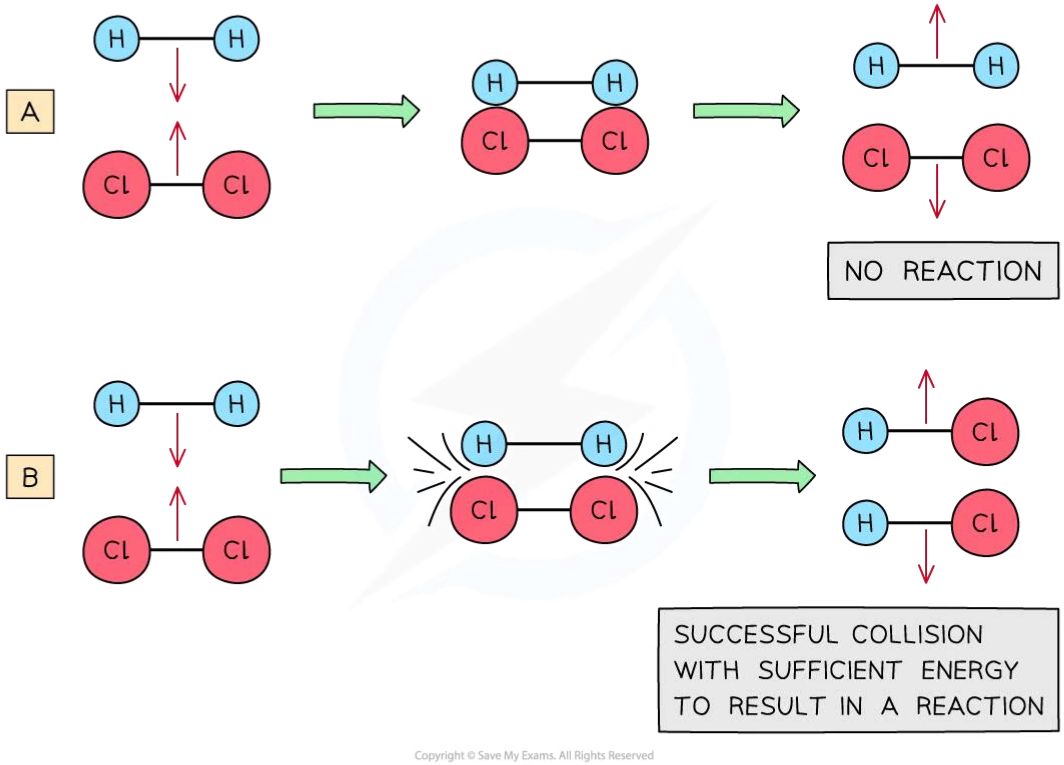
- The **collision theory** states that for a chemical reaction to take place the particles need to **collide** with each other in the correct **orientation** and with enough **energy**

Collision Theory Table



	Effective Collision	Ineffective Collision
Orientation	Correct orientation	Wrong orientation
Energy	Enough energy (E_a)	Not enough energy
Chemical Reaction	Yes	No

- An **ineffective collision** is when particles collide in the wrong orientation or when they don't have enough energy and **bounce off** each other without causing a chemical reaction



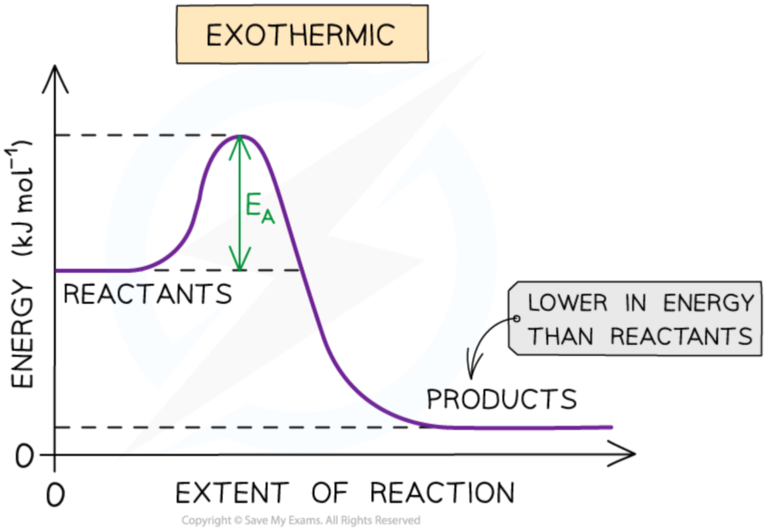
(a) shows an ineffective collision due to the particles not having enough energy whereas (b) shows an effective collision where the particles have the correct orientation and enough energy for a chemical reaction to take place

Increase in reaction rate

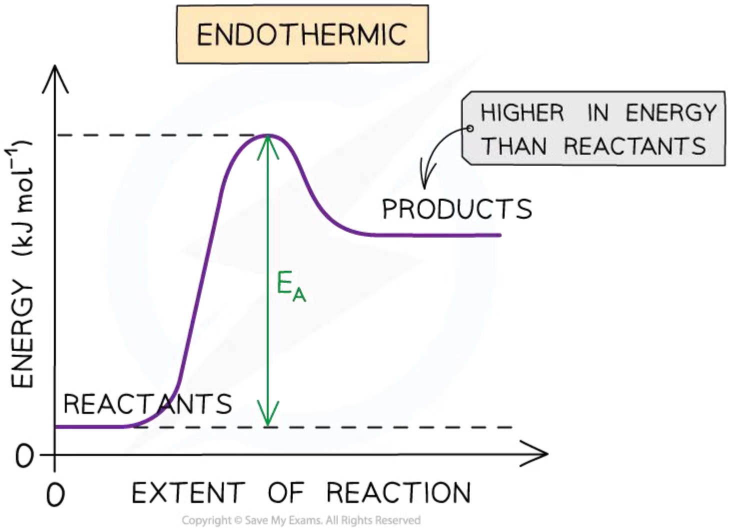
- The **collision frequency** is the number of collisions per unit time
- When more collisions per unit time take place, the number of particles with energy greater than the E_a increases
- This causes an **increase** in the **rate of reaction**

Activation Energy

- For a reaction to take place, the reactant particles need to overcome a minimum amount of energy
- This energy is called the **activation energy (E_a)**
- In **exothermic reactions** the reactants are higher in energy than the products
- In **endothermic reactions** the reactants are lower in energy than the products
- Therefore, the E_a in **endothermic reactions** is relatively larger than in exothermic reaction



The diagram shows that the reactants are higher in energy than the products in the exothermic reaction, so the energy needed for the reactants to go over the energy barrier is relatively small

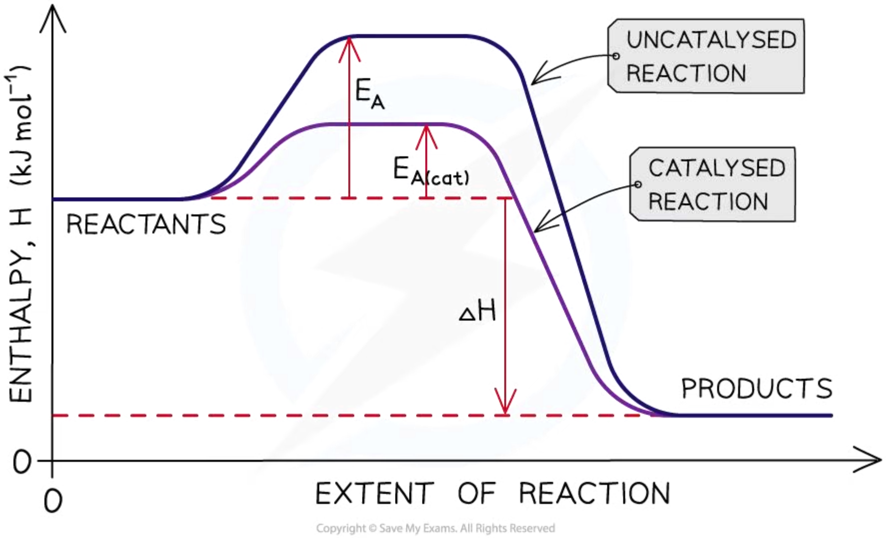


The diagram shows that the reactants are lower in energy than the products in the endothermic reaction, so the energy needed for the reactants to go over the energy barrier is relatively large

- Even though particles collide with each other in the same orientation, if they don't possess a minimum energy that corresponds to the E_a of that reaction, the reaction will **not** take place
- Therefore, for a collision to be **effective** the reactant particles must collide in the correct orientation **AND** possess a minimum energy equal to the E_a of that reaction

Catalysts and activation energy

- A **catalyst** is a substance that **increases** the **rate of reaction** without taking part in the chemical reaction by providing the particles an alternative mechanism with a lower activation energy



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A catalyst increases the rate of a reaction by providing an alternative pathway which has a lower activation energy

Exam Tip

The activation energy is the energy needed to 'activate' the reactant particles in order for them to collide effectively and cause a chemical reaction.

1.7.2 Measuring Rates of Reaction

Measuring the Rate of a Reaction

Reaction rate

- The **rate of reaction** is the speed at which a chemical reaction takes place and has units **mol dm^{-3} s^{-1}** or **mol dm^{-3} min^{-1}**
- The rate of a reaction can be calculated using:

$$\text{RATE OF A REACTION} = \frac{\text{CHANGE IN AMOUNT OF REACTANTS OR PRODUCTS (mol dm}^{-3}\text{)}}{\text{TIME (s)}}$$

Worked Example

Calculating the rate of reaction Calculate the rate of reaction, in mol dm^{-3} s^{-1}, if 0.0440 g of ethyl ethanoate, $CH_3COOC_2H_5$, (M = 88.0 g mol^{-1}) is formed in 1.00 min from a reaction mixture of total volume 400 cm^3

Answer

Step 1: Calculate the amount of ethyl ethanoate in moles:

$$\text{number of moles} = \frac{mass\ of\ substance\ in\ grams}{molar\ mass\ (g\ mol^{-1})}$$

amount of ethyl ethanoate = 0.0440 g ÷ 88.0 g mol^{-1}

= 0.0005 mol

Step 2: Calculate the concentration of the product:

$$\text{concentration(mol dm}^{-3}\text{)} = \frac{number\ of\ moles\ of\ solute\ (mol)}{volume\ of\ solution\ (dm^3)}$$

concentration of ethyl ethanoate = 0.0005 mol ÷ 0.400 dm^3

= 0.00125 mol dm^{-3}

Step 3: Calculate the rate:

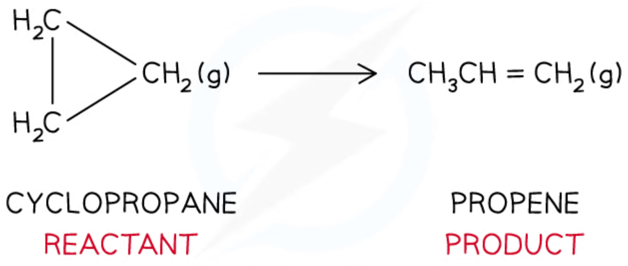
rate of reaction = 0.00125 mol dm^{-3} ÷ 60 s

rate of reaction = **2.08 x 10^{-5} mol dm^{-3} s^{-1}**

Measuring a rate from a graph

- During a reaction, the **reactants** are used up and changed into **products**
- This means that as the reaction proceeds, the concentration of the reactants is **decreasing** and the concentration of the products is **increasing**
- Because of this, the **rate of the reaction** is not the same throughout the reaction but **changes**

- The rate of reaction during the reaction can be calculated from a **concentration–time graph**
- The **isomerisation of cyclopropane** to propene is used as an example:



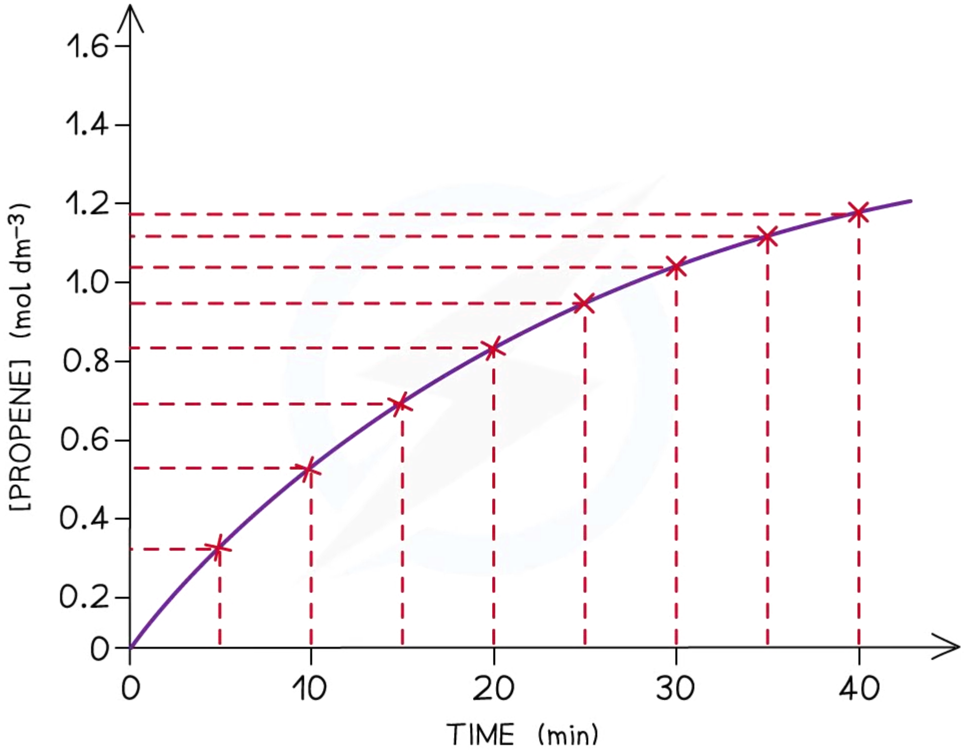
Isomerisation of cyclopropane

- The concentrations of reactant (cyclopropane) and product (propene) over time can be measured by experiment

Concentrations of Cyclopropane & Propene Table

Time (min)	[cyclopropane] (mol dm^{-3})	[propene] (mol dm^{-3})
0	1.50	0.00
5	1.23	0.27
10	1.00	0.50
15	0.82	0.68
20	0.67	0.83
25	0.55	0.95
30	0.45	1.05
35	0.37	1.13
40	0.33	1.17

- When taking the measurements, the **temperature** should be kept constant as a **change** in temperature will change the **rate of reaction**
- A **concentration–time graph** for the concentration of propene as well as cyclopropane can be obtained from the above results
    - As an example, the concentration-time graph for propene is shown below:



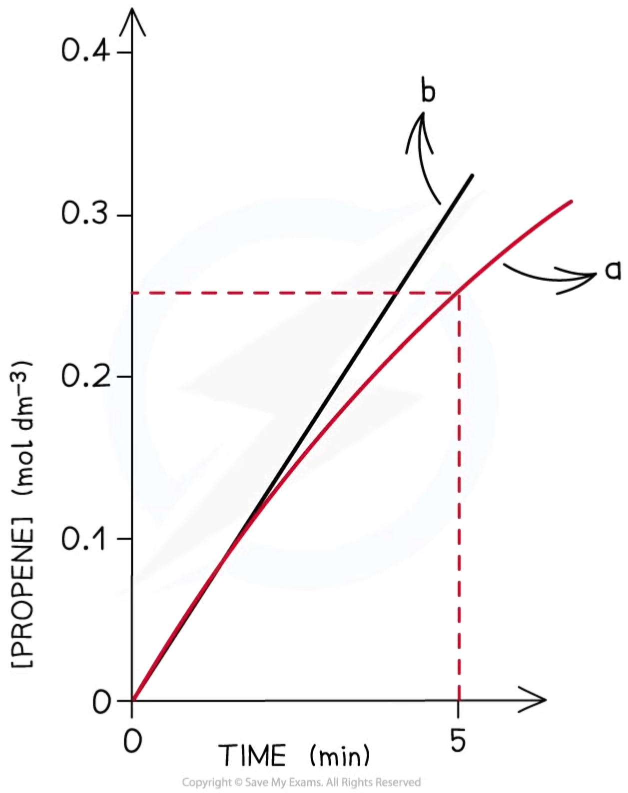
The graph shows that the concentration of propene increases with time

Calculating the rate at the start of a reaction

- At the start of the reaction, the concentration-time curve looks almost linear
- The rate at this point can therefore be found by treating the curve as a linear line and by using:

$$\text{RATE OF A REACTION} = \frac{\text{CHANGE IN AMOUNT OF REACTANTS OR PRODUCTS (mol dm}^{-3}\text{)}}{\text{TIME (s)}}$$

- Using the graph, the average rate of the reaction over the first 5 minutes for propene is:



Line a shows the average rate over the first five minutes whereas line b shows the actual initial rate found by drawing a tangent at the start of the curve. The calculated rates are very similar for both methods

$$\text{Rate} = \frac{0.27}{300}$$

$$= \mathbf{0.0009\ mol\ dm^{-3}\ s^{-1}}$$

Calculating the rate as the reaction proceeds

- The curve becomes shallower with time which means that the rate decreases with time
- The rate of reaction can be calculated by taking short time intervals

  Eg. you can calculate the rate of reaction from 15 to 20 mins during which the concentration of propene increases from 0.68 to 0.83 mol dm^{-3}:

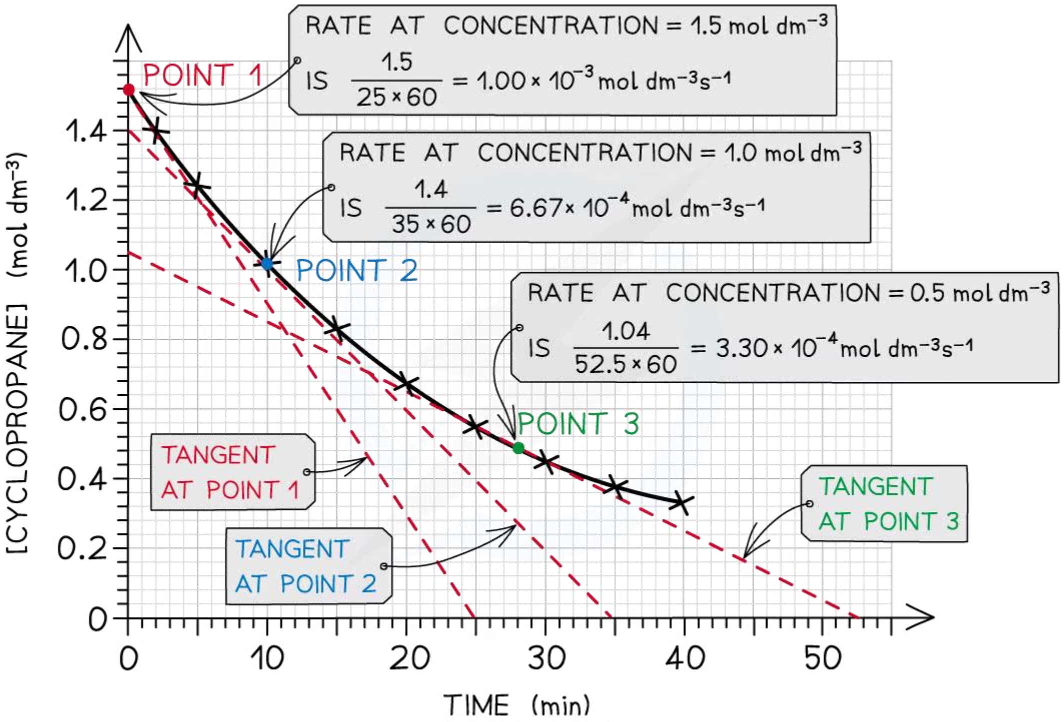
$$\text{Rate} = \frac{(0.83) - (0.68)}{(1200) - (900)}$$

$$= \frac{0.15}{300}$$

$$= \mathbf{0.0005\ mol\ dm^{-3}\ s^{-1}}$$

- The smaller the time intervals, the more accurate the reaction rate value is
- It is even more accurate to find the rate of reaction at **different concentrations** of reactant or product at **particular time points**

- This can be done by drawing **tangents** at several points on the graph
  - As an example, the rates of reaction at different concentrations of cyclopropane are calculated by drawing the appropriate tangents:

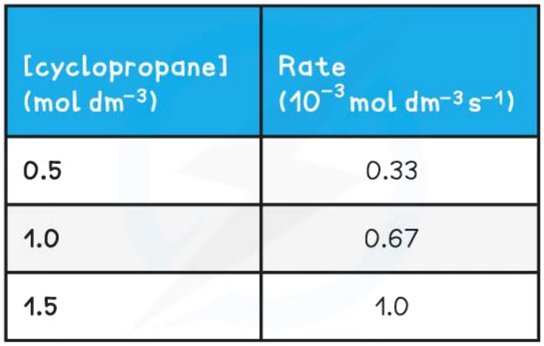


The rate of reaction at three different concentrations of cyclopropane is calculated by drawing tangents at those points in the graph

Rate-concentration graph

- The calculated rates can then be summarised in a table to show how the rate of reaction changes with changing concentration of the reactants or products

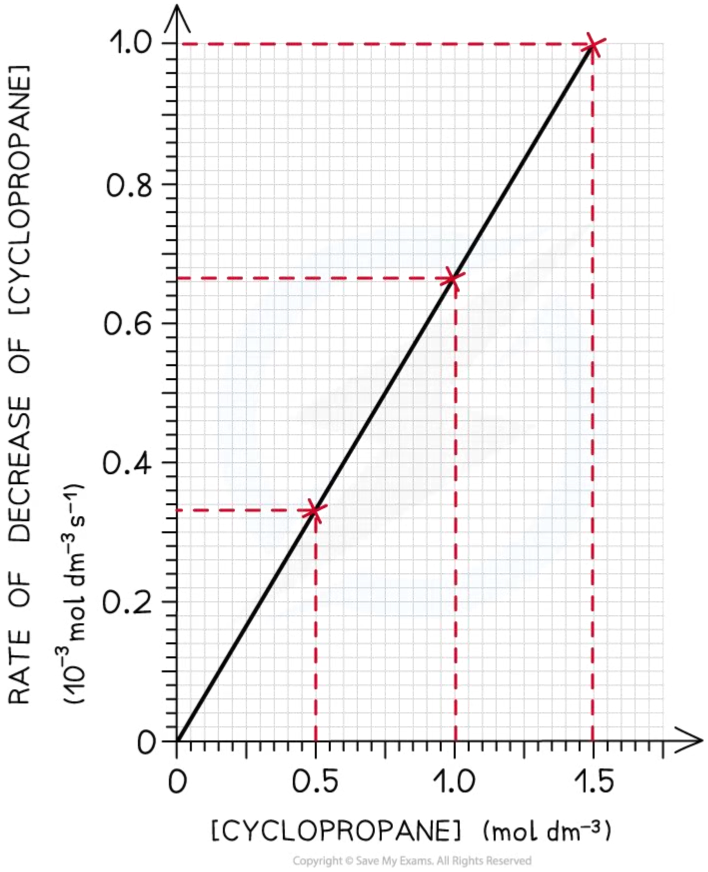
Change in rate with Increasing Concentration of Cyclopropane



[cyclopropane] (mol dm^{-3})	Rate (10^{-3} mol dm^{-3} s^{-1})
0.5	0.33
1.0	0.67
1.5	1.0

- This data can then be used to plot a rate-concentration graph

- The graph shows that the rate is directly proportional to the concentration of cyclopropane
  - If you double the concentration of cyclopropane the rate of reaction will double too



The graph shows a directly proportional correlation between the concentration of cyclopropane and the rate of reaction

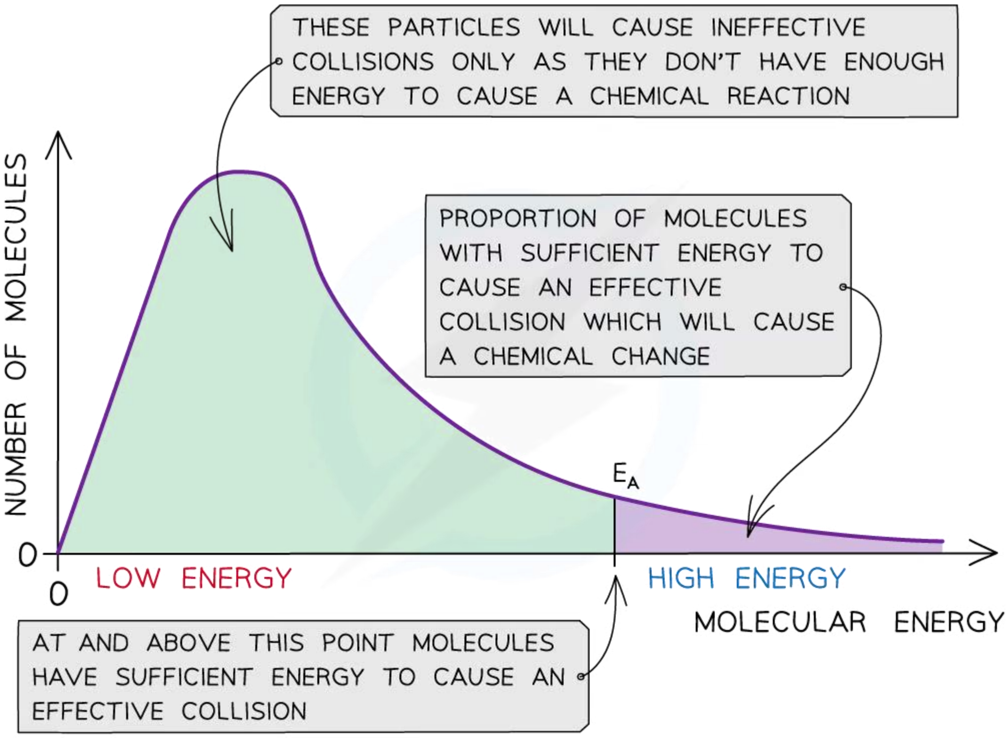
Exam Tip

To calculate the rate of reaction you can either use the increase in concentration of products (like in the example above) or the decrease in concentration of reactants.

Maxwell-Boltzmann Distribution Curve - Temperature

Maxwell-Boltzmann distribution curve

- A **Maxwell-Boltzmann distribution curve** is a graph that shows the distribution of **energies** at a certain **temperature**
- In a sample of a gas, a few particles will have very low energy, a few particles will have very high energy, but most particles will have energy in between



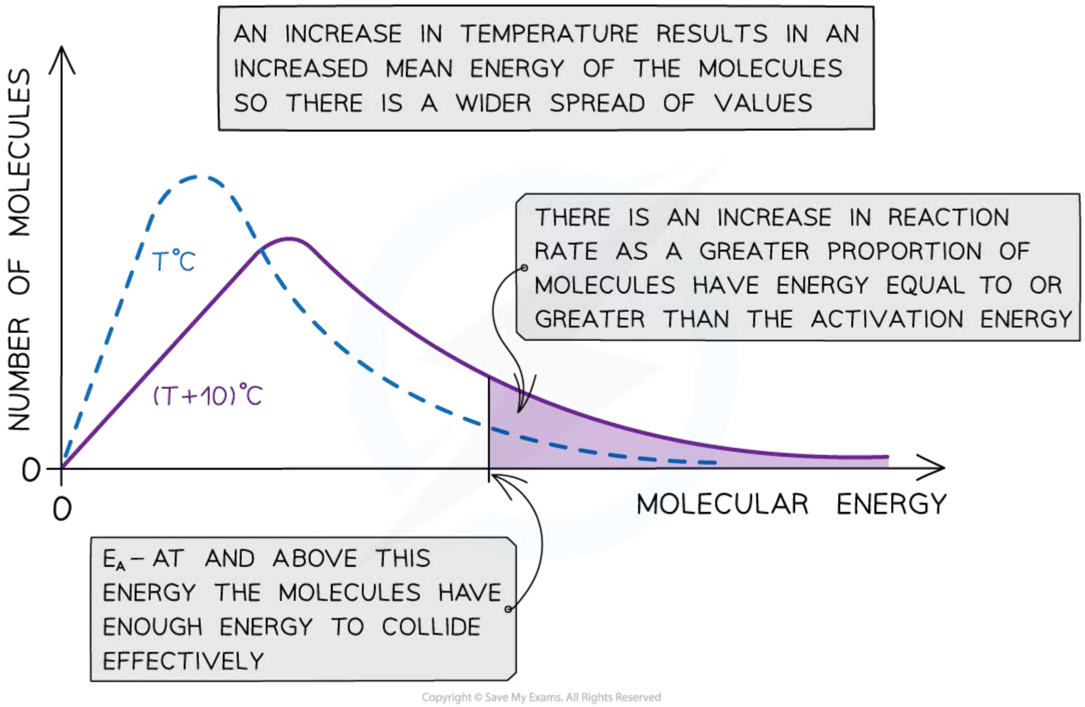
The Maxwell-Boltzmann distribution curve shows the distribution of the energies and the activation energy

- The graph shows that only a small proportion of molecules in the sample have enough energy for an **effective collision** and for a **chemical reaction** to take place

Changes in temperature

- When the temperature of a reaction mixture is increased, the particles gain more kinetic energy
- This causes the particles to move around faster resulting in more **frequent collisions**
- Furthermore, the proportion of **successful collisions** increases, meaning a higher **proportion** of the particles possess the minimum amount of energy (activation energy) to cause a chemical reaction

- With higher temperatures, the Boltzmann distribution curve **flattens** and the peak **shifts** to the right



The Maxwell–Boltzmann distribution curve at T °C and when the temperature is increased by 10 °C

- Therefore, an increase in temperature causes an increased rate of reaction due to:
    - There being **more effective collisions** as the particles have **more kinetic energy**, making them move around faster
    - A **greater proportion** of the molecules having **kinetic energy** greater than the **activation energy**

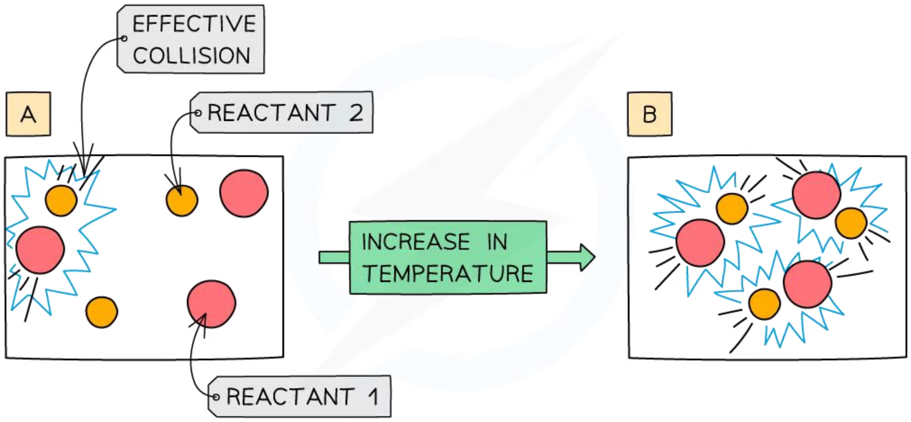
Exam Tip

The increase in proportion of molecules having kinetic energy greater than the activation has a greater effect on the rate of reaction than the increase in effective collisions

Temperature & Rate of Reaction

Temperature & Rate of Reaction

- Increasing the temperature of the reaction mixture increases the **rate of reaction** in the following two ways:
    - At higher temperatures, the particles are moving faster, so collide more frequently. A higher number of collisions in total mean a higher **number** of successful collisions
    - At higher temperatures, a higher proportion of the molecules have the activation energy or more. This means that a higher **proportion** of collisions are **successful**



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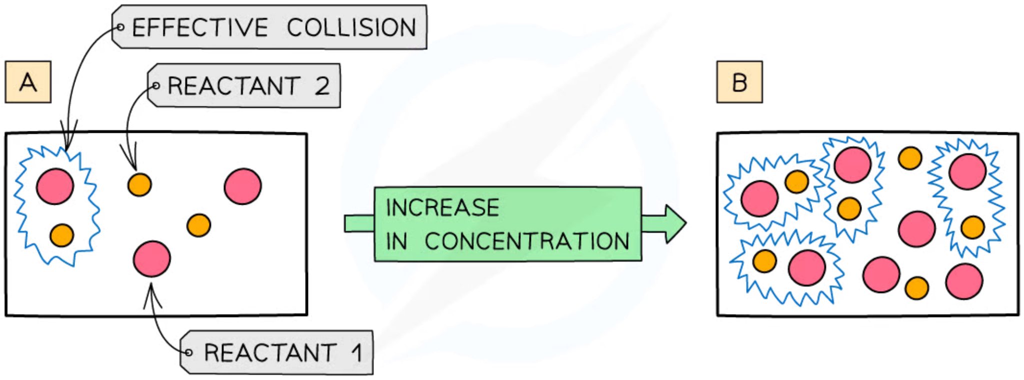
An increase in temperature causes an increase in the kinetic energy of the particles. The number of collisions increases and the proportion of successful collisions increases

Concentration, Pressure & Rate of Reaction

Concentration

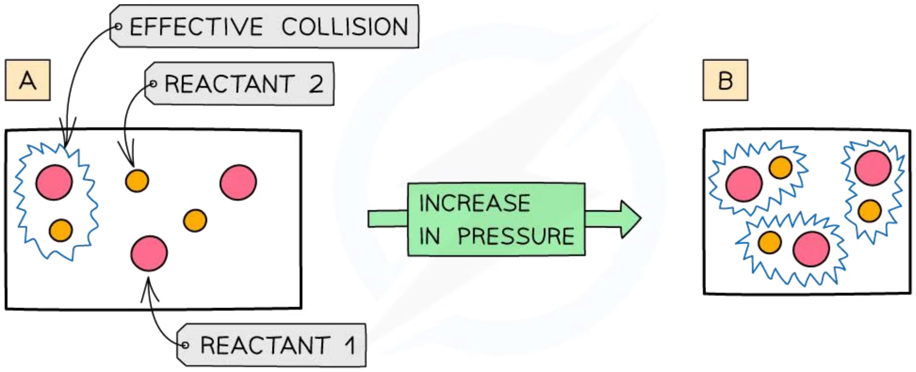
- The more **concentrated** a solution is, the **greater** the number of **particles** in a given volume of solvent
- An increase in **concentration** causes in an increased **collision frequency** and therefore an increased **rate of reaction**



The diagram shows a higher concentration of particles in (b) which means that there are more particles present in the same volume than (a) so the chances and frequency of collisions between reacting particles is increased causing an increased rate of reaction

Pressure

- An increase in pressure in reactions that involve gases has the same effect as an increase in the concentrations of solutions
- When the **pressure** is increased, the molecules have less space in which they can move
- This means that the number of **effective collisions** increases due to an increased **collision frequency**
- An increase in pressure therefore increases the **rate of reaction**



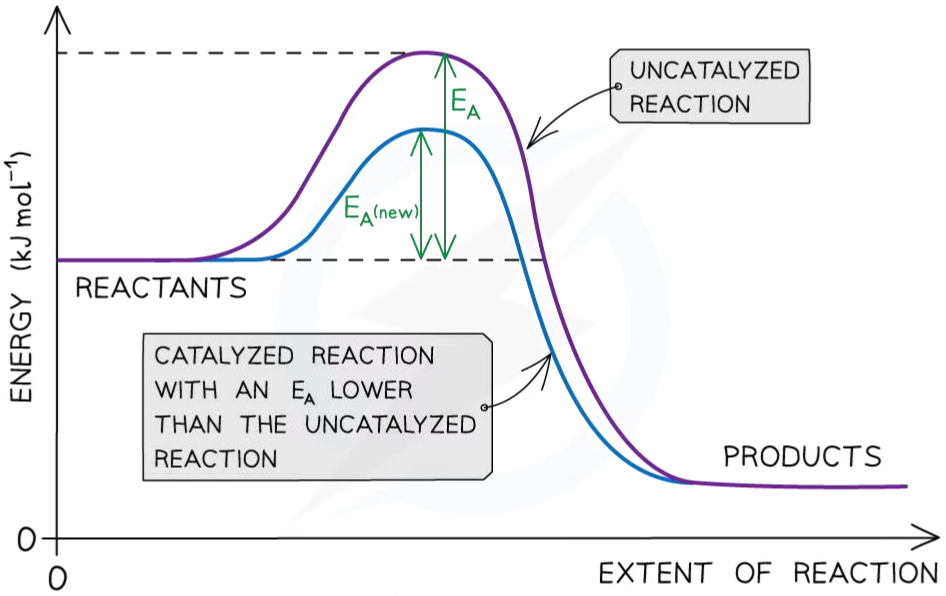
The diagram shows a higher pressure in (b) which means that the same number of particles occupy a smaller volume, resulting in an increased collision frequency and therefore increased rate of reaction

Maxwell-Boltzmann Distribution Curve - Catalyst

- **Catalysis** is the process in which the rate of a chemical reaction is increased, by adding a **catalyst**
- A catalyst increases the rate of a reaction by providing the reactants with an **alternative reaction pathway** which is **lower in activation energy** than the uncatalysed reaction
- Catalysts can be divided into two types:
  - Homogeneous catalysts
  - Heterogeneous catalysts

- **Homogeneous** means that the catalyst is in the **same phase** as the reactants
  - For example, the reactants and the catalysts are all in solution

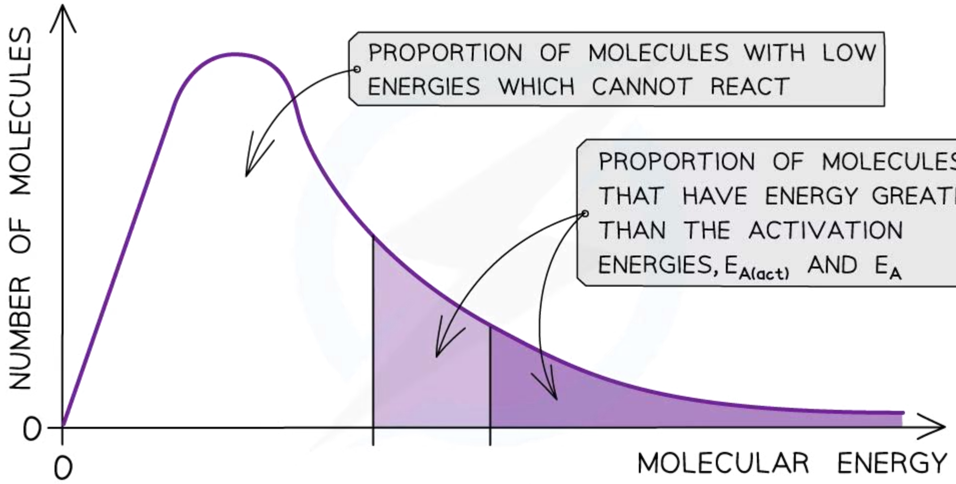
- **Heterogeneous** means that the catalyst is in a **different phase** to the reactants
  - For example, the reactants are gases but the catalyst used is a solid



The diagram shows that the catalyst allows the reaction to take place through a different mechanism, which has a lower activation energy than the original reaction

Maxwell-Boltzmann distribution curve

- **Catalysts** provide the reactants another pathway which has a lower activation energy
- By lowering E_a, a **greater proportion** of molecules in the reaction mixture have the activation energy, and therefore have sufficient energy for an **effective collision**
- As a result of this, the rate of the catalysed reaction is increased compared to the uncatalyzed reaction



The diagram shows that the total shaded area (both dark and light shading) under the curve shows the number of particles with energy greater than the E_a **when a catalyst is present. This area is much larger than the dark shaded area which shows the number of particles with energy greater than the E_a without a catalyst**

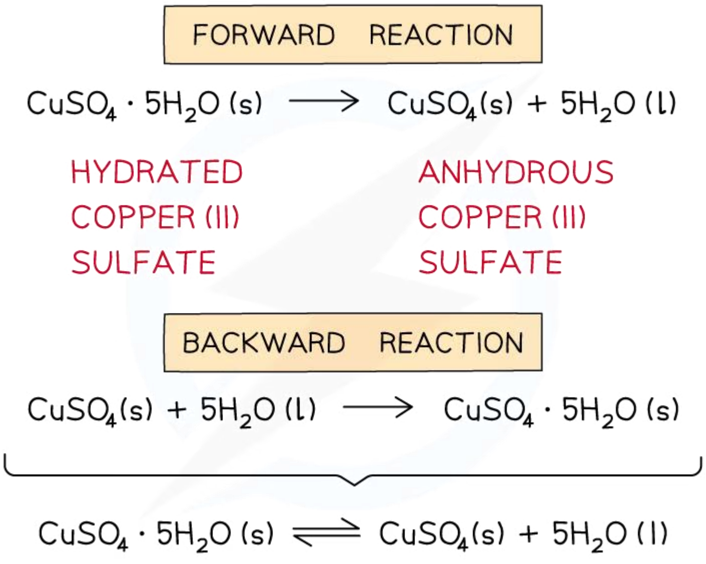
1.8 Chemical Equilibria, Le Chatelier's Principle & Kc

1.8.1 Chemical Equilibria

Reversible Reactions & Dynamic Equilibrium

Reversible reaction

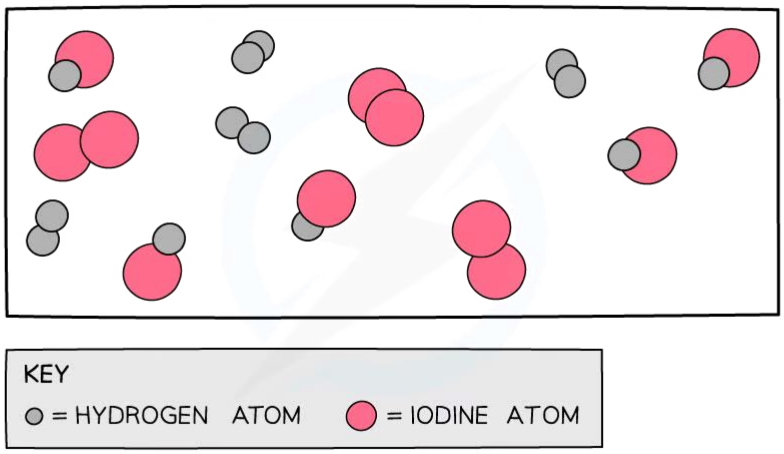
- Some reactions go to completion where the reactants are used up to form the products and the reaction stops when all of the reactants are used up
- In **reversible reactions** the products can react to reform the original reactants
- To show a reversible reaction, two opposing half arrows are used: ⇌



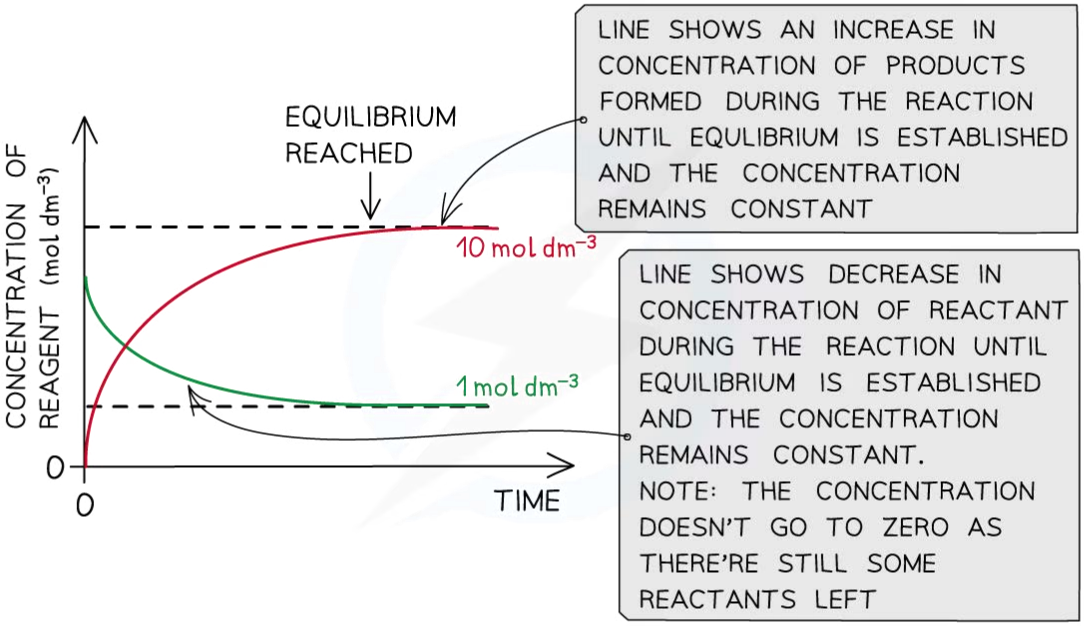
The diagram shows an example of a forward and backward reaction that can be written as one equation using two half arrows

Dynamic equilibrium

- In a **dynamic equilibrium** the reactants and products are **dynamic** (they are constantly moving)
- In a dynamic equilibrium the **rate** of the **forward** reaction is the same as the rate of the **backward** reaction in a **closed system**, and the **concentrations** of the **reactants** and **products** is **constant**



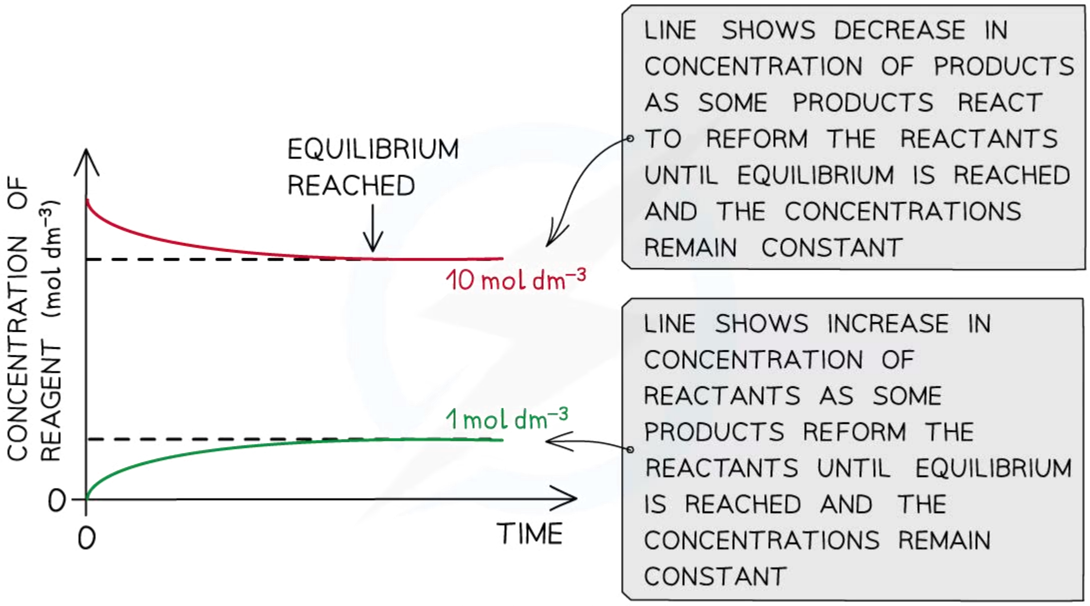
The diagram shows a snapshot of a dynamic equilibrium in which molecules of hydrogen iodide are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules are reacting together to form hydrogen iodide



LINE SHOWS AN INCREASE IN CONCENTRATION OF PRODUCTS FORMED DURING THE REACTION UNTIL EQULIBRIUM IS ESTABLISHED AND THE CONCENTRATION REMAINS CONSTANT

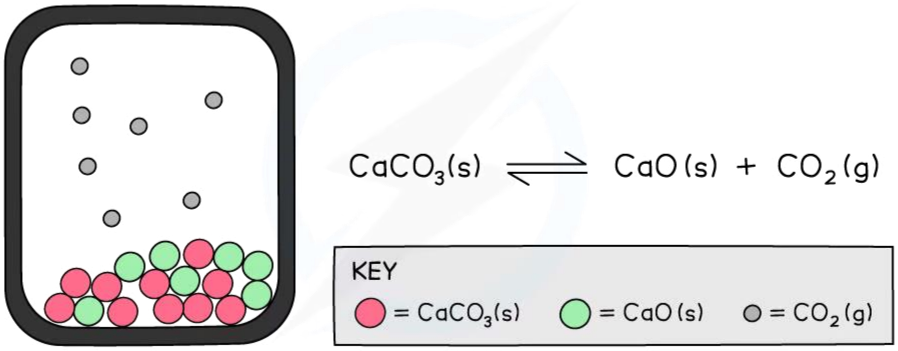
LINE SHOWS DECREASE IN CONCENTRATION OF REACTANT DURING THE REACTION UNTIL EQUILIBRIUM IS ESTABLISHED AND THE CONCENTRATION REMAINS CONSTANT.
NOTE: THE CONCENTRATION DOESN'T GO TO ZERO AS THERE'RE STILL SOME REACTANTS LEFT

The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)

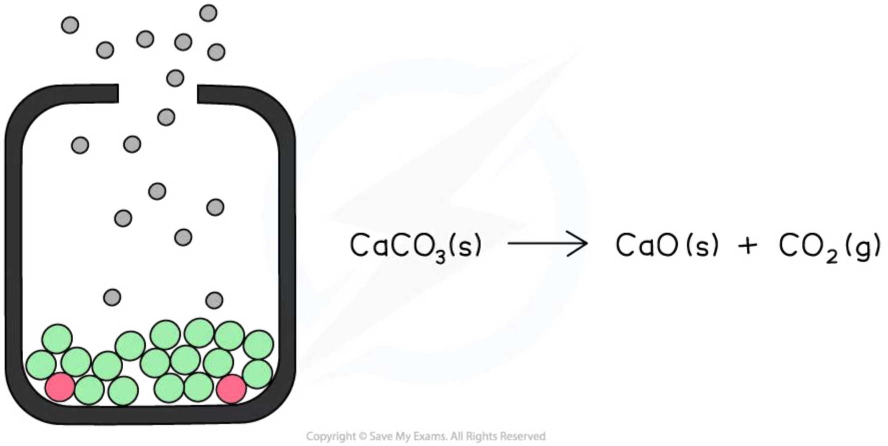


The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using products)

- A **closed system** is one in which none of the reactants or products escape from the reaction mixture
- In an **open system**, matter and energy can be lost to the surroundings
- When a reaction takes place entirely in solution, equilibrium can be reached in open flasks as a negligible amount of material is lost through evaporation
- If the reaction involves gases, equilibrium can only be reached in a closed system



The diagram shows a closed system in which no carbon dioxide gas can escape and the calcium carbonate is in equilibrium with the calcium oxide and carbon dioxide



The diagram shows an open system in which the calcium carbonate is continually decomposing as the carbon dioxide is lost causing the reaction to eventually go to completion

Exam Tip

A common misconception is to think that the concentrations of the reactants and products are **equal.** However, they are **not equal** but they **remain constant** at dynamic equilibrium (i.e. the concentrations are not changing).The concentrations will change as the reaction progresses, only **until the equilibrium** is reached.

Le Chatelier's Principle

Position of the equilibrium

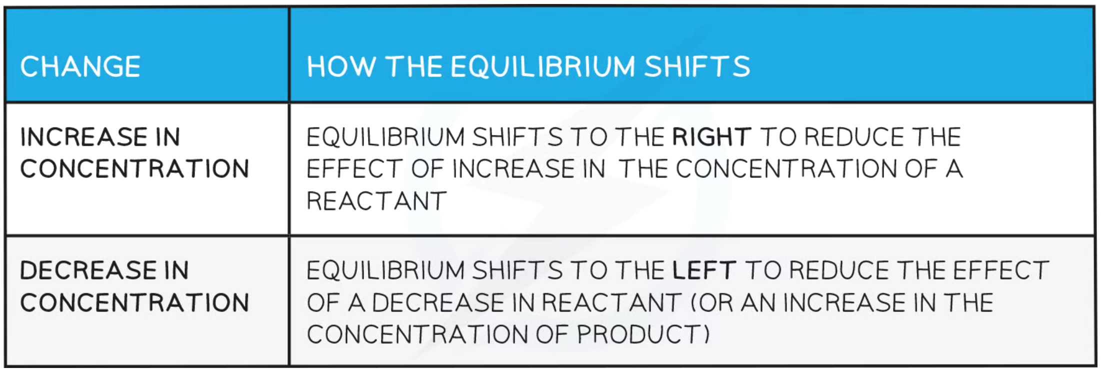
- The **position of the equilibrium** refers to the relative amounts of products and reactants in an equilibrium mixture
- When the position of equilibrium shifts to the **left**, it means the concentration of **reactants** increases
- When the position of equilibrium shifts to the **right**, it means the concentration of **products** increases

Le Chatelier's principle

- **Le Chatelier's principle** says that if a change is made to a system in dynamic equilibrium, the position of the equilibrium moves to counteract this change
- The principle is used to predict changes to the position of equilibrium when there are changes in temperature, pressure or concentration

Effects of concentration

- How the equilibrium shifts with concentration changes:



CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN CONCENTRATION	EQUILIBRIUM SHIFTS TO THE **RIGHT** TO REDUCE THE EFFECT OF INCREASE IN THE CONCENTRATION OF A REACTANT
DECREASE IN CONCENTRATION	EQUILIBRIUM SHIFTS TO THE **LEFT** TO REDUCE THE EFFECT OF A DECREASE IN REACTANT (OR AN INCREASE IN THE CONCENTRATION OF PRODUCT)

Worked Example

Changes in equilibrium position Using the reaction below:

$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$

Explain what happens to the position of equilibrium when:

1. **More $CH_3COOC_2H_5$ is added**
2. **Some C_2H_5OH is removed**

Using the reaction below:

$Ce^{4+}\ (aq) + Fe^{2+}\ (aq) \rightleftharpoons Ce^{3+}\ (aq) + Fe^{3+}\ (aq)$

Explain what happens to the position of equilibrium when

3. **Water is added to the equilibrium mixture**

Answer 1:

- The position of the equilibrium moves to the left and more ethanoic acid and ethanol are formed.
- The reaction moves in this direction to oppose the effect of added ethyl ethanoate, so the ethyl ethanoate decreases in concentration.

Answer 2:

- The position of the equilibrium moves to the left and more ethanoic acid and ethanol are formed.
- The reaction moves in this direction to oppose the removal of ethanol so more ethanol (and ethanoic acid) are formed from ethyl ethanoate and water.

Answer 3:

- There is no effect as the water dilutes all the ions equally so there is no change in the ratio of reactants to products.

Effects of pressure

- Changes in pressure only affect reactions where the reactants or products are gases
- How the equilibrium shifts with pressure changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **SMALLER** NUMBER OF MOLECULES OF GAS TO DECREASE THE PRESSURE AGAIN
DECREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **LARGER** NUMBER OF MOLECULES OF GAS TO INCREASE THE PRESSURE AGAIN

Worked Example

Changes in pressure Predict the effect of increasing the pressure on the following reactions:

1. $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$
2. $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

Predict the effect of decreasing the pressure on the following reaction:

3. $2NO_2\ (g) \rightleftharpoons 2NO\ (g) + O_2\ (g)$

Answer 1:

- The equilibrium shifts to the left as there are fewer gas molecules on the left
- This causes a decrease in pressure

Answer 2:

- The equilibrium shifts to the left as there are no gas molecules on the left but there is CO_2 on the right
- This causes a decrease in pressure

Answer 3:

- The equilibrium shifts to the right as there is a greater number of gas molecules on the right
- This causes an increase in pressure

Effects of temperature

- How the equilbrium shifts with temperature changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **ENDOTHERMIC** DIRECTION TO REVERSE THE CHANGE
DECREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **EXOTHERMIC** DIRECTION TO REVERSE THE CHANGE

Worked Example

Changes in temperature Using the reaction below:

$H_2 (g) + CO_2 (g) \rightleftharpoons H_2O (g) + CO (g) \quad \Delta H = +41.2 \text{ kJ mol}^{-1}$

1. **Predict the effect of increasing the temperature on this reaction**

Using the reaction below:

$Ag_2CO_3 (s) \rightleftharpoons Ag_2O (s) + CO_2 (g)$

2. **Increasing the temperature increases the amount of CO_2(g) at constant pressure. Is this reaction exothermic or endothermic?**

Explain your answer

Answer 1:

- The reaction will absorb the excess energy and since the forward reaction is endothermic, the equilibrium will shift to the right.

Answer 2:

- The reaction will absorb the excess energy and since this causes a shift of the equilibrium towards the right (as more CO_2(g) is formed) this means that the reaction is endothermic.

Effects of catalysts

- A catalyst is a substance that increases the rate of a chemical reaction (they increase the rate of the **forward** and **reverse** reaction **equally**)
- Catalysts only cause a reaction to reach equilibrium **faster**
- Catalysts therefore have **no effect** on the **position of the equilibrium** once this is reached

The Equilibrium Constant, Kc

Equilibrium expression & constant

- The **equilibrium expression** links the **equilibrium constant**, K_c, to the **concentrations of reactants and products** at equilibrium taking the **stoichiometry** of the equation into account
- So, for a given reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the K_c is defined as follows:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[A] AND [B] = EQUILIBRIUM REACTANT CONCENTRATIONS ($mol\ dm^{-3}$)

[C] AND [D] = EQUILIBRIUM PRODUCT CONCENTRATIONS ($mol\ dm^{-3}$)

a, b, c AND d = NUMBER OF MOLES OF REACTANTS AND PRODUCTS

Equilibrium expression linking the equilibrium concentration of reactants and products at equilibrium

- **Solids** are ignored in equilibrium expressions
- The K_c of a reaction is specific and only changes if the **temperature** of the reaction changes

Worked Example

Deducing equilibrium expressions

Deduce the equilibrium expression for the following reactions:

1. $Ag^+ (aq) + Fe^{2+} (aq) \rightleftharpoons Ag (s) + Fe^{3+} (aq)$
2. $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$
3. $2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$

Answer 1:

- $K_c = \frac{[Fe^{3+} (aq)]}{[Fe^{2+} (aq)]\ [Ag^+ (aq)]}$
- [Ag (s)] is not included in the equilibrium expression as it is a solid

Answer 2:

- $K_c = \dfrac{[NH_3(g)]^2}{[N_2(g)]\,[H_2(g)]^3}$

Answer 3:

- $K_c = \dfrac{[SO_3(g)]^2}{[SO_2(g)]^2\,[O_2(g)]}$

1.8.4 Calculations Involving the Equilibrium Constant

Kc Calculations

Calculations involving K_c

- In the equilibrium expression each figure within a square bracket represents the concentration in **mol dm^{-3}**
- The **units** of K_c therefore depend on the form of the equilibrium expression
- Some questions give the **number of moles** of each of the reactants and products at equilibrium together with the volume of the reaction mixture
- The concentrations of the reactants and products can then be calculated from the number of moles and total volume

$$\text{CONCENTRATION (mol dm}^{-3}) = \frac{\text{NUMBER OF MOLES}}{\text{VOLUME (dm}^3)}$$

Equation to calculate concentration from number of moles and volume

Worked Example

Ethanoic acid and ethanol react according to the following equation:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

At equilibrium, 500 cm^3 of the reaction mixture contained 0.235 mol of ethanoic acid and 0.035 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water.

Calculate the value of K_c for this reaction.

Answer

Step 1: Calculate the concentrations of the reactants and products

$$[CH_3COOH(l)] = \frac{0.235}{0.500} = 0.470\ \text{mol dm}^{-3}$$

$$[C_2H_5OH(l)] = \frac{0.035}{0.500} = 0.070\ \text{mol dm}^{-3}$$

$$[CH_3COOC_2H_5(l)] = \frac{0.182}{0.500} = 0.364\ \text{mol dm}^{-3}$$

$$[H_2O(l)] = \frac{0.182}{0.500} = 0.364\ \text{mol dm}^{-3}$$

Step 2: Write out the balanced chemical equation with the concentrations of beneath each substance

$$\begin{array}{ccccccc} CH_3COOH(l) & + & C_2H_5OH(l) & \rightleftharpoons & CH_3COOC_2H_5(l) & + & H_2O(l) \\ 0.470\ mol\ dm^{-3} & & 0.070\ mol\ dm^{-3} & & 0.364\ mol\ dm^{-3} & & 0.364\ mol\ dm^{-3} \end{array}$$

Step 3: Write the equilibrium constant for this reaction in terms of concentration

$$K_c = \frac{[H_2O]\,[CH_3COOC_2H_5]}{[C_2H_5OH]\,[CH_3COOH]}$$

Step 4: Substitute the equilibrium concentrations into the expression

$$K_c = \frac{(0.364)\ x\ (0.364)}{(0.070)\ x\ (0.470)}$$

$$= 4.03$$

Step 5: Deduce the correct units for K_c

$$K_c = \frac{(mol\ dm^{-3})\ x\ (mol\ dm^{-3})}{(mol\ dm^{-3})\ x\ (mol\ dm^{-3})}$$

All units cancel out

Therefore, K_c = **4.03**

Note that the smallest number of significant figures used in the question is 3, so the final answer should also be given to 3 significant figures

- Some questions give the **initial and equilibrium concentrations** of the reactants but not the products
- An initial, change and equilibrium table should be used to determine the equilibrium concentration of the products **using the molar ratio of reactants and products in the stoichiometric equation**

Worked Example

Calculating K_c of ethyl ethanoate

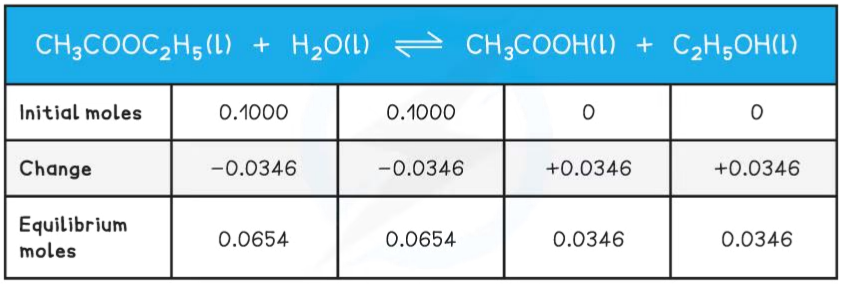
Ethyl ethanoate is hydrolysed by water:

$$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$$

0.1000 mol of ethyl ethanoate are added to 0.1000 mol of water. A little acid catalyst is added and the mixture made up to 1dm^3. At equilibrium 0.0654 mol of water are present. Use this data to calculate a value of K_c for this reaction.

Answer

Step 1: Write out the balanced chemical equation with the concentrations of beneath each substance using an initial, change and equilibrium table



	$CH_3COOC_2H_5(l)$ +	$H_2O(l)$ ⇌	$CH_3COOH(l)$ +	$C_2H_5OH(l)$
Initial moles	0.1000	0.1000	0	0
Change	−0.0346	−0.0346	+0.0346	+0.0346
Equilibrium moles	0.0654	0.0654	0.0346	0.0346

Step 2: Calculate the concentrations of the reactants and products

$$[CH_3COOC_2H_5(l)] = \frac{0.0654}{1.000} = 0.0654 \text{ mol dm}^{-3}$$

$$[H_2O(l)] = \frac{0.0654}{1.000} = 0.0654 \text{ mol dm}^{-3}$$

$$[CH_3COOH(l)] = \frac{0.0346}{1.000} = 0.0346 \text{ mol dm}^{-3}$$

$$[C_2H_5OH(l)] = \frac{0.0346}{1.000} = 0.0346 \text{ mol dm}^{-3}$$

Step 3: Write the equilibrium constant for this reaction in terms of concentration

$$K_c = \frac{[C_2H_5OH]\,[CH_3COOH]]}{[H_2O]\,[CH_3COOC_2H_5]}$$

Step 4: Substitute the equilibrium concentrations into the expression

$$K_c = \frac{(0.0346)\ x\ (0.0346)}{(0.0654)\ x\ (0.0654)}$$

= 0.28

Step 5: Deduce the correct units for K_c

$$K_c = \frac{(mol\ dm^{-3})\ x\ (mol\ dm^{-3})}{(mol\ dm^{-3})\ x\ (mol\ dm^{-3})}$$

All units cancel out

Therefore, K_c = **0.28**

Changes Affecting the Equilibrium Constant

Changes in concentration

- If all other conditions stay the same, the equilibrium constant K_c is **not affected** by any changes in concentration of the reactants or products
- For example, the decomposition of hydrogen iodide:

$$2HI \rightleftharpoons H_2 + I_2$$

The equilibrium expression is:

$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2} = 6.25 \times 10^{-3}$$

Adding more HI makes the ratio of [products] to [reactants] smaller

To restore equilibrium, $[H_2]$ and $[I_2]$ increases and [HI] decreases

Equilibrium is restored when the ratio is 6.25×10^{-3} again

Changes in pressure

- A change in pressure **only** changes the **position of the equilibrium** (see Le Chatelier's principle)
- If all other conditions stay the same, the equilibrium constant K_c is **not affected** by any changes in pressure of the reactants and products

Changes in temperature

- Changes in temperature **affect** the value of the equilibrium constant, K_c
- For an endothermic reaction such as:

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g) \qquad K_c = \frac{[H_2][I_2]}{[HI]^2}$$

An increase in temperature:

$[H_2]$ and $[I_2]$ **increases**

[HI] **decreases**

Because $[H_2]$ and $[I_2]$ are **increasing** and [HI] is **decreasing**, the equilibrium constant K_c **increases**

- For an exothermic reaction such as:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

An increase in temperature:

$[SO_3]$ **decreases**

$[SO_2]$ and $[O_2]$ **increases**

Because $[SO_3]$ **decreases** and $[SO_2]$ and $[O_2]$ **increases** the equilibrium constant K_c decreases

Presence of a catalyst

- If all other conditions stay the same, the equilibrium constant K_c is **not affected** by the presence of a catalyst
- A catalyst speeds up both the forward and reverse reactions at the same rate so the ratio of [products] to [reactants] remains unchanged

Worked Example

Factors affecting K_c

An equilibrium is established in the reaction

$$AB\ (aq) + CD\ (aq) \rightleftharpoons AC\ (aq) + BD\ (aq) \qquad \Delta H = +180\ kJ\ mol^{-1}$$

Which factors would affect the value of K_c in this equilibrium?

Answer

- Only a change in temperature will affect the value of K_c and any other changes in conditions would result in the position of the equilibrium moving in such way to oppose this change.
- Adding a catalyst will increase the rate of reaction meaning the state of equilibrium will be reached faster but will have no effect on the position of the equilibrium and therefore K_c is unchanged.

Choosing Conditions to Maximise Yield

- Equilibrium reactions are involved in some stages of the large-scale production of certain chemicals
- An understanding of equilibrium and Le Chatelier's principle is therefore very important in the chemical industry

Haber process

- The Haber process involves the synthesis of ammonia according to:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H_r = -92\ \text{kJ mol}^{-1}$$

- Le Chatelier's principle is used to get the best yield of ammonia

Maximising the ammonia yield

Pressure

- An increase in **pressure** will result in the equilibrium shifting in the direction of the fewest molecules of gas formed to reduce the pressure
- In this case, the equilibrium shifts towards the right so the yield of ammonia increases
- An increase in pressure will cause the particles to be closer together and therefore increasing the number of successful collisions leading to an increased reaction rate
- Very high pressures are expensive to produce therefore a **compromise pressure** of 200 atm is chosen

Temperature

- To get the maximum yield of ammonia the position of equilibrium should be shifted as far as possible to the right as possible
- Since the Haber process is an exothermic reaction, according to Le Chatelier's principle the equilibrium will shift to the right if the temperature is lowered
- A decrease in **temperature** will decrease the energy of the surroundings so the reaction will go in the direction in which energy is released to counteract this
- Since the reaction is exothermic, the equilibrium shifts to the right
- **However,** at a low temperature the gases won't have enough kinetic energy to collide and react and therefore equilibrium would not be reached therefore a **compromise temperature** of 400-450^{o}C is used in the Haber process
- **A heat exchanger** warms the incoming gas mixture to give molecules more **kinetic energy** such that the gas molecules **collide more frequently** increasing the likelihood of a reaction

Removing ammonia

- **Removing ammonia by condensing it to a liquid** causes the equilibrium position to shift to the right to replace the ammonia causing more ammonia to be formed from hydrogen and nitrogen
- The recovered ammonia is stored at **very low temperatures** and there is **no catalyst** present with the stored ammonia so the decomposition reaction of

ammonia to decompose back into hydrogen and nitrogen will be too slow to be a problem

Catalysts

- In the absence of a catalyst the reaction is so slow that hardly anything happens in a reasonable time!
- Adding an iron catalyst speeds up the rate of reaction

Contact process

- The Contact process involves the synthesis of sulfuric acid according to:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H_r = -197 \text{ kJ mol}^{-1}$$

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

- Le Chatelier's principle is used to get the best yield of sulfuric acid

Maximising the sulfuric acid yield

Pressure

- An increase in **pressure** will result in the equilibrium shifting in the direction of the fewest molecules of gas formed to reduce the pressure
- In this case, the equilibrium shifts towards the right so the yield of sulfur trioxide increases
- In practice, the reaction is carried out at only 1 atm
- This is because *Kc* for this reaction is already very high meaning that the position of the equilibrium is already far over to the right
- Higher pressures than 1 atm will be unnecessary and expensive

Temperature

- The same principle applies to increasing the temperature in the Contact process as in the Haber process
- A **compromise temperature** of 450 °C is used

Removing sulfuric acid

- In practice, SO_3 is removed by absorbing it in 98% sulfuric acid
- This is because adding SO_3 directly to water produces an uncontrollable and hazardous exothermic reaction
- The SO_3 reacts with the sulfuric acid to make oleum, $H_2S_2O_7$, which is then carefully diluted to make more H_2SO_4

Catalysts

- The Contact process uses vanadium(V) oxide as a catalyst to increase the rate of reaction

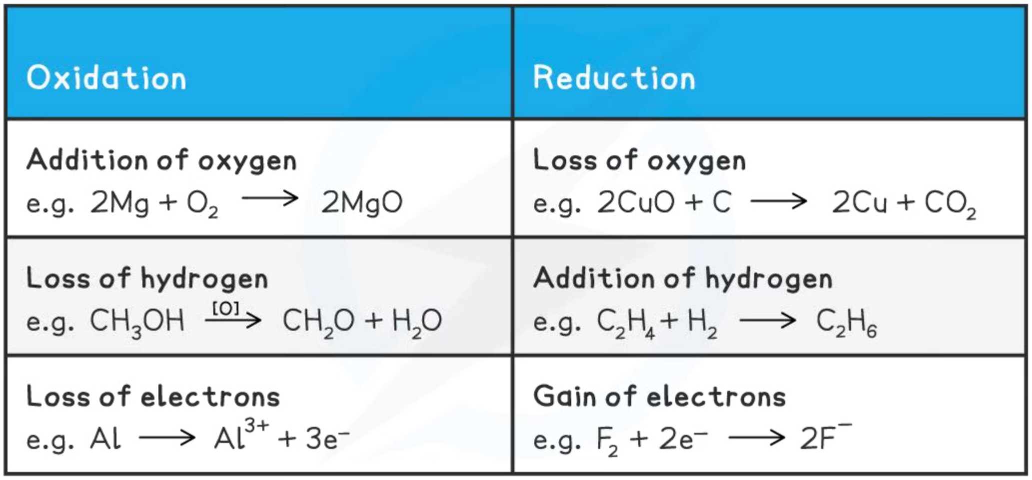
1.9 Oxidation, Reduction & Redox Equations

1.9.1 Oxidation & Reduction

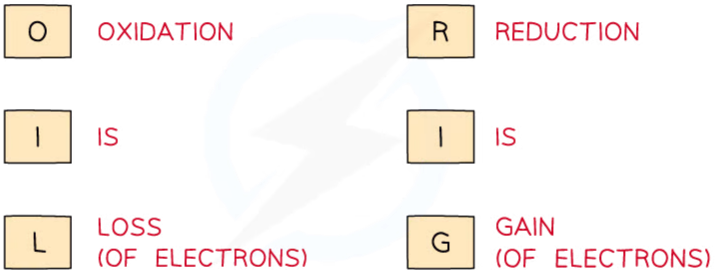
Oxidation & Reduction

- There are three definitions of **oxidation** and **reduction** used in different branches of chemistry
- **Oxidation** and **reduction** can be used to describe any of the following processes

Definitions and Examples of Oxidation & Reduction



Oxidation	Reduction
Addition of oxygen e.g. $2Mg + O_2 \longrightarrow 2MgO$	**Loss of oxygen** e.g. $2CuO + C \longrightarrow 2Cu + CO_2$
Loss of hydrogen e.g. $CH_3OH \xrightarrow{[O]} CH_2O + H_2O$	**Addition of hydrogen** e.g. $C_2H_4 + H_2 \longrightarrow C_2H_6$
Loss of electrons e.g. $Al \longrightarrow Al^{3+} + 3e^-$	**Gain of electrons** e.g. $F_2 + 2e^- \longrightarrow 2F^-$

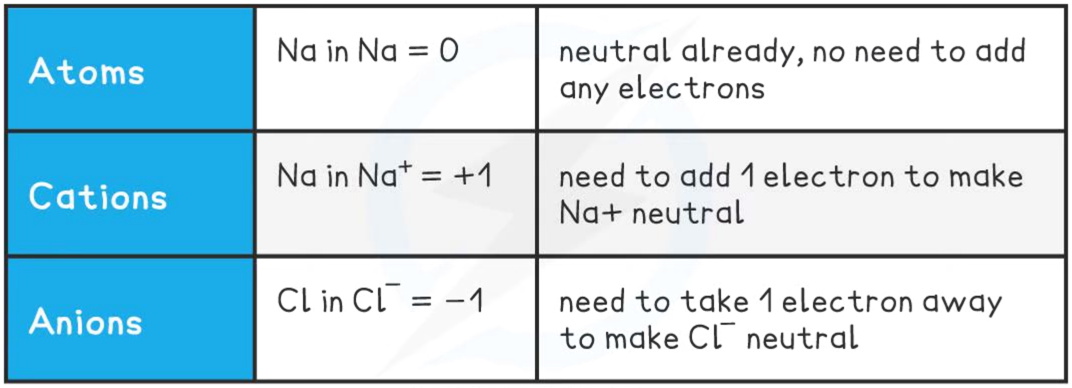


Use the acronym "Oil Rig" to help you remember the definitions of oxidation and reduction

Oxidation States

- The **oxidation state** of an atom is the charge that would exist on an individual atom if the bonding were completely ionic
- It is like the electronic 'status' of an element
- **Oxidation states** are used to
  - Tell if oxidation or reduction has taken place
  - Work out what has been oxidised and/or reduced
  - Construct half equations and balance redox equations

Oxidation States of Simple Ions



Atoms	Na in Na = 0	neutral already, no need to add any electrons
Cations	Na in Na^+ = +1	need to add 1 electron to make Na+ neutral
Anions	Cl in Cl^- = −1	need to take 1 electron away to make Cl^- neutral

Worked Example

What are the oxidation states of the elements in the following species?

a) C b) Fe^{3+} c) Fe^{2+} d) O^{2-} e) He
f) Al^{3+}

Answers:

a) 0 b) +3 c) +2 d) −2 e) 0 f) +3

- So, in simple ions, the oxidation stateof the atom is the charge on the ion:
    - Na^+, K^+, H^+ all have an oxidation state of +1
    - Mg^{2+}, Ca^{2+}, Pb^{2+} all have an oxidation state of +2Cl^-
    - , Br^-, I^- all have an oxidation state of −1
    - O^{2-}, S^{2-} all have an oxidation state of −2

Exam Tip

Oxidation state and oxidation number are often used interchangeably, though IUPAC does not distinguish between the two terms.Oxidation states are represented by Roman numerals according to IUPAC

Oxidising & Reducing Agents

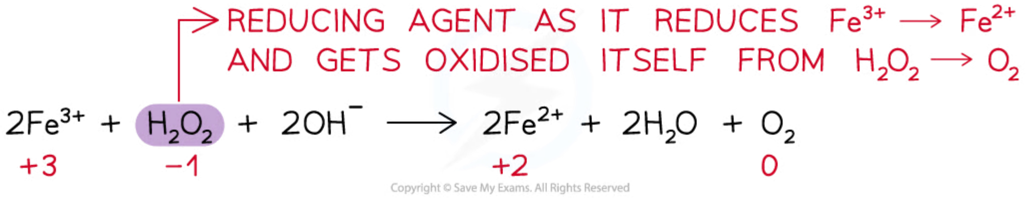
Oxidising agent

- **An oxidising agent** is a substance that **oxidises** another atom or ion by causing it to lose electrons
- An oxidising agent itself gets **reduced – it gains electrons**
- Therefore, the **oxidation state** of the oxidising agent **decreases**

Example of an oxidising agent in a chemical reaction

Reducing agent

- **A reducing agent** is a substance that **reduces** another atom or ion by causing it to gain electrons
- A reducing agent itself gets **oxidised – it loses/donates electrons**
- Therefore, the **oxidation state** of the reducing agent **increases**



Example of a reducing agent in a chemical reaction

- For a reaction to be a redox reaction, there must be both an oxidising and reducing agent present
- Some substances can act both as oxidising and reducing agents – look at the two roles of H_2O_2 in the previous examples
- The role they take is dependent on what they are reacting with and the reaction conditions

Worked Example

Oxidising & reducing agents Four reactions are shown. In which reaction is the species in bold acting as an oxidising agent?

1. $Cr_2O_7^{2-}$ + $8H^+$ + **$3SO_3^{2-}$** → $2Cr^{3+}$ + $4H_2O$ + $3SO_4^{2-}$
2. Mg + **Fe^{2+}** → Mg^{2+} + Fe
3. Cl_2 + **$2Br^-$** → $2Cl^-$ + Br_2
4. Fe_2O_3+ **3CO** → 2Fe + $3CO_2$

Answer

The correct option is **2**

  - Oxidising agents are substances that oxidise other species, gain electrons and are themselves reduced.
  - Write down the oxidation numbers of each species in the reaction

$$\overset{0}{Mg} + \overset{+2}{Fe^{2+}} \rightarrow \overset{+2}{Mg^{2+}} + \overset{0}{Fe^{-}}$$

  - In equation 2, Fe^{2+} oxidises Mg(0) to Mg^{2+}(+2) and is itself reduced from Fe^{2+} (+2) to Fe(0)

Roman numerals

- Roman numerals are used to show the oxidation states of **transition metals** which can have more than one oxidation state
- Iron can be both +2 and +3 so Roman numerals are used to distinguish between them
  - **Fe^{2+}** in FeO is written as **iron(II) oxide**
  - **Fe^{3+}** in Fe_2O_3 is written as **iron(III) oxide**

Worked Example

Systematic names of compounds Give the full systematic names of the following compounds:

1. $FeCl_2$
2. $HClO_4$
3. NO_2
4. $Mg(NO_3)_2$
5. K_2SO_4

Answer

Answer 1: Iron(II) chloride: the oxidation state of 2 Cl atoms is –2 and $FeCl_2$ has no overall charge so the oxidation state of Fe is +2

Answer 2: Chloric(VII) acid: the oxidation state of H is +1, 4 O atoms is –8 and $HClO_4$ has no overall charge so the oxidation state of Cl is +7

Answer 3: Nitrogen(IV) oxide: the oxidation state of 2 O atoms is –4 and NO_2 has no overall charge so the oxidation state of N is +4

Answer 4: Magnesium nitrate: this is a salt of the common acid, so it is named without including the oxidation state of the non–metal

Answer 5: Potassium sulfate: this is a salt of the common acid, so it is named without including the oxidation state of the non–metal

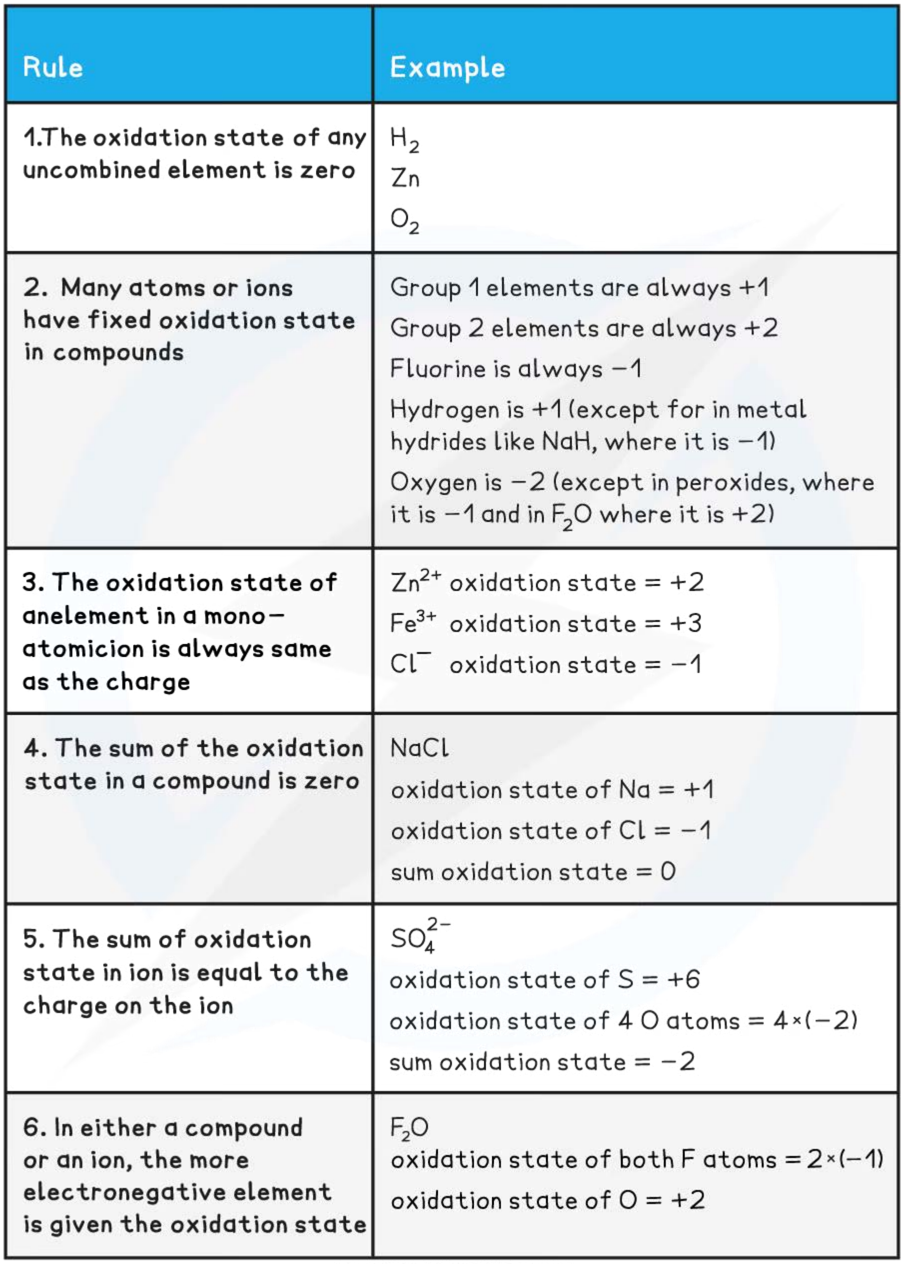
1.9.2 Oxidation States: The Rules

Oxidation States

Oxidation State Rules

- A few simple rules help guide you through the process of determining the oxidation state of any element
- Remember, you are determining the oxidation state of a *single* atom

Oxidation Rules Table

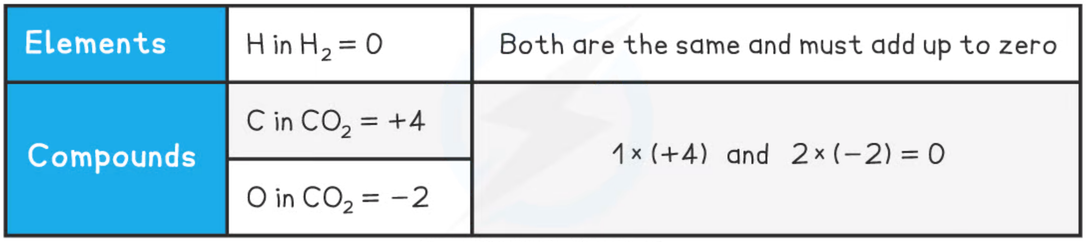


Rule	Example
1.The oxidation state of any uncombined element is zero	H_2 Zn O_2
2. Many atoms or ions have fixed oxidation state in compounds	Group 1 elements are always +1 Group 2 elements are always +2 Fluorine is always −1 Hydrogen is +1 (except for in metal hydrides like NaH, where it is −1) Oxygen is −2 (except in peroxides, where it is −1 and in F_2O where it is +2)
3. The oxidation state of anelement in a mono−atomicion is always same as the charge	Zn^{2+} oxidation state = +2 Fe^{3+} oxidation state = +3 Cl^- oxidation state = −1
4. The sum of the oxidation state in a compound is zero	NaCl oxidation state of Na = +1 oxidation state of Cl = −1 sum oxidation state = 0
5. The sum of oxidation state in ion is equal to the charge on the ion	SO_4^{2-} oxidation state of S = +6 oxidation state of 4 O atoms = 4×(−2) sum oxidation state = −2
6. In either a compound or an ion, the more electronegative element is given the oxidation state	F_2O oxidation state of both F atoms = 2×(−1) oxidation state of O = +2

Molecules or Compounds

- In molecules or compounds, the sum of the oxidation states on the atoms is zero

Oxidation State in Molecules or Compounds



Elements	H in $H_2 = 0$	Both are the same and must add up to zero
Compounds	C in $CO_2 = +4$	$1 \times (+4)$ and $2 \times (-2) = 0$
	O in $CO_2 = -2$	

- Because CO_2 is a neutral molecule, the sum of the oxidation states must be zero
- For this, one element must have a positive oxidation state and the other must be negative

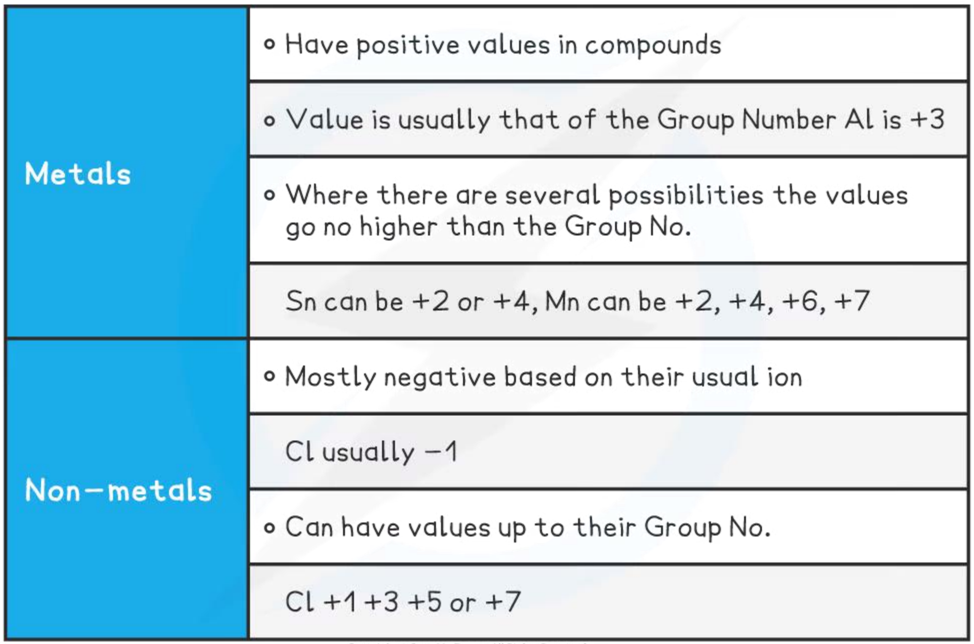
How do you determine which is the positive one?

- The more electronegative species will have the negative value
- Electronegativity increases across a period and decreases down a group
- O is further to the right than C in the periodic table so it has the negative value

How do you determine the value of an element's oxidation state?

- From its position in the periodic table and/or
- The other element(s) present in the formula
- The oxidation states of all other atoms in their compounds can vary
- By following the oxidation state rules, the oxidation state of any atom in a compound or ion can be deduced
- The position of an element in the periodic table can act as a guide to the oxidation state

Oxidation States & the Periodic Table



Metals	◦ Have positive values in compounds
	◦ Value is usually that of the Group Number Al is +3
	◦ Where there are several possibilities the values go no higher than the Group No.
	Sn can be +2 or +4, Mn can be +2, +4, +6, +7
Non–metals	◦ Mostly negative based on their usual ion
	Cl usually −1
	◦ Can have values up to their Group No.
	Cl +1 +3 +5 or +7

- Test your understanding on the following examples:

Worked Example

Deducing oxidation states Give the oxidation state of the elements in **bold** in these compounds or ions:

a. $\mathbf{P_2}O_5$

b. $\mathbf{S}O_4^{2-}$

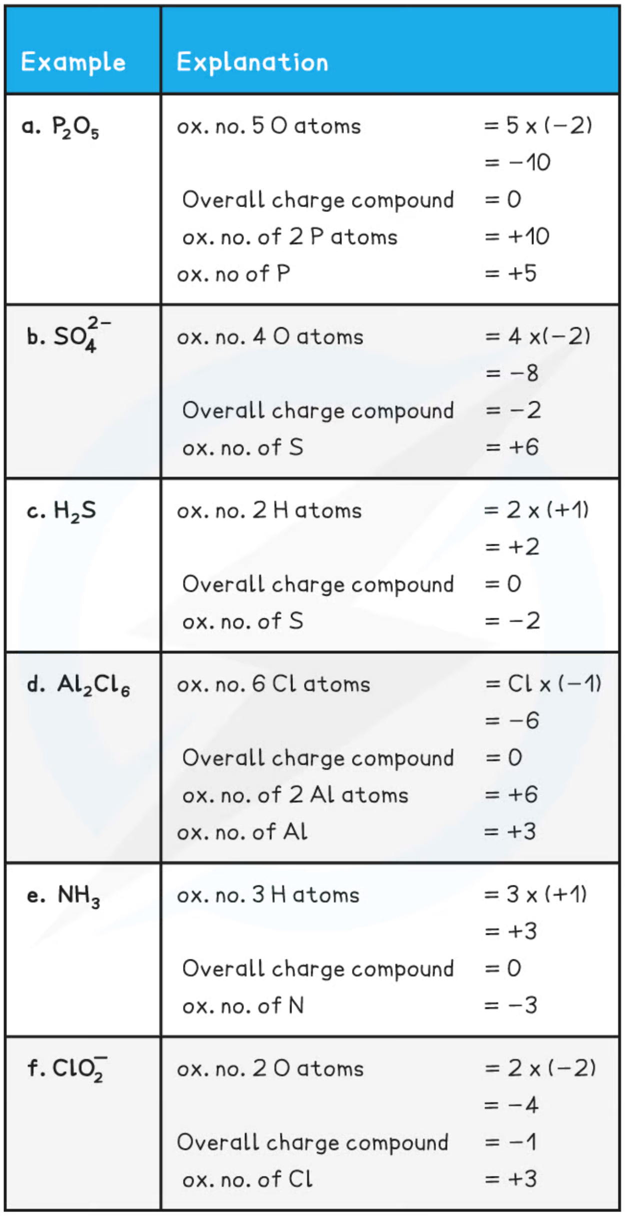
c. $H_2\mathbf{S}$

d. $\mathbf{Al_2}Cl_6$

e. $\mathbf{N}H_3$

f. $\mathbf{Cl}O_2^-$

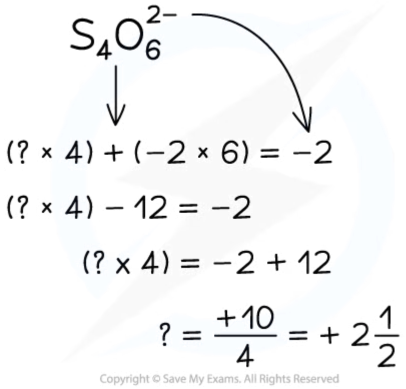
Answers



Example	Explanation	
a. P_2O_5	ox. no. 5 O atoms Overall charge compound ox. no. of 2 P atoms ox. no of P	= 5 x (−2) = −10 = 0 = +10 = +5
b. SO_4^{2-}	ox. no. 4 O atoms Overall charge compound ox. no. of S	= 4 x(−2) = −8 = −2 = +6
c. H_2S	ox. no. 2 H atoms Overall charge compound ox. no. of S	= 2 x (+1) = +2 = 0 = −2
d. Al_2Cl_6	ox. no. 6 Cl atoms Overall charge compound ox. no. of 2 Al atoms ox. no. of Al	= Cl x (−1) = −6 = 0 = +6 = +3
e. NH_3	ox. no. 3 H atoms Overall charge compound ox. no. of N	= 3 x (+1) = +3 = 0 = −3
f. ClO_2^-	ox. no. 2 O atoms Overall charge compound ox. no. of Cl	= 2 x (−2) = −4 = −1 = +3

Are oxidation states always whole numbers?

- The answer is yes and no
- When you try and work out the oxidation state of sulfur in the tetrathionate ion $S_4O_6^{2-}$ you get an interesting result!



The oxidation state of sulfur in $S_4O_6^{2-}$ is a fraction

- The fact that the oxidation state comes out to +2.5 does not mean it is possible to get half an oxidation state
- This is only a mathematical consequence of four sulfur atoms sharing +10 oxidation state
- Single atoms can only have an integer oxidation states, because you cannot have half an electron!

Exam Tip

Although there is a slight technical difference between the terms, oxidation state and oxidation number can be used interchangeably in your exams and examiners will know what you are talking about!

Balancing Redox Reactions

- Balancing equations using redox principles is a useful skill and is best illustrated by following an example
- It is important to follow a methodical step-by-step approach so that you don't get lost:

Worked Example

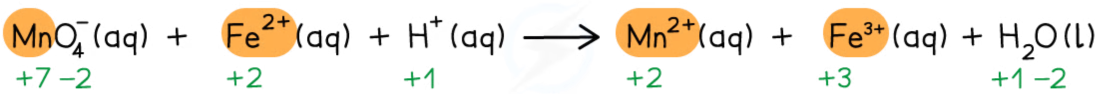
Writing overall redox reactions

Manganate(VII) ions (MnO_4^-) react with Fe^{2+} ions in the presence of acid (H^+) to form Mn^{2+} ions, Fe^{3+} ions and water

Write the overall redox equation for this reaction

Answer

Step 1: Write the unbalanced equation and identify the atoms which change in oxidation state



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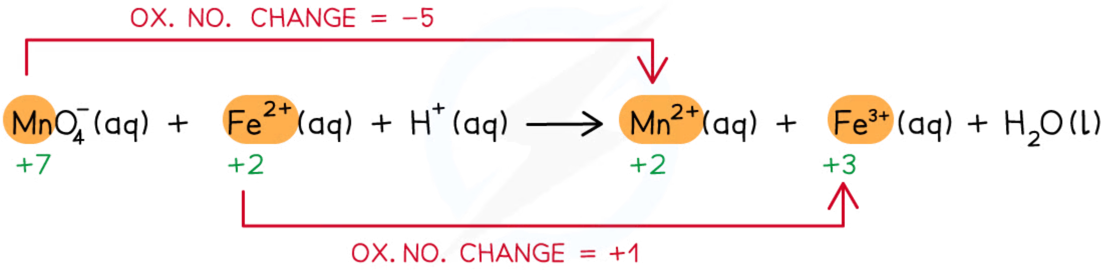
Step 2: Deduce the oxidation state changes



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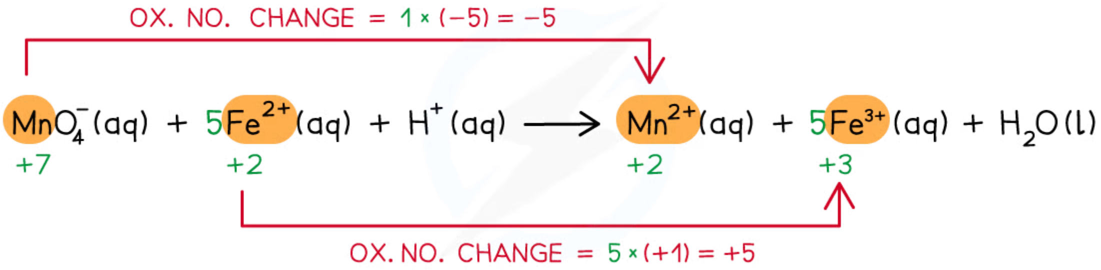
Step 3: Balance the oxidation state changes



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Step 4: Balance the charges

$$\underline{MnO_4^-}(aq) + \underline{5Fe^{2+}}(aq) + H^+(aq) \longrightarrow \underline{Mn^{2+}}(aq) + \underline{5Fe^{3+}}(aq) + H_2O(l)$$

IGNORING H^+

- ∘ TOTAL ⊕ CHARGE = (5 × 2+) = 10+
- ∘ TOTAL ⊖ CHARGE = 1−

TOTAL CHARGE REACTANTS = 9+

- ∘ TOTAL ⊕ CHARGE = 5 × (3+) + (2+)= 17+
- ∘ TOTAL ⊖ CHARGE = 0

TOTAL CHARGE PRODUCTS = 17+

THUS $8H^+$ IONS ARE NEEDED TO BALANCE THE CHARGES ON BOTH SIDES

Step 5: Finally, balance the atoms

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Redox & Disproportionation Reactions

Oxidation

- Oxidation is the **gain of oxygen**, eg:

$$\mathbf{Cu + H_2O \rightarrow CuO + H_2}$$

(Cu has gained an oxygen and is oxidised)

- Oxidation is also the **loss of hydrogen**, eg:

$$\mathbf{2NH_3 + 3Br_2 \rightarrow N_2 + 6HBr}$$

(NH_3 has lost hydrogen and is oxidised)

- Oxidation is also the **loss of electrons**, eg:

$$\mathbf{Cu^{2+} + Mg \rightarrow Mg^{2+} + Cu}$$

(Mg has lost two electrons and is oxidised)

- Oxidation causes an **increase in oxidaiton state**, eg:

$$\mathbf{Cu^{2+} + Mg \rightarrow Mg^{2+} + Cu}$$

(change in ox. no. of Mg is +2 thus Mg is oxidised)

Reduction

- Reduction is the **loss of oxygen**, eg:

$$\mathbf{Cu + H_2O \rightarrow 2CuO + H_2}$$

(H_2O has been reduced)

- Reduction is also the **gain of hydrogen**, eg:

$$\mathbf{2NH_3 + 3Br_2 \rightarrow N_2 + 6HBr}$$

(Br has been reduced)

- Reduction is also the **gain of electrons**, eg:

$$\mathbf{Cu^{2+} + Mg \rightarrow Mg^{2+} + Cu}$$

(Cu has been reduced)

- Reduction causes a **decrease in oxidation number**, eg:

$$\mathbf{Cu^{2+} + Mg \rightarrow Mg^{2+} + Cu}$$

(the change in oxidation state of Cu is −2 thus Cu is reduced)

Redox reactions

- Redox reactions are reactions in which oxidation and reduction take place simultaneously
- While one species is oxidising, another is reducing in the same reaction, eg:

$$Cu^{2+} + Mg \rightarrow Mg^{2+} + Cu$$

(Cu has been reduced and Mg has been oxidised)

Worked Example

Oxidation and reduction In each of the following equations, state which reactant has been oxidised and which has been reduced.

1. $Na^+ + Cl^- \rightarrow NaCl$
2. $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$
3. $CO + Ag_2O \rightarrow 2Ag + CO_2$

Answer

Answer 1:

- Oxidised: Cl^- as the oxidation state has increased by 1
- Reduced: Na^+ as the oxidation state has decreased by 1

Answer 2:

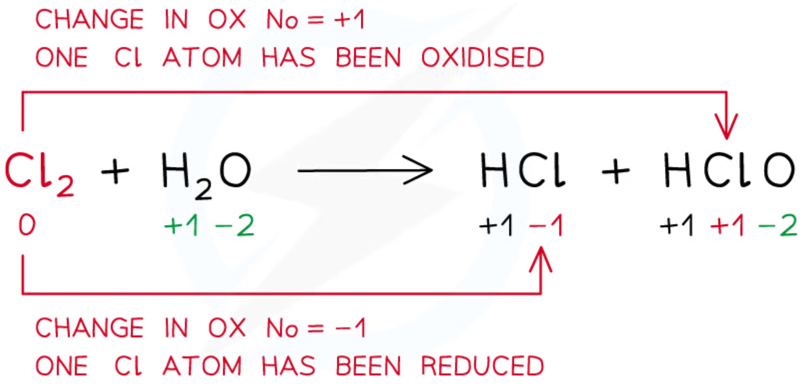
- Oxidised: Mg as the oxidation state has increased by 2
- Reduced: Fe^{2+} as the oxidation state has decreased by 2

Answer 3:

- Oxidised: C as it has gained oxygen
- Reduced: Ag as it has lost oxygen

Disproportionation reactions

- A **disproportionation reaction** is a reaction in which the same species is both oxidised and reduced



Example of a disproportion reaction in which the same species (chlorine in this case) has been both oxidised and reduced

YOUR NOTES
↓

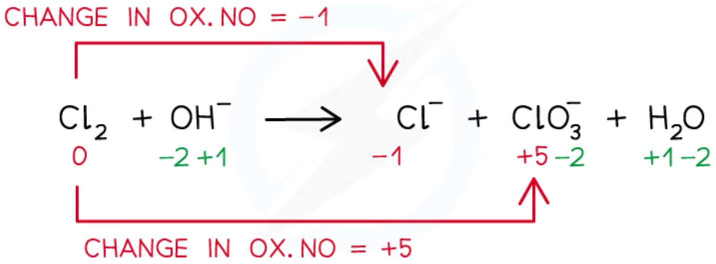
Worked Example

Balancing disproportionation reactions Balance the disproportionation reaction which takes place when chlorine is added to hot concentrated aqueous sodium hydroxideThe products are Cl^- and ClO_3^- ions and water

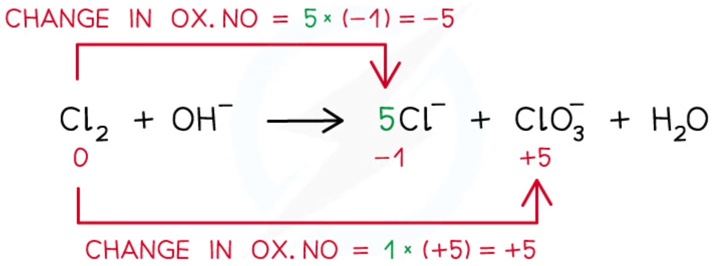
Answer

Step 1: Write the unbalanced equation and identify the atoms that change in oxidation state:

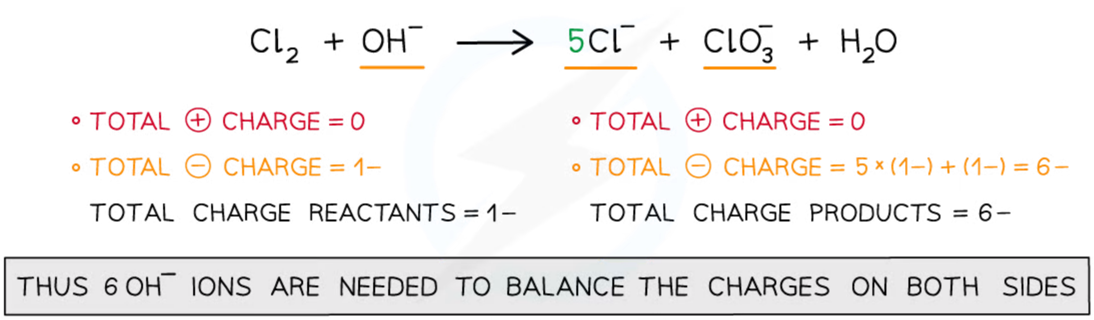
Step 2: Deduce the oxidation state changes:



Step 3: Balance the oxidation state changes:



Step 4: Balance the charges



$$Cl_2 + \underline{OH^-} \longrightarrow \underline{5Cl^-} + \underline{ClO_3^-} + H_2O$$

- TOTAL ⊕ CHARGE = 0
- TOTAL ⊖ CHARGE = 1−

TOTAL CHARGE REACTANTS = 1−

- TOTAL ⊕ CHARGE = 0
- TOTAL ⊖ CHARGE = 5 × (1−) + (1−) = 6−

TOTAL CHARGE PRODUCTS = 6−

THUS 6 OH^- IONS ARE NEEDED TO BALANCE THE CHARGES ON BOTH SIDES

Step 5: Balance the atoms

$$3Cl_2 + 6OH^- \longrightarrow 5Cl^- + ClO_3^- + 3H_2O$$