

A Level Chemistry Edexcel

YOUR NOTES



1. Physical Chemistry

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1.1 Atomic Structure

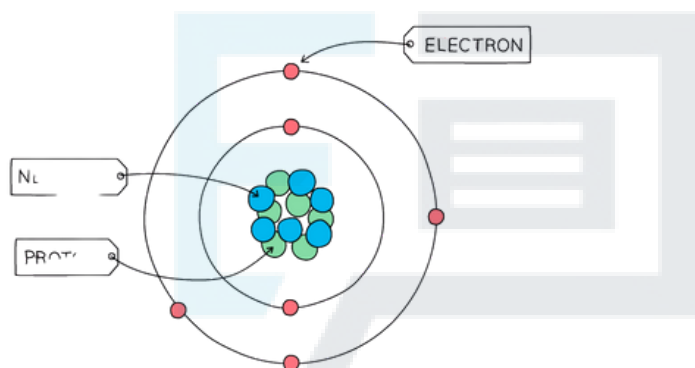
1.1.1 Structure of the Atom

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Structure of the 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 Mass & Charge

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- 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.

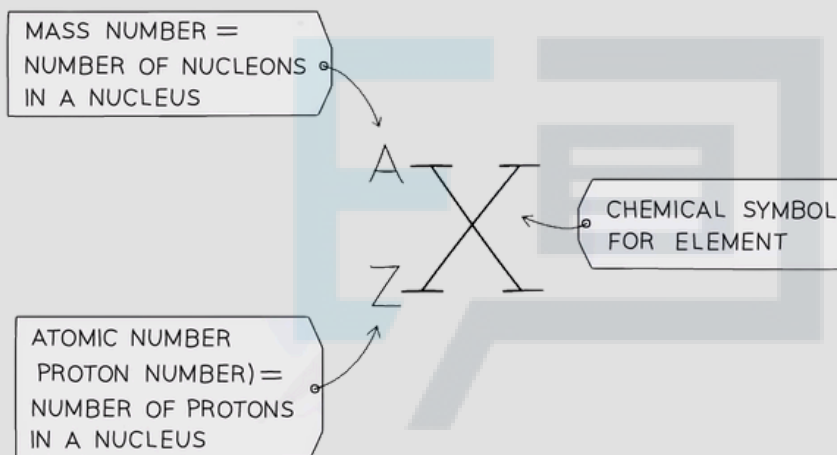
Atomic & Mass Numbers

- 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:

$$\text{Number of neutrons} = \text{mass number} - \text{atomic number}$$

- 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

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1.1.2 Isotopes

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Atomic Structure Calculations

- 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:

$$\text{Mass number} = \text{number of protons} + \text{number of neutrons}$$

$$\text{Number of protons} = \text{mass number} - \text{number of neutrons}$$



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

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

$$\text{Number of protons} = \text{mass number} - \text{number of neutrons}$$

$$\text{Number of protons} = 63 - 34 \quad \text{Number of protons} = 29$$

- 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. Mg²⁺ 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 Mg²⁺ 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)

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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

$$\begin{aligned} \text{Number of neutrons} &= \text{mass number (A)} - \text{number of protons (Z)} \\ \text{Number of neutrons} &= 24 - 12 \quad \text{Number of neutrons} = 12 \end{aligned}$$

- 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

$$\begin{aligned} \text{Number of neutrons} &= \text{mass number (A)} - \text{number of protons (Z)} \\ \text{Number of neutrons} &= 12 - 6 \quad \text{Number of neutrons} = 6 \end{aligned}$$

- 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

$$\begin{aligned} \text{Number of neutrons} &= \text{mass number (A)} - \text{number of protons (Z)} \\ \text{Number of neutrons} &= 63 - 29 \quad \text{Number of neutrons} = 34 \end{aligned}$$

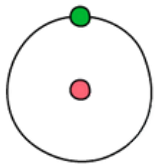
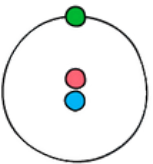
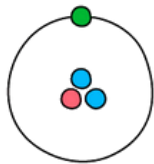
- The neutral atom of element X has 34 neutrons in its nucleus

Defining & Calculating Isotopes

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

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	PROTIUM	DEUTERIUM	TRITIUM
			
PROTONS	1	1	1
NEUTRONS	0	1	2
ISOTOPIC SYMBOL	${}^1_1\text{H}$	${}^2_1\text{H}$	${}^3_1\text{H}$
	 = ELECTRON = PROTON = NEUTRON		

The atomic structure and symbols of the three isotopes of hydrogen

1.1.3 Relative Mass

Isotopic & Atomic Mass

- The relative mass of an atom uses the carbon-12 isotope as the international standard
- One atom of carbon-12 has an accepted mass of $1.992646538 \times 10^{-26}$ kg
- It is not realistic to work with this value so the mass of a carbon-12 atom is fixed as exactly 12 atomic mass units / 12u
- The standard mass for atomic mass is 1u
 - Therefore, the standard mass for comparison is the mass of 1/12 of a carbon-12 atom

Relative isotopic mass

- Relative isotopic mass is defined as the mass of an isotope relative to 1/12 of a carbon-12 atom
- For A Level Chemistry it is common to work with mass values rounded to one decimal place, for example:
- The accurate relative isotopic mass of nitrogen is 14.00307401 but this is rounded to 14.0
- The accurate relative isotopic mass of oxygen is 15.99491464 but this is rounded to 16.0

Relative atomic mass

Most elements on the Periodic Table represent a mixture of different isotopes, which is shown as their relative atomic mass (A_r)

- The relative atomic mass is the weighted mean / average mass of an atom relative to 1/12 of the mass of a carbon-12 atom

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Molecular & Formula Mass

- We have seen previously that the symbol for the relative atomic mass is A_r
- This is calculated from the mass number and relative abundances of all the isotopes of a particular element
- The symbol for the relative formula mass is M_r and it refers to the total mass of the substance
 - The term relative formula mass should be used for compounds with giant structures e.g. ionic compounds such as sodium chloride
 - If the substance is molecular you can use the term relative molecular mass
- To calculate the M_r of a substance, you have to add up the relative atomic masses of all the atoms present in the formula

Relative Formula Mass Calculations Table

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

☐ Exam Tip

It is expected that you will use relative atomic mass values from the Periodic Table

- This means that your values will be more accurate
- e.g. potassium carbonate = $(2 \times 39.1) + 12.0 + (3 \times 16.0) = 138.2$

If you are in any doubt whether to use relative molecular mass or relative formula mass, use the latter because it applies to all compounds whether they are ionic or covalent.

1.1.4 Mass Spectrometry

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Interpreting Mass Spectra

- Isotopes are different atoms of the same element that contain the same number of protons and electrons but a different number of neutrons
- Therefore, 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

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

- The relative abundance of an isotope is either given or can be read off the mass spectrum



Worked Example

Calculate the relative atomic mass of oxygen A_r if a sample of oxygen contains the following isotopes:

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

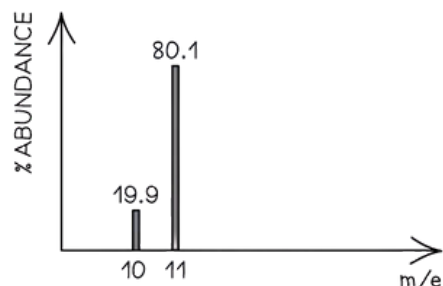
What is the relative atomic mass A_r , of oxygen in this sample, to 2dp?

Answer

- $A_r = \frac{(99.76 \times 16) + (0.04 \times 17) + (0.2 \times 18)}{100}$
- $A_r = 16.0044$
- $A_r = 16.00$

☐ **Worked Example**
Calculating relative atomic mass of boron

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



Answer

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

☐ **Exam**

Tip You can be expected to work with tables or graphs of data to calculate relative atomic mass

You can also be expected to do these calculations backwards to determine the abundance of one isotope given sufficient information

Predicting Mass Spectra

- You can also predict how a mass spectrum might appear for a given compound, e.g. ethanol, $\text{CH}_3\text{CH}_2\text{OH}$
 - The methyl, CH_3^+ , fragment has a mass of 15.0
 - The ethyl, CH_3CH_2^+ , fragment has a mass of 29.0
 - The base ion, $\text{CH}_3\text{CH}_2\text{OH}^+$, fragment has a mass of 31.0
 - The whole molecule has a mass of 46.0
- Predicting mass spectra becomes more complex with the inclusion of halogen isotopes such as chlorine and bromine

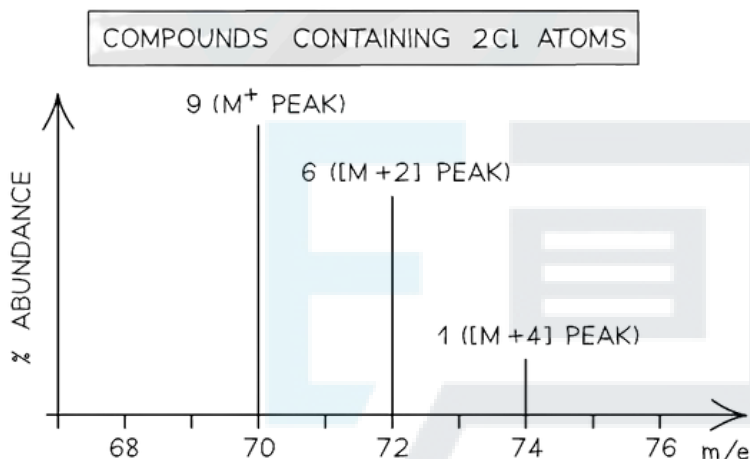
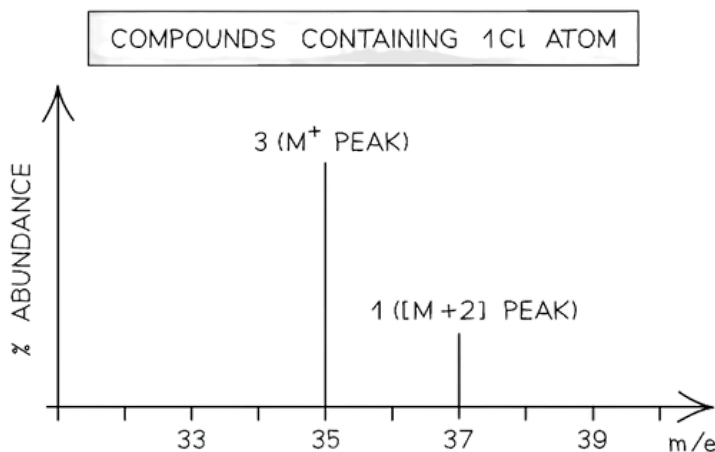
Chlorine

Chlorine exists as two isotopes, ^{35}Cl and ^{37}Cl

- A compound containing **one** chlorine atom will therefore have two molecular ion peaks due to the two different isotopes it can contain
 - $^{35}\text{Cl} = \text{M}^+$ peak
 - $^{37}\text{Cl} = [\text{M}+2]$ peak
 - The ratio of the peak heights is 3:1 (as the relative abundance of ^{35}Cl is 3x greater than that of ^{37}Cl)
- A diatomic chlorine molecule or a compound containing **two** chlorine atoms will have three molecular ion peaks due to the different combinations of chlorine isotopes they can contain
 - $^{35}\text{Cl} + ^{35}\text{Cl} = \text{M}^+$ peak
 - $^{35}\text{Cl} + ^{37}\text{Cl} = [\text{M}+2]$ peak
 - There is an alternative of $^{37}\text{Cl} + ^{35}\text{Cl}$ doubling the $[\text{M}+2]$ peak
 - $^{37}\text{Cl} + ^{37}\text{Cl} = [\text{M}+4]$ peak
 - The ratio of the peak heights is 9:6:1
 - This ratio can be deduced by using the probability of each chlorine atom being ^{35}Cl or ^{37}Cl
 - $^{35}\text{Cl} + ^{35}\text{Cl} = 3 \times 3 = 9$
 - $^{35}\text{Cl} + ^{37}\text{Cl} = 3 \times 1 = 3$ / but this doubles for the $^{37}\text{Cl} + ^{35}\text{Cl}$ option, therefore 6
 - $^{37}\text{Cl} + ^{37}\text{Cl} = 1 \times 1 = 1$
- The presence of bromine or chlorine atoms in a compound gives rise to a $[\text{M}+2]$ and possibly $[\text{M}+4]$ peak

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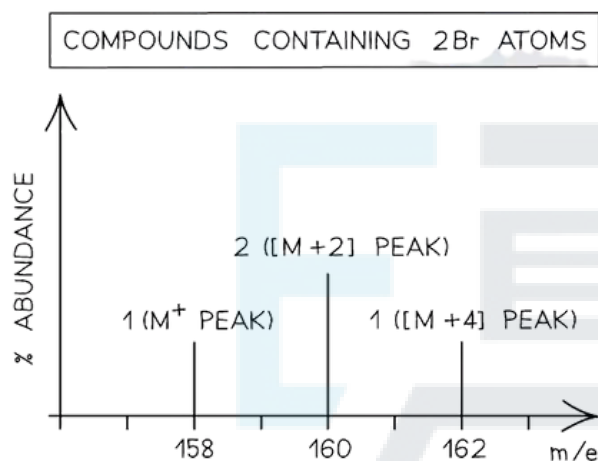
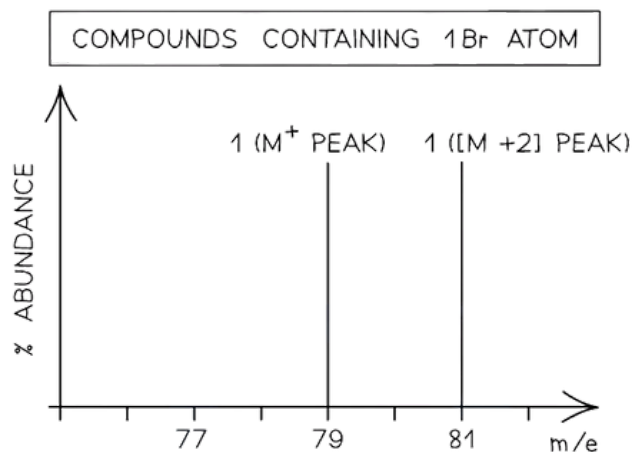
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Mass spectrum of compounds containing one chlorine atom (1) and two chlorine atoms (2)

Bromine

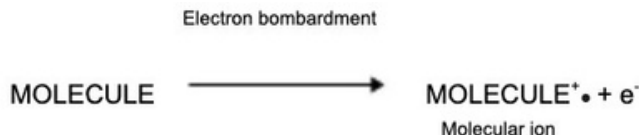
- Bromine too exists as two isotopes, ^{79}Br and ^{81}Br A compound containing
- **one** bromine atom will have two molecular ion peaks
 - $^{79}\text{Br} = \text{M}^+$ peak
 - $^{81}\text{Br} = [\text{M}+2]$ peak
 - The ratio of the peak heights is 1:1 (they are of similar heights as their relative abundance is the same!)
- A diatomic molecule of bromine or a compound containing **two** bromine atoms will have three molecular ion peaks
 - $^{79}\text{Br} + ^{79}\text{Br} = \text{M}^+$ peak
 - $^{79}\text{Br} + ^{81}\text{Br} = [\text{M}+2]$ peak
 - $^{81}\text{Br} + ^{81}\text{Br} = [\text{M}+4]$ peak
 - The ratio of the peak heights is 1:2:1



Mass spectrum of compounds containing one bromine atom

Mass Spectra & Mr

- When a compound is analysed in a mass spectrometer, vaporised molecules are bombarded with a beam of high-speed electrons. These knock off an electron
- from some of the molecules, creating molecular ions:



- The relative abundances of the detected ions form a **mass spectrum**: a kind of molecular fingerprint that can be identified by computer using a spectral database
- The peak with the highest m/z value is the molecular ion (M^+) peak which gives information about the **molecular mass** of the compound. This value of m/z is equal to
- the **relative molecular mass** of the compound

The $M+1$ peak

- The $[M+1]$ peak is a smaller peak which is due to the natural abundance of the isotope **carbon-13**. The height of the $[M+1]$ peak for a particular ion depends on
- how many carbon atoms are present in that molecule; The more carbon atoms, the larger the $[M+1]$ peak is
 - For example, the height of the $[M+1]$ peak for an hexane (containing six carbon atoms) ion will be greater than the height of the $[M+1]$ peak of an ethane (containing two carbon atoms) ion

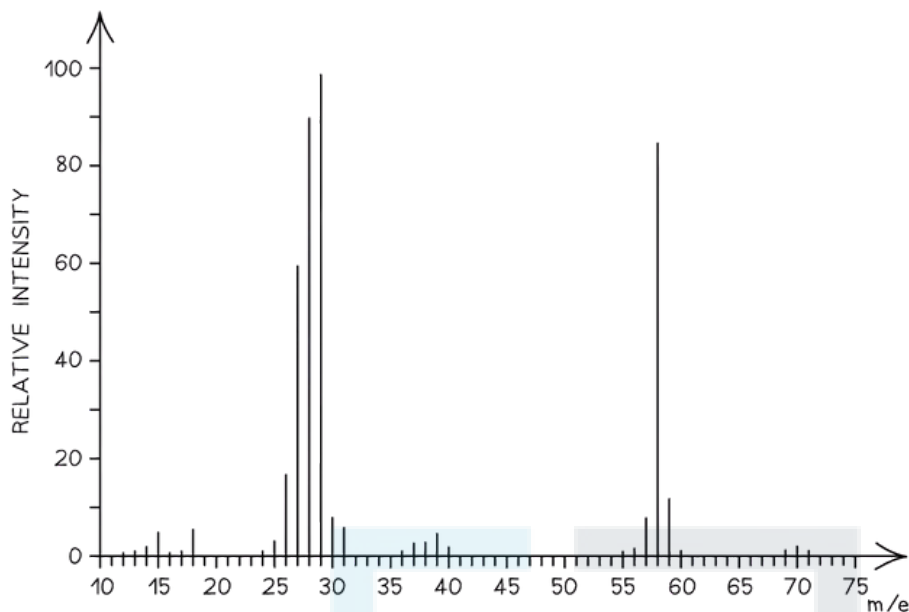
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☐ Worked

Example

Determine whether the following mass spectrum belongs to propanal or butanal



Answer :

- The mass spectrum corresponds to **propanal** as the molecular ion peak is at $m/z = 58$
- Propanal arises from the $\text{CH}_3\text{CH}_2\text{CHO}^+$ ion which has a molecular mass of 58
- Butanal arises from the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}^+$ ion which has a molecular mass of 72

☐ Exam Tip

A mass spectrum can give lots of information about fragments of the overall compound being analysed

Your specification states that this is not expected knowledge, you are only required to know the implications of the M+1 peak from a mass spectrum

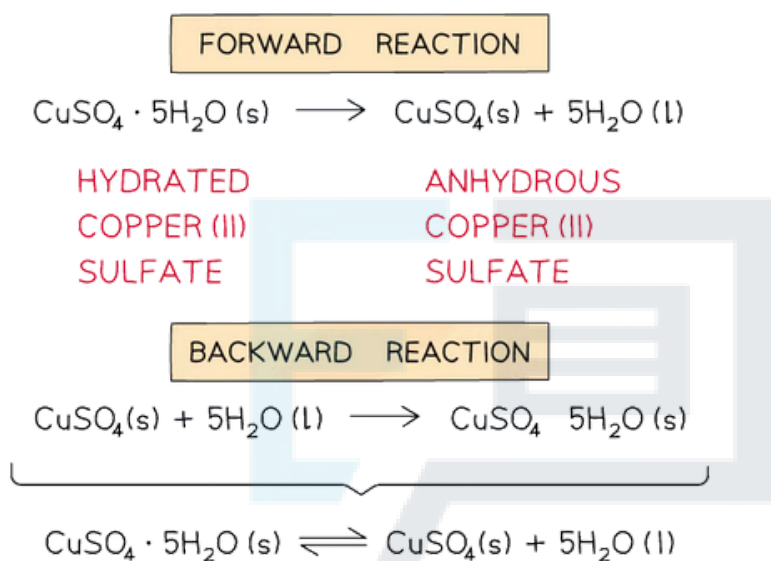
1.10 Equilibrium I

1.10.1 Dynamic Equilibrium

Dynamic Equilibrium

Reversible reaction

- Some reactions go to completion where the reactants are used up to form the products
 - 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: $\rightleftharpoons$



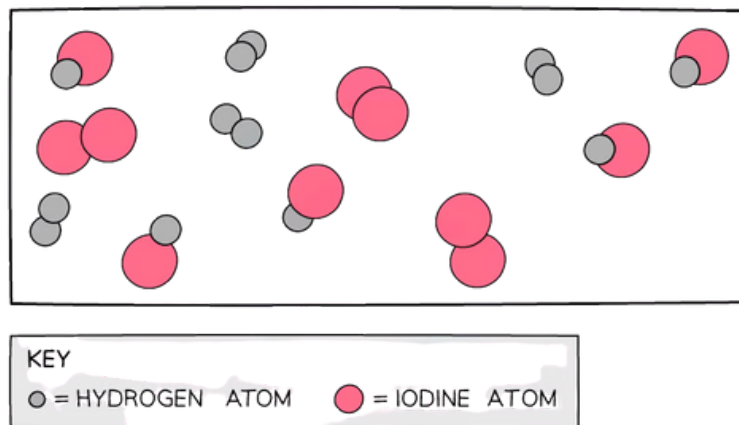
The diagram shows an example of a forward and backward reaction that can be written as one equation using two half arrows

Dynamic equilibrium

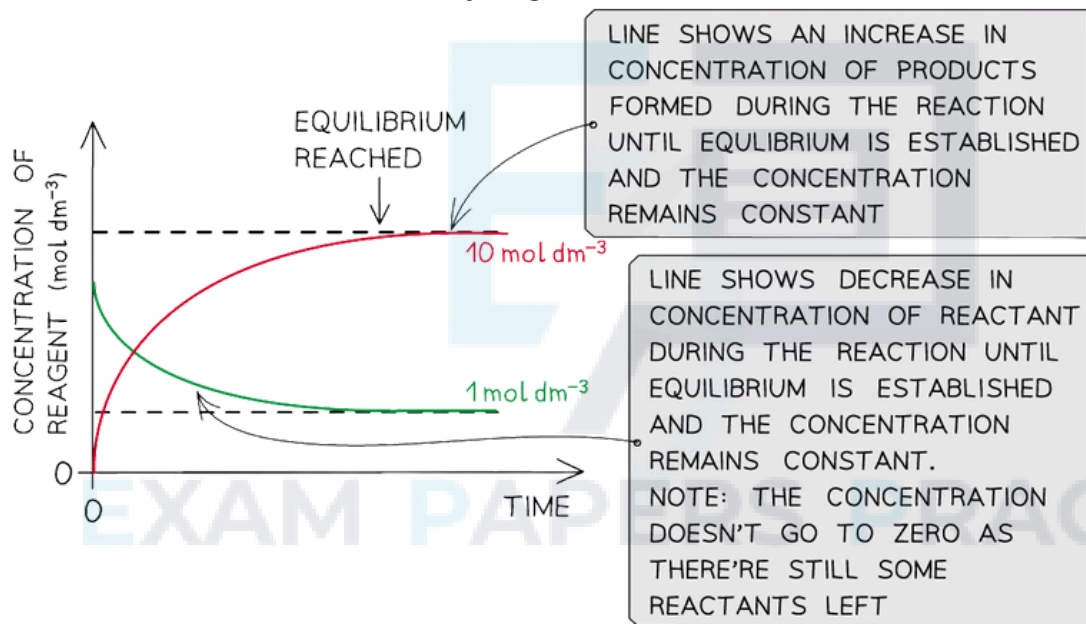
- In a **dynamic equilibrium**, the reactants and products are dynamic (they are constantly moving)
- In a dynamic equilibrium, the **rate of the forward reaction** is the same as the rate of the **backward reaction** in a closed system, and the concentrations of the reactants and products are constant

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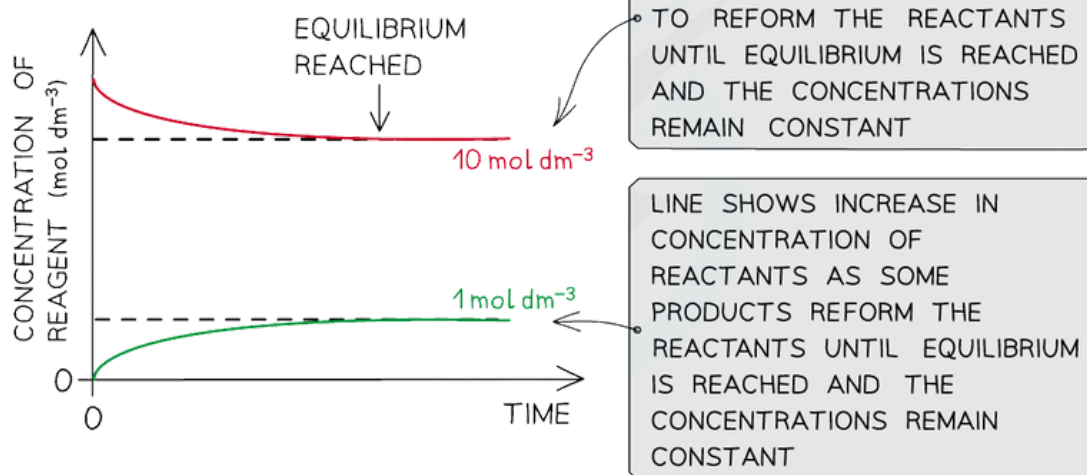




The diagram shows a snapshot of a dynamic equilibrium in which molecules of hydrogen iodide are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules are reacting together to form hydrogen iodide

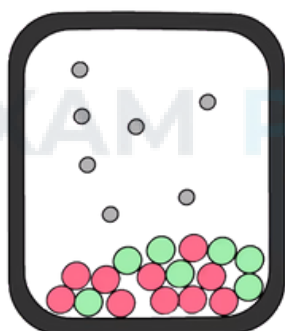


The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)



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)

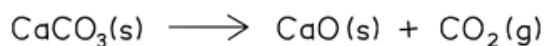
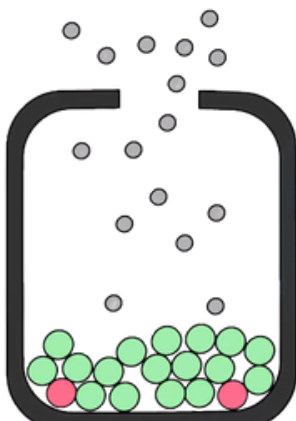
- A closed system is one in which none of the reactants or products escape from the reaction mixture In an open system, matter and energy can be lost to the surroundings
- When a reaction takes place entirely in solution, equilibrium can be reached in open flasks as a negligible amount of material is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



KEY

● = $\text{CaCO}_3(\text{s})$ ● = $\text{CaO}(\text{s})$ ● = $\text{CO}_2(\text{g})$

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.

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.

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EXAM PAPERS PRACTICE

1.10.2 Le Chatelier's Principle

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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

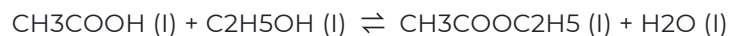
Effects of concentration

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)

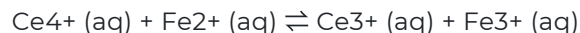
☐ Worked Example

Changes in equilibrium position Using the reaction below:



Explain what happens to the position of equilibrium when:

1. More $\text{CH}_3\text{COOC}_2\text{H}_5$ is added
2. Some $\text{C}_2\text{H}_5\text{OH}$ is removed Using the reaction below:



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. $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g})$

2. $\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$ Predict the effect of decreasing the pressure on the following reaction:

3. $2\text{NO}_2 (\text{g}) \rightleftharpoons 2\text{NO} (\text{g}) + \text{O}_2 (\text{g})$

$\rightleftharpoons$

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

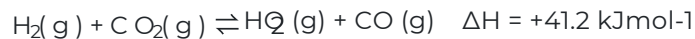
Effects of

temperature How the equilibrium 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:



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

Using the reaction below: $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Ag}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$

2. Increasing the temperature increases the amount of $\text{CO}_2(\text{g})$ at constant pressure. Is this reaction exothermic or endothermic?

Explain your answer

YOUR NOTES



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 $\text{CO}_2(\text{g})$ is formed) this means that the reaction is endothermic

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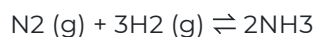
1.10.3 The Rate & Yield Compromise

YOUR NOTES

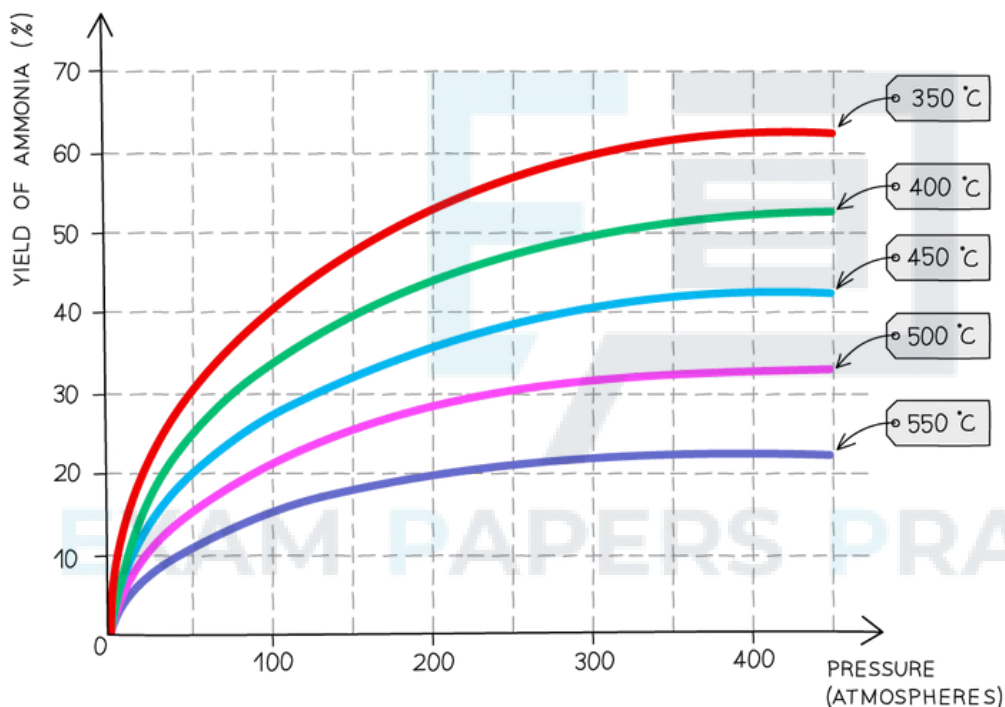


Industrial Compromises

- The Haber Process is, once again, a good example of the need for a compromise of reaction conditions in industrial processes



- The reaction is endothermic in the forward direction
 - Therefore, an increase in temperature may increase the rate of reaction but it will decrease the overall yield as the equilibrium shifts to the left
- An increase in pressure will increase the yield
 - This is because there are 4 moles of reactant compared to only 2 moles of product
- The overall effect of changing the pressure at different temperatures can be seen:



The yield of ammonia with varying conditions for the Haber Process

- Temperature is the first compromise in conditions 450 °C is used as this still produces an acceptable yield of ammonia (roughly 35%) but also within an acceptable time frame
 - Higher temperatures are not used because of the lower yields combined with the increased costs to achieve these temperatures

- Lower temperatures are not used because the rate is too slow despite an increased yield

YOUR NOTES



☐ Exam Tip

In very simplistic terms, this temperature compromise can be thought of as the following question:

Is it better to produce 100 g per hour or 1000 g per day?

- For 100 g per hour, less product is being made but it is being made more quickly
- For 1000g per day, more product is being made but it is being made much more slowly
- Overall, 100 g per hour is better as this results in a total of 2400 g per day

- The second compromise in conditions is pressure A pressure of around 20 MPa
- (or 200 atmospheres) is used, which produces an acceptable yield (around 35%)
 - Doubling the pressure to around 40 MPa (roughly 400 atmospheres, only increases the yield by around 7% However, this comes with the financial and
 - energy costs of producing the pressure requires along with the health and safety considerations of working at such high pressure
- While industry aims for a high yield where possible, sometimes this is balanced and compromised by:
 - Financial and profit considerations - is the cost of altered reaction conditions balanced out by a sufficient increase in yield and, therefore, profit? Energy and
 - environmental considerations - will altering the reaction conditions have an effect on the energy needs (linking back to finance) and will there be an increased use of fossil fuels resulting from the change of conditions? Health and safety considerations - are the proposed reaction conditions actually safe to work with? What potential harm to workers and the manufacturing plant could happen? Is this balanced out by the increase in yield and, therefore, profit?

☐ Exam Tip

The Haber Process has been used as the example for industrial considerations as you should be relatively familiar with this process

However, you can be expected to apply the ideas shown here to any potential industrial reaction

1.10.4 Deducing K_c Expressions

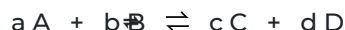
YOUR NOTES



Deducing K_c Expressions

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:



- 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)

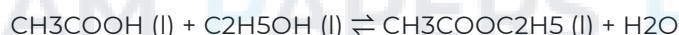
a, b, c AND d = NUMBER OF MOLES OF REACTANTS AND PRODUCTS

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

- The K_c of a reaction is specific and only changes if the temperature of the reaction changes

Homogeneous systems K_c

and a homogeneous system is where all of the reactants and products are in the same physical state, e.g.

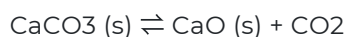


- For this reaction, all of the reactants and products are in the same, liquid state / phase and will, therefore, all feature in the K_c expression

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}] [\text{C}_2\text{H}_5\text{OH}]}$$

Heterogeneous systems K_c

and a heterogeneous system is where not all of the reactants and products are in the same physical state, e.g.



- Solids are ignored in equilibrium expressions
 - This leads to a K_c expression of $K_c = [\text{CO}_2]$

☐ Exam Tip

Expressions, it is important that you use square brackets as sometimes examiners are instructed to be strict about the appearance of brackets in expressions

Square brackets implies concentration

☐ Worked Example

Deducing equilibrium expressions Deduce the equilibrium

expression for the following reactions:

1. $\text{Ag}^+ (\text{aq}) + \text{Fe}^{2+} (\text{aq}) \rightleftharpoons \text{Ag} (\text{s}) + \text{Fe}^{3+} (\text{aq})$
2. $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g})$
3. $2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2\text{SO}_3 (\text{g})$

Answer 1:

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

Answer 2:

- $K_c = \frac{[\text{NH}_3 (\text{g})]^2}{[\text{N}_2 (\text{g})][\text{H}_2 (\text{g})]^3}$

Answer 3:

- $K_c = \frac{[\text{SO}_3 (\text{g})]^2}{[\text{SO}_2 (\text{g})]^2 [\text{O}_2 (\text{g})]}$

1.2 Ions & Electrons

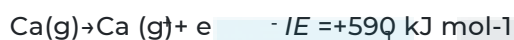
1.2.1 Ionisation Energy

Factors Affecting Ionisation Energy

Ionisation energy

- 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 (IE₁)** is the energy required to remove **one mole of electrons** from one mole of gaseous atoms of an element to form one mole of gaseous 1+ ions.

◦ E.g. the first ionisation energy of gaseous calcium:



Successive ionisation energies of an element

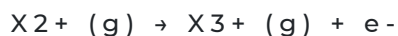
- More than one electron can be removed from an atom and each time you remove an electron there is a successive ionisation energy. These are called second, third ionisation energy and so on.
- The **second ionisation energy (IE₂)** is defined as
 - is the energy required to remove **one mole of electrons** from one mole of gaseous 1+ ions to form one mole of gaseous 2+ ions.
- And can be represented as



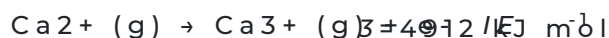
OR (for calcium)



- The **third ionisation energy (IE₃)** of an element can be represented as



OR (for calcium)



- 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.

YOUR NOTES



- 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

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First Ionisation Energy – Period

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**

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 IE1 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 1s² 2s²
 - **Boron** has a first ionisation energy of 800 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p¹_x
- There is a slight **decrease** in IE1 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 1s² 2s² 2p³ 2p¹_z
 - **Oxygen** has a first ionisation energy of 1310 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p²_x 2p²_z
 - 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**

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First Ionisation Energy – Group

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

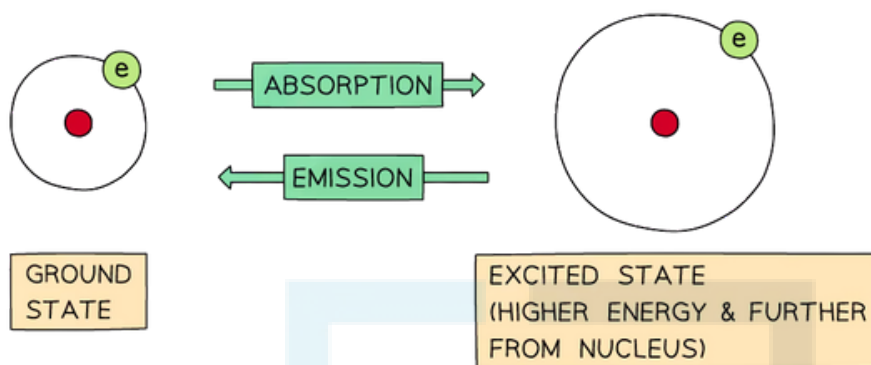
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1.2.2 Quantum Shells

Developing Electronic Configuration

- Electrons move rapidly around the nucleus in energy shells
- If their energy is increased, then they can jump to a higher energy level. The process is reversible, so electrons can return to their original energy levels
 - When this happens, they emit energy
- The frequency of energy is exactly the same, it is just being emitted rather than absorbed:



The difference between absorption and emission depends on whether electrons are jumping from lower to higher energy levels or the other way around

- The energy they emit is a mixture of different frequencies. This is thought to correspond to the many possibilities of electron jumps between energy shells. If the emitted energy is in the visible region, it can be analysed by passing it through a diffraction grating. The result is a line emission spectrum.

Line emission spectra



The line emission (visible) spectrum of hydrogen

- Each line is a specific energy value
 - This suggests that electrons can only possess a limited choice of allowed energies
- These packets of energy are called 'quanta' (plural quantum)
- What you should notice about this spectrum is that the lines get closer together towards the blue end of the spectrum

YOUR NOTES

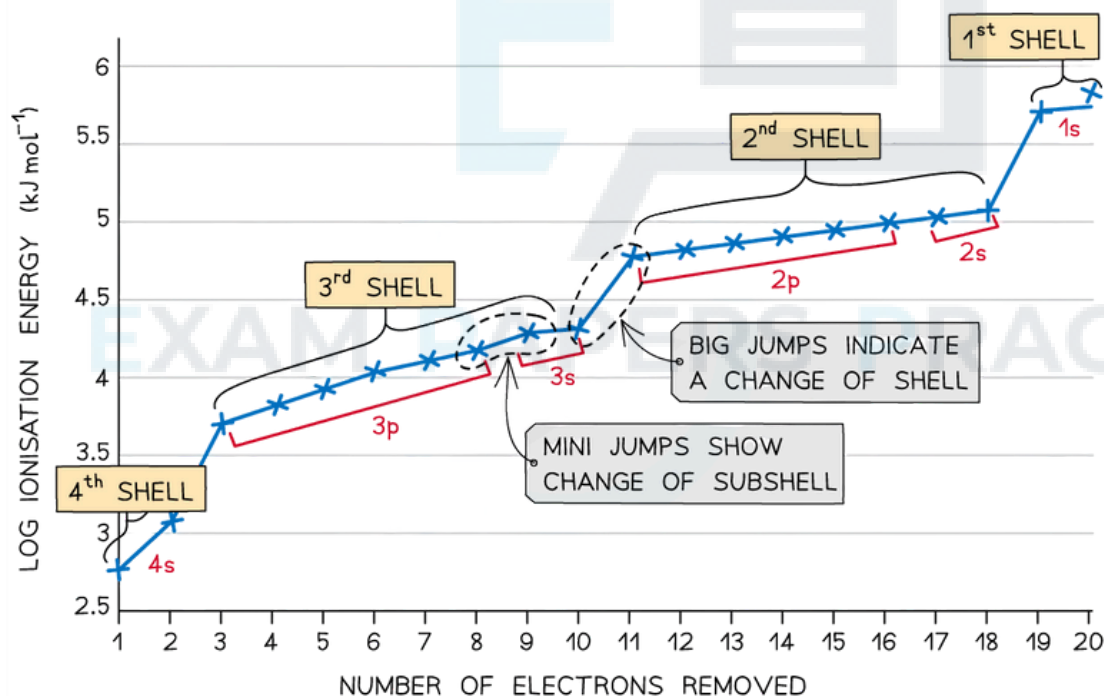
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- This is called **convergence** and the set of lines is **converging** towards the higher energy end, so the electron is reaching a maximum amount of energy. This maximum corresponds to the **ionisation energy** of the electron. These lines were first observed by the Swiss school teacher Johannes **Balmer**, and they are named after him. We now know that these lines correspond to the electron jumping from higher levels down to the **second** or $n = 2$ energy level.

Successive ionisation energies

- The **first** electron removed has a low $|E|$ 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.



Successive ionisation energies for the element calcium

Filling Quantum 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

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1.2.3 Orbitals

YOUR NOTES



Orbital Shapes

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 ($1 \times 2 =$ total of 2 electrons)
 - **p** : three orbitals ($3 \times 2 =$ total of 6 electrons)
 - **d** : five orbitals ($5 \times 2 =$ total of 10 electrons)
 - **f** : seven orbitals ($7 \times 2 =$ 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

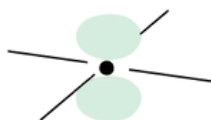
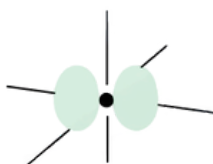
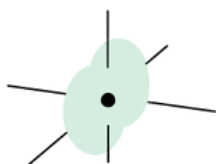
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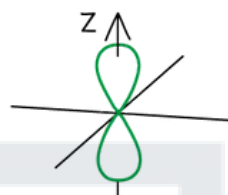
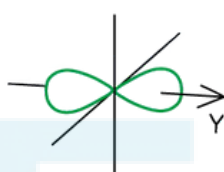
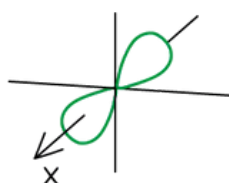
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a. s ORBITALS



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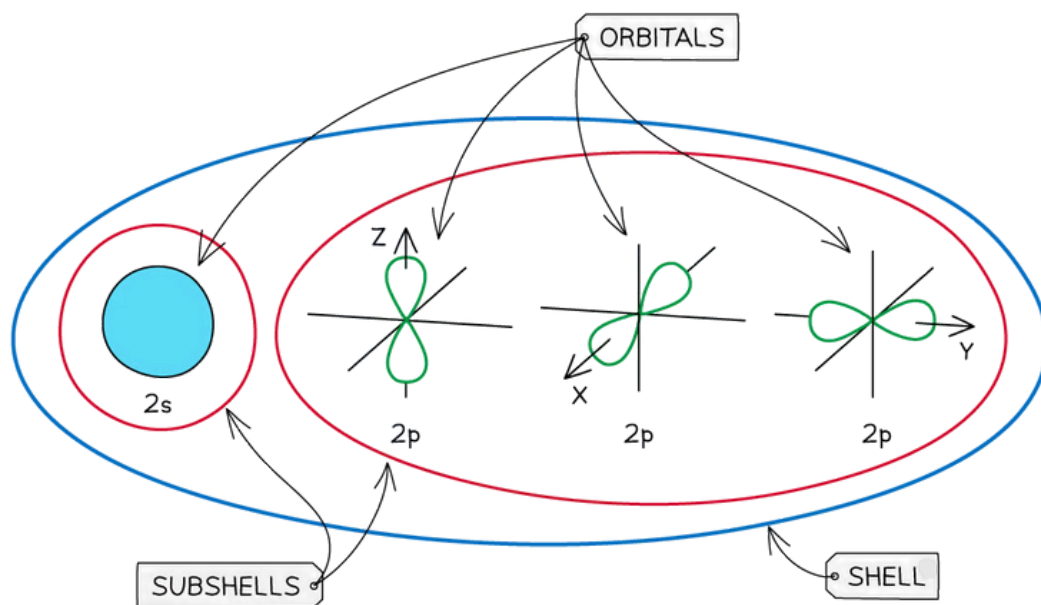


b. p ORBITALS

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

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

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

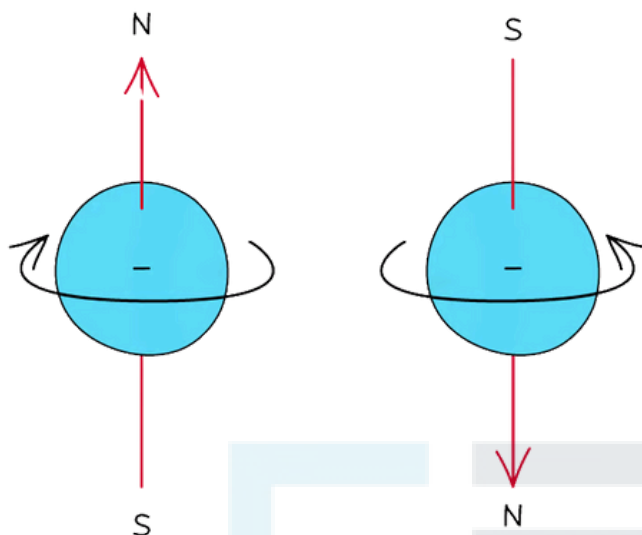
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Filling Orbitals

YOUR NOTES

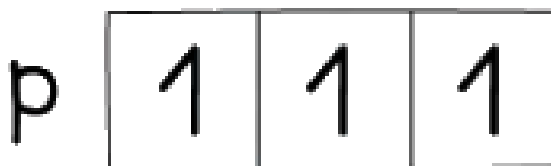


- Electrons can be imagined as small spinning charges which rotate around their own axis in either a **clockwise** or **anticlockwise** direction
 - The spin of the electron is represented by its direction. The spin creates a tiny magnetic field with N-S pole pointing up or down.



Electrons can spin either in a clockwise or anticlockwise direction around their own axis

- Electrons with the same spin repel each other which is also called **spin-pair repulsion**
 - Therefore, electrons will occupy separate orbitals in the same subshell first to minimise this repulsion and have their **spin** in the same direction. They will then pair up, with a second electron being added to the first p orbital, with its spin in the **opposite** direction.
- This is known as **Hund's Rule**
 - 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.



Electron configuration: three electrons in a p subshell

- The principal quantum number indicates the energy level of a particular shell but also indicates the energy of the electrons in that shell.

- A 2p electron is in the second shell and therefore has an energy corresponding to $n = 2$

- Even though there is repulsion between negatively charged electrons, they
 - occupy the same region of space in orbitals
 - An orbital can only hold two electrons and they must have opposite spin - this is known as the **Pauli Exclusion Principle**
 - This is because the energy required to jump to a higher empty orbital is **greater** than the inter-electron repulsion
- For this reason, they pair up and occupy the lower energy levels first

YOUR NOTES



EXAM PAPERS PRACTICE

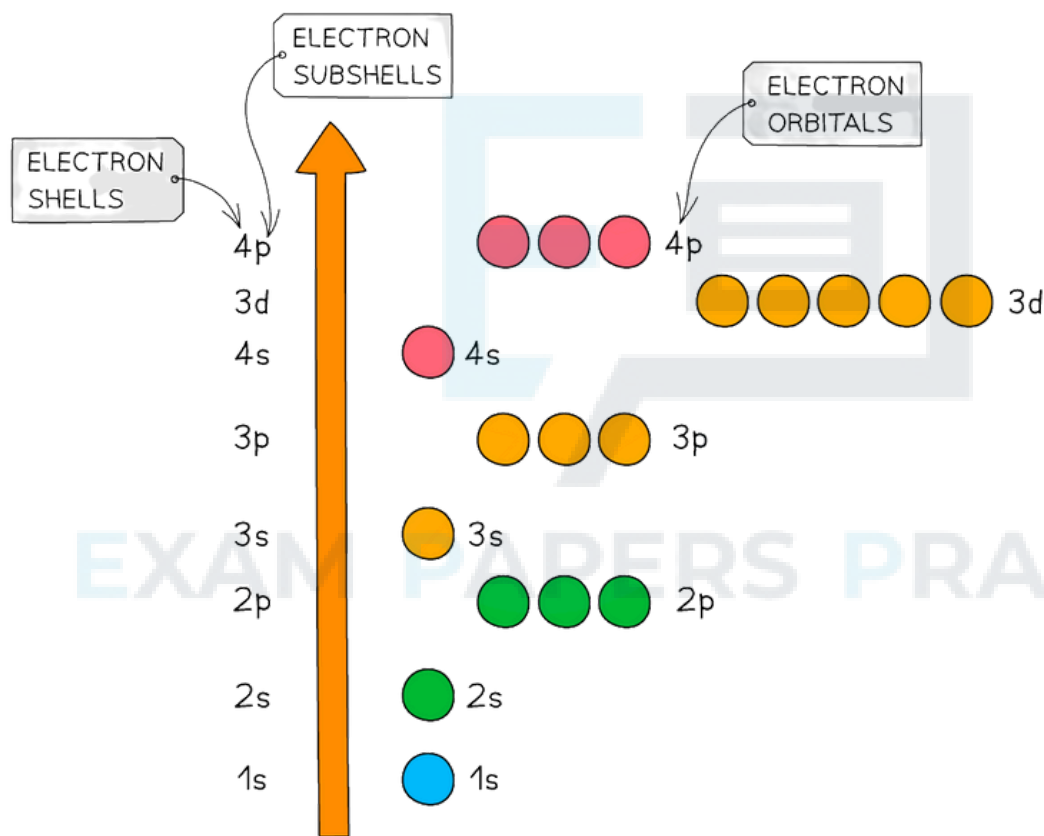
1.2.4 Electronic Configurations

YOUR NOTES



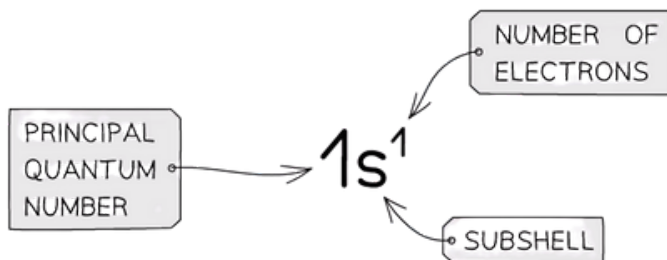
Electronic Configurations of Atoms & Ions

- 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

Configuration has 1 single electron

- The electron is in the s orbital of the first shell
- Its electron configuration is 1s¹
- 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 1s² 2s² 2p⁶ 3s² 3p⁶ 4s¹

Shorthand Electron

Configuration 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] 4s¹

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 $[\text{Ar}] 4s^2$ 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:

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

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

- 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

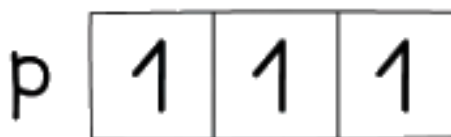
also $1s^2 2s^2 2p^6 3s^2 3p^6$

Exceptions

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

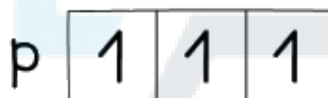
Presenting the Electron Configuration

- 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 px, py and pz orbital



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 px 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



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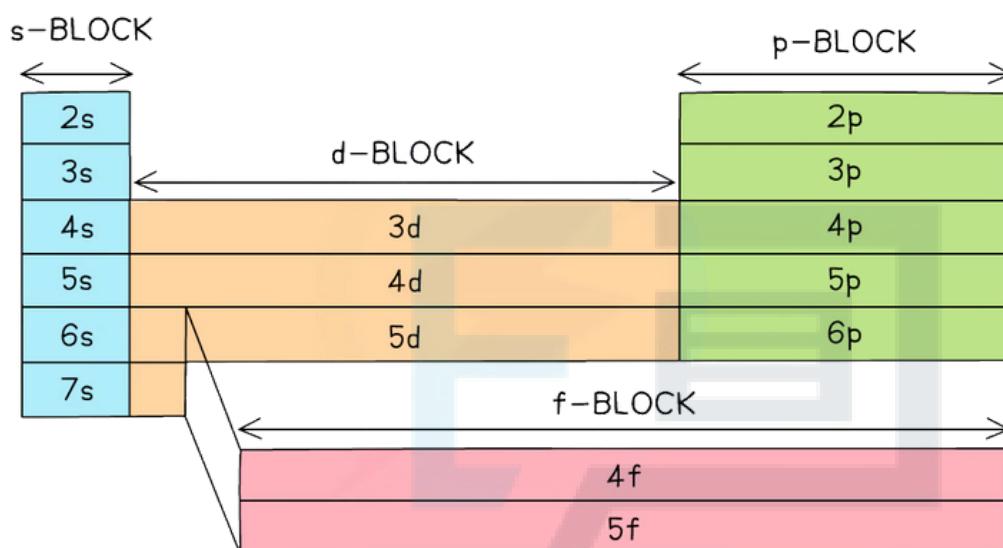


The electrons in titanium are arranged in their orbitals as shown. Electrons occupy the lowest energy levels first before filling those with higher energy

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Classifying Elements

- 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



Electronic Configuration & Chemical Properties

- The way an element reacts with other elements is determined by a number of factors, but in particular the **electronic configuration** of its atoms
- The Periodic Table is arranged in **periods (horizontal)** and **groups (vertical)**
 - All the elements in the same period have the same number of shells (principle quantum number)
 - All the elements in the same group have the same number of outer electrons
- The elements in each group of period show particular trends and characteristics in their chemical and physical properties that can be explained in terms of their atomic numbers
- This provides valuable information about what is **likely to happen** when particular elements react
- The properties of the elements are a function of their atomic numbers
- Using this information as well as the location of the elements in the different blocks we can predict the properties
- For example:
 - Helium, neon and argon all have electronic structures with full sub shells as well as high ionisation energies
 - This confirms that the **electronic arrangement** is very stable explaining why they rarely react with other chemicals

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1.3 The Periodic Table

1.3.1 Periodicity

Melting & Boiling Point Trends

- Elements in the periodic table are arranged in order of increasing atomic number and placed in vertical columns (groups) and horizontal rows (periods)
- The elements across the periods show repeating patterns in chemical and physical properties. This is called periodicity.

PERIODIC TABLE OF THE ELEMENTS

KEY

MASS NUMBER
ELEMENT SYMBOL
ATOMIC NUMBER
NAME

AT ROOM TEMPERATURE

- METALS
- NON-METALS - SOLID
- NON-METALS - GAS
- LIQUIDS
- METALLOID

All elements are arranged in the order of increasing atomic number from left to right.

Melting point

- Period 2 and 3 elements follow the same pattern in relation to their melting points

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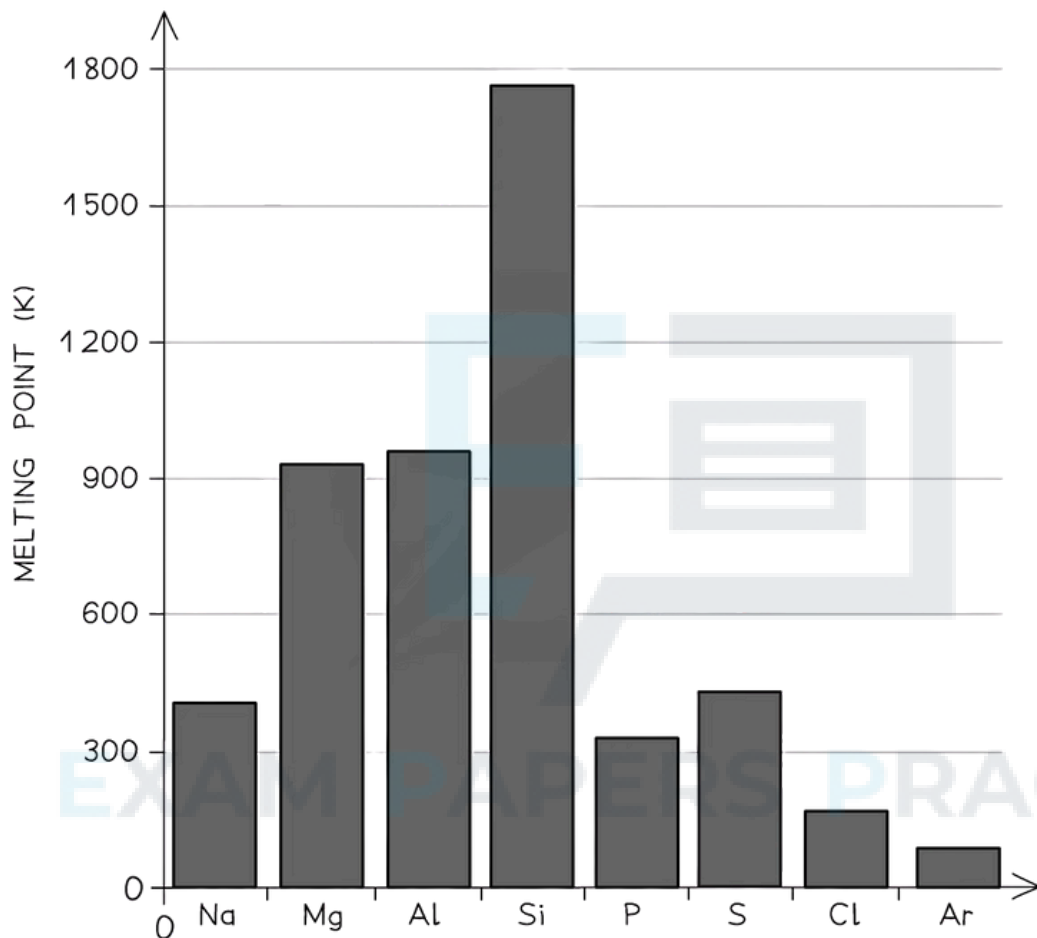


Melting points of the elements across Period 3 table

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Period 3 Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting Point (K)	371	923	932	1683	317	392	172	84



Ions of Period 3 elements with increasing positive charge (metals) and increasing of number of outer electrons across the period

- A general increase in **melting point** for the Period 3 elements up to silicon is observed **Silicon** has the highest **melting point** After the Si element the melting points of the elements **decreases** significantly
- The above trends can be explained by looking at the bonding and structure of the elements

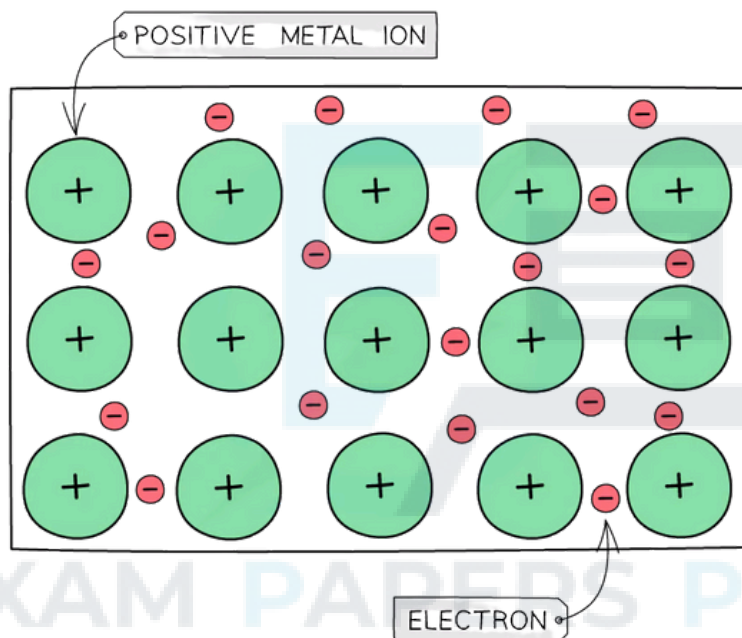
Bonding & structure of the elements table

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Period 3 Element	Na	Mg	Al	Si	P	S	Cl	Ar
Bonding	Metallic	Metallic	Metallic	Covalent	Covalent	Covalent	Covalent	–
Structure	Giant metallic	Giant metallic	Giant metallic	Giant molecular	Simple molecular	Simple molecular	Simple molecular	Simple molecular

- The table shows that Na, Mg and Al are metallic elements which form positive ions arranged in a **giant lattice** in which the ions are held together by a 'sea' of delocalised electrons



Metal cations form a giant lattice held together by electrons that can freely move around

- The electrons in the 'sea' of delocalised electrons are those from the **valence shell** of the atoms
- Na will donate one electron into the 'sea' of delocalised electrons, Mg will donate two and Al three electrons
- As a result of this, the metallic bonding in Al is stronger than in Na
- This is because the electrostatic forces between a $3+$ ion and the larger number of negatively charged delocalised electrons is much larger compared to a $1+$ ion and the smaller number of delocalised electrons in Na
- Because of this, the **melting points** increase going from Na to Al

- Si has the highest melting point due to its giant molecular structure in which each Si atom is held to its neighbouring Si atoms by **strong covalent bonds**
- P, S, Cl and Ar are non-metallic elements and exist as **simple molecules** (P₄, S₈, Cl₂ and Ar as a single atom)
- The **covalent bonds** within the molecules are strong, however, **between** the molecules, there are only weak **instantaneous dipole-induced dipole forces**
- It doesn't take much energy to break these **intermolecular forces**
- Therefore, the melting points decrease going from P to Ar (note that the melting point of S is higher than that of P as sulphur exists as larger S₈ molecules compared to the smaller P₄ molecule)

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Atomic radius

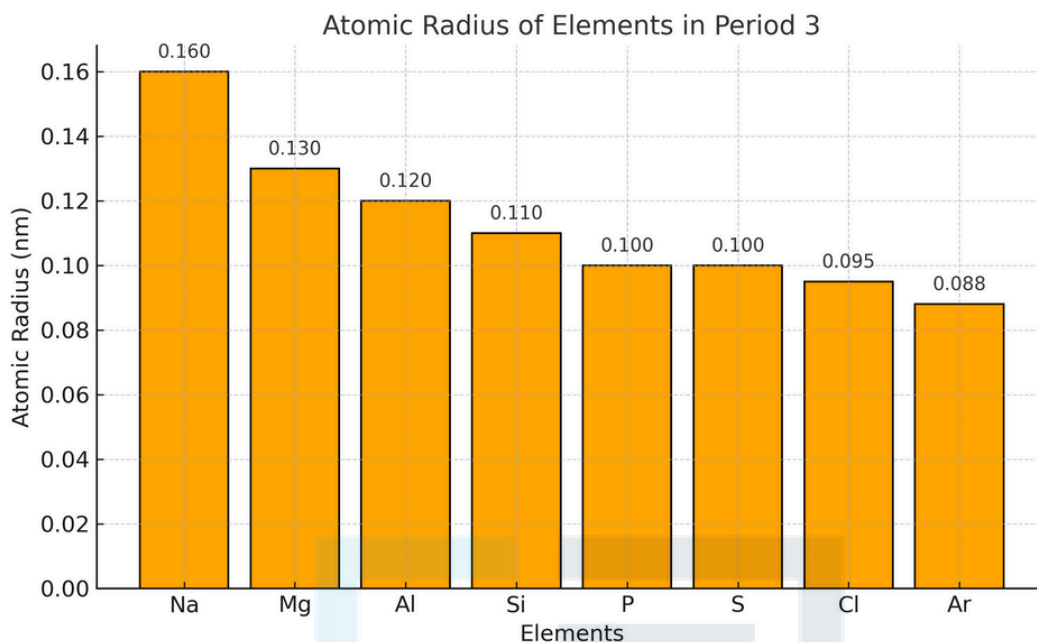
- The **atomic radius** is the distance between the nucleus and the outermost electron of an atom. The atomic radius is measured by taking two atoms of the same element, measuring the distance between their nuclei and then halving this distance. In **metals** this is also called the **metallic radius** and in **non-metals**,
- the **covalent radius**

Atomic radii of period 3 elements

- You can see a clear trend across the period which also **repeated** in period 2

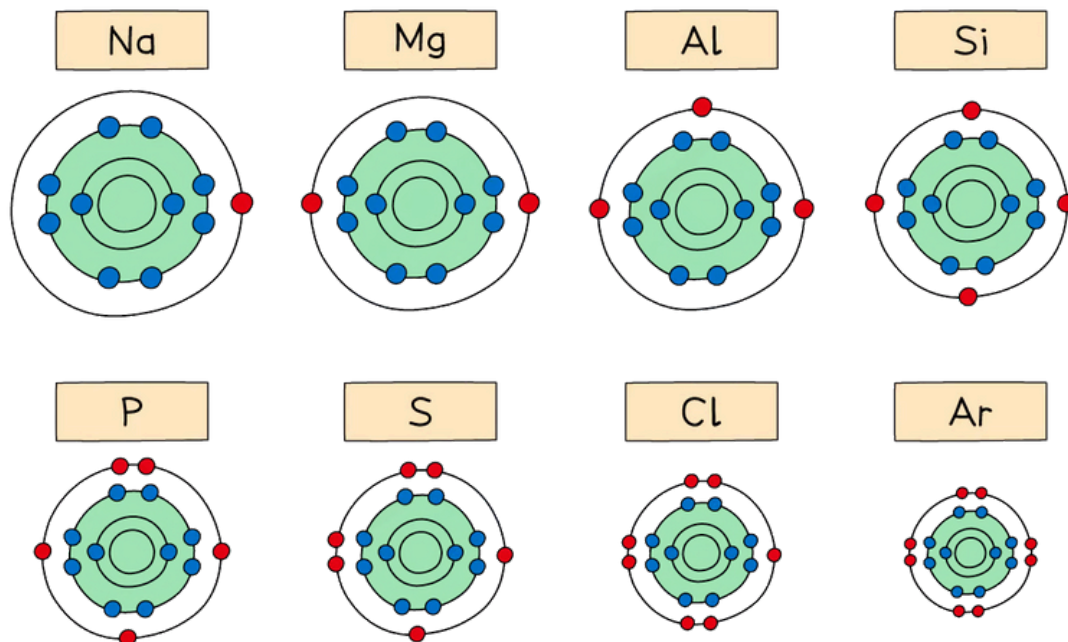
Period 3 Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic Radius (nm)	0.157	0.136	0.125	0.117	0.110	0.104	0.099	No data

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The graph shows a decrease in atomic radii of period 3 elements across the period

- Across the period, the atomic radii decrease
- This is because the number of protons (**the nuclear charge**) and the number of **electrons** increases by one every time you go an element to the right
- The elements in a period all have the same number of shells (so the **shielding effect** is the same)
- This means that as you go across the period the nucleus attracts the electrons more **strongly pulling them closer** to the nucleus. Because of this, the atomic radius (and thus the size of the atoms) **decreases** across the period



The diagram shows that across period 3, the elements gain extra electrons in the same principal quantum shell

Ionisation Energy Trends

Ionisation energy across period 2 and 3

- 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 for period 2

- There is a slight **decrease in I_E** 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 1s² 2s²
 - Boron has a first ionisation energy of 800 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p¹
- There is a slight **decrease in I_E** between **nitrogen** and **oxygen** due to **spin-pair repulsion** in the 2p orbital of oxygen
 - Nitrogen has a first ionisation energy of 1400 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p³ (↑↑↑)
 - Oxygen has a first ionisation energy of 1310 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p⁴ (↑↑↓↑)
- In oxygen, there are 2 electrons in the 2p orbital, so the repulsion between those electrons makes it slightly easier for one of those electrons to be removed

Dips in the trend for period 3

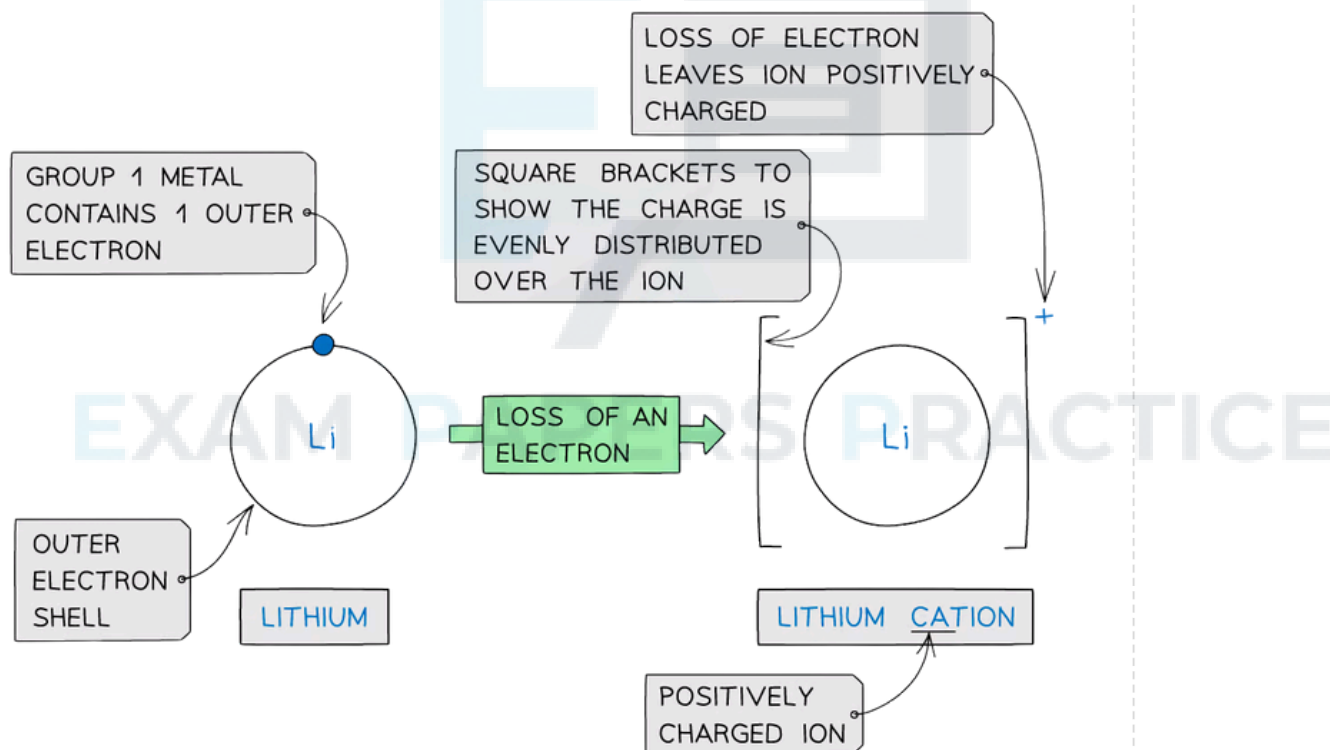
- There is again a slight decrease between **magnesium** and **aluminium** as the thirteenth electron in aluminium is in the 3p subshell, which is further away from the nucleus than the 3s subshell of magnesium
 - Magnesium has a first ionisation energy of 738 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p⁶ 3s²
 - Aluminium has a first ionisation energy of 578 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p⁶ 3s² 3p¹
- There is a slight decrease in I_E between **phosphorus** and **sulfur** due to **spin-pair repulsion** in the 3p orbital of oxygen
 - Phosphorus has a first ionisation energy of 1012 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p⁶ 3s² 3p³ (↑↑↑)
 - Sulfur has a first ionisation energy of 1000 kJ mol⁻¹ as its electron configuration is 1s² 2s² 2p⁶ 3s² 3p⁴ (↑↑↓↑)
- In sulfur, there are 2 electrons in the 3p orbital, so the repulsion between those electrons makes it slightly easier for one of those electrons to be removed

1.4 Bonding

1.4.1 Ionic Bonding Overview

Ionic Bonds

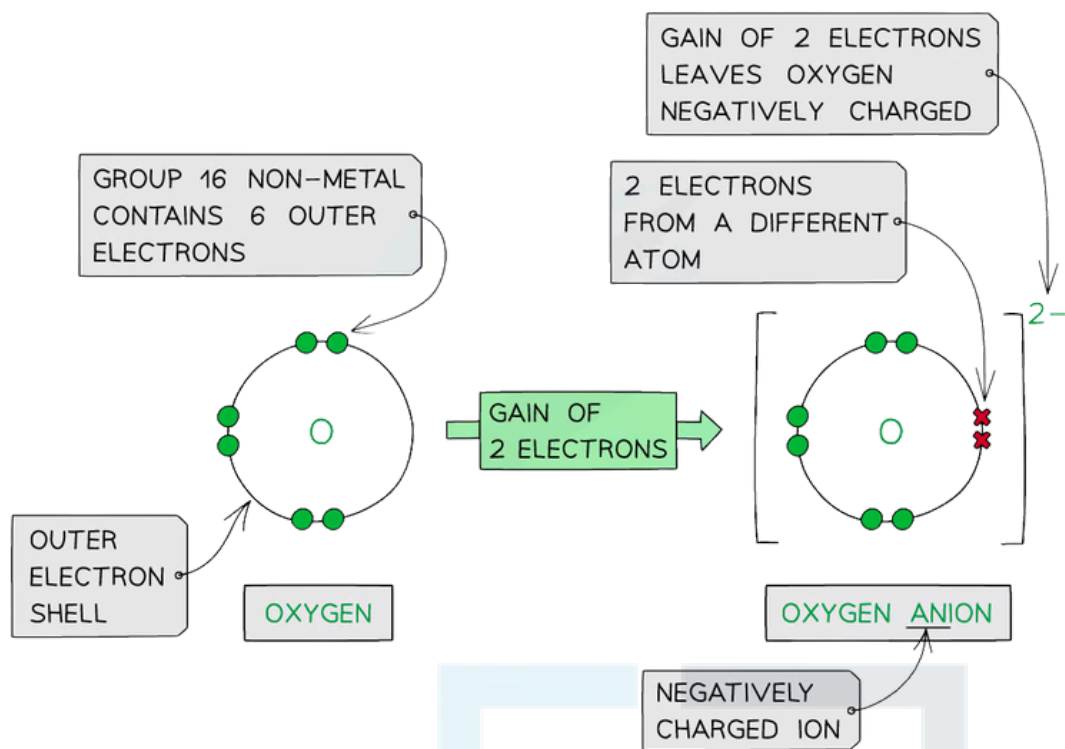
- As a general rule, **metals** are on the left of the periodic table and **nonmetals** are on the right-hand side. **Ionic bonding** involves the **transfer** of electrons from
- a **metallic** element to a **non-metallic** element. Transferring electrons usually leaves the metal and the non-metal with 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

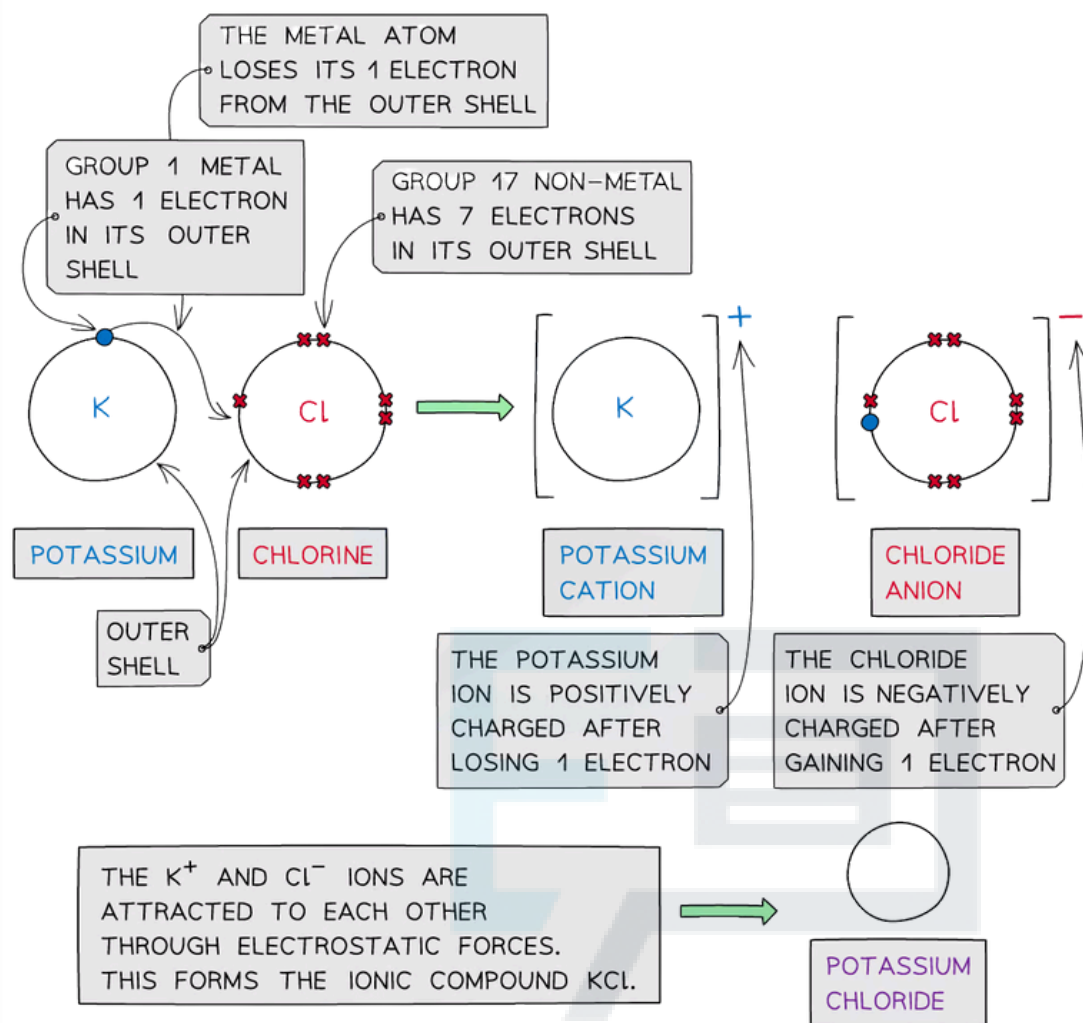
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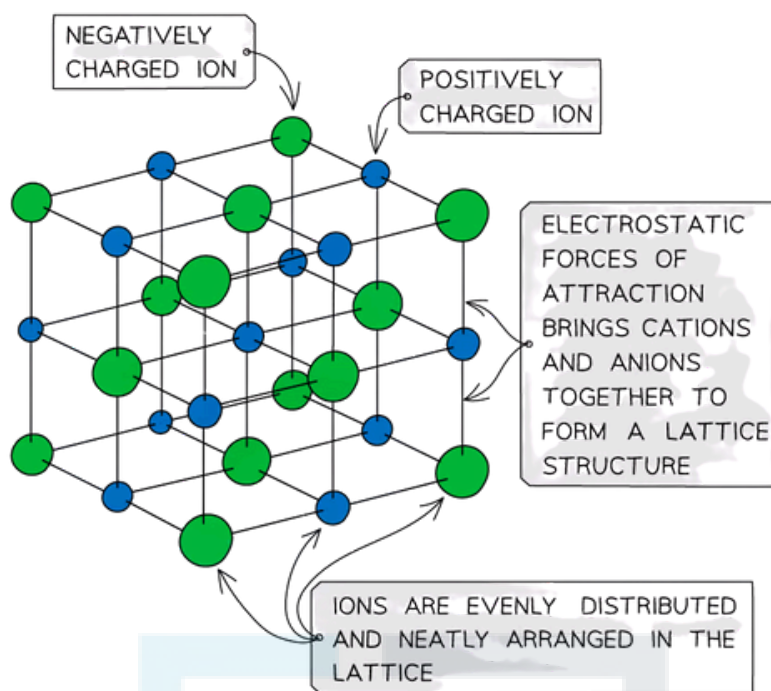
Forming anions by the addition of electrons to nonmetals

- 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

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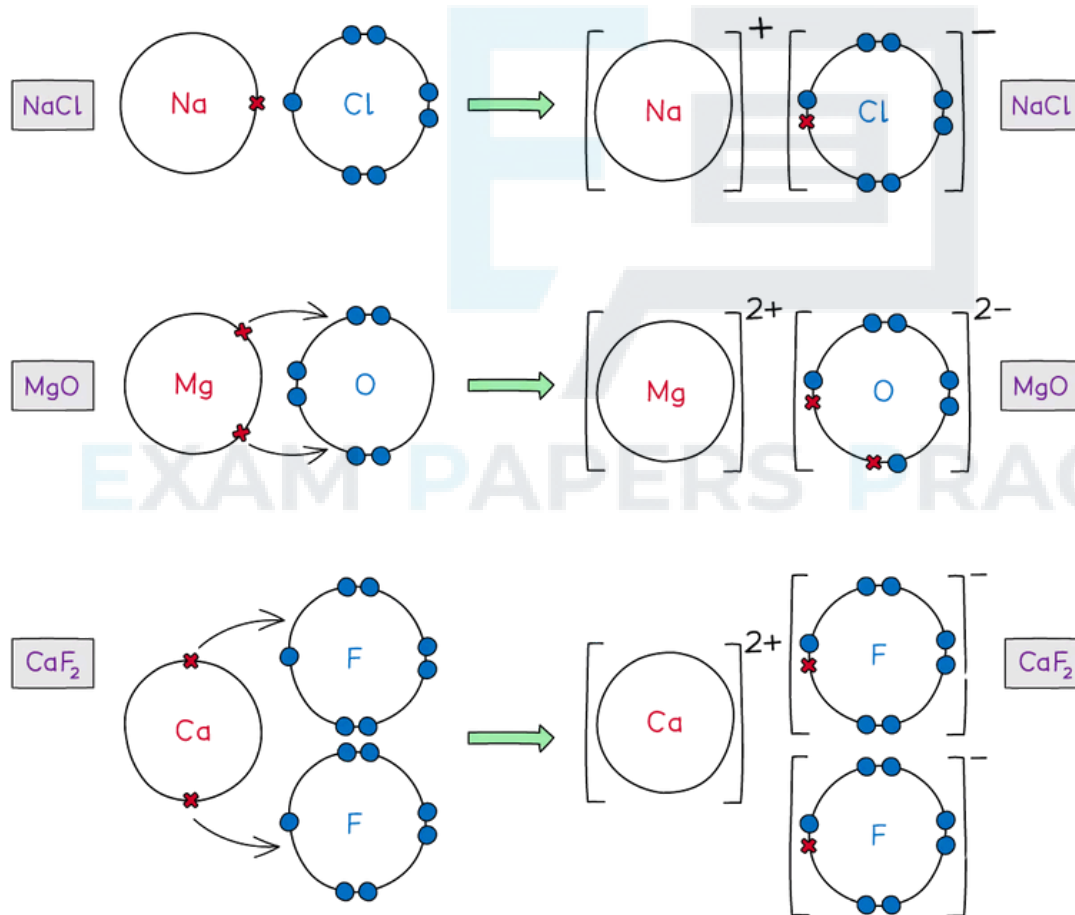
1.4.2 Representing Ionic Bonding

Ionic Dot-and-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 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

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Calcium fluoride

- Calcium is a Group 2 **metal**
 - It **loses** its 2 outer electrons to form a calcium ion with a +2 charge (Ca^{2+})
- Fluorine is a Group 7 **non-metal**
 - It **gains** 1 electron to form a fluoride ion with a -1 charge (F^-)
- As before, the positive and negative ions are attracted to each other via an ionic bond
- However, to cancel out the 2+ charge of the calcium ion, 2 fluorine atoms are needed
 - Each fluorine atom can only accept 1 electron from the calcium atom
 - 2 fluoride ions will be formed
- Calcium fluoride is made when 1 calcium ion and 2 fluoride ions form ionic bonds, CaF_2
- The final ionic solid of CaF_2 is **neutral** in charge

☐ Worked Example

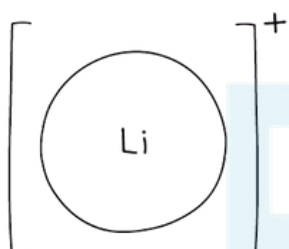
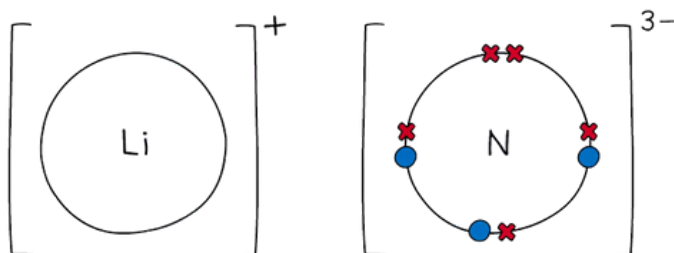
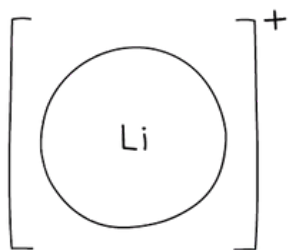
Draw a dot cross diagram for lithium nitride

Answer

- Lithium is a Group 1 **metal**
- It **loses** its outer electron to form a lithium ion with a +1 charge (Li^+)
- Nitrogen is a Group 5 **non-metal**
- It **gains** 3 electrons to form a nitride ion with a -3 charge (N^{3-})
- To cancel out the -3 charge of the nitride ion, 3 lithium atoms are needed and 3 lithium ions will be formed
- Lithium nitride is made when 1 nitride ion and 3 lithium ions form ionic bonds
- The final ionic solid of Li_3N is **neutral** in charge

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Dot and cross diagram to show the ionic bonding in lithium nitride

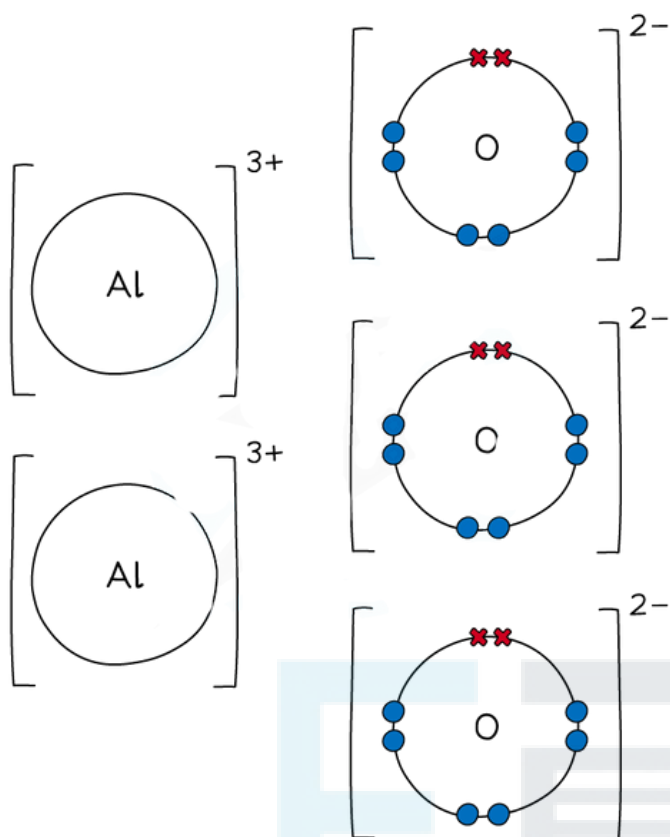


Worked Example

Draw a dot and cross diagram for aluminium oxide

Answer

- Aluminium is a Group 3 **metal**
- It **loses** its outer electrons to form an aluminium ion with a +3 charge (Al^{3+})
- Oxygen is a Group 6 **non-metal**
- It **gains** 2 electrons to form an oxide ion with a -2 charge (O^{2-})
- To cancel out the negative and positive charges, 2 aluminium and 3 oxygen atoms are needed
- Aluminium oxide is made when 2 aluminium ions and 3 oxygen ions form ionic bonds
- The final ionic solid of Al_2O_3 is **neutral** in charge



Dot and cross diagram to show the ionic bonding in aluminium oxide

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1.4.3 Ionic Trends

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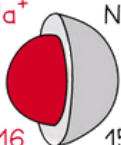
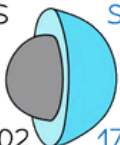
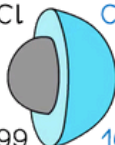
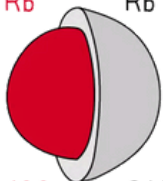
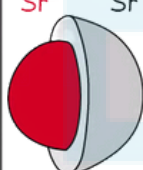
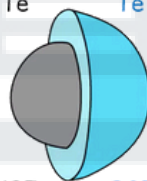
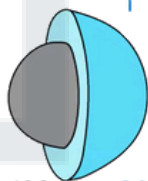


Ionic Radius

Ionic radius

- The **ionic radius** of an element is a measure of the size of an ion
- Ionic radii show predictable patterns
 - Ionic radii **increase** with increasing **negative charge**
 - Ionic radii **decrease** with increasing **positive charge**
- For negative ions
 - They are formed by atoms **gaining** electrons
 - The outermost electrons are further away from the positively charged nucleus and are therefore held only weakly to the nucleus which **increases the ionic radius**
 - The greater the negative charge, the larger the ionic radius
- For positive ions
 - Positively charged ions are formed by atoms **losing** electrons
 - The nuclear charge remains the same but there are now fewer electrons which undergo a greater electrostatic force of attraction to the nucleus which **decreases the ionic radius**
 - The greater the positive charge, the smaller the ionic radius

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SIZES OF ATOMS AND THEIR IONS IN PM					
	GROUP 1	GROUP 2	GROUP 13	GROUP 16	GROUP 17
PERIOD 2	Li^+ Li  90 134	Be^{2+} Be  59 90	B  41 82	O^{2-}  73 126	F^-  71 119
PERIOD 3	Na^+ Na  116 154	Mg^{2+} Mg  86 130	Al^{3+} Al  68 118	S S^{2-}  102 170	Cl Cl^-  99 167
PERIOD 4	K^+ K  152 196	Ca^{2+} Ca  114 174	Ga^{3+} Ga  76 126	Se Se^{2-}  116 184	Br Br^-  114 182
PERIOD 5	Rb^+ Rb  166 211	Sr^{2+} Sr  132 192	In^{3+} In  94 144	Te Te^{2-}  135 207	I^-  133 206

Trends in the ionic radii across a period and down a group

Isoelectronic Ions

- These are ions that have the **same electronic configuration**
- For example the following ions all have the electronic configuration of $1s^2 2s^2 2p^6$
- However, they all have different numbers of protons, therefore will have a different ionic radius
 - N^{3-} (7 protons)
 - O^{2-} (8 protons)
 - F^- (9 protons)
 - Na^+ (11 protons)
 - Mg^{2+} (12 protons)
 - Al^{3+} (13 protons)
- As the number of protons in the nucleus of the ion increases, the electrons get pulled in more closely to the nucleus. The radii of the isoelectronic ions
- therefore fall across this series of ions
 - N^{3-} has an ionic radius of 0.171 nm and Al^{3+} has an ionic radius of 0.054 nm

1.4.4 Physical Properties of Ionic Compounds

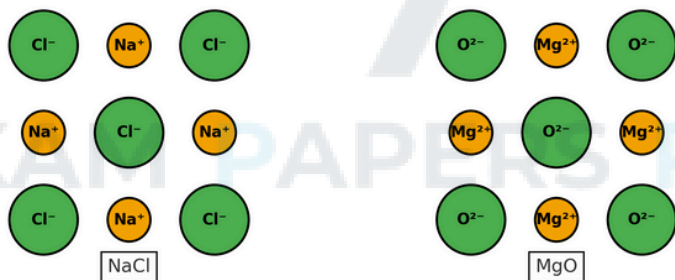
Physical Properties of Ionic Compounds

- 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**

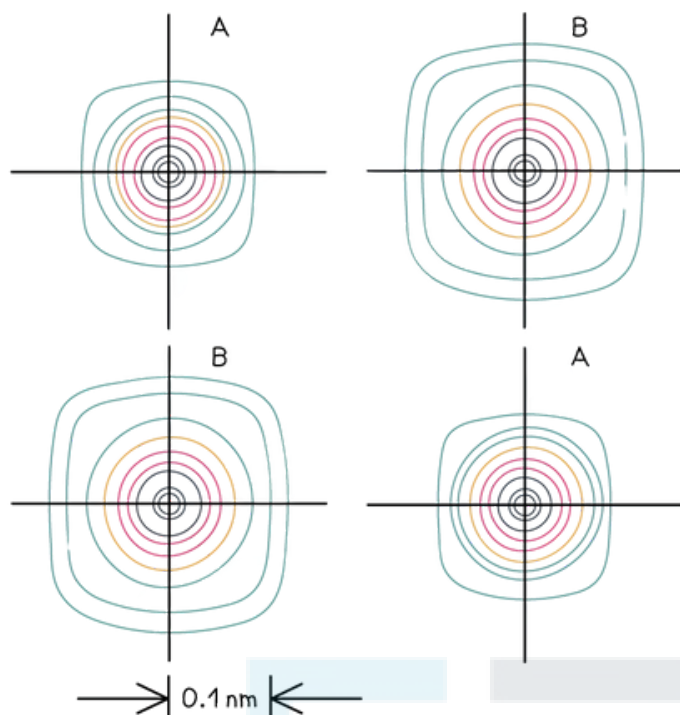
Negative ions (anions) are bigger than positive ions (cations)



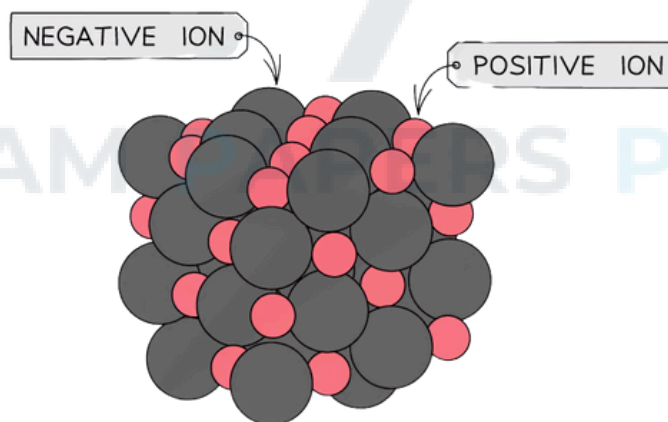
Ionic lattices of the ionic compounds NaCl and MgO

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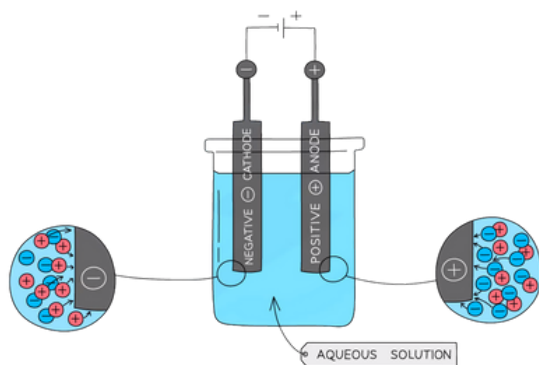
Electron density maps shown above show the likelihood of finding electrons in a region. This shows the electron density map for NaCl. The contours are lines of equal electron density. A = Na^+ ions (smaller), B = Cl^- ions (larger). Between the ions the electron density falls to zero.



General ionic lattice which shows the actual packing of the ions

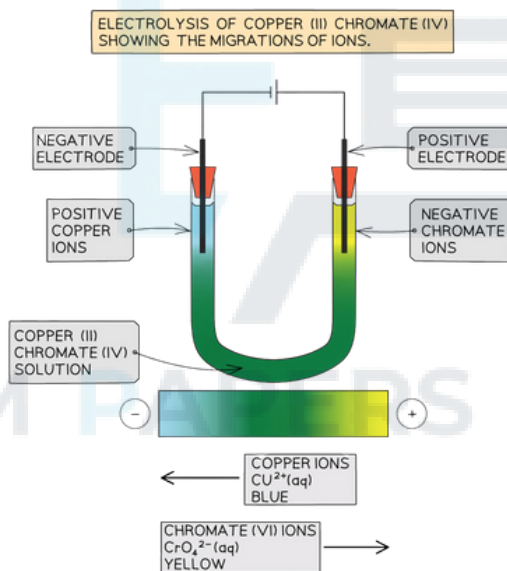
Evidence

- The behaviour of ionic substances during electrolysis is a clear piece of evidence for the existence of ions
 - Positive ions in solution are attracted to the negative electrode
 - Negative ions in solution are attracted to the positive electrode



Set up of electrolysis

- An example which is simple to see the separation is using copper(II) chromate(VI), CuCrO_4
- The solution contains
 - Cu^{2+} ions (blue)
 - CrO_4^{2-} ions (yellow)



- Overall the solution is an olive green colour, but when the solution undergoes electrolysis a blue colour appears around the negative electrode, and a yellow colour appears around the positive electrode
- This is because the Cu^{2+} ions are attracted to the negative electrode and their blue colour is observed and the CrO_4^{2-} their yellow colour is observed

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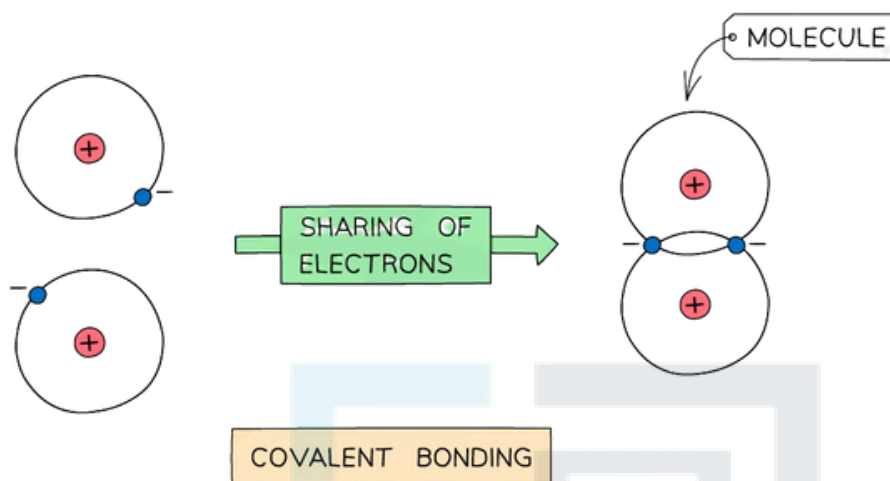
1.4.5 Covalent Bonding Overview

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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

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1.4.6 Covalent Dot-and-Cross Diagrams

Covalent Dot-and-Cross Diagrams

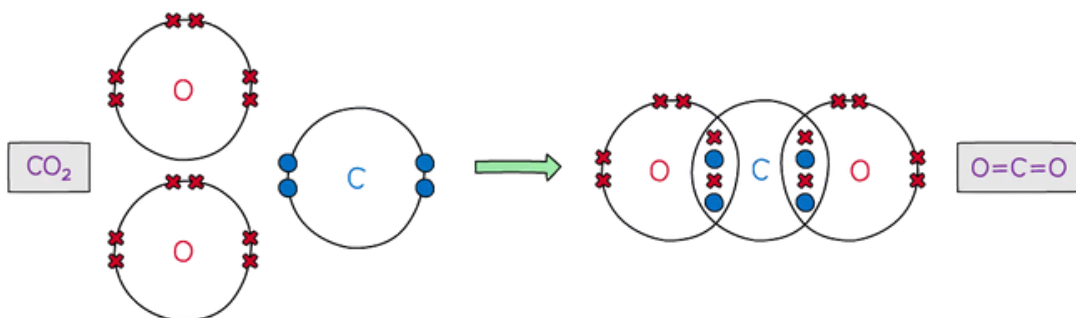
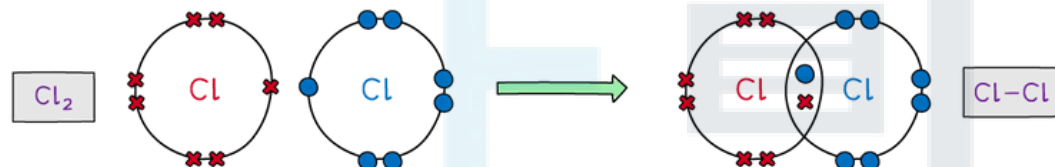
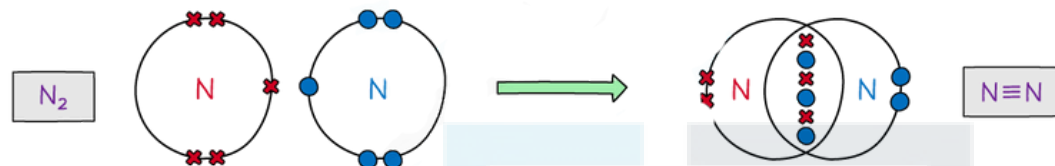
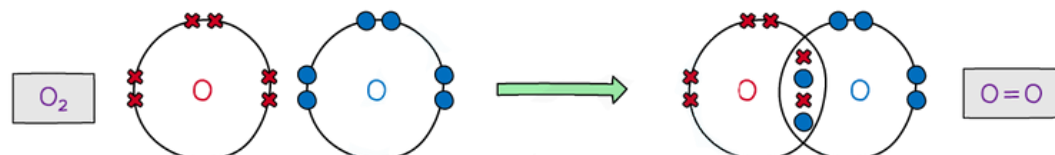
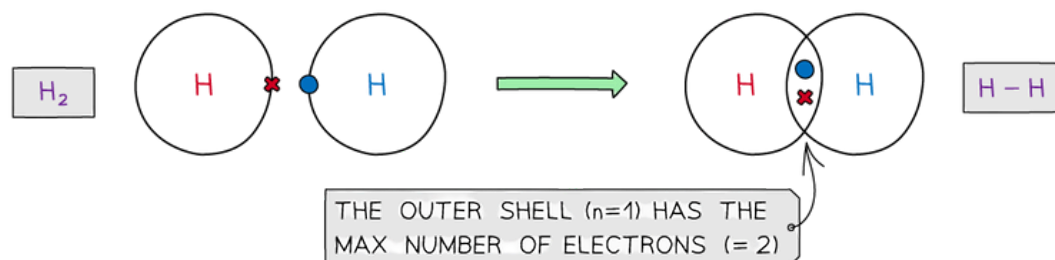
Covalent compounds

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

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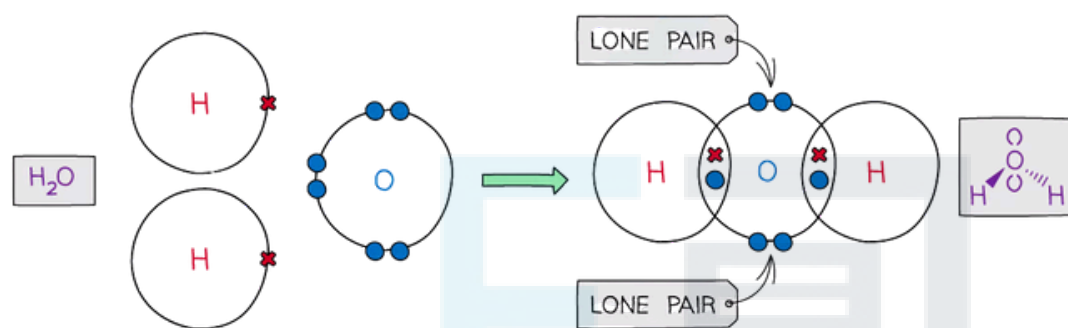
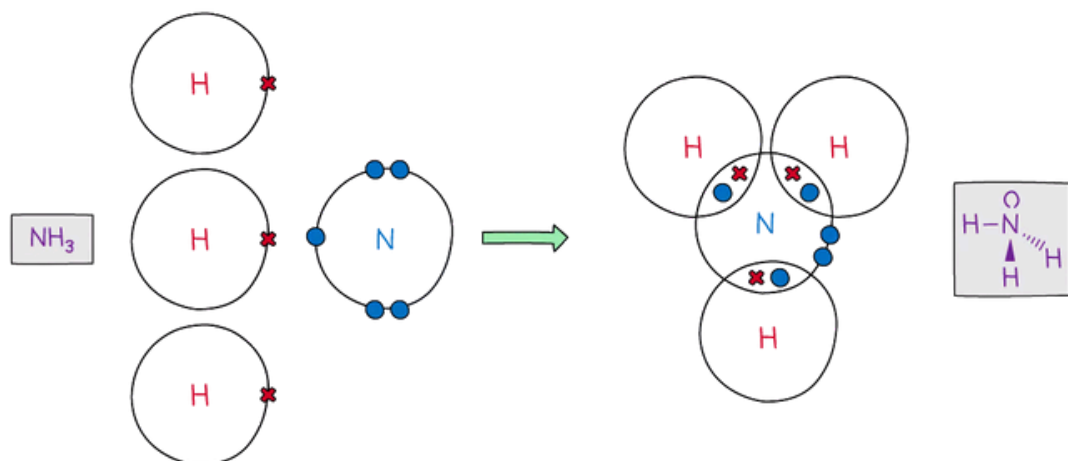


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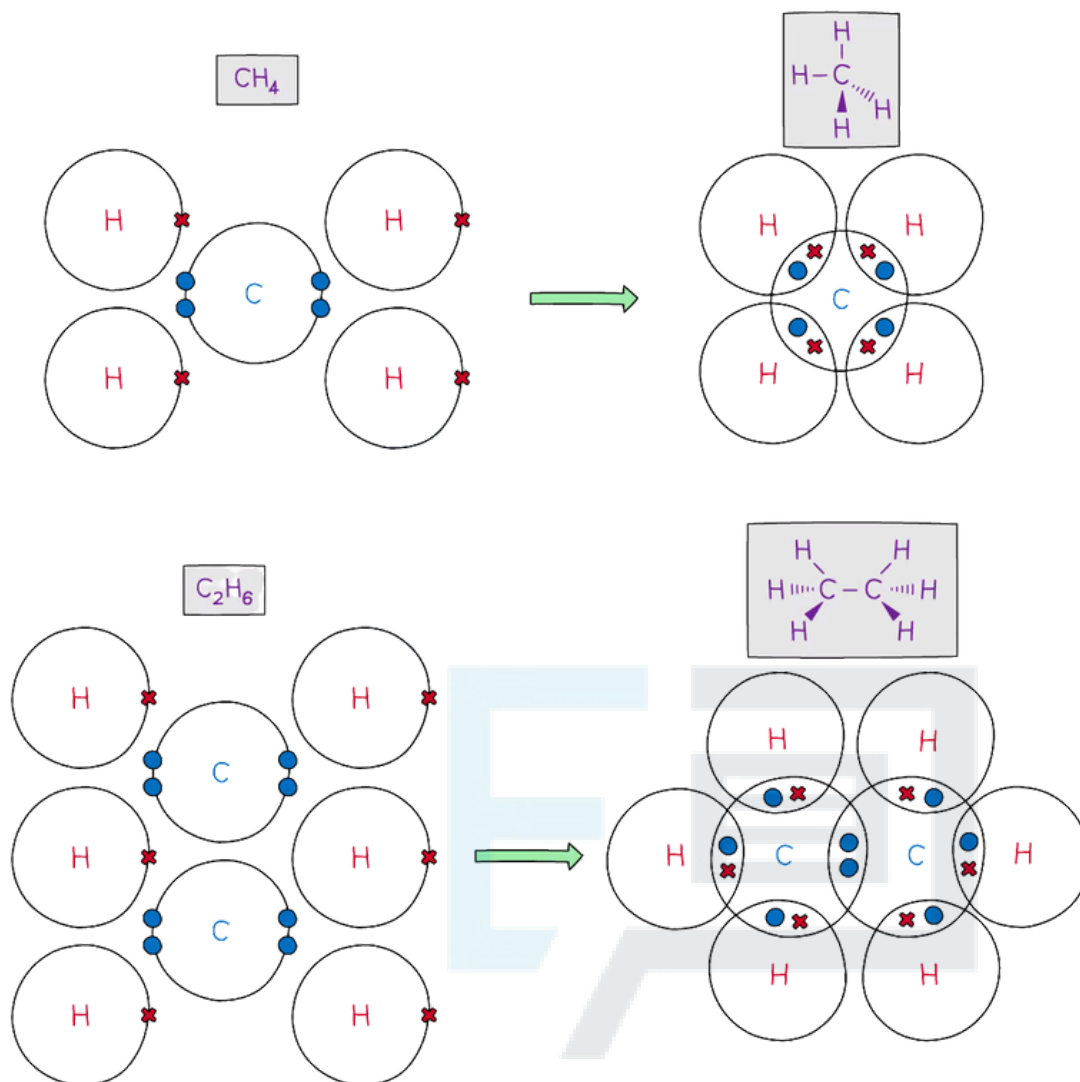


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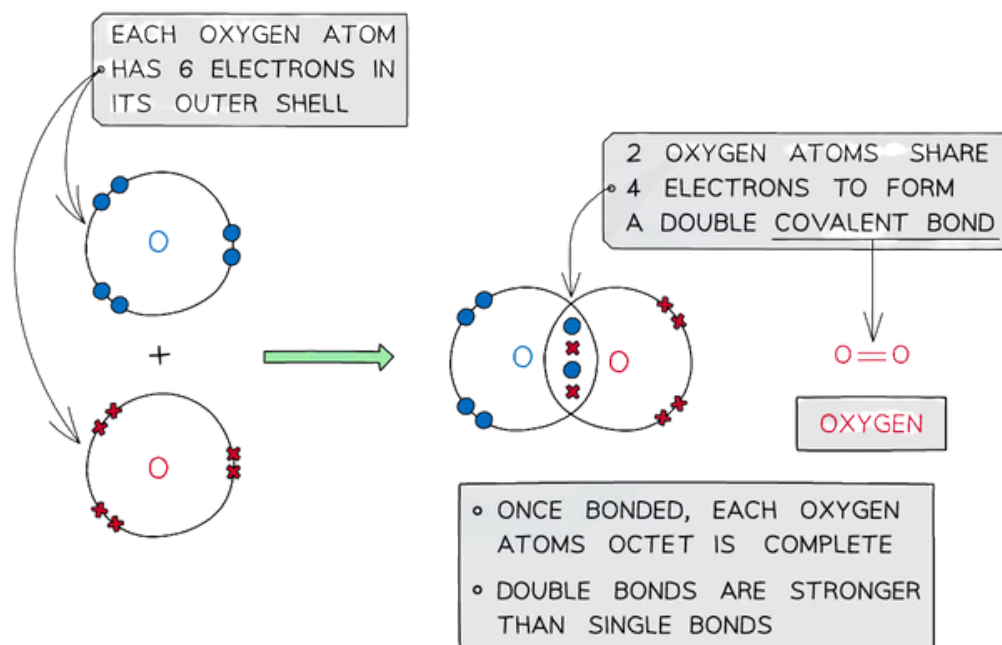


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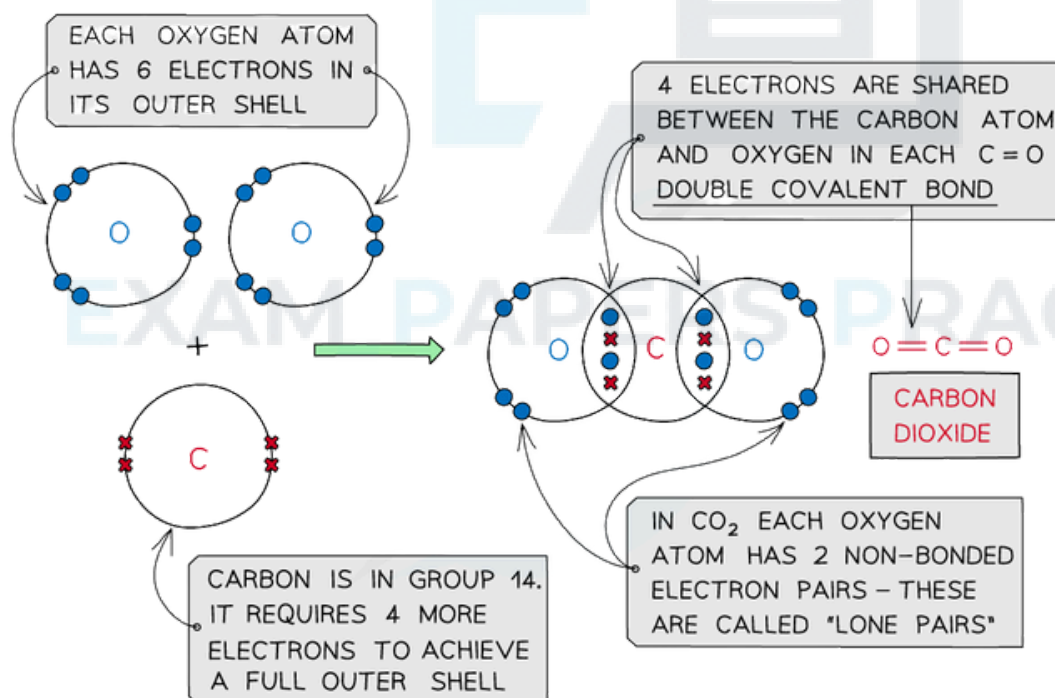
Dot-and-cross diagrams of covalent compounds in which the atoms share their valence electrons

Double covalent
bonding
Oxygen, O₂



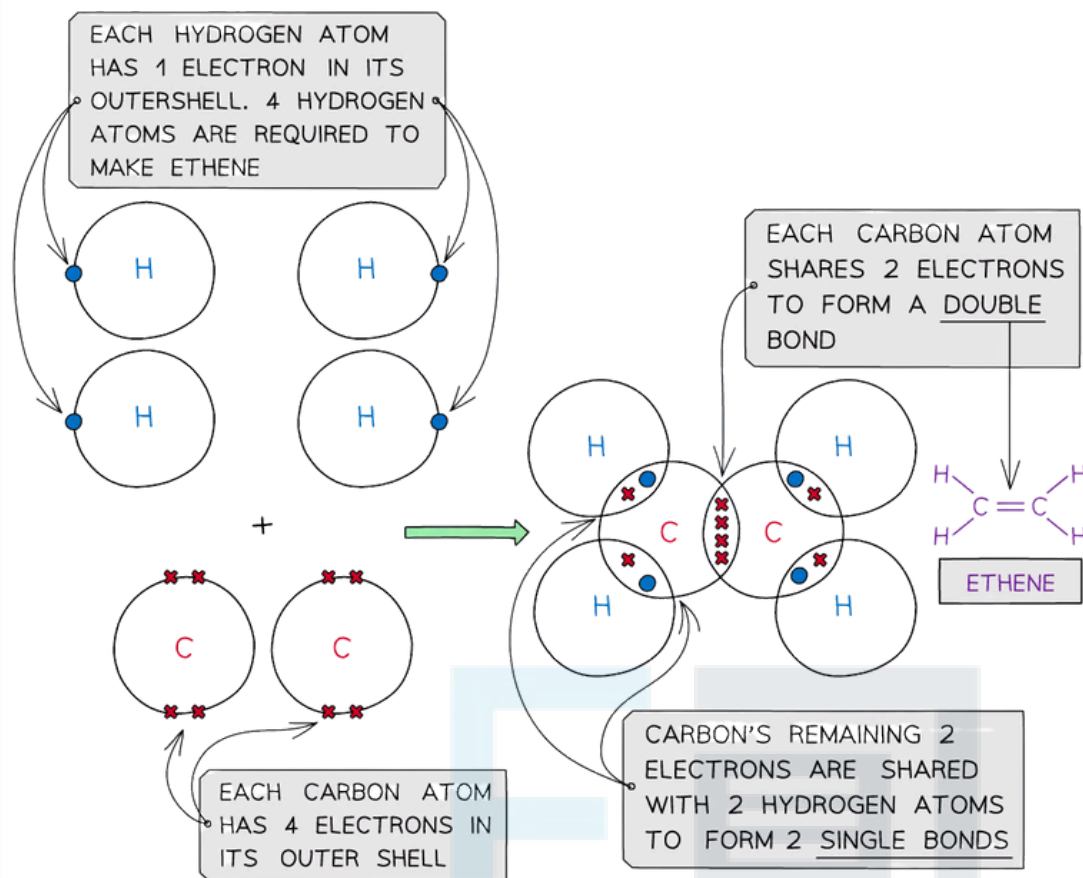
Covalent bonding in oxygen

Carbon dioxide, CO₂



Covalent bonding in carbon dioxide

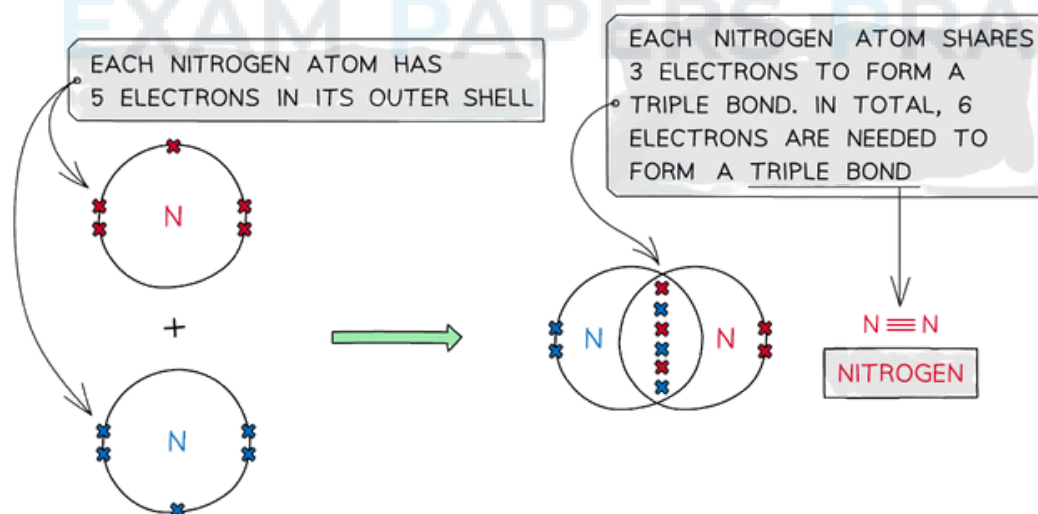
Ethene, C₂H₄



Covalent bonding in ethene

Triple covalent bonding

Nitrogen, N₂

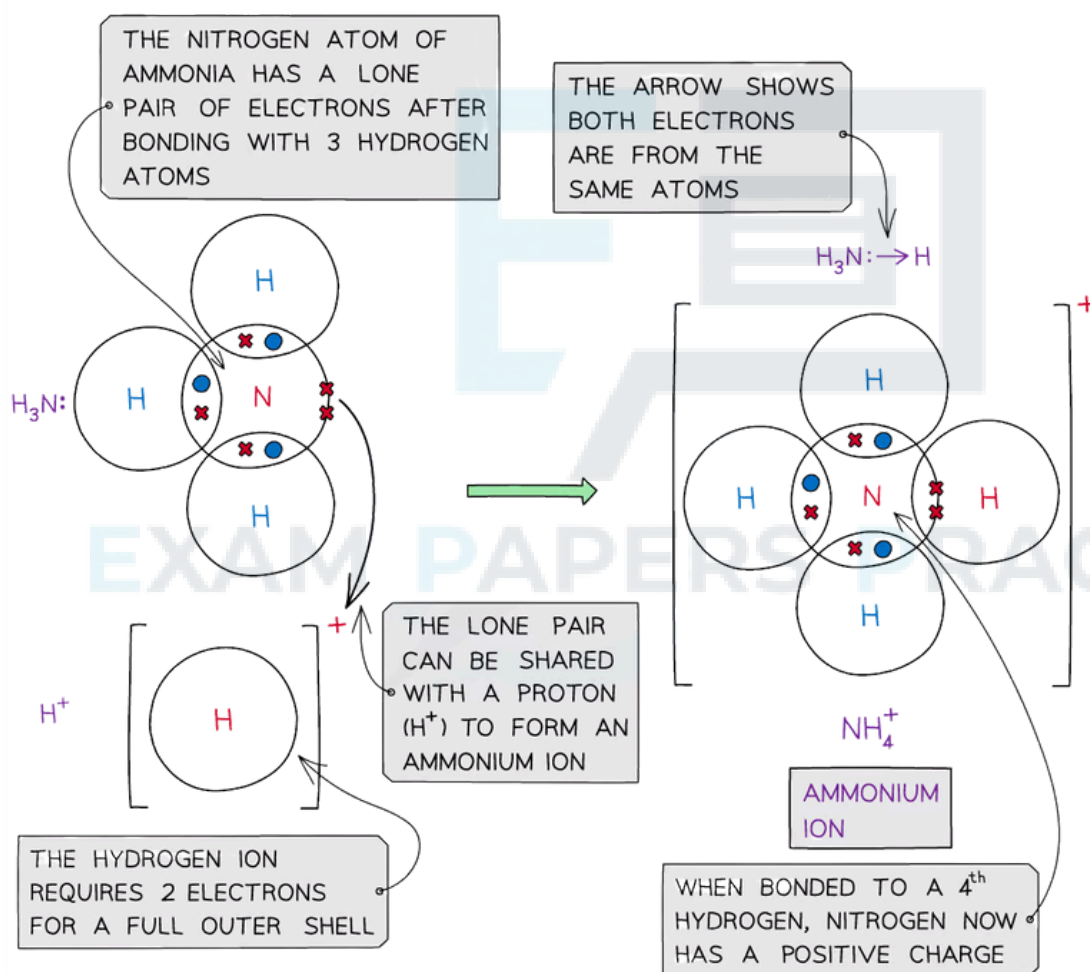


Covalent bonding in nitrogen

YOUR NOTES

Dative covalent bonding

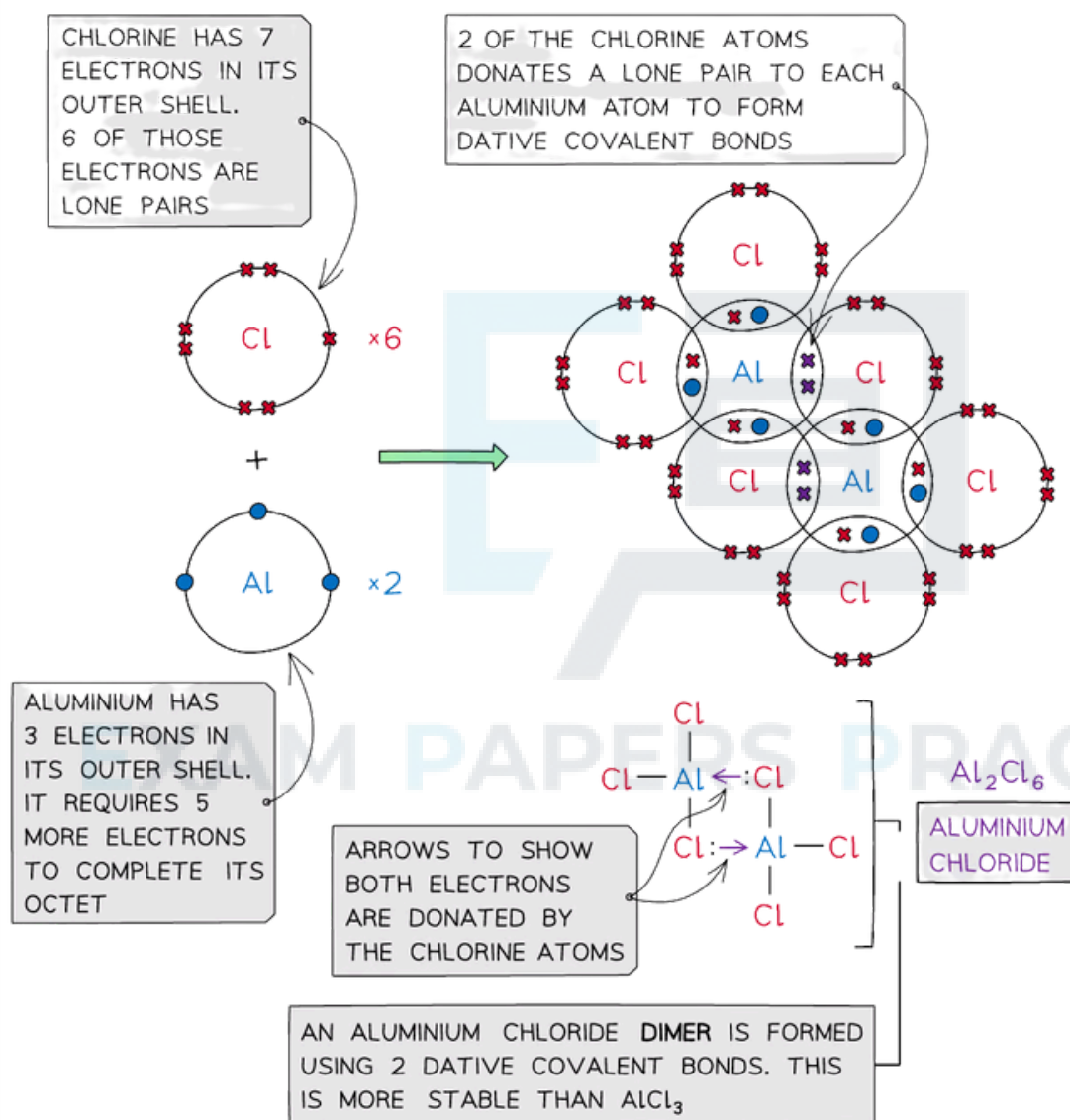
- In simple covalent bonds, the two atoms involved share electrons
- Some molecules have a **lone pair** of electrons that can be donated to form a bond with an **electron-deficient** atom
 - An electron-deficient atom is an atom that has an **unfilled outer orbital**
- So **both electrons** are from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



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

Aluminium chloride

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



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



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.

YOUR NOTES



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1.4.7 Bond Length & Bond Strength

YOUR NOTES



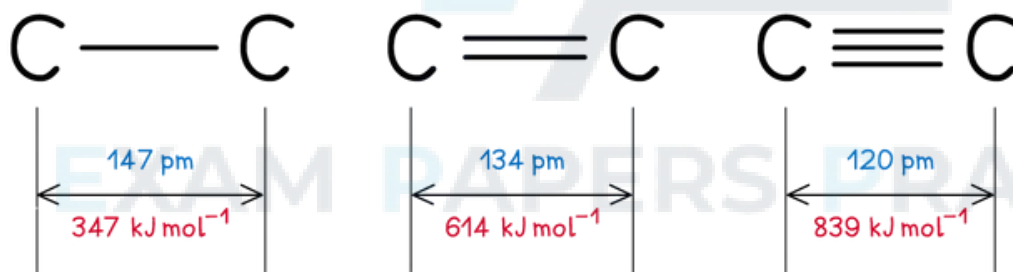
Bond Length & Bond Strength

Bond energy

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

Bond length

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



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

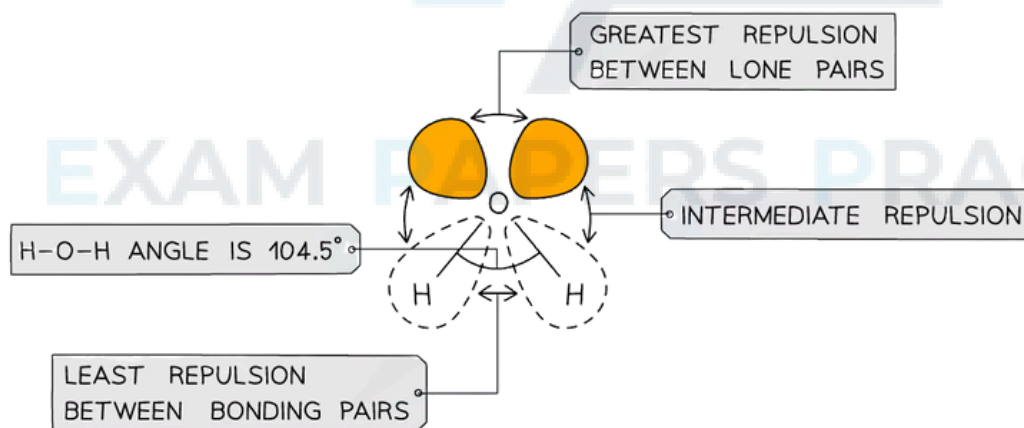
1.4.8 Shapes of Covalent Compounds

YOUR NOTES



Electron Pair Repulsion & Shape

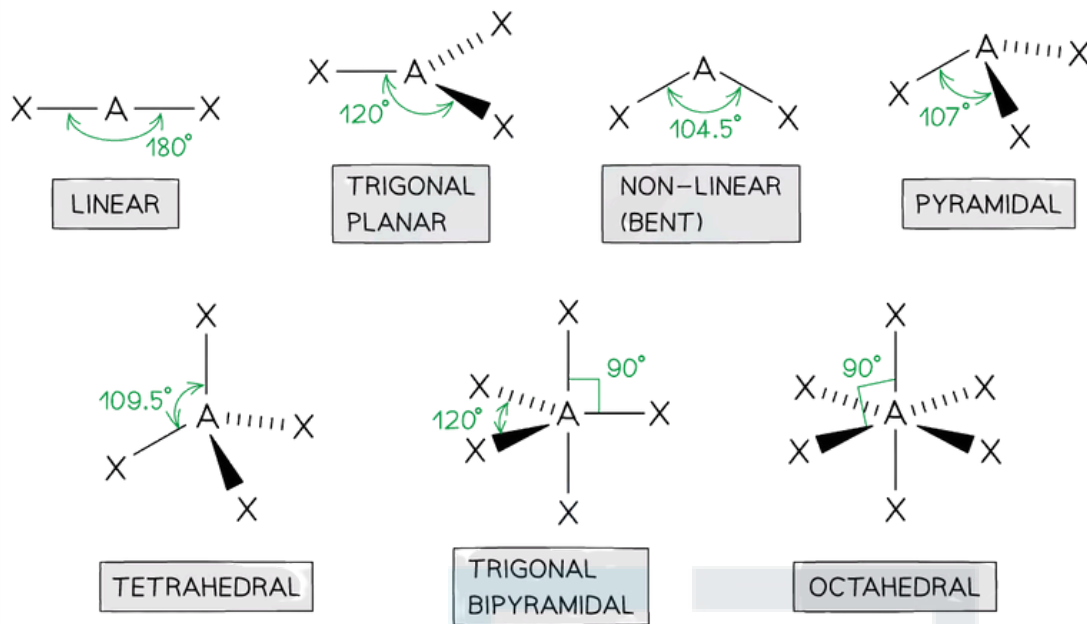
- The valence shell electron pair repulsion theory (VSEPR) predicts the shape and bond angles of molecules
- Electrons are **negatively charged** and will repel other electrons when close to each other
- In a molecule, the **bonding pairs of electrons** will repel other electrons around the **central 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 & Angles

- Molecules can adapt the following shapes and bond angles:

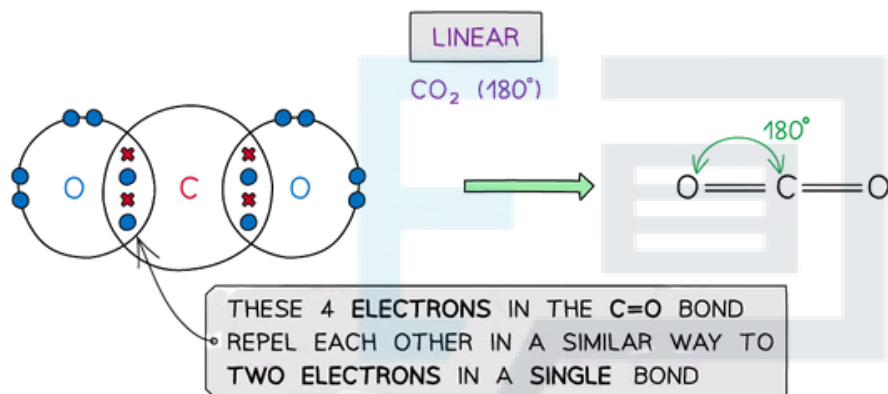
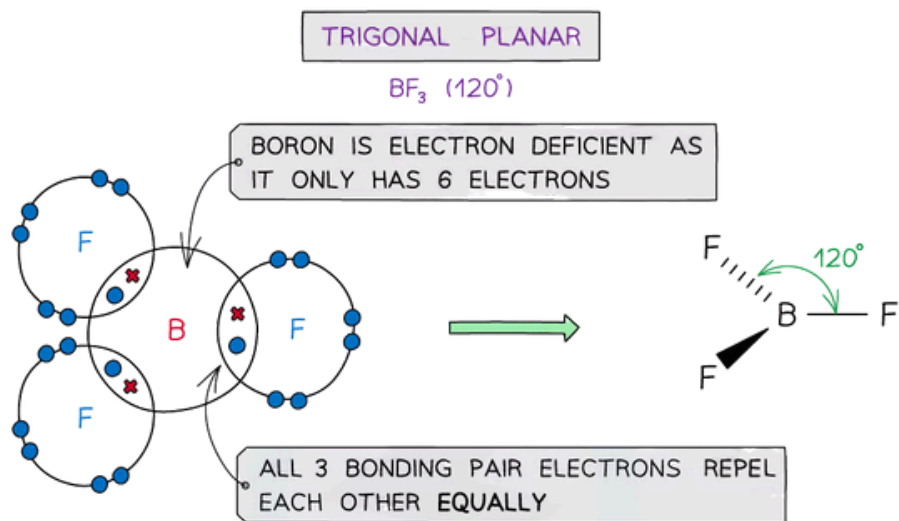


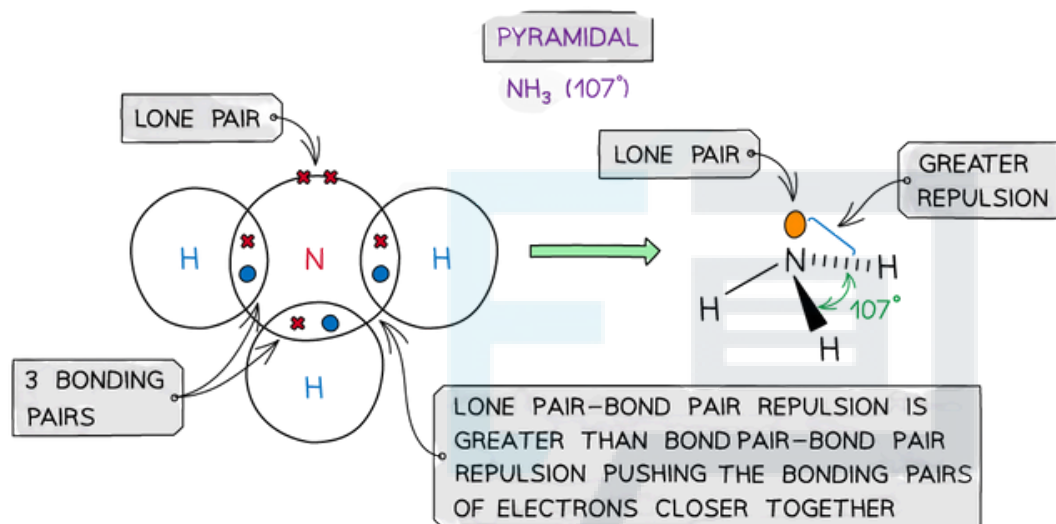
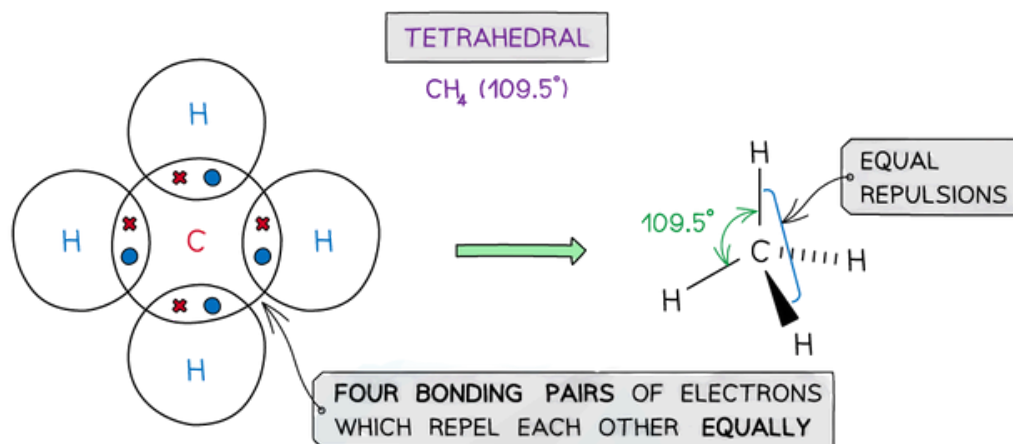
Molecules of different shapes can adapt with their corresponding bond angles

Examples

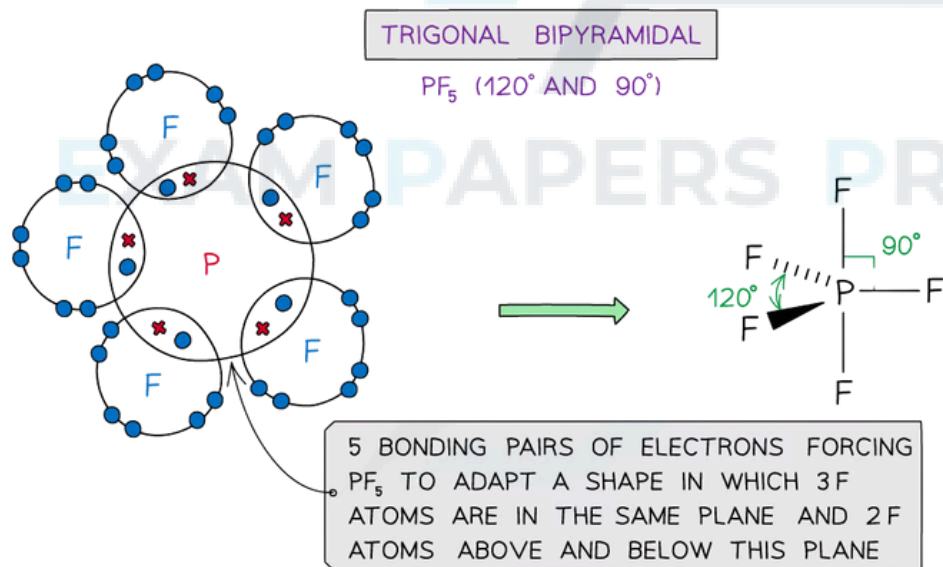
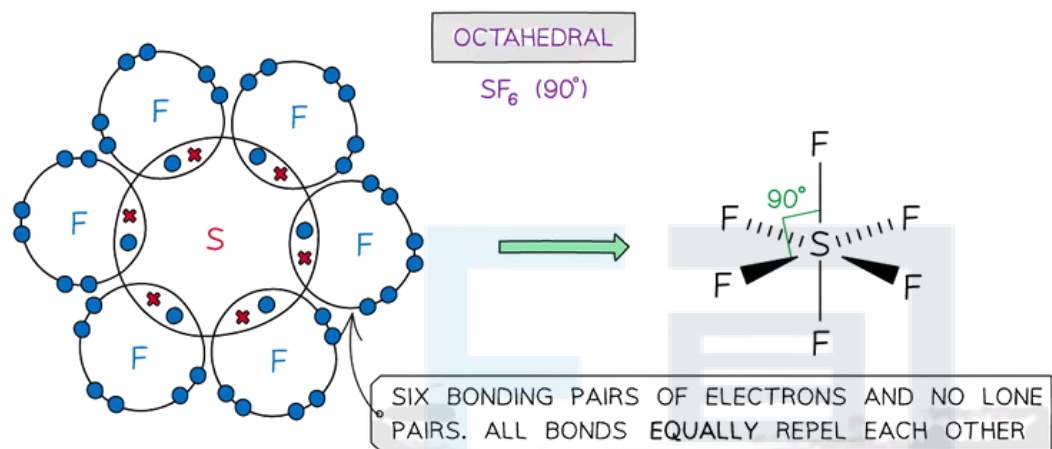
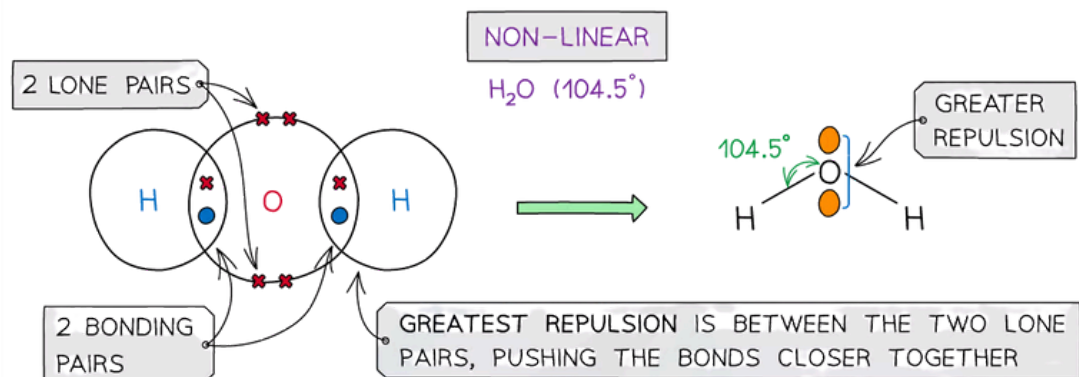
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Examples of molecules with different shapes and bond angles

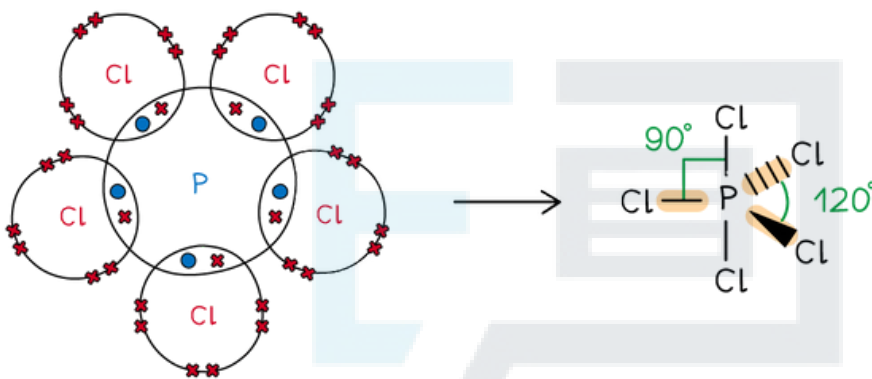
☐ **Worked Example**
VSEPR & shapes of molecules

Draw the shape of the following molecules:

1. Phosphorus(V) chloride
2. $\text{N}(\text{CH}_3)_3$
3. CCl_4

Answer 1:

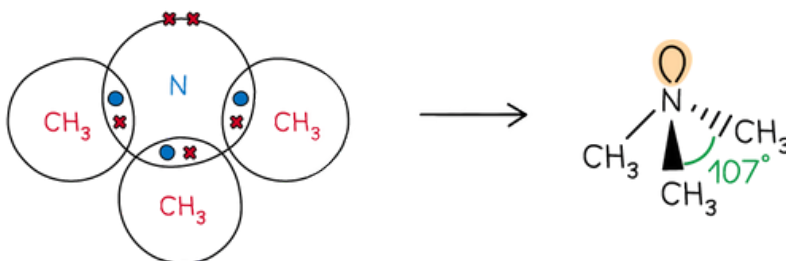
- Phosphorus is in group 15, so has 5 valence electrons; Cl is in group 17, so has 7 valence electrons
- All 5 electrons are used to form covalent bonds with Cl and there are no lone pairs
- This gives a trigonal (or triangular) bipyramidal shape:



Phosphorus pentachloride or phosphorus (V) chloride

Answer 2:

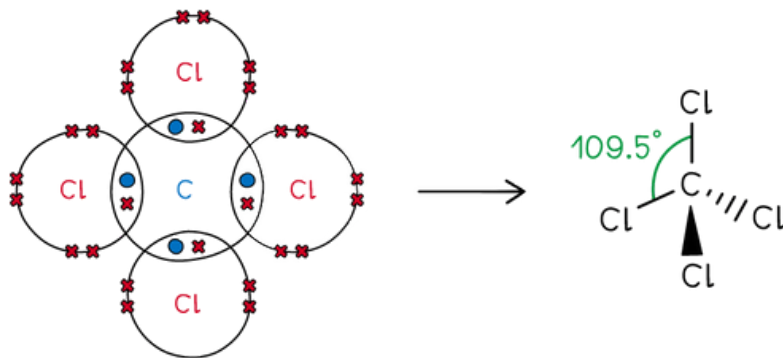
- Nitrogen is in group 15, so has 5 valence electrons; carbon is in group 14, so has 4 valence electrons, 3 of which are already used in the covalent bonds with hydrogen
- Three of the valence electrons in N are used to form bonding pairs, so there is one lone pair left
- $\text{N}(\text{CH}_3)_3$ has 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 used to bond with chlorine and there are no lone pairs
- The shape of CCl_4 is tetrahedral



Tetrachloromethane

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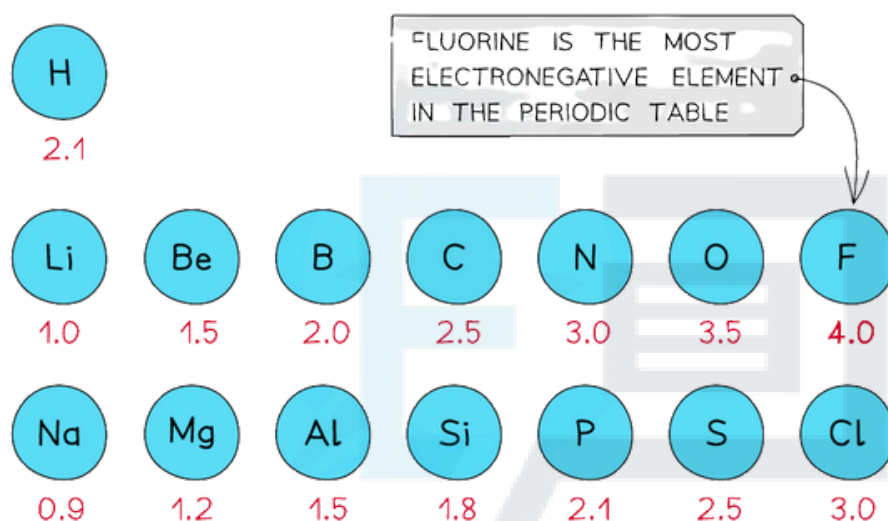
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1.5 Structure

1.5.1 Electronegativity

Defining 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.
-

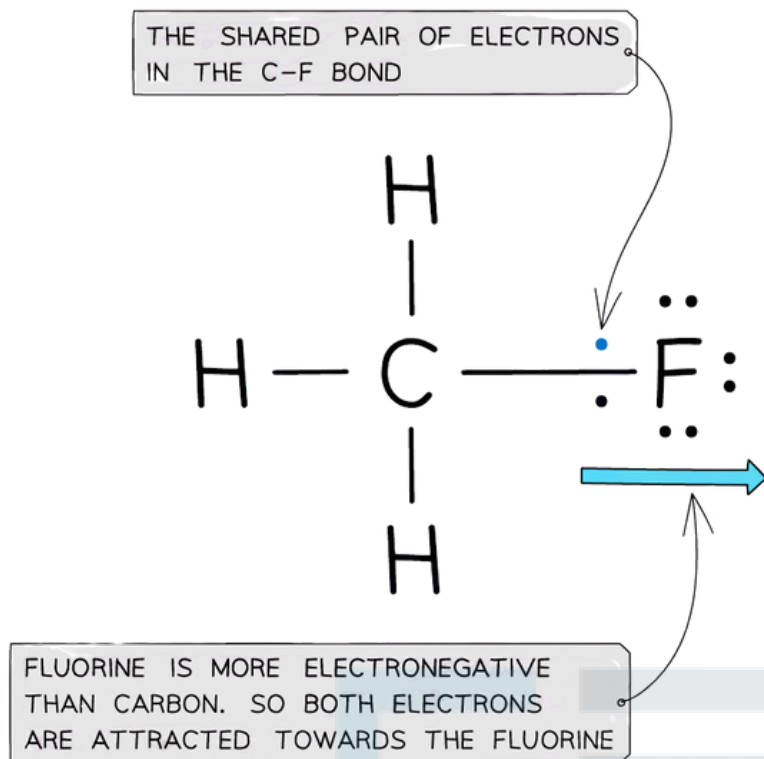


First three rows of the periodic table showing electronegativity values

- 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.

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□



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

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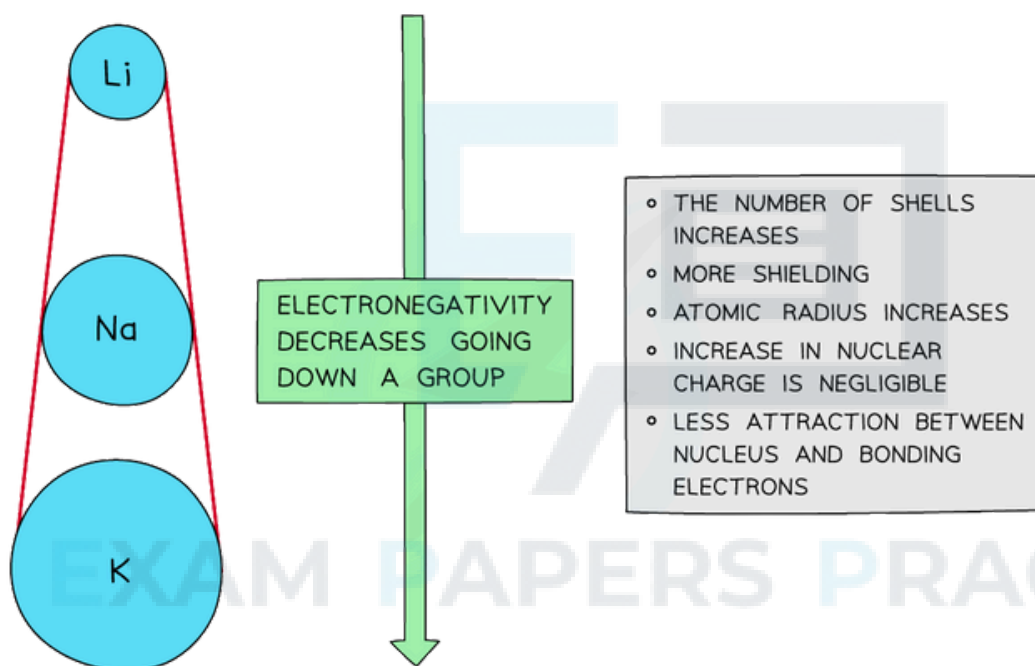
- Thus, an increased number of inner shells and subshells will result in a decreased electronegativity

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

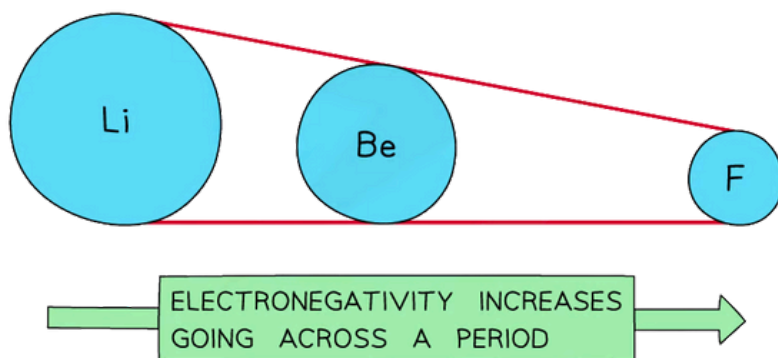


Electronegativity decreases going down the groups of the periodic table

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

- NUCLEAR CHARGE INCREASES
- ATOMIC RADIUS DECREASES
- GREATER ATTRACTION BETWEEN NUCLEUS AND BONDING ELECTRONS

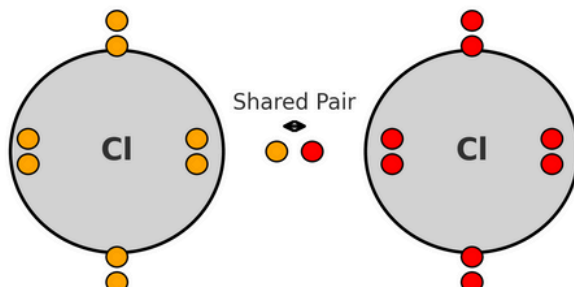


Electronegativity increases going across the periods of the Periodic Table

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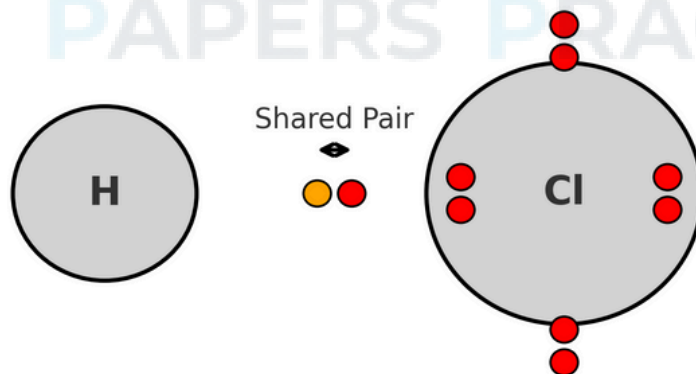
Bond Polarity

- 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

- The difference in electronegativities will dictate the type of bond that is formed
- When the electronegativities are very different (difference of more than 1.7) then ions will be formed and the bond will be ionic
- When two atoms in a covalent bond have a difference in electronegativities of 0.3 to 1.7 a covalent bond is formed and the bond will be polar
 - The electrons will be drawn towards the more electronegative atom
- As a result of this:
 - The negative charge centre and positive charge centre do not coincide with each other. This means that the electron distribution is asymmetric
 - The less electronegative atom gets a partial charge of δ^+ (delta positive)
 - The more electronegative atom gets a partial charge of δ^- (delta negative)
 -
- The greater the difference in electronegativity the more polar the bond becomes



Cl has a greater electronegativity than H causing the electrons to be more attracted towards the Cl atom which becomes delta negative and the H delta positive

1.5.2 Intermolecular Forces

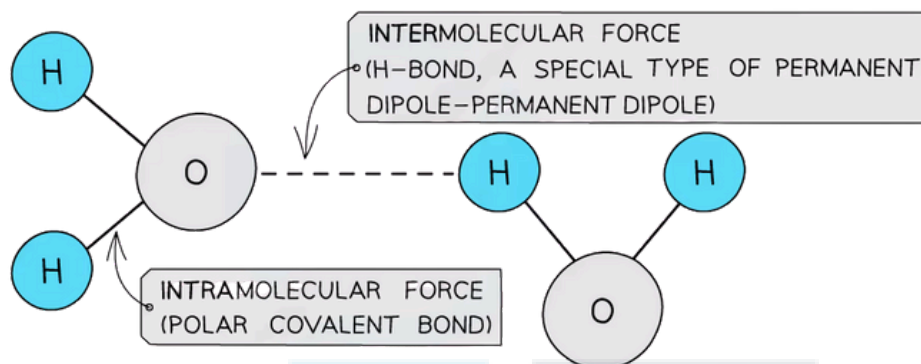
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Intermolecular Forces

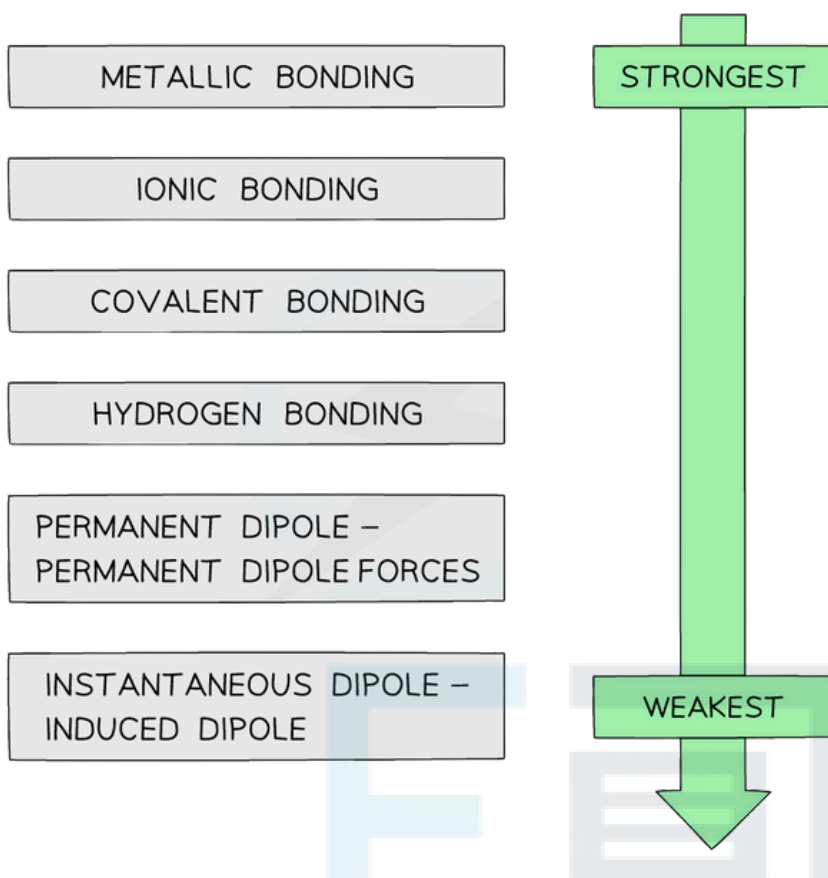
Intramolecular forces

- 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:



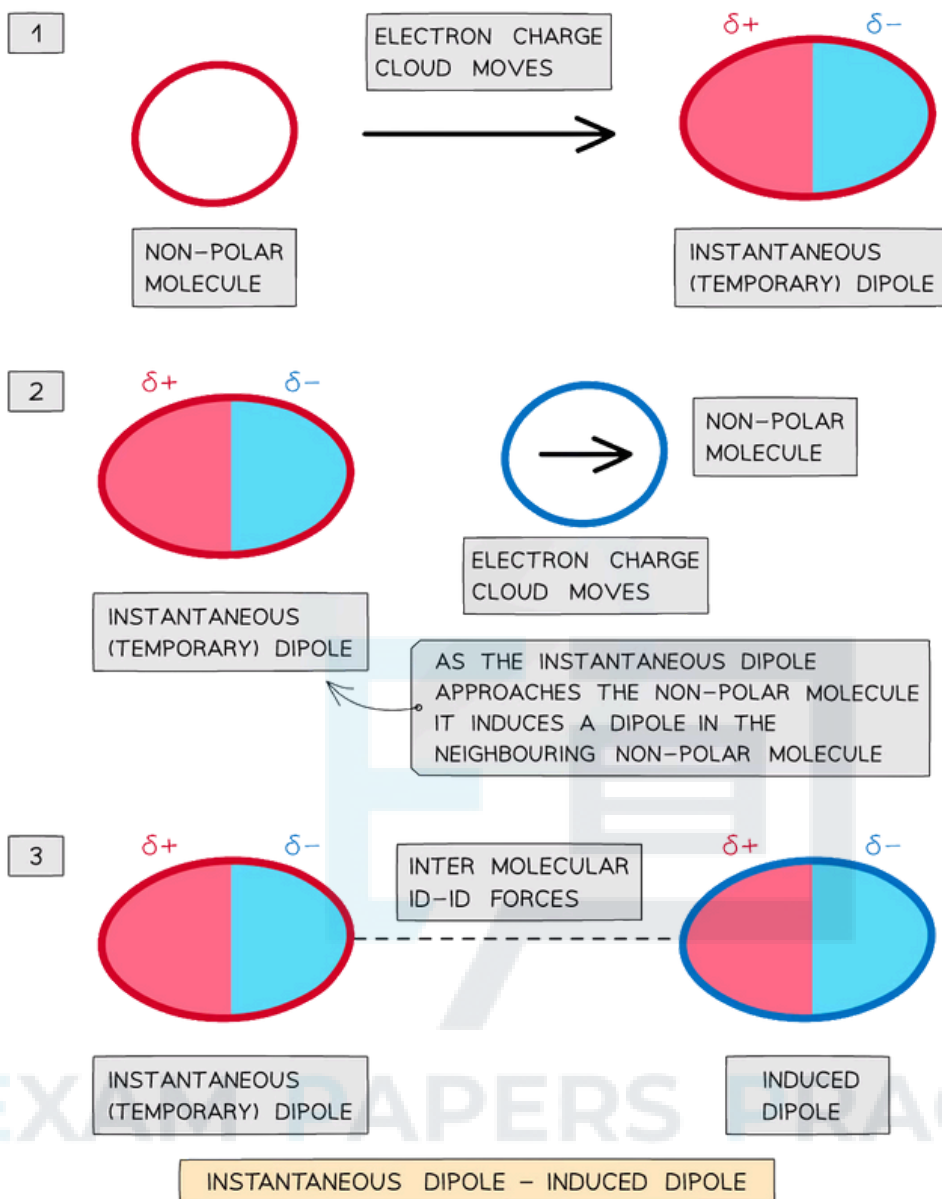
The varying strengths of different types of bonds

Induced dipole-dipole forces:

- Induced dipole - dipole forces exist between all atoms or molecules

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◦ They are also known as London dispersion forces



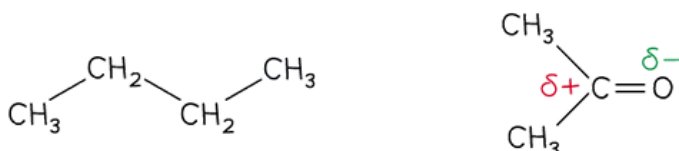
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- The **electron charge cloud** in non-polar molecules or atoms are constantly moving
- During this movement, the electron charge cloud can be more on one side of the atom or molecule than the other
- This causes a **temporary dipole** to arise
- This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

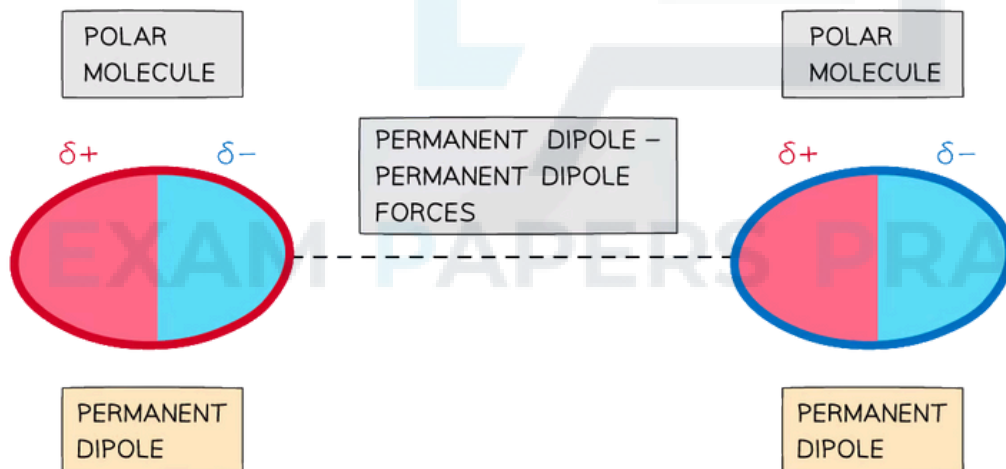
- For small molecules with the same number of electrons, permanent dipoles are stronger than induced dipoles
 - Butane and propanone have the same number of electrons
 - Butane is a nonpolar molecule and will have induced dipole forces
 - Propanone is a polar molecule and will have permanent dipole forces
 - 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

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 $\delta+$ end of the dipole in one molecule and the $\delta-$ end of the dipole in a neighbouring molecule are attracted towards each other

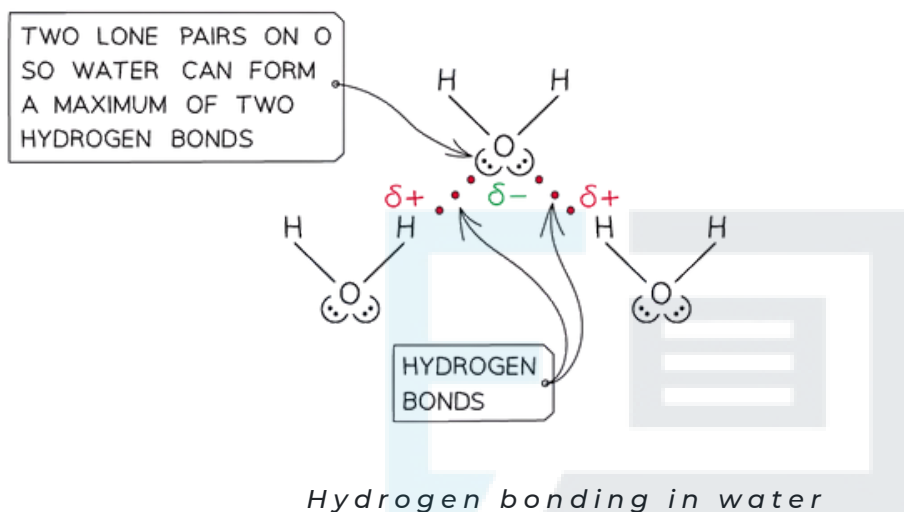
Hydrogen bonding

- Hydrogen bonding is the strongest form of intermolecular bonding
 - Intermolecular bonds are bonds between molecules

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- 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 **$\delta+$** 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



☐ 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.

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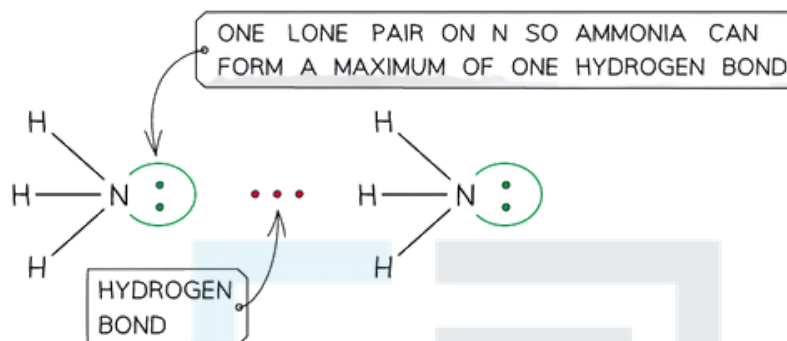
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1.5.3 Hydrogen Bonding

Hydrogen Bonding Interactions

Examples of compounds that can form hydrogen bonds are:

- Alcohols (contains an O-H bond)
- Ammonia (contains an N-H bond)
- Amines (contains an N-H bond)
- Carboxylic acids (contains an O-H bond)
- Hydrogen fluoride (contains an H-F bond)
- Proteins (contains an N-H bond)



Ammonia can form a maximum of one hydrogen bond per molecule

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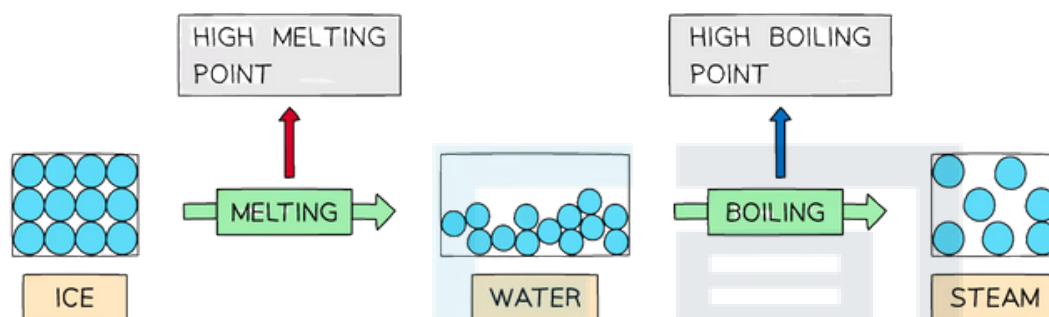
Anomalous Properties of Water

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 **strong intermolecular forces** of hydrogen bonding between the molecules in both ice (solid H₂O) and water (liquid H₂O)
- A lot of energy is therefore required to separate the water molecules and melt or boil them

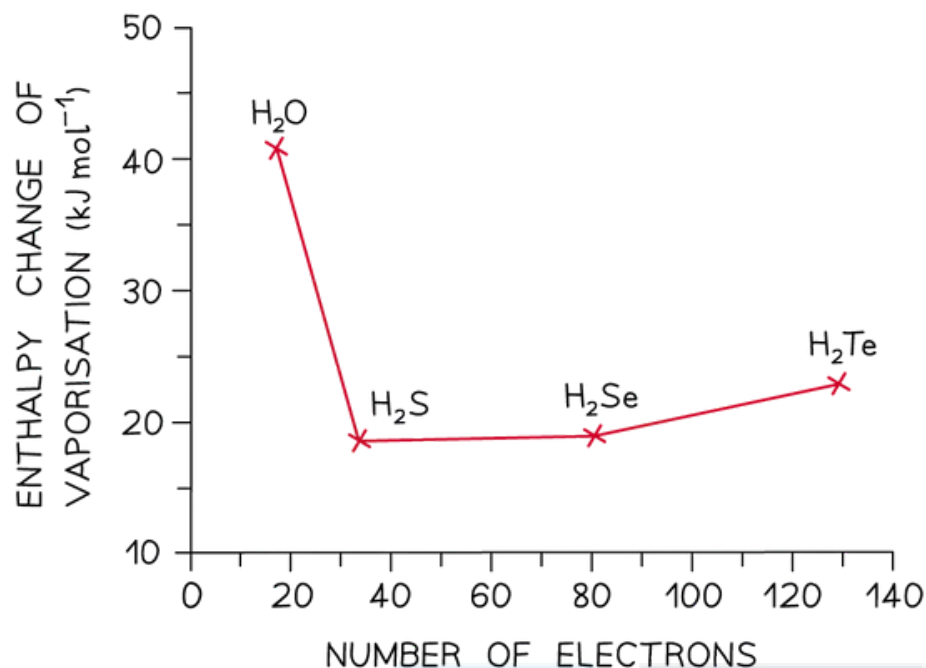


Hydrogen bonds are strong intermolecular forces which are harder to break causing water to have a higher melting and boiling point than would be expected for a molecule of such a small size

- The graph below compares the **enthalpy of vaporisation** (energy required to boil a substance) of different hydrides
- The enthalpy changes **increase** going from H₂S to H₂Te 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, H₂O 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

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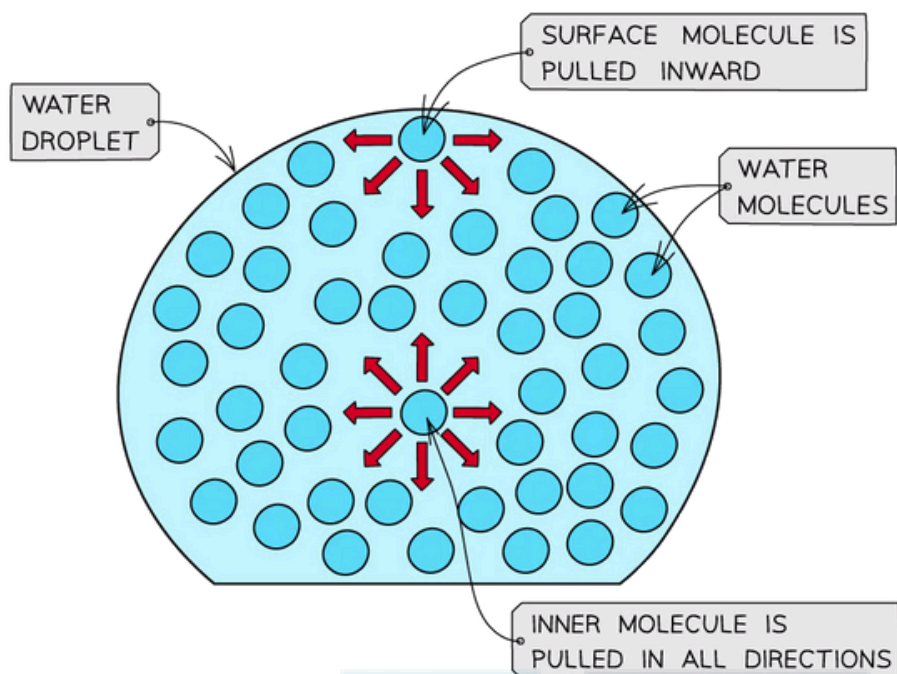
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The high enthalpy change of evaporation of water suggests that instantaneous dipole-induced dipole forces are not the only forces present in the molecule – there are also strong hydrogen bonds, which cause the high boiling point

High surface tension

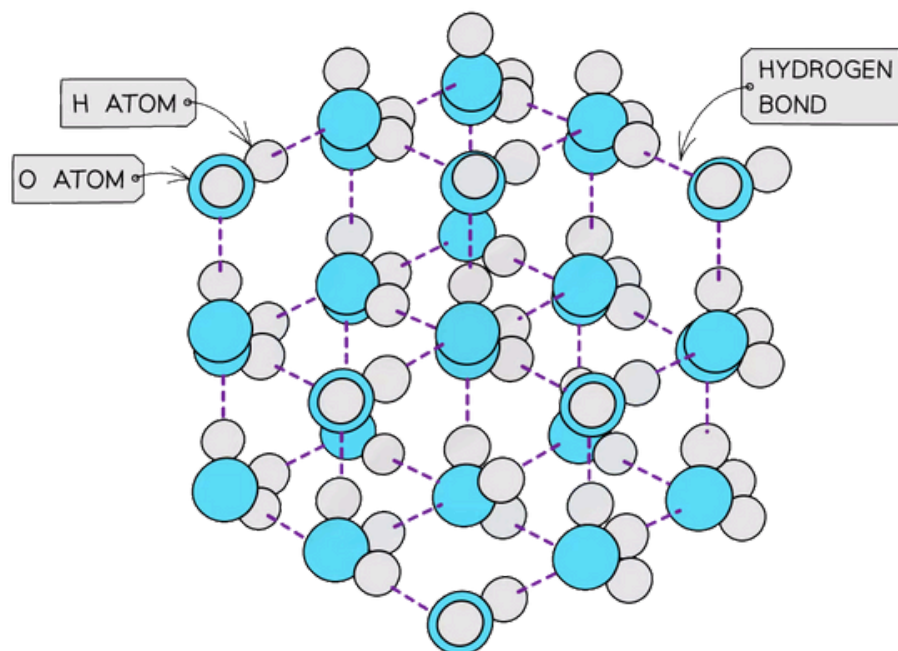
- Water has a high surface tension
- Surface tension is the ability of a liquid surface to resist any external forces (i.e. to stay unaffected by forces acting on the surface)
- The water molecules at the surface of liquid are bonded to other water molecules through hydrogen bonds
- These molecules pull 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

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1.5.4 Intermolecular Forces & Physical Properties

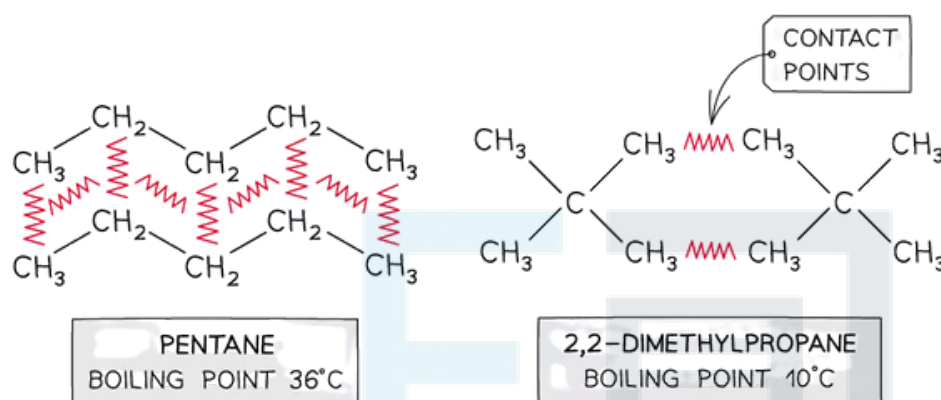
YOUR NOTES



Intermolecular Forces & Physical Properties

Branching

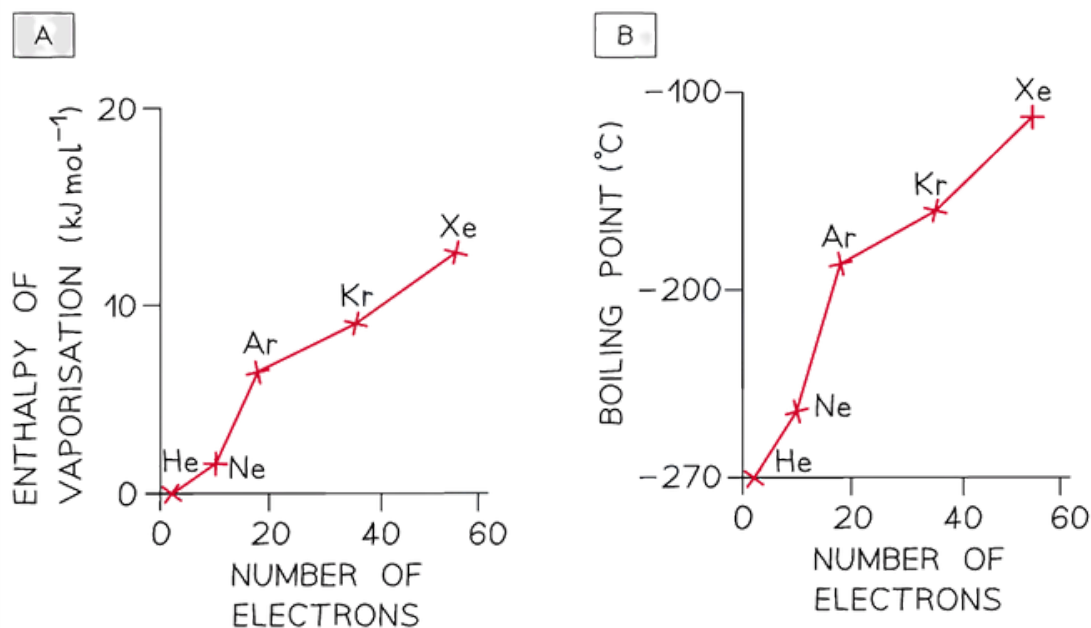
- The larger the surface area of a molecule, the more contact it will have with adjacent molecules
- The surface area of a molecule is **reduced by branching**
- The greater its ability to induce a dipole in an adjacent molecule, the greater the **London (dispersion) forces** and the higher the melting and boiling points
- This point can be illustrated by comparing different isomers containing the same number of electrons:



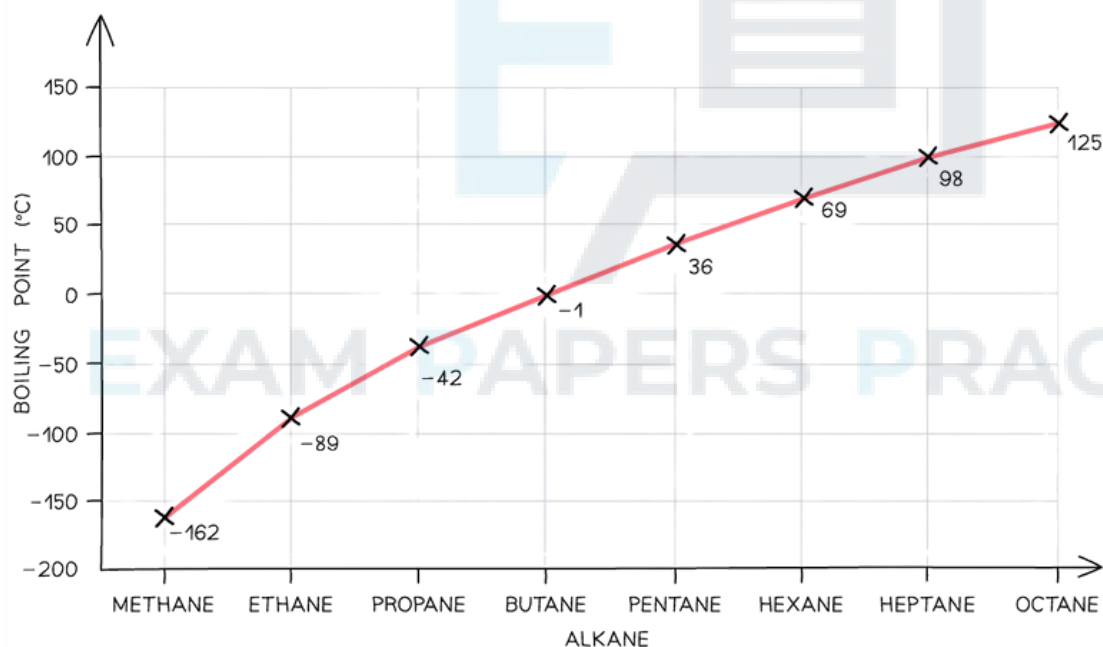
Boiling points of molecules with the same numbers of electrons but different surface areas

Number of electrons

- The greater the number of electrons (or the greater the molecular mass) in a molecule, the greater the likelihood of a distortion and thus the greater the frequency and magnitude of the temporary dipoles
- The dispersion forces between the molecules are stronger and the enthalpy of vaporisation, melting and boiling points are larger
- The greater boiling points of the noble gases illustrate this factor:



As the number of electrons increases more energy is needed to overcome the forces of attraction between the noble gases atoms



Graph showing the increase in boiling point as the number of electrons increases
Alcohols

- Hydrogen bonding occurs between molecules where you have a hydrogen atom attached to one of the very electronegative elements - fluorine, oxygen or nitrogen
- In an alcohol, there are O-H bonds present in the structure



Therefore hydrogen bonds set up between the slightly positive hydrogen atoms ($\delta^+ \text{H}$) and lone pairs on oxygens in other molecules. The hydrogen atoms are slightly positive because the bonding electrons are pulled away from them towards the very electronegative oxygen atoms. In **alkanes**, the only intermolecular forces are **temporary induced dipole-dipole forces**. Hydrogen bonds are much stronger than these and therefore it takes more energy to separate alcohol molecules than it does to separate alkane molecules. Therefore, the boiling point of alkanes is lower than the boiling point of the respective alcohols. For example, the boiling point of propane is -42°C and the boiling point of propanol is 97°C .

Hydrogen Halides

-
- The boiling points of the hydrogen halides are as follows

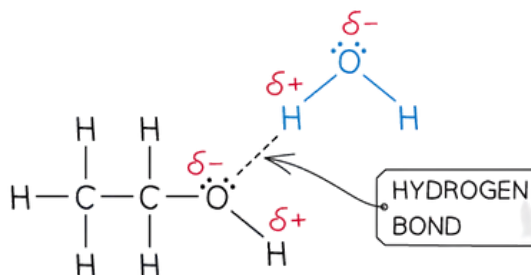
Hydrogen Halide	Boiling Point (K)
HF	293
HCl	188
HBr	207
HI	238

- The boiling points of the rest of the hydrogen halides **increase** as the molecules become larger
- The extra electrons allow greater temporary dipoles and so increase the amount of London dispersion forces between the molecules. Hydrogen fluoride also has
- hydrogen bonding between the HF molecules. The bond is very polar so that the
- hydrogen has a significant amount of positive charge and the fluorine a significant amount of negative charge. In addition, the fluorine has small intense lone pairs. Hydrogen bonds can form between the hydrogen on one molecule and a lone pair on the fluorine in its neighbour
-

Choosing Solvents

Solubility

- The general principle is that 'like dissolves like' so non-polar substances mostly dissolve in non-polar solvents, like hydrocarbons and they form dispersion forces between the solvent and the solute. Polar covalent substances generally dissolve
- in polar solvents as a result of dipole-dipole interactions or the formation of hydrogen bonds between the solute and the solvent. A good example of this is seen in organic molecules such as alcohols and water:



Hydrogen bonds form between ethanol and water

- As covalent molecules become larger their solubility can decrease as the polar part of the molecule is only a smaller part of the overall structure
 - This effect is seen in alcohols for example where ethanol, C_2H_5OH , is readily soluble but hexanol, $C_6H_{13}OH$, is not
- Polar covalent substances are unable to dissolve well in non-polar solvents as their dipole-dipole attractions are unable to interact well with the solvent
- Giant covalent substances generally don't dissolve in any solvents as the energy needed to overcome the strong covalent bonds in the lattice structures is too great

YOUR NOTES

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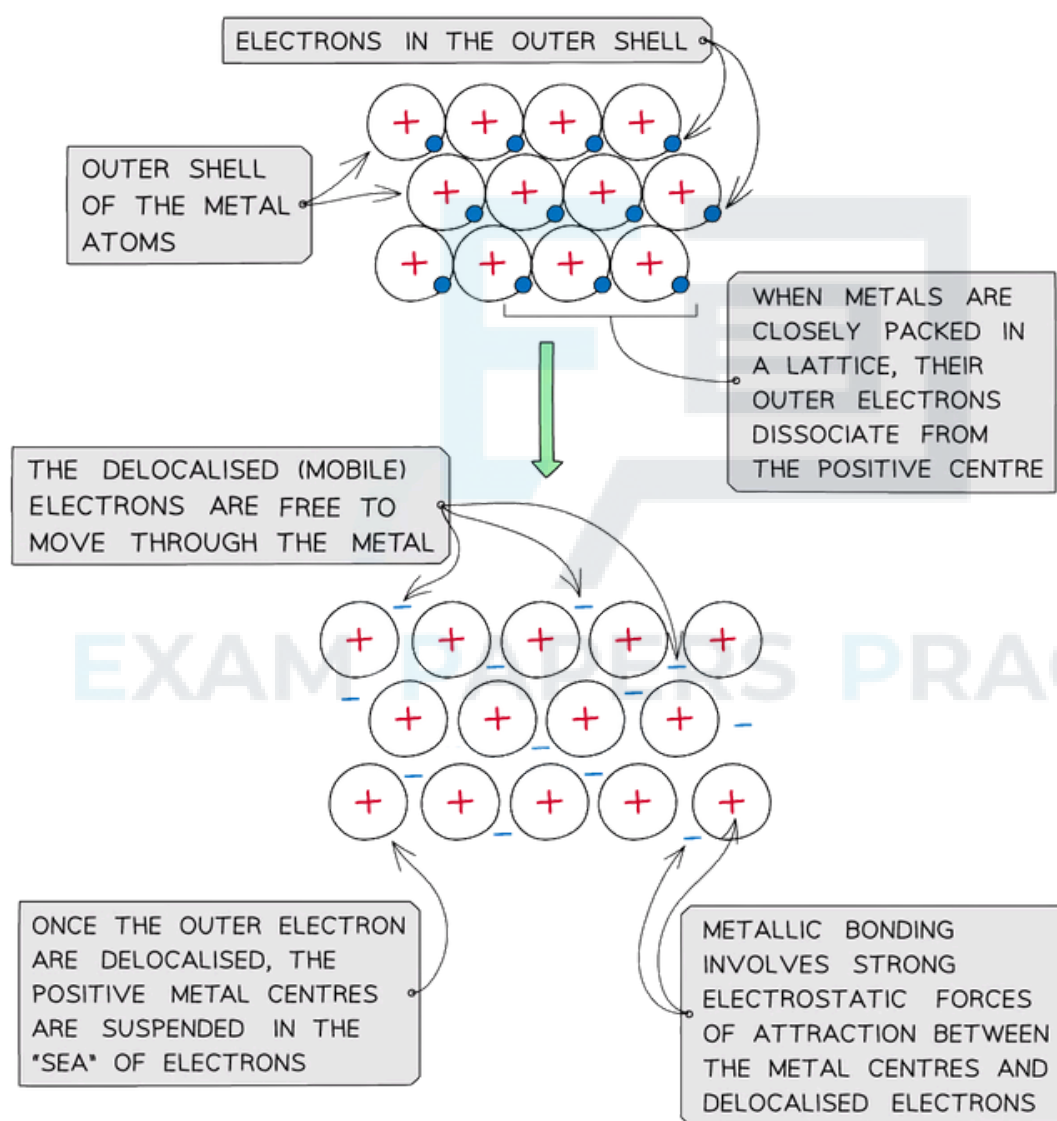
1.5.5 Metallic Bonding

YOUR NOTES

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Metallic Bonding

- 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

1.5.6 Giant Lattices

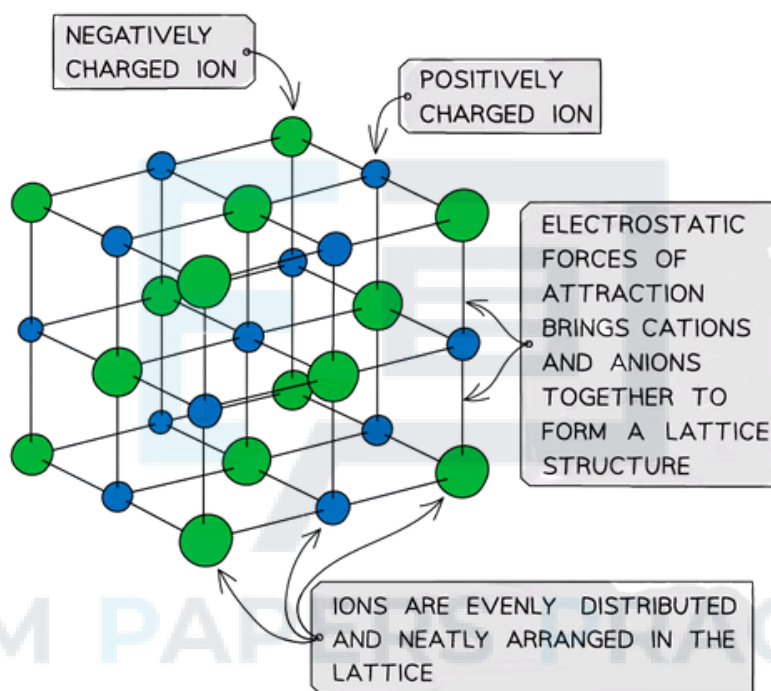
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Giant Lattices

Ionic Lattices

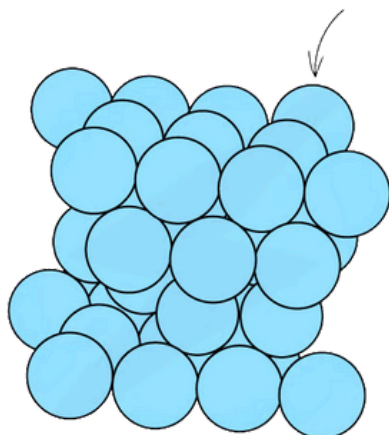
- The ions form a **lattice structure** which is an evenly distributed crystalline structure Ions in a lattice are arranged in a **regular repeating pattern** so
- that positive charges cancel out negative charges The attraction between the cations and anions is occurring in all directions Each ion is 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

Metallic Lattices

- 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

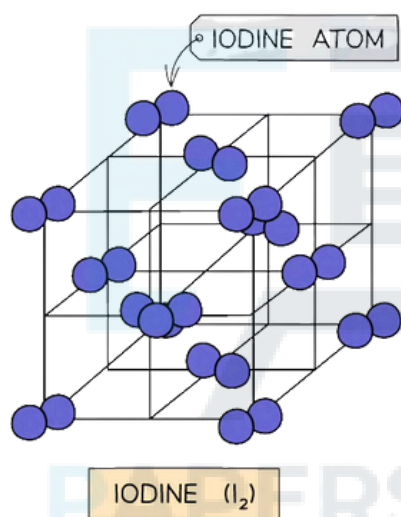
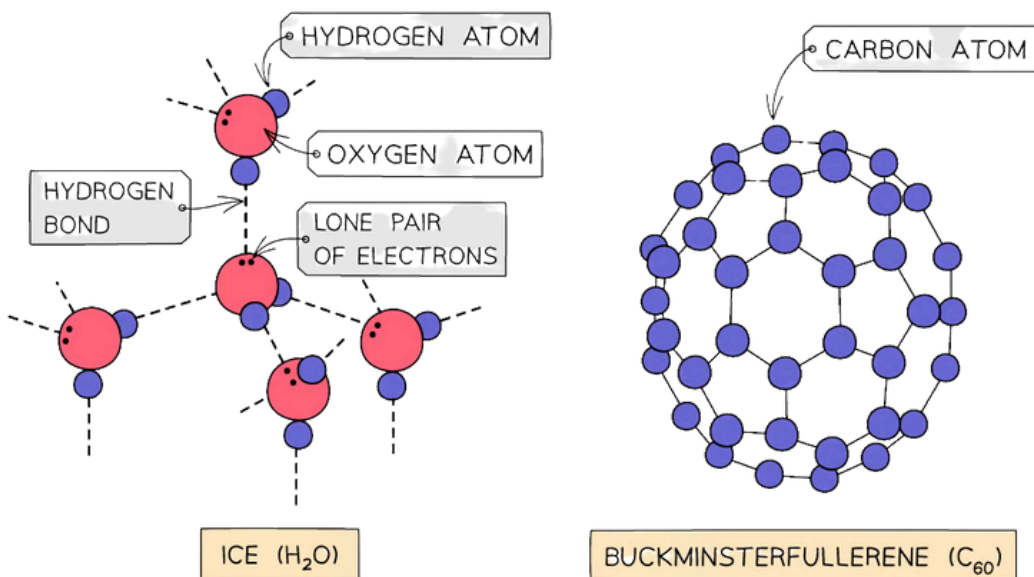


Layers of copper ions (the delocalised electrons are not shown in the diagram)

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 (C₆₀) and ice
 - Giant molecular: silicon(IV) oxide, graphite and diamond

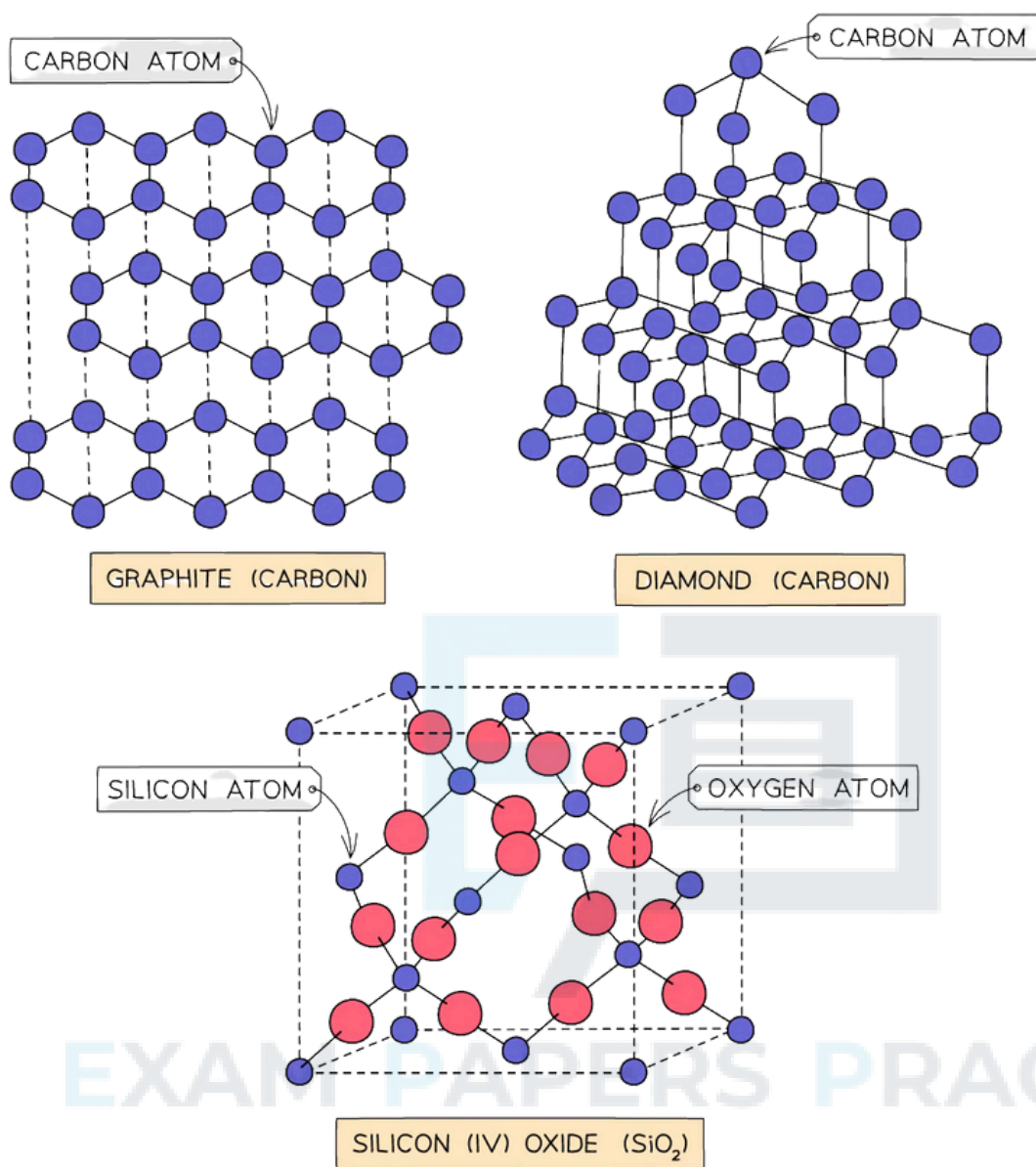
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Simple molecular lattices

YOUR NOTES

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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).

1.5.7 Covalent Structures

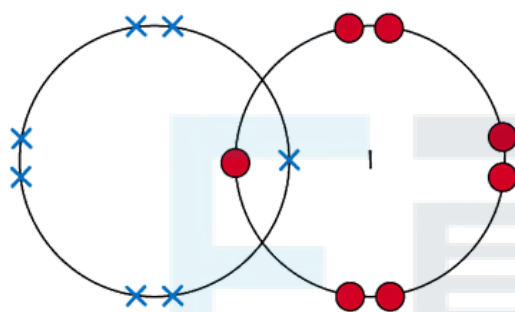
YOUR NOTES



Simple Molecular Compounds

Simple Molecular Compounds

- Covalent substances tend to have small molecular structures, such as Cl_2 , H_2O or CO_2
- These small molecules are known as **simple molecules**
- Hydrogen (H_2), chlorine (Cl_2), oxygen (O_2), nitrogen (N_2), hydrogen chloride (HCl), water (H_2O), ammonia (NH_3) and methane (CH_4) are also examples of simple molecules
- Iodine is a simple molecule and can be represented but it exists as a crystalline structure involving a regular structure held together by weak London dispersion forces



Dot cross diagram of an iodine molecule

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Carbon Allotropes

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

Graphite

- Each carbon atom in graphite is bonded to **three** others forming **layers** of **hexagons**, leaving one free electron per carbon atom. These free electrons migrate along the layers and are free to move and carry charge, hence graphite can **conduct electricity**. The covalent bonds within the layers are very strong, but the layers are attracted to each other by weak **intermolecular forces**, so the layers can **slide** over each other making graphite **soft** and **slippery**.

YOUR NOTES



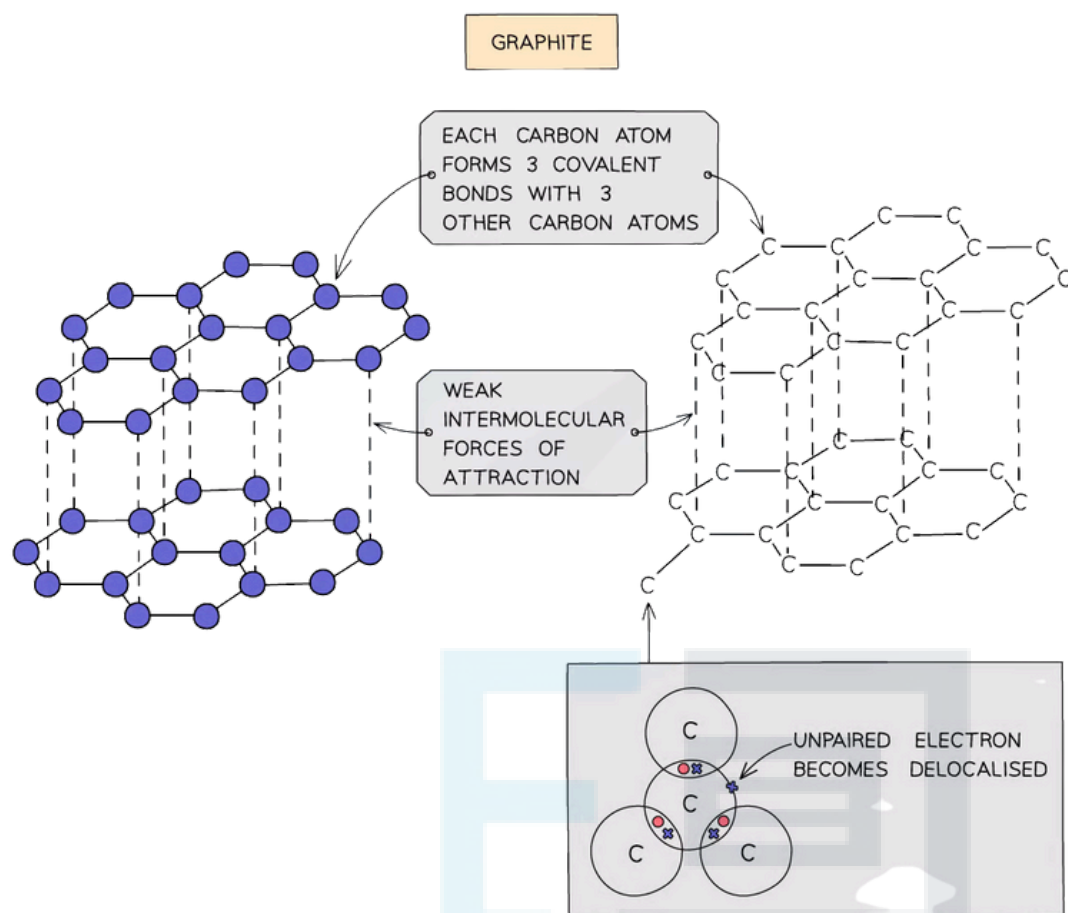


Diagram showing the structure and bonding arrangement in graphite

Diamond

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

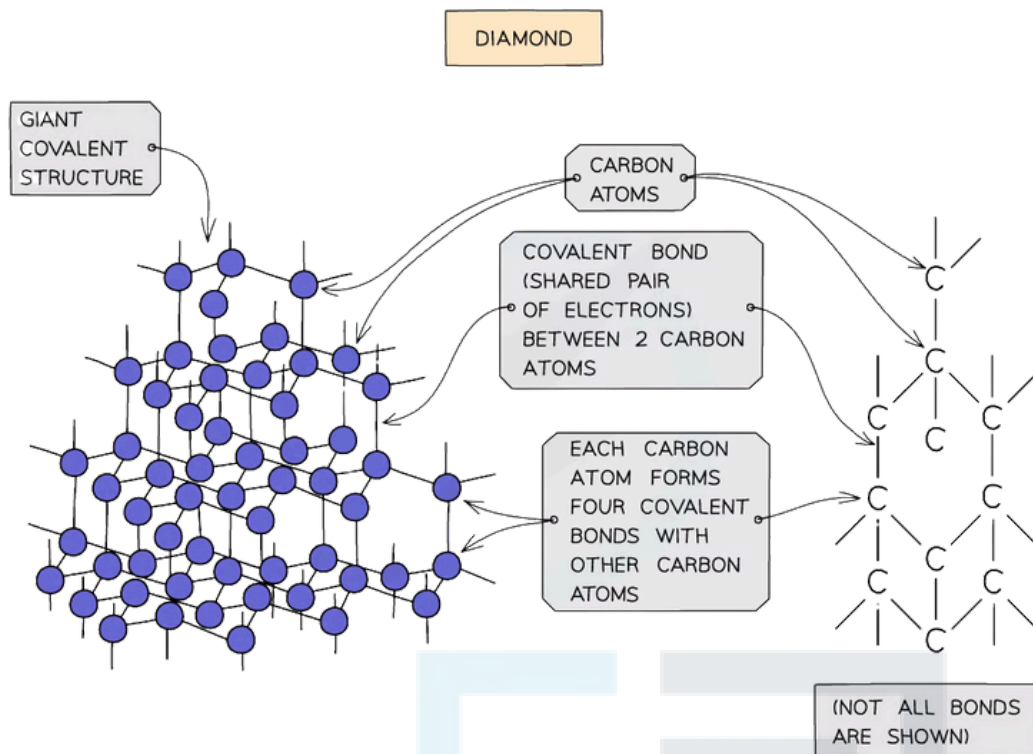
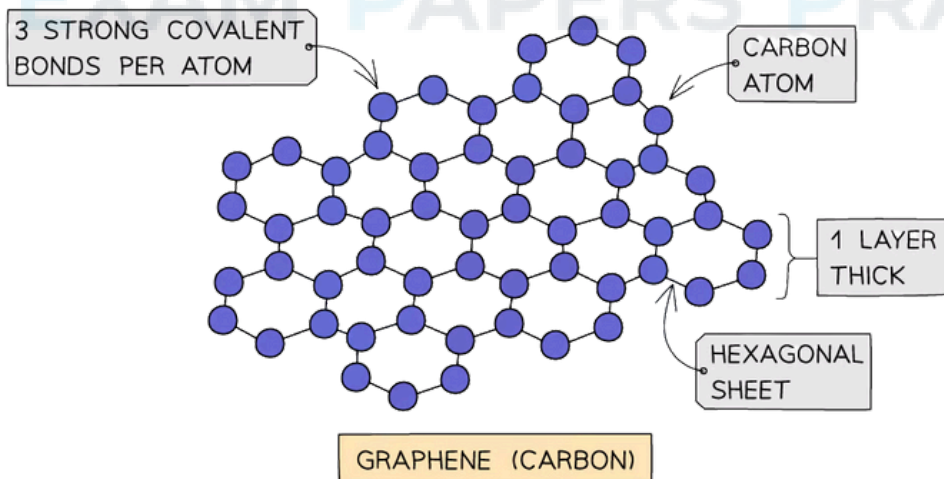


Diagram showing the structure and bonding arrangement in diamond

Graphene

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



Graphene is a truly remarkable material that has some unexpected properties

1.5.8 Predicting Structures

YOUR NOTES



Predicting Structure & Bonding

- 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

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

Predicting Physical Properties

☐ 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**.

YOUR NOTES

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☐ **Worked Example**
Bonding & structure

Compound X has the following properties:

Melting point	Electrical conductivity	
	solid	
		poor

What is the most probable structure of X?

- A. Network covalent
- B. Polar covalent molecule
- C. Ionic lattice
- D. Metallic lattice

Answer :

The correct option is A

- A high melting point is characteristic of a giant structure, which could be metallic, ionic or covalent
- The poor conductivity as a liquid and solid would match a giant covalent or network covalent structure

YOUR NOTES

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1.6 Formulae, Equations & Avogadro

1.6.1 Empirical & Molecular Formulae

Empirical & Molecular Formula Definitions

- 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 $\text{C}_2\text{H}_4\text{O}_2$
- 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

YOUR NOTES



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Empirical & Molecular Formula Calculations

YOUR NOTES

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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	$= \frac{10}{1.0}$ $= 10 \text{ mol}$	$= \frac{80}{16}$ $= 5.0 \text{ mol}$
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.

Empirical Formula Calculation

Given:

C = 85.7%

H = 14.3%

Step 1: Assume 100 g sample

C = 85.7 g

H = 14.3 g

Step 2: Convert to moles

C: $85.7 / 12 = 7.14 \text{ mol}$

H: $14.3 / 1 = 14.3 \text{ mol}$

Step 3: Divide by smallest

C: $7.14 / 7.14 = 1$

H: $14.3 / 7.14 = 2$

Empirical Formula = CH₂

YOUR NOTES



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 C₄H₁₀S and the relative molecular mass of X is 180.2

What is the molecular formula of X?

(Ar data: C = 12.0, H = 1.0, S = 32.1)

Answer Step 1: Calculate relative mass of the empirical formula

- Relative empirical mass = (C × 4) + (H × 10) + (S × 1)
- Relative empirical mass = (12.0 × 4) + (1.0 × 10) + (32.1 × 1)
- Relative empirical mass = 90.1

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

- Ratio between Mr of X and the Mr of the empirical formula = $180.2 / 90.1$
- Ratio between Mr of X and the Mr of the empirical formula = 2

Step 3: Multiply each number of elements by 2

- (C₄ × 2) + (H₁₀ × 2) + (S × 2) = (C₈) + (H₂₀) + (S₂)

- Molecular Formula of X is $C_8H_{20}S_2$

Ideal Gas Equation

- The ideal gas equation is:

$$PV = nRT$$

- P = pressure in pascals (Pa)
- V = volume in cubic metres (m^3)
- n = the amount of substance in moles (mol)
- R = the gas constant, which is given in the Data Booklet as $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$
- T = temperature in Kelvin (K)

☐ Exam Tip

There are several calculations in Chemistry where you need to convert the units to or from SI units

The ideal gas equation has three:

1. Pressure is often quoted in kPa but the calculation needs pressure in Pa
 - kPa to Pa = multiply by 1000 or 10^3
2. Volume is usually quoted in cm^3 or dm^3 but the calculation needs volume in m^3
 - cm^3 to m^3 = divide by 1000000 or multiply by 10^{-6}
 - dm^3 to m^3 = divide by 1000 or multiply by 10^{-3}
3. Temperature can be quoted in Kelvin or Celsius
 - Celsius to Kelvin = + 273

This is why you should always show your working! Examiners can't take all of your marks for one error, if you show your working then they should check through for errors and award marks accordingly

- The ideal gas equation can be used to find the amount of moles in a gaseous substance
 - It can also be used for volatile liquids at temperatures above their boiling point
- If the mass of the substance is known, then the molar mass can be calculated
 - This can then be used with empirical formula data to determine the molecular formula of a compound

YOUR NOTES



Worked Example

An unknown compound was analysed and found to contain 66.7% of carbon, 11.1% hydrogen and the remainder was oxygen

0.135 g of the unknown compound had a volume of 56.0 cm³ at a temperature of 90 °C and a pressure of 101 kPa

Determine the molecular formula of the unknown compound

Answer Step 1: Calculate the number of moles of carbon, hydrogen and oxygen

Carbon: $\frac{66.7}{12.0} = 5.558$ moles	Hydrogen: $\frac{11.1}{1.00} = 11.1$ moles	Oxygen: $\frac{(100 - 66.7 - 11.1)}{16.0} = 1.3875$ moles
---	--	---

Step 2: Divide by the smallest answer to get the ratio

Carbon: $\frac{5.558}{1.3875} = 4$	Hydrogen: $\frac{11.1}{1.3875} = 8$	Oxygen: $\frac{1.387}{1.387} = 1$
------------------------------------	-------------------------------------	-----------------------------------

Step 3: State the empirical formula

- The empirical formula is C₄H₈O

Step 4: Calculate the amount in moles, using $PV = nRT$

$$n = \frac{PV}{RT} = \frac{(101 \times 10^3) \times (56.0 \times 10^{-6})}{831 \times (90 + 273)} = 1.875 \times 10^{-3} \text{ moles}$$

Step 5: Calculate the molar mass

$$\text{Molar mass} = \frac{0.135}{1.875 \times 10^{-3}} = 72$$

Step 6: Deduce the molecular formula

- The empirical formula, C₄H₈O, has a mass of $(4 \times 12.0) + (8 \times 1.0) + 16.0 = 72.0$
- Therefore, the molecular formula is also C₄H₈O

1.6.2 Balanced Equations

YOUR NOTES



Writing Balanced 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 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



Worked Example

Balance the following equation:



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

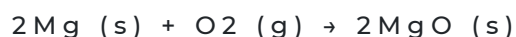


Step 2: Count the numbers of atoms in each reactant and product



	Mg	O
Reactants	1	2
Products	1	1

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



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

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

1. Balance the following equation



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

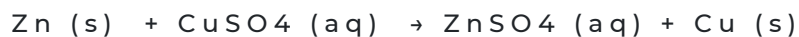


Step 2: Count the numbers of atoms in each reactant and product. The equation is already balanced



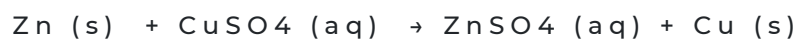
	Zn	Cu	S	O
Reactants	1	1	1	4
Products	1	1	1	4

Step 3: Use appropriate state symbols in the equation

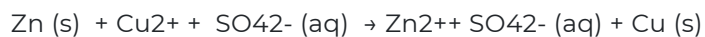


Answer 2:

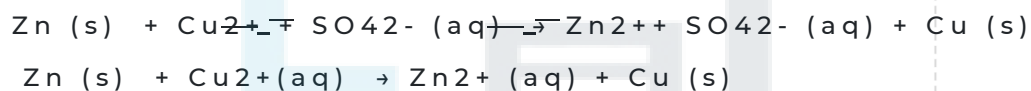
Step 1: The full chemical equation for the reaction is



Step 2: Break down reactants into their respective ions



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



1.6.3 Applying Equations

YOUR NOTES



Relating Observations to Chemical Equations

- Chemical equations give information about the reaction that is taking place
 - Balanced equations show the number of particles participating in the reaction and the number of products being formed
 - Balanced equations can be used to calculate the number of moles involved in reactions
 - Balanced equations can, also, be used to calculate masses and volumes involved in reactions
 - Ionic equations only show the reacting particles
 - Ionic equations allow you to identify spectator ion

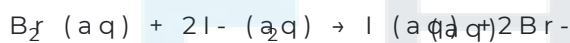
Types of reaction

- Chemical equations can be used to determine the type of reaction taking place

Displacement reactions



- In this reaction, the more reactive bromine **displaces** the less reactive iodide in potassium iodide
- This can also be seen in the ionic equation for the reaction



□ Exam Tip

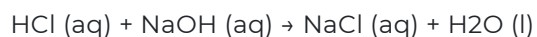
The use of chemical equations can help identify risks and hazards in the reaction and suggest appropriate precautions where necessary

For example, the use of aqueous bromine in the above example should suggest the potential use of a fume cupboard and nitrile gloves because:

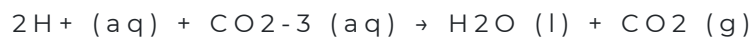
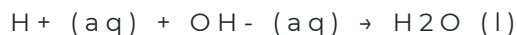
- Bromine liquid is **toxic, corrosive and harmful to the environment**
- Bromine water with a concentration of 0.2 mol dm³ is corrosive
- With a concentration of between 0.06 mol dm³ and 0.2 mol dm³, bromine water is an **irritant**
- Only below concentrations of 0.06 mol dm³ is bromine water considered a **low hazard**

Neutralisation reactions

- These can be identified by the presence of reactant acids and bases as well as the formation of a **neutral salt solution** and water (and sometimes other compounds such as carbon dioxide)



- The ionic equations can more clearly demonstrate the neutralisation of an acid and a base:



☐ Exam Tip

For neutralisation reactions, the main hazards are linked to:

- The concentration of the acid
- The type of acid
 - This could mean **strong**, e.g. HCl, or **weak**, e.g. CH₃COOH
 - This could also mean **monoprotic**, e.g. HNO₃, **diprotic**, e.g. H₂SO₄, or **triprotic**, e.g. H₃PO₄
- The concentration of the base
- The strength of the base
- The physical state of the base, e.g. NaOH (s) is arguably considered more corrosive than a high concentration solution of NaOH (aq)

Precipitation reactions

- These are shown by the reaction of two aqueous solutions to form products which include one solid



- The ionic equation shows the precipitation reactions more clearly as there are no other products considered



☐ Exam Tip

A precipitation reaction is a clear example of where consideration for further practical procedures is most obvious

The formation of a solid product should tell you that any purification of the product should include filtering or decanting as a minimum

YOUR NOTES

☐

1.6.4 The Mole & the Avogadro Constant

YOUR NOTES



The Mole & Avogadro

- The **Avogadro constant** (N_A) 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 $6.02 \times 10^{23} \text{ g mol}^{-1}$
- The mass of a substance with this number of particles is called a **mole** (mol)
 - This can be called the **molar mass**
 - This is the mass of substance that contains the same number of fundamental units as exactly 12.00g of carbon-12
- The amount / number of moles of a substance, n , the mass of the substance, m , and the molar mass, M , are linked by the equation:

$$n = \frac{\text{mass, } m}{\text{Molar mass, } M}$$

- 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 6.02×10^{23} atoms of carbon, you would have a mass of 12.00 g
 - One mole of water would have a mass of $(2 \times 1 + 16) = 18 \text{ g}$

□ Worked Example

1. What is the molar mass of water? 2. How many moles are there in 100 g of water? 3. How many water molecules are there in 100 g of water?

Answers

1. Molar mass of water, $H_2O = (2 \times 1.0) + 16.0 = 18.0 \text{ g mol}^{-1}$
2. Moles $\frac{\text{mass}}{\text{molar mass}} = \frac{100}{18.0} = 5.56 \text{ moles (to 3 s.f.)}$
3. Number of molecules = number of moles $\times$ Avogadro's constant = $5.56 \times (6.02 \times 10^{23}) = 3.35 \times 10^{24} \text{ molecules}$

□ Worked Example

What is the mass of the following:

1. Five hundred million atoms of platinum
2. (1.31×10^{22}) molecules of ethanol

Answer 1:



$$\text{Number of moles} = \frac{\text{number of particles}}{\text{Avogadro's constant, } N_A} = \frac{500 \times 10^6}{6.02 \times 10^{23}} = 8.31 \times 10^{-16} \text{ moles}$$

Mass = moles x molar mass = $(8.31 \times 10^{-16}) \times 195.1 = 1.62 \times 10^{-13} \text{ g}$ (lots of atoms, a tiny mass)

Answer 2: Molar mass of ethanol, $\text{CHOH} = (2 \times 12.0) + (5 \times 1.0) + 16.0 + 1.0 = 46.0 \text{ g mol}^{-1}$

1 25

$$\text{Number of moles} = \frac{\text{number of particles}}{\text{Avogadro's constant, } N_A} = \frac{1.31 \times 10^{22}}{6.02 \times 10^{23}} = 0.0218 \text{ moles}$$

Mass = moles x molar mass = $0.0218 \times 46.0 = 1.00 \text{ g}$ (an exceptionally large number of molecules in just 1 g)

□ Exam Tip

- When you are completing calculations using Avogadro's constant, you may end up with answers that seem very large or very small - don't automatically assume that they must be wrong. Remember,
- Avogadro's constant is a VERY large number:
 - 6.02×10^{23} or 602 000 000 000 000 000 000 000
- So when you multiply or divide by Avogadro's constant, your answers will, naturally, become very large or very small

EXAM PAPERS PRACTICE

1.6.5 Amount of Substance Calculations

YOUR NOTES



Amount of Substance Calculations

- As previously discussed, the amount of substance can be defined as the number of particles in a substance, n , measured in moles (often abbreviated to mol)
- In reality, amount of substance is used as a blanket term to cover most chemical calculations, especially those that involve moles
- The two main calculations for amount of substance are:

$$\text{Moles, } n = \frac{\text{mass } m}{\text{molar mass, } M}$$

$$\text{Moles, } n = \text{concentration} \times \text{volume}$$

- Other common calculations for amount of substance include:

$$\text{Moles, } n = \frac{\text{number of particles}}{\text{Avogadro's constant}}$$

$$\text{Moles, } n = \frac{PV}{RT} \text{ from the ideal gas equation}$$

EXAM PAPERS PRACTICE

Reacting Mass Calculations

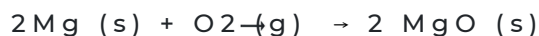
- Chemical equations can be used to calculate the moles or masses of reactants and products. To do this, information given in the question is used to find the amount
- in moles of the substances being considered. Then, the ratio between the substances is identified using the balanced chemical equation. Once the moles
- have been determined, they can then be converted into grams using the relative atomic or relative formula masses
-

YOUR NOTES



□ Worked Example

Example 1 Calculate the mass of magnesium oxide that can be made by completely burning 6.0 g of magnesium in oxygen in the following reaction:



Answer

$$\text{MOLES} = \frac{\text{MASS}}{M_r}$$

$$\text{MOLES} = \frac{6}{24} = 0.25$$



RATIO IS THUS 1:1

SO 0.25 MOLES Mg
PRODUCES 0.25 MOLES MgO

$$\text{MASS} = \text{MOLES} \times M_r$$

$$\text{MASS} = 0.25 \times 40 = 10\text{g}$$

STEP 1: CALCULATE THE
MOLES OF MAGNESIUM
USED IN THE REACTION

STEP 2: FIND THE RATIO OF
Mg TO MgO USING THE
MOLAR RATIO FROM THE
BALANCED EQUATION

STEP 3: CALCULATE THE
MASS OF MgO

□ Worked Example

Example 2 Calculate the mass of aluminium, in tonnes, that can be produced from 51 tonnes of aluminium oxide. The equation for the reaction is:





Answer

$$\begin{aligned}\text{MASS OF Al}_2\text{O}_3 \text{ IN g} &= 51 \times 10^6 \\ &= 51,000,000 \text{ g}\end{aligned}$$

$$\text{MOLES} = \frac{\text{MASS}}{M_r}$$

$$\text{MOLES} = \frac{51,000,000}{102} = 500,000$$



RATIO IS THUS 1:2

SO 500,000 MOLES Al_2O_3
PRODUCES 1,000,000 MOLES AL

STEP 1: CALCULATE THE
MOLES OF ALUMINIUM OXIDE
USED

STEP 2: FIND THE RATIO
OF Al_2O_3 TO AL USING
THE MOLAR RATIO FROM
BALANCED EQUATION

$$\text{MASS} = \text{MOLES} \times M_r$$

$$\begin{aligned}\text{MASS} &= 1,000,000 \times 27 \\ &= 27,000,000 \text{ g}\end{aligned}$$

STEP 3: CALCULATE THE
MASS OF AL

$$\begin{aligned}\text{MASS IN TONNES} &= \frac{27,000,000}{10^6} \\ &= 27 \text{ TONNES}\end{aligned}$$

STEP 4: CONVERT MASS
FROM GRAMS TO TONNES

□ Exam Tip

As long as you are consistent it doesn't matter whether you work in grams or tonnes or any other mass unit as the reacting masses will always be in proportion to the balanced equation.

Balancing Equations using Reacting Masses

- If the masses of reactants and products of a reaction are known then we can use them to write a balanced equation for that reaction
- This is done by converting the **masses** to **moles** and simplifying to find the **molar ratios**

□ Worked Example

Example 3 A student reacts 1.2 g of carbon with 16.2 g of zinc oxide. The resulting products are 4.4 g of carbon dioxide and 13 g of zinc. Determine the balanced equation for the reaction.

Answer



$$\begin{aligned} \text{C} &= 12 \\ \text{ZnO} &= 65 + 16 = 81 \\ \text{CO}_2 &= 12 + (2 \times 16) = 44 \\ \text{Zn} &= 65 \end{aligned}$$

STEP 1: WRITE DOWN THE RELATIVE ATOMIC/MOLECULAR MASSES OF EACH SUBSTANCE

$$\begin{aligned} \text{C} &= \frac{1.2}{12} = 0.1 \\ \text{ZnO} &= \frac{16.2}{81} = 0.2 \\ \text{CO}_2 &= \frac{4.4}{44} = 0.1 \\ \text{Zn} &= \frac{13}{65} = 0.2 \end{aligned}$$

STEP 2: CALCULATE THE MOLES OF EACH SUBSTANCE USING THE FORMULA:

$$\text{MOLES} = \frac{\text{MASS}}{\text{Mr}}$$

$$\begin{aligned} \text{C} &= 1 \\ \text{ZnO} &= 2 \\ \text{CO}_2 &= 1 \\ \text{Zn} &= 2 \end{aligned}$$

STEP 3: DIVIDE ACROSS BY THE SMALLEST NUMBER WHICH IS 0.1. IF ANY FRACTIONS OR DECIMALS APPEAR AT THIS STAGE THEN MULTIPLY ACROSS BY THE SAME NUMBER TO PRODUCE WHOLE NUMBERS



STEP 4: THEY ARE ALL WHOLE NUMBERS SO NO FURTHER WORK IS REQUIRED. THESE ARE THE MOLAR RATIOS IN THE REACTION AND SO THE BALANCED EQUATION CAN NOW BE WRITTEN

□ Exam Tip

These questions look hard but they are actually quite easy to do, as long as you follow the steps and organise your work neatly.

Remember the molar ratio of a balanced equation gives you the ratio of the amounts of each substance in the reaction.

1.7 Reaction Calculations

1.7.1 Reacting Volume Calculations

Reacting Volume Calculations

- Reacting volume calculations are commonly associated with the reactions of gases
- All gases occupy the same volume under the same conditions
 - At room temperature and pressure (r.t.p.), the molar gas volume of any gas is 24.0 dm³
 - Room temperature and pressure are 293 K / 20 °C and 101.3 kPa respectively
 - At standard temperature and pressure (s.t.p.), the molar gas volume of any gas is 22.4 dm³
 - Standard temperature and pressure are 273 K / 0 °C and 101.3 kPa respectively
- The equation to calculate the number of moles for any volume of gas is:

$$\text{Number of moles} = \frac{\text{Volume of gas (dm}^3\text{)}}{\text{Molar gas volume (dm}^3\text{)}}$$

☐ Worked Example

Molar gas volume calculations Calculate the number of moles present in 4.5 dm³ of carbon dioxide at:

1. Room temperature and pressure
2. Standard temperature and pressure

Answers

$$1. \text{ Number of moles} = \frac{\text{Volume of gas (dm}^3\text{)}}{\text{Molar gas volume (dm}^3\text{)}} = \frac{4.5}{24} = 0.1875 \text{ moles}$$

$$2. \text{ Number of moles} = \frac{\text{Volume of gas (dm}^3\text{)}}{\text{Molar gas volume (dm}^3\text{)}} = \frac{4.5}{22.4} = 0.201 \text{ moles (to 3 s.f.)}$$

- Volumes of gas can also be calculated using
 - Number of moles calculations
 - Volume calculations
- This can help determine the size of the equipment that you use in an experiment

YOUR NOTES

☐

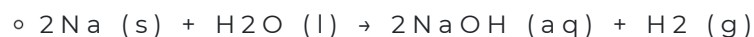
☐ Worked Example

Calculating gas volumes from moles Calculate the volume of gas

produced when 1.50 g of sodium reacts with water at standard temperature and pressure.

Answer

Step 1: Write the balanced equation for the reaction



Step 2: Calculate the number of moles of sodium

$$\text{Number of moles} = \frac{\text{mass (g)}}{\text{molar mass (g mol}^{-1}\text{)}} = \frac{1.5}{23.0} = 0.0652 \text{ moles (to 3 s.f.)}$$

Step 3: Use the stoichiometry of the equation to calculate the number of moles of hydrogen

◦ The stoichiometric ratio of Na : H₂ is 2 : 1

◦ Therefore, the number of moles of hydrogen is $\frac{0.0652}{2} = 0.0326 \text{ moles}$

Step 4: Calculate the volume of hydrogen gas evolved

◦ Volume of gas = number of moles x molar gas volume

◦ Volume of gas = $0.0326 \times 22.4 = 0.730 \text{ dm}^3 \text{ (to 3 s.f.)}$

☐ Worked Example

Calculating gas volumes from other volumes Calculate the total

volume of gas produced when 6.50 dm³ of propane combusts completely

Answer

Step 1: Write the balanced equation for the reaction



Step 2: Determine the number of moles of gas produced

◦ One mole of propane produces 3 moles of carbon dioxide and 4 moles of water

◦ Therefore, one mole of propane produces a total of 7 moles of gas

Step 3: Calculate the volume of gas that is produced

◦ 6.50 dm³ of propane will produce $7 \times 6.50 \text{ dm}^3 \text{ of gas} = 45.5 \text{ dm}^3 \text{ gas}$

Ideal Gases

YOUR NOTES



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 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 ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)
- 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

- $P = 220 \text{ kPa} = 220\,000 \text{ Pa}$
- $n = 0.781 \text{ mol}$
- $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
- $T = 21 \text{ }^{\circ}\text{C} = 294 \text{ K}$



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

□ Worked Example

Calculating the molar mass of a gas A flask of volume 1000 cm³ 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

- $P = 300 \text{ kPa} = 300\,000 \text{ Pa}$
- $V = 1000 \text{ cm}^3 = 1 \text{ dm}^3 = 0.001 \text{ m}^3$
- $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
- $T = 23 \text{ °C} = 296 \text{ K}$

$$n = \frac{300000 \times 0.001}{8.31 \times 296} = 0.12 \text{ mol}$$

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

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

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

□ Exam Tip

To calculate the temperature in Kelvin, add 273 to the Celsius temperature, e.g. 100 °C 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!

1.7.2 Titrations

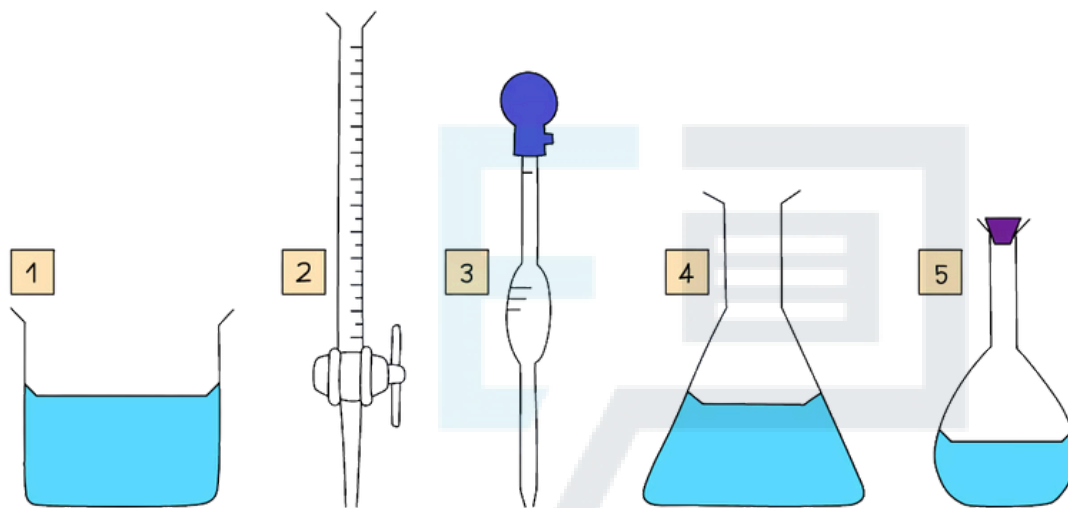
YOUR NOTES



Titration Calculations

Volumetric Analysis

- Volumetric analysis is a process that uses the volume and concentration of one chemical reactant (**standard solution**) to determine the concentration of another unknown solution
- The technique most commonly used is a **titration**
- The volumes are measured using two precise pieces of equipment, a **volumetric or graduated pipette** and a **burette**
- Before the titration can be done, the standard solution must be prepared
- Specific apparatus must be used both when preparing the standard solution and when completing the titration, to ensure that volumes are measured precisely

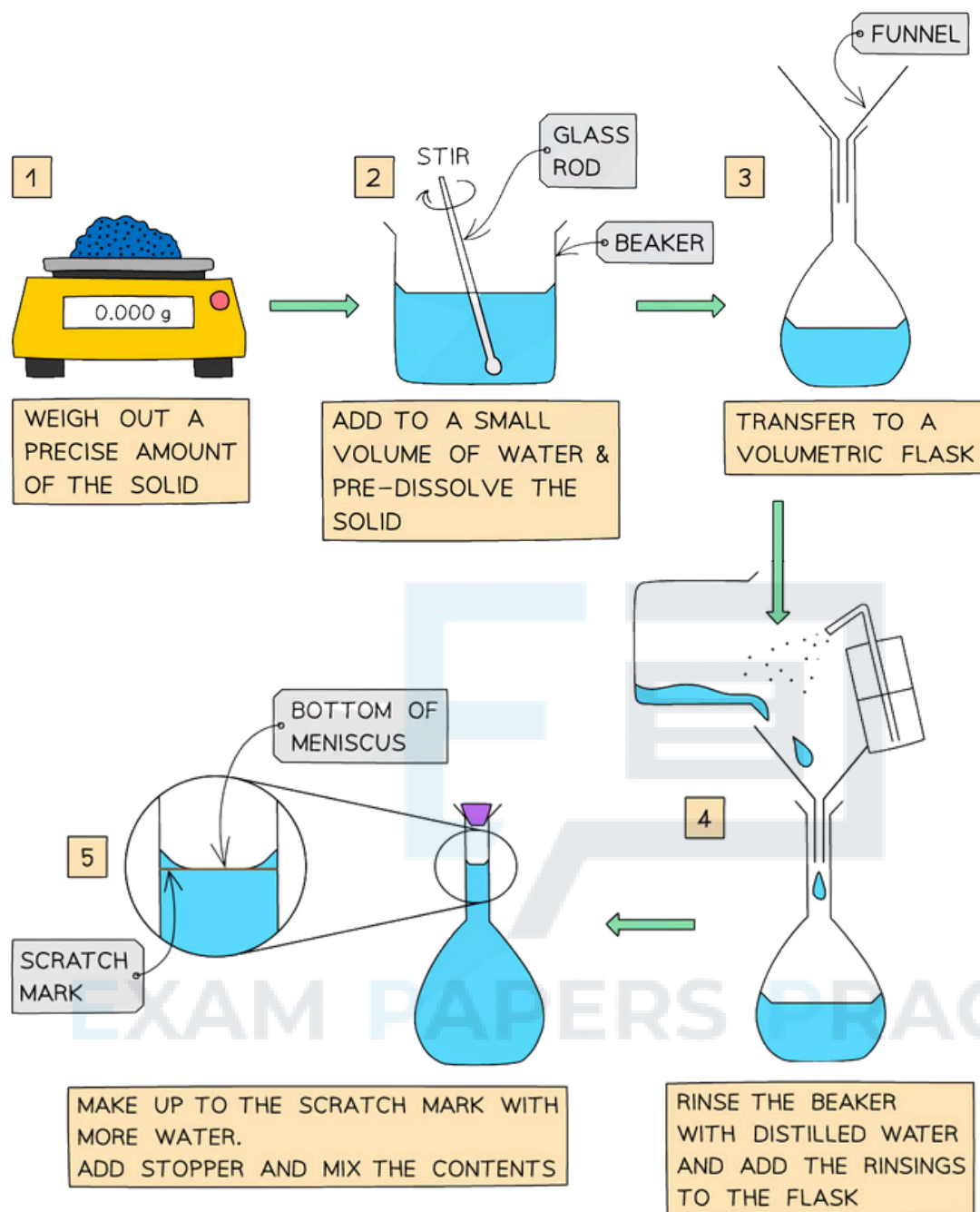


Some key pieces of apparatus used to prepare a volumetric solution and perform a simple titration

1. Beaker
2. Burette
3. Volumetric Pipette
4. Conical Flask
5. Volumetric Flask

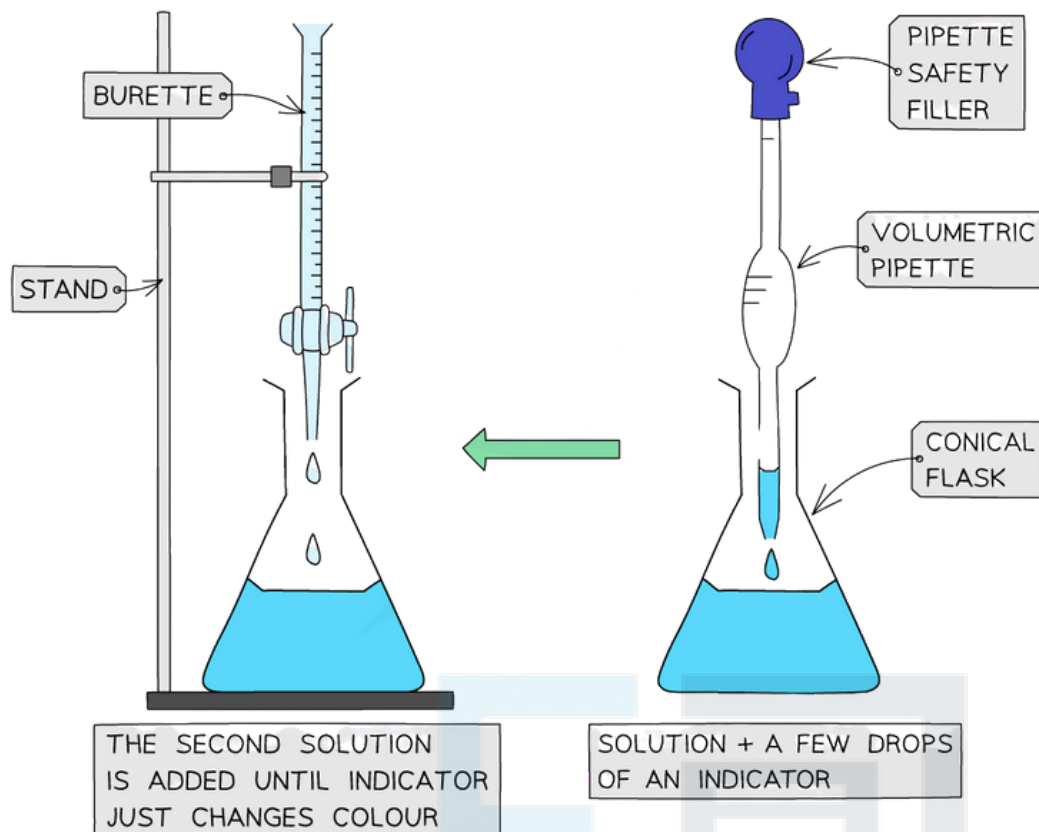
Making a Standard Solution

- Chemists routinely prepare solutions needed for analysis, whose concentrations are known precisely
- These solutions are termed **volumetric solutions** or **standard solutions**
- They are made as accurately and precisely as possible using three decimal place balances and volumetric flasks to reduce the impact of measurement uncertainties
- The steps are:



Performing the Titration

- The key piece of equipment used in the titration is the burette
- Burettes** are usually marked to a precision of 0.10 cm³
 - Since they are analogue instruments, the uncertainty is recorded to half the smallest marking, in other words to ± 0.05 cm³
- The **end point** or **equivalence point** occurs when the two solutions have reacted completely and is shown with the use of an indicator



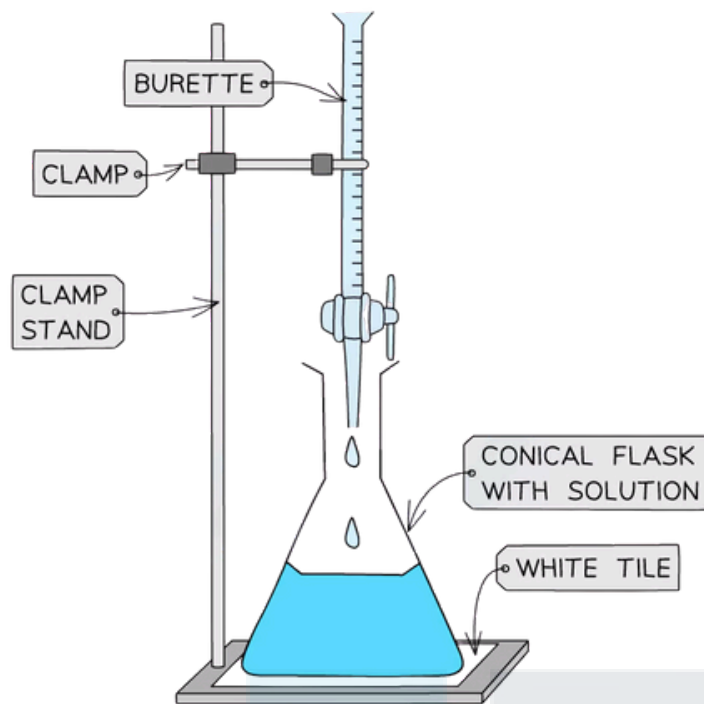
YOUR NOTES

□

The steps in a titration

- A white tile is placed under the conical flask while the titration is performed, to make it easier to see the colour change

EXAM PAPERS PRACTICE



The steps in a titration

- The steps in a titration are:
 - Measuring a known volume (usually 20 or 25 cm³) of one of the solutions with a volumetric pipette and placing it into a conical flask. The other solution is placed in the burette.
 - To start with, the burette will usually be filled to 0.00 cm³
 - A few drops of the indicator are added to the solution in the conical flask
 - The tap on the burette is carefully opened and the solution added, portion by portion, to the conical flask until the indicator starts to change colour
 - As you start getting near to the end point, the flow of the burette should be slowed right down so that the solution is added dropwise.
 - You should be able to close the tap on the burette after one drop has caused the colour change
 - Multiple runs are carried out until **concordant** results are obtained.
 - Concordant results are within 0.1 cm³ of each other

Recording and processing titration results

- Both the initial and final burette readings should be recorded and shown to a precision of ± 0.05 cm³, the same as the uncertainty

ALL RESULTS ARE RECORDED TO 2 DECIMAL PLACES INCLUDING ZERO READINGS

	Rough	Run 1	Run 2	Run 3
Initial burette reading $\pm 0.05 \text{ ml}$	0.00	23.15	0.20	23.00
Final burette reading $\pm 0.05 \text{ ml}$	23.75	45.95	23.00	46.10
Volume delivered $\pm 0.10 \text{ ml}$	23.75	22.80 ✓	22.80 ✓	23.10

THE FINAL DIGIT IS 0 OR 5

DOUBLE THE UNCERTAINTY

THE ROUGH RESULT IS USUALLY FAR OVER THE END-POINT

THIS RESULT IS DISCARDED AS IT IS TOO HIGH

✓ = CONCORDANT RESULTS

USED TO CALCULATE THE AVERAGE

A typical layout and set of titration results

- The volume delivered (titre) is calculated and recorded to an uncertainty of $\pm 0.10 \text{ cm}^3$
 - The uncertainty is doubled, because two burette readings are made to obtain the titre ($V_{\text{final}} - V_{\text{initial}}$), following the rules for propagation of uncertainties
- Concordant results are then averaged, and non-concordant results are discarded
- The appropriate calculations are then done

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

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

- A **concentrated** solution is a solution that has a **high** concentration of solute A
- A **dilute** solution is a solution with a **low** concentration of solute
- When carrying out calculations involving 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

$$\text{number of moles (mol)} = \text{concentration (mol dm}^{-3}\text{)} \times \text{volume (dm}^3\text{)}$$
- ◦ Multiply the moles of solute by its molar mass

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

☐ Worked Example

Neutralisation calculation 25.0 cm³ of 0.050 mol dm⁻³ sodium carbonate was completely neutralised by 20.00 cm³ of dilute hydrochloric acid. Calculate the concentration in mol dm⁻³ of hydrochloric acid.

Answer Step 1: Write the balanced symbol

equation



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 cm³ to dm³

$$\text{Amount (Na}_2\text{CO}_3\text{)} = 0.025 \text{ dm}^3 \times 0.050 \text{ mol dm}^{-3} = 0.00125 \text{ mol}$$

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

- 1 mol of Na₂CO₃ reacts with 2 mol of HCl, so the molar ratio is 1 : 2
- Therefore 0.00125 moles of Na₂CO₃ react with 0.00250 moles of HCl

Step 4: Calculate the concentration, in mol dm⁻³, of hydrochloric acid

$$\text{[HCl]} = \frac{\text{amount (mol)}}{\text{volume (dm}^3\text{)}} = \frac{0.00250}{0.0200} = 0.125 \text{ mol dm}^{-3}$$

YOUR NOTES

☐

1.7.3 Error & Uncertainty

YOUR NOTES



Error & Uncertainty

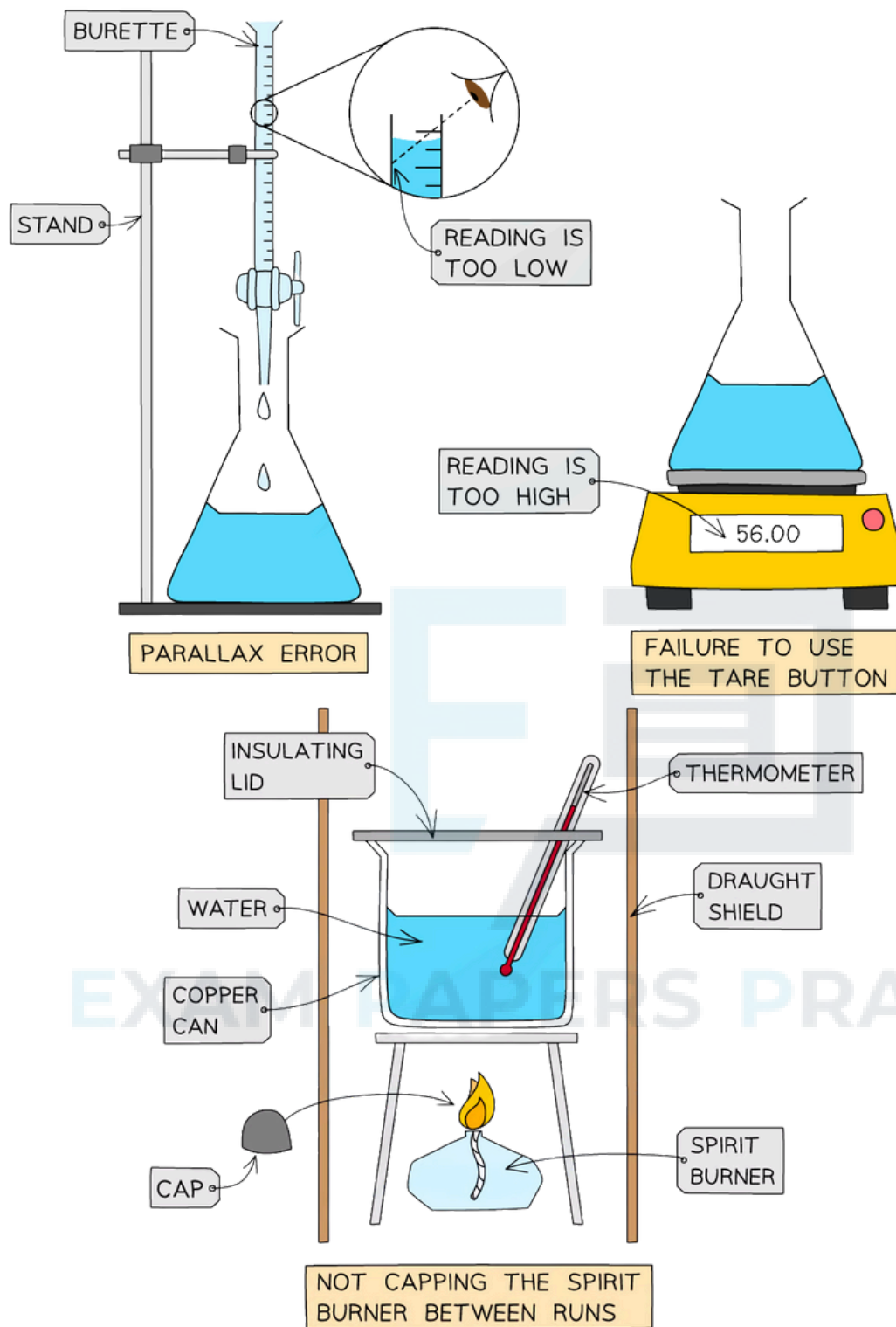
- An error is the difference between a value or quantity obtained in an experiment and an accepted or literature value for an experiment
- There are two types of errors in experiments, **random errors** and **systematic errors**

Random Errors

- When you are reading an instrument and estimate the final digit, there is an equal chance that you may read it slightly too high or slightly too low
 - This is a **random error**
- **Random errors** can be affected by:
 - How easily the instrument or scale is to read
 - The person reading the scale poorly
 - Changes in the environment, for example
 - fluctuations in the temperature of the lab
 - air currents in the room
- **Random errors** will pull a result away from an accepted value in either direction (either too high or too low)
- Repeating the experiment and working with the mean average of the results can help to reduce the effects of random errors

Systematic Errors

- **Systematic errors** are errors that occur as a result of a faulty or poorly designed experimental procedure
- **Systematic errors** will always pull the result away from the accepted value in the **same** direction (always too high or always too low)
- For example,
 - If you forget to zero an electronic balance (using the tare button) the mass weighings will always be higher than they should be
 - If you don't read the volume in a burette at eye level, the volumes will always be smaller than they should be due to a parallax error
 - If you fail to keep a cap on a spirit burner in a calorimetry experiment, the alcohol will evaporate and give you a larger mass loss
- Repeating the experiment and working with the average value will not remove any systematic errors



Systematic errors

Percentage Uncertainties

- **Percentage uncertainties** are a way to compare the significance of an **absolute uncertainty** on a measurement
- This is not to be confused with **percentage error**, which is a comparison of a result to a literature value
- The formula for calculating percentage uncertainty is as follows:

$$\text{Percentage uncertainty} = \frac{\text{absolute uncertainty}}{\text{measured value}} \times 100$$

- Some examples of percentage uncertainty calculations for common

laboratory
apparatus:

YOUR NOTES

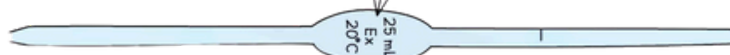


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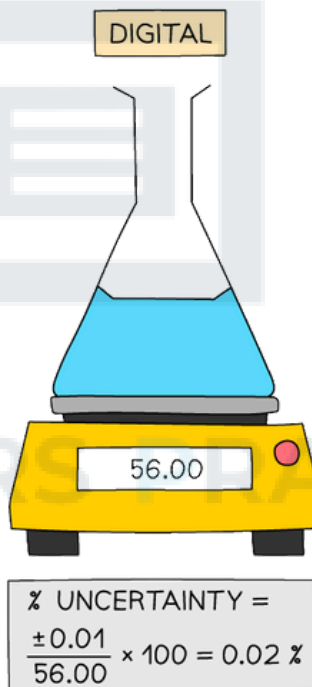
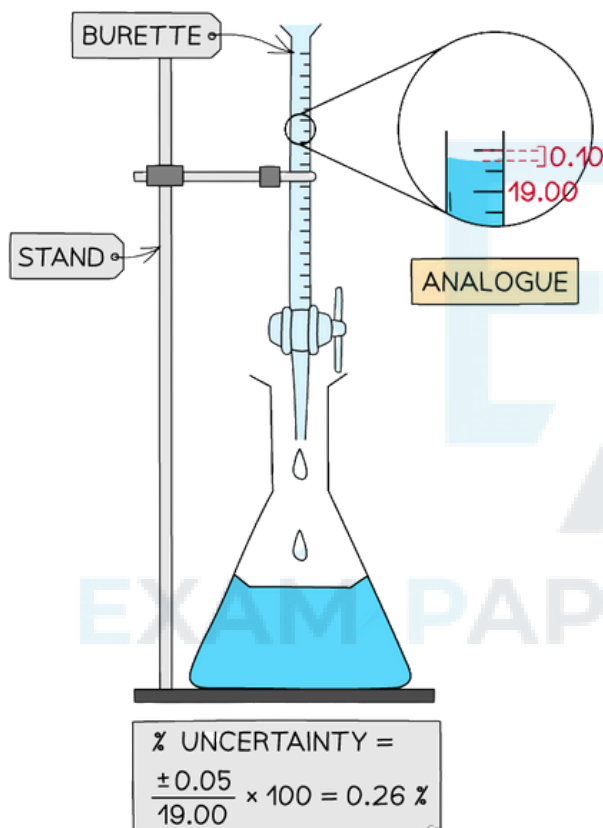
ANALOGUE

PIPETTES WILL USUALLY HAVE THE UNCERTAINTY PRINTED ON THEM



A VOLUMETRIC PIPETTE

$$\% \text{ UNCERTAINTY} = \frac{\pm 0.08}{25.00} \times 100 = 0.32 \%$$



Calculating Percentage Uncertainty

Adding or subtracting measurements

- When you are adding or subtracting two measurements then you add together the **absolute** measurement uncertainties
- For example,
 - Using a balance to measure the initial and final mass of a container

- Using a thermometer for the measurement of the temperature at the start and the end
- Using a burette to find the initial reading and final reading
- In all these examples you have to read the instrument **twice** to obtain the quantity
- If each time you read the instrument the measurement is 'out' by the stated uncertainty, then your final quantity is potentially 'out' by **twice** the uncertainty

Multiplying or dividing measurements

- When you multiply or divide experimental measurements then you **add together the percentage uncertainties**
- You can then calculate the **absolute uncertainty** from the sum of the percentage uncertainties

☐ Exam Tip

If you are multiplying or dividing data you should quote the answer to the same number of significant figures as the least precise data.

When you add or subtract data you should use the same number of decimal places as the least precise data value

YOUR NOTES



EXAM PAPERS PRACTICE

1.7.4 Yield & Atom Economy

YOUR NOTES



Yield & Atom Economy

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**
 - Products are **lost** during separation and purification
- 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:

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

- The **actual yield** is the number of moles or mass of product obtained **experimentally**
- The **theoretical yield** is the number of moles or mass obtained by a reacting mass calculation



Worked Example

In an experiment to displace copper from copper(II) sulfate, 6.5 g of zinc was added to an excess of copper(II) sulfate solution. The resulting 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 balanced symbol equation is:



Step 2: Calculate the amount of zinc reacted in moles

$$\text{number of moles} = \frac{6.5 \text{ g}}{65.4 \text{ g mol}^{-1}} = 0.10 \text{ mol}$$

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)

$$\begin{aligned}\text{mass} &= \text{mol} \times M \\ \text{mass} &= 0.10 \text{ mol} \times 63.55 \text{ g mol}^{-1} \\ \text{mass} &= 6.4 \text{ g (2 sig figs)}\end{aligned}$$

Step 5: Calculate the percentage yield of copper

$$\text{percentage yield} = \frac{4.6 \text{ g}}{6.1 \text{ g}} \times 100 = 75\%$$

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 M_r 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:



- The atom economy could also be calculated using mass, instead of M_r . 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
- Questions about atom economy often ask in qualitative or quantitative terms



Worked Example

Qualitative atom economy Ethanol can be produced by various reactions, such as:



Explain which reaction has a higher atom economy.

Answer Hydration of ethene has a higher atom economy (of 100%) because all of the reactants are converted into products, whereas the substitution of bromoethane produces NaBr as a waste product

☐ **Worked Example**
Quantitative atom economy

The blast furnace uses carbon monoxide to reduce iron(III) oxide to iron.



Calculate the atom economy for this reaction, assuming that iron is the desired product.

(Ar / Mr data: $\text{Fe}_2\text{O}_3 = 159.6$, $\text{CO} = 28.0$, $\text{Fe} = 55.8$, $\text{CO}_2 = 44.0$)

Answer

Step 1: Write the equation:

$$\text{Atom economy} = \frac{\text{molecular mass of desired product}}{\text{sum of molecular masses of ALL reactants}} \times 100$$

Step 2: Substitute values and evaluate:

$$\text{Atom economy} = \frac{2 \times 55.8}{159.6 + (3 \times 28.0)} \times 100 = 45.8\%$$

☐ **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.

1.8 Energetics I

1.8.1 Enthalpy Changes

Enthalpy Change Definitions

- 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 ΔH° 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

YOUR NOTES





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	$\Delta H_{\text{neut}}^\ominus$	Exothermic

□ Exam Tip

You will see various enthalpy change symbols used with subtle changes, e.g.

ΔH or $\Delta_c H$ for enthalpy of combustion

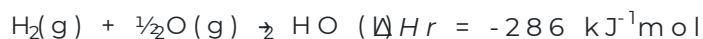
Whichever symbol you use must have the following basic points:

- Δ to represent change
- H to represent enthalpy
- $^\ominus$ to represent standard conditions
- A symbol to represent the type of enthalpy change occurring, e.g.
 - c for combustion
 - f for formation
 - neut for neutralisation
 - r for reaction

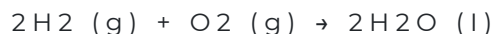


Worked Example

Calculating the enthalpy change of reaction One mole water is formed from hydrogen and oxygen, releasing 286 kJ of energy



Calculate ΔH_r for the reaction below:



Answer

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



Worked Example

Calculating the enthalpy change Calculate ΔH_r

for the reaction below, given that

$$\Delta H_f[\text{Fe}_2\text{O}_3(\text{s})] = -824.2 \text{ kJ mol}^{-1}$$



Answer

- Since two moles of $\text{Fe}_2\text{O}_3(\text{s})$ are formed the total change in enthalpy for the reaction above is:
- $\Delta H_r = 2 \times (-824.2 \text{ kJ mol}^{-1}) = -1648.4 \text{ kJ}$



Worked Example

Calculating enthalpy changes

Identify each of the following as ΔH_f , ΔH_c or ΔH_r

- $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$
- $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

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 as one mole of water is formed from the reaction between an
neut 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}

YOUR NOTES

☐



EXAM PAPERS PRACTICE

1.8.2 Enthalpy Level Diagrams

YOUR NOTES



Enthalpy Level Diagrams

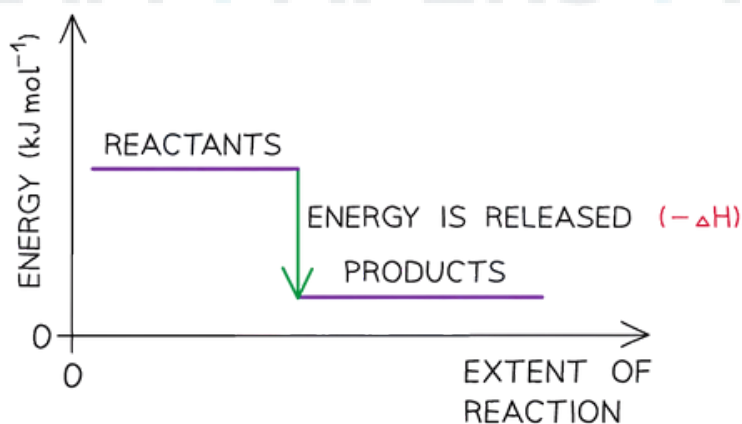
- The total chemical energy inside a substance is called the **enthalpy** (or heat content). When chemical reactions take place, changes in chemical energy take place and therefore the enthalpy changes.
- An **enthalpy change** is represented by the symbol ΔH (Δ = change; H = enthalpy).
- An enthalpy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

□ Exam Tip

Activation energy is not shown in enthalpy level diagrams.
Activation is shown in reaction profile diagrams.

Exothermic reactions

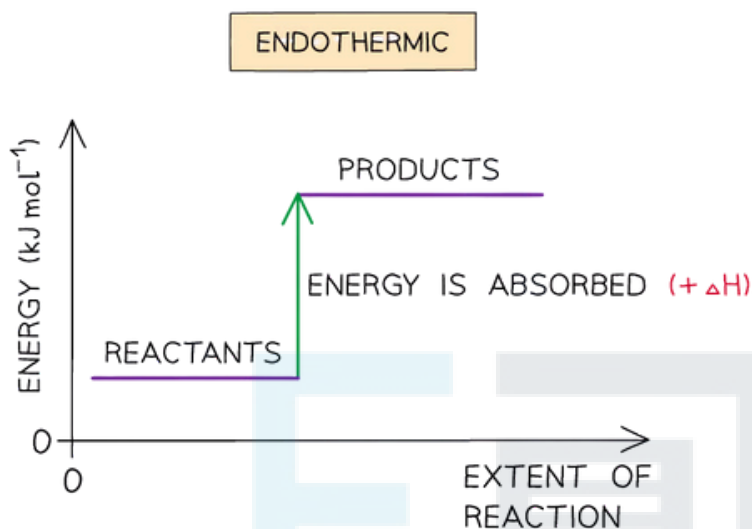
- A reaction is exothermic when the products have less energy than the reactants. Heat energy is **given off** by the reaction to the surroundings.
 - The **temperature** of the environment **increases** - this can be measured with a thermometer.
 - The **energy** of the system **decreases**.
- There 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

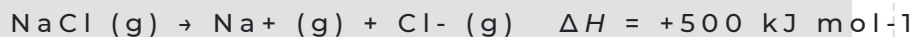
- A reaction is endothermic when the products have more energy than the reactants
- Heat energy is **absorbed** by the reaction from the surroundings
 - The **temperature** of the **environment decreases** - this can be measured with a thermometer
 - The **energy** of the **system increases**
- There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



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).

YOUR NOTES

☐

1.8.3 Calorimetry

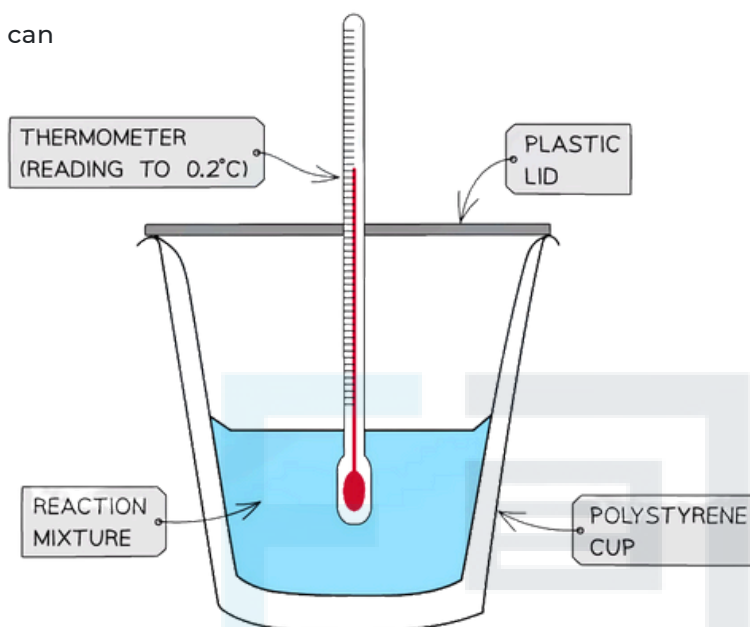
YOUR NOTES



Calculating Energy Transferred, Q

Measuring enthalpy changes

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



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 K⁻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 °C⁻¹
 ΔT = THE TEMPERATURE CHANGE, °C

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 °C. The specific heat capacity of water is 4.18 J g⁻¹ K⁻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:

- $q = 500 \times 4.18 \times 43 = 89\,870 \text{ J}$

Step 3:

- This is only 30% of the total energy released by methane
- Total energy $\times 0.3 = 89\,870 \text{ J}$
- Total energy = 299 567 J

Step 4:

- This is released by 2.50 g of methane
- Energy released by 1.00 g of methane = $299\,567 \div 2.50 = 120\,000 \text{ J g}^{-1}$ (to 3 s.f.) or 120 kJ g⁻¹



Calculating Enthalpy Changes

- 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:

q

$$\Delta H = \text{or } \frac{m \times c \times \Delta T}{n}$$

- When there is a rise in temperature, the value for ΔH becomes negative suggesting that the reaction is exothermic
 - This means that your value should be negative for an exothermic reaction, e.g. combustion
- When the temperature falls, the value for ΔH becomes positive suggesting that the reaction is endothermic
 - This means that your value should be positive for an endothermic reaction, e.g. combustion

□ Worked Example

1.50 g of an organic liquid ($M_r = 58.0$) underwent complete combustion.
The heat formed raised the temperature of 100 g of water from 20 °C to 75 °C.

Calculate the enthalpy of combustion for the organic liquid

Answer

Step 1: Calculate the energy released by the organic liquid

- $Q = mc\Delta T$
- $Q = 100 \times 4.18 \times (75 - 20)$
- $Q = 22990 \text{ J}$
- $Q = 22.99 \text{ kJ}$

Step 2: Calculate the number of moles of the organic liquid

- Number of moles $= \frac{\text{mass}}{\text{molar mass}} = \frac{1.50}{58.0} = 0.0259 \text{ moles (to 3 s.f.)}$

Step 3: Calculate the enthalpy change of combustion

- $\Delta_c H^\theta = \frac{Q}{n} = \frac{22.99}{0.0259} = -887 \text{ kJ mol}^{-1} \text{ (to 3 s.f.)}$
 - Remember, combustion is an exothermic process and will, therefore, be a negative enthalpy change value

1.8.4 Hess Cycles

YOUR NOTES



Constructing Hess Cycles

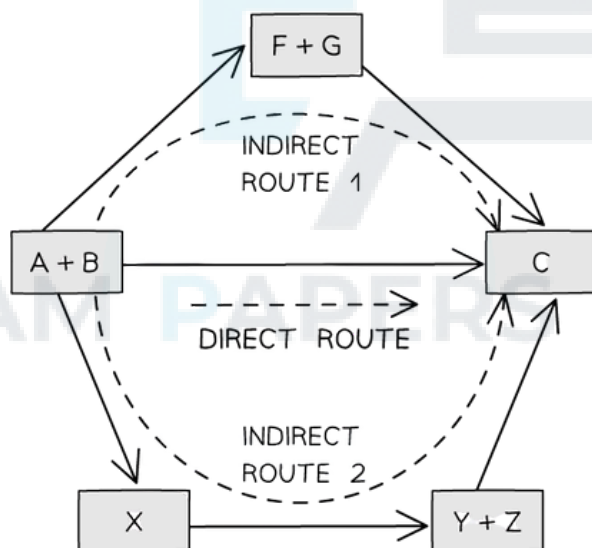
- In 1840, the Russian chemist Germain Hess formulated a law which went on to be known as **Hess's Law**
- This went on to form the basis of one of the laws of thermodynamics. The first law of thermodynamics relates to the **Law of Conservation of Energy**
- It is sometimes expressed in the following form:

Energy cannot be created or destroyed, it can only change form

- This means that in a **closed system**, the total amount of energy present is always constant
- Hess's law can be used to calculate the standard enthalpy change of a reaction from known standard enthalpy changes
- Hess's Law states that:

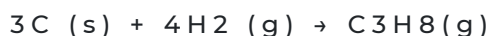
"The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

- This means that whether the reaction takes place in one or two steps, the total enthalpy change of the reaction will still be the same



The diagram above illustrates Hess' Law: the enthalpy change of the direct route, going from reactants (A+B) to product (C) is equal to the enthalpy change of the indirect routes

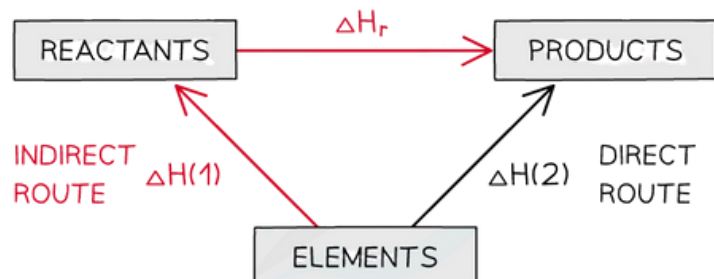
- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using calorimetry, e.g.:



- $\Delta_f H$ (propane) can't be found experimentally as hydrogen and carbon don't react under standard conditions

Calculating $\Delta_r H$ from $\Delta_f H$ using Hess's Law energy cycles

- You can see the relationships on the following diagram:



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

- The products can be directly formed from the elements = ΔH_2
- OR
- The products can be indirectly formed from the elements = $\Delta H_1 + \Delta H_r$
- Equation

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

Therefore for energy to be conserved,

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

☐ Exam Tip

You do not need to learn Hess's Law word for word as it is not a syllabus requirement, but you do need to understand the principle as it provides the foundation for all the problem solving in Chemical Energetics

YOUR NOTES

☐

Hess Cycle Calculations

- Hess cycles can be used to calculate various enthalpy changes as long as sufficient information about the other sides of the cycle is known

YOUR NOTES



Worked Example

Calculating the enthalpy change of reaction

Calculate the ΔH_f for the following reaction:



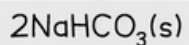
The table below shows the standard enthalpy of formations (ΔH_f) relevant

to this reaction:

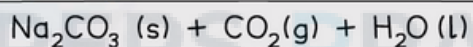
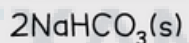
Molecule	ΔH_f (kJ mol ⁻¹)
NaHCO ₃ (s)	-950.8
Na ₂ CO ₃ (s)	-1130.7
CO ₂ (g)	-393.5
H ₂ O(l)	-285.8

Answer

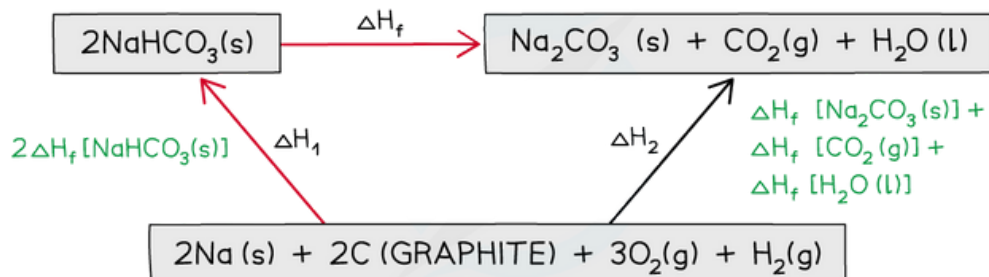
Step 1: Write the balanced equation at the top



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

- $\Delta_r H = \Delta H_2 - \Delta H_1$
 - It is minus ΔH_1 because you have to go in the opposite direction of the arrow
- ΔH_2 is $\Delta_f H [\text{Na}_2\text{CO}_3(\text{s})] + \Delta_f H [\text{CO}_2(\text{g})] + \Delta_f H [\text{H}_2\text{O}(\text{l})]$
- ΔH_1 is $2 \times \Delta_f H [\text{NaHCO}_3(\text{s})]$
- $\Delta_r H = (\Delta_f H [\text{Na}_2\text{CO}_3(\text{s})] + \Delta_f H [\text{CO}_2(\text{g})] + \Delta_f H [\text{H}_2\text{O}(\text{l})]) - (2\Delta_f H [\text{NaHCO}_3(\text{s})])$
- $\Delta_r H = ((-1130.7) + (-393.5) + (-285.8)) - (2 \times (-950.8))$
- $\Delta_r H = +91.6 \text{ kJ mol}^{-1}$



Exam Tip

Keep your enthalpy values inside their own brackets so that you don't accidentally lose a minus sign

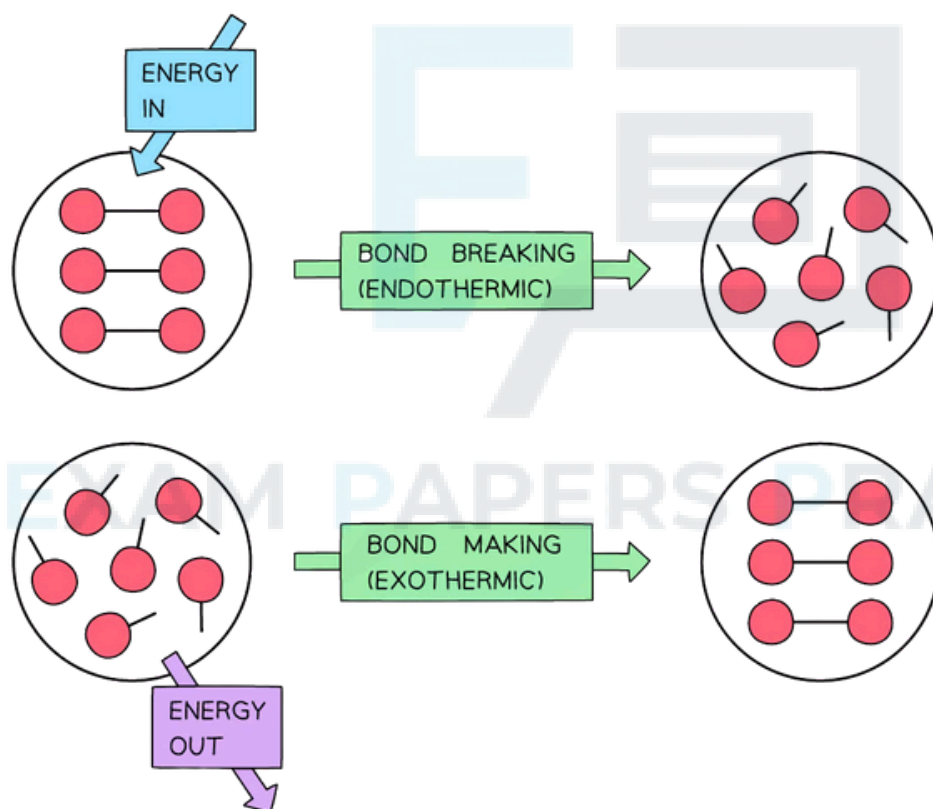
1.8.5 Bond Enthalpy

YOUR NOTES



Bond Enthalpy Definitions

- When bonds are broken or made enthalpy changes take place
 - A chemical bond is a force of attraction between two atoms Breaking the bond requires the input of energy it is therefore an **endothermic** process
- The energy change required to break the bond depends on the atoms that form the bond
 - The energy required to break a particular bond is called the **bond dissociation enthalpy**
 - This is usually just shortened to **bond enthalpy** or **bond energy**
- Bond formation is the opposite of bond breaking and so energy is released when bonds are formed
 - It is therefore an **exothermic** process



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

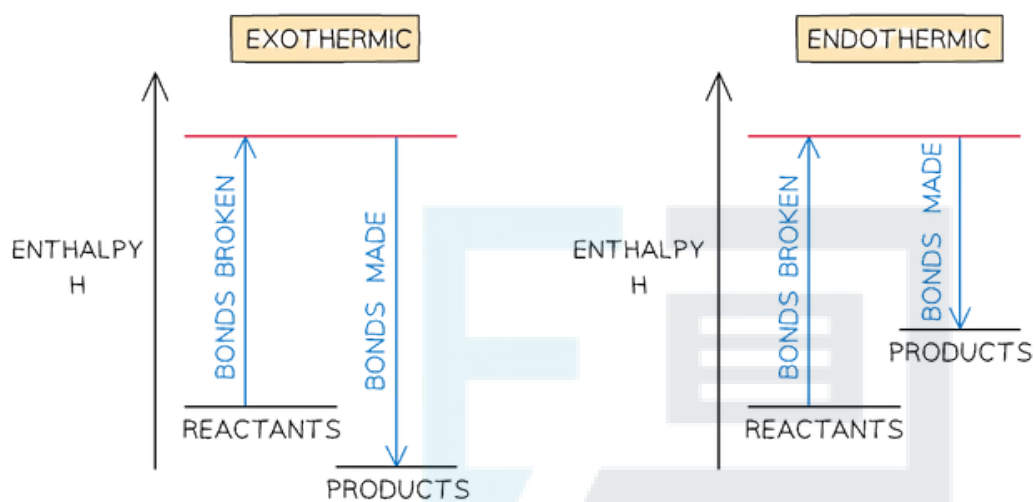
- The amount of energy released when a particular bond is formed has the same magnitude as the energy taken in when the bond is broken but has the opposite



sign

Overall enthalpy changes

- If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is **exothermic**
 - The products are **more stable** than the reactants
- If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is **endothermic**
 - The products are **less stable** than the reactants
- The relationship between bond breaking and bond making can be shown graphically like this:

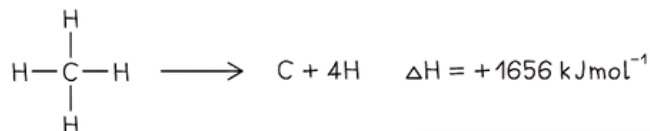


Bond enthalpy profiles

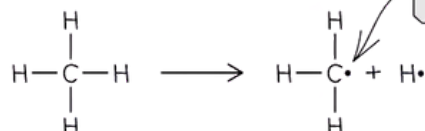
Average bond energy

- 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** and is defined as

'The energy needed to break one mole of bonds in a gaseous molecule averaged over similar compounds'



FIRST STEP



THE REMAINING Hs ARE HELD MORE STRONGLY

SECOND STEP



IT TAKES MORE ENERGY TO REMOVE MORE H ATOMS

AVERAGE BOND ENTHALPY $\Delta H = \frac{+1656}{4} = +414 \text{ kJmol}^{-1}$

Average bond enthalpy of C-H in methane

- The average bond enthalpy of C-H is found by taking the bond dissociation enthalpy for the whole molecule and dividing it by the number of C-H bonds
- The first C-H bond is easier to break than the second as the remaining hydrogens are pulled more closely to the carbon
- However, since it is impossible to measure the energy of each C-H bond an average is taken
- This value is also compared with a range of similar compounds to obtain an accepted value for the average bond enthalpy

☐ Exam Tip

A lot of students mix up endothermic / exothermic and bond breaking / bond making.

An easy way to remember is that ENDOTHERMIC leads to the poetic phrase the 'end o' the bond'

Calculating Bond Enthalpies

YOUR NOTES

- Bond energies are used to find the enthalpy of reaction when this cannot be done experimentally. The process is a step-by-step summation of the bond enthalpies of all the molecules present finishing with this formula:

$$\Delta H^\theta_r =$$

$$\text{enthalpy change for bonds broken} + \text{enthalpy change for bonds formed}$$

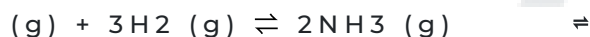
- These two worked examples show how to lay out your calculation

☐ Worked Example

Calculate the enthalpy of reaction for the Haber process reaction. 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: The chemical equation for the Haber process is:



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

Bonds Broken (kJ mol ⁻¹)	Bonds formed (kJ mol ⁻¹)
$1 \times \text{N} \equiv \text{N} = 1 \times 945 = 945$ $3 \times \text{H} - \text{H} = 3 \times 436 = 1308$	$6 \times \text{N} - \text{H} = 6 \times 391$
Total = +2253	Total = -2346

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

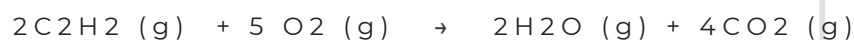


Step 3: Calculate the standard enthalpy of reaction

- $\Delta_r H^\theta$ = enthalpy change for bonds broken + enthalpy change for bonds formed
- $\Delta_r H^\theta = (+2253 \text{ kJ mol}^{-1}) + (-2346 \text{ kJ mol}^{-1})$
- $\Delta_r H^\theta = -93 \text{ kJ mol}^{-1}$

□ Worked Example

The complete combustion of ethyne, C_2H_2 , is shown in the equation below:



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 $\equiv$ C	839
O = O	498
C = O	804
O – H	463
O – C	358

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



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



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

- $\Delta_r H^\theta$ = enthalpy change for bonds broken + enthalpy change for bonds formed
- $\Delta_r H^\theta = (+2912 \text{ kJ mol}^{-1}) + (-4142 \text{ kJ mol}^{-1}) = -1230 \text{ kJ mol}^{-1}$
- $\Delta_r H^\theta$

□ Exam Tip

The key to success in bond enthalpy calculations is to be very careful when accounting for every bond present. Always draw out the full displayed structures of the molecules so you don't miss any of the bonds.

Watch out for coefficients in the balanced equations as students often miss those, forget to multiply them by the bond enthalpies and get the answer wrong! It is super important to show your steps because bond enthalpy

calculations

often carry 3 marks, 2 of which could be for workings if you get the final answer wrong

EXAM PAPERS PRACTICE

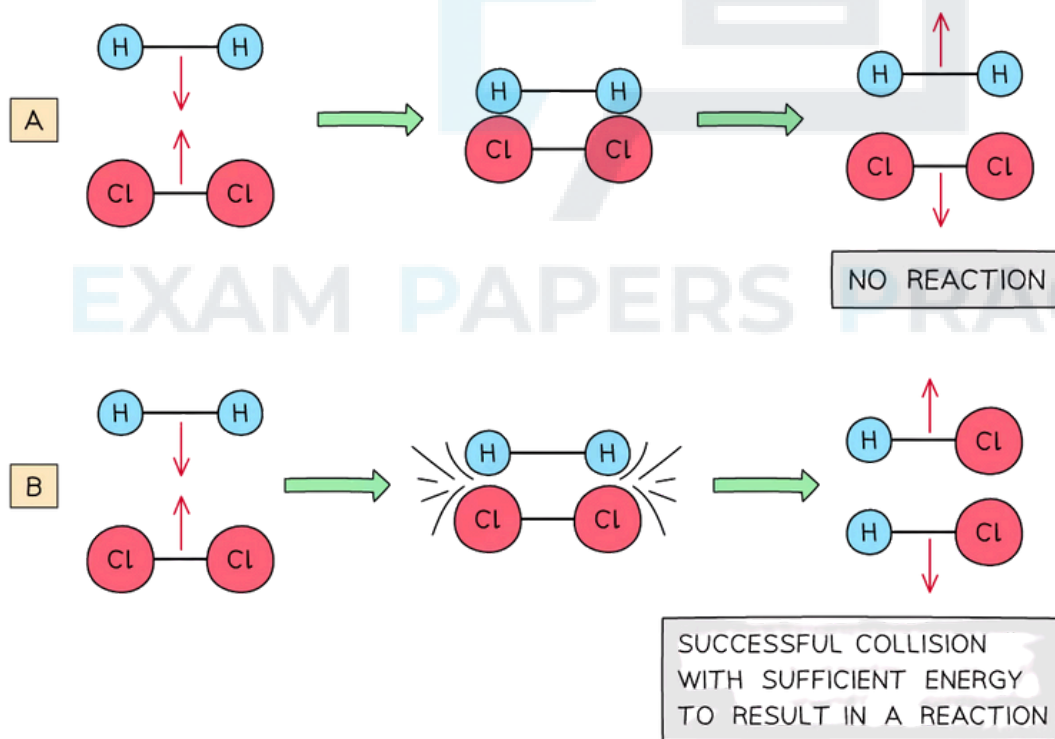
1.9 Kinetics I

1.9.1 Collision Theory & Rates

Collision Theory & Rates

Collision Theory

- When reactants come together the kinetic energy they possess means their particles will collide and some of these collisions will result in chemical bonds being broken and some new bonds being formed
- The rate of a chemical reaction depends on factors including:
 - collision frequency
 - collision energy
 - activation energy
- Ultimately, the rate of reaction depends on the number of successful / effective collisions that happen per unit time
 - A **successful / effective collision** is where the particles collide in the correct orientation and with sufficient energy for a chemical reaction to occur
 - An **unsuccessful / 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



YOUR NOTES

□



(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

Collision frequency

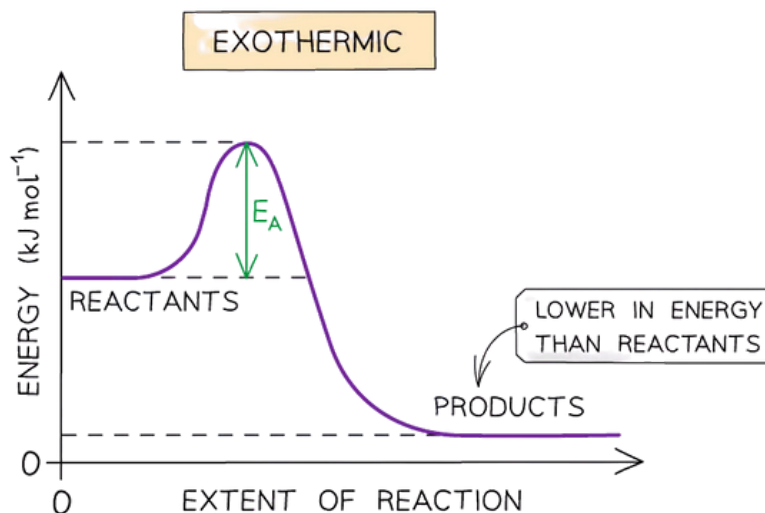
- If a chemical reaction is to take place between two particles, they must first collide
- The number of collisions between particles per unit time in a system is known as the **collision frequency**. The collision frequency of a given system can be altered by:
 - Changing the **concentration** of the reactants
 - Increasing the concentration will mean that there are more particles available to react in the same volume / amount of space leading to more frequent, successful collisions
 - Changing the total **pressure**
 - Increasing the pressure means that there will be the same number of particles but in a smaller volume leading to more frequent, successful collisions
 - Changing the **temperature**
 - This will increase the kinetic energy of the reacting particles, ultimately, resulting in more frequent, successful collisions
 - Changing the **size** of the reacting particles
 - This is achieved by increasing the **surface area** which means that there are more particles available to react in the same volume / amount of space leading to more frequent, successful collisions

Collision energy

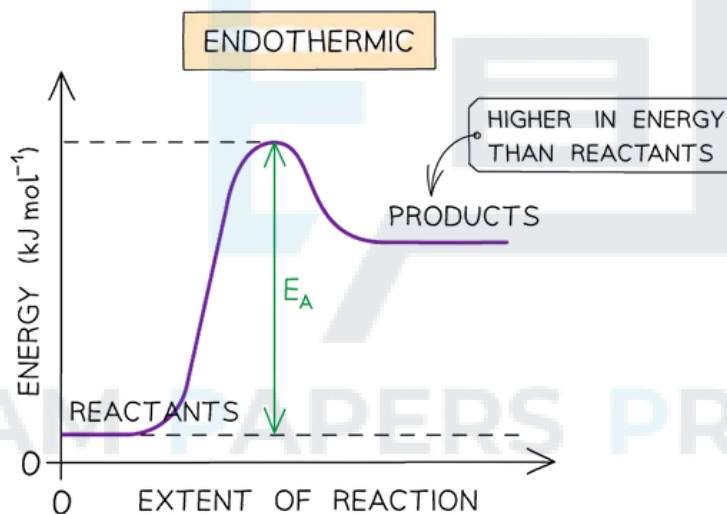
- Not all collisions result in a chemical reaction
 - Most collisions just result in the colliding particles bouncing off each other
 - Collisions which do not result in a reaction are known as **unsuccessful collisions**
- **Unsuccessful collisions** happen when the colliding species do not have enough energy to break the necessary bonds
- If they do not have sufficient energy, the collision will not result in a chemical reaction
- If they have sufficient energy, they will react, and the collision will be successful

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

The success of a reaction can be measured using the rate of reaction, which could be achieved by measuring:

The amount of reactant lost

- The amount of product formed The time it takes for a
- specific colour change to happen The time it takes for a
- certain amount of precipitate to form

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1.9.2 Calculating Rates of Reaction

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Calculating Rates of Reaction

- To measure the **rate of a reaction**, we need to be able to measure either how quickly the reactants are used up or how quickly the products are formed
- The method used for measuring depends on the substances involved
- There are a number of ways to measure a reaction rate in the lab; they all depend on some property that changes during the course of the reaction
- That property is taken to be **proportional** to the concentration of the reactant or product, e.g., colour, mass, volume
- Some reaction rates can be measured as the reaction proceeds (this generates more data);
 - faster reactions can be easier to measure when the reaction is over, by averaging a collected measurement over the course of the reaction
- Commonly used techniques are:
 - **mass loss**
 - **gas production**

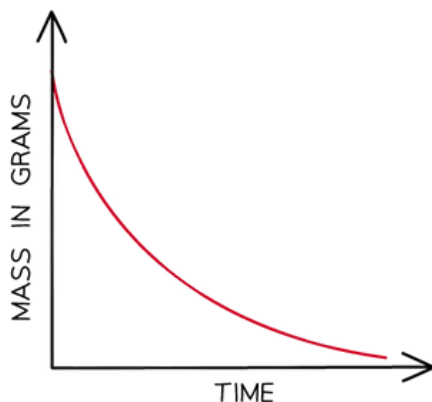
Changes in mass

- When a gas is produced in a reaction it usually escapes from the reaction vessel, so the mass decreases
 - This can be used to measure the rate of reaction. For example, the reaction of calcium carbonate with hydrochloric acid produces CO_2
 - The mass is measured every few seconds and change in mass over time is plotted as the CO_2 escapes



Measuring changes in mass using a balance

- The mass loss provides a measure of the amount of reactant, so the graph is the same as a graph of amount of reactant against time



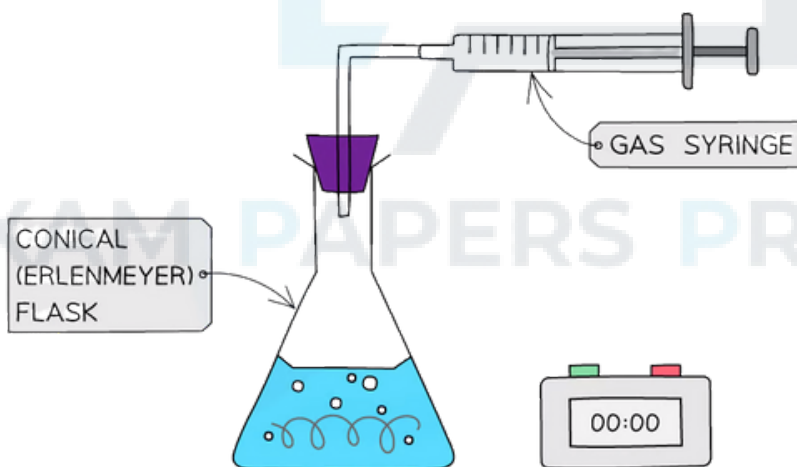
Mass loss of a product against time

- However, one limitation of this method is the gas must be sufficiently dense or the change in mass is too small to measure on a 2 or 3 d.p. balance

So carbon dioxide would be suitable ($M_r = 44.0$) but hydrogen would not ($M_r = 2.0$)

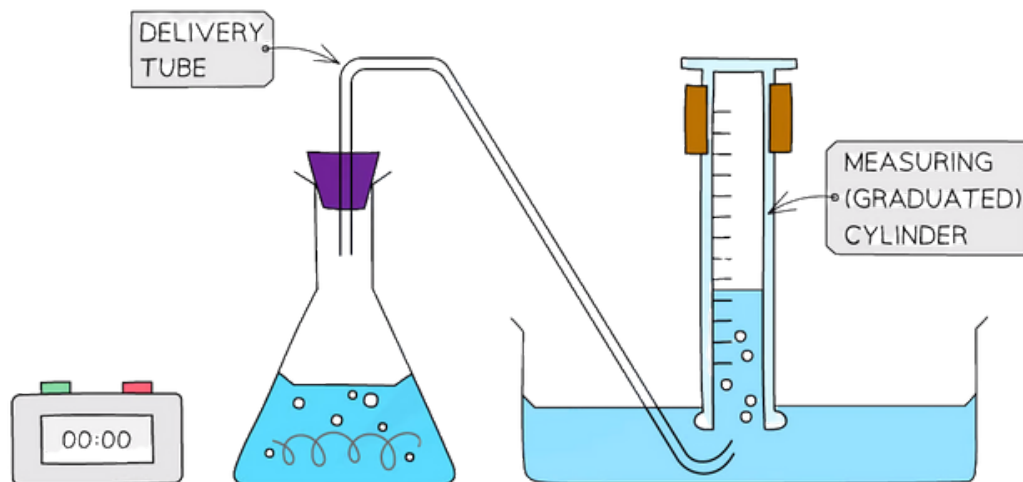
Volumes of gases

- When a gas is produced in a reaction, it can be trapped and its volume measured over time
 - This can be used to measure the rate of reaction. For example, the
 - reaction of magnesium with hydrochloric acid produces hydrogen



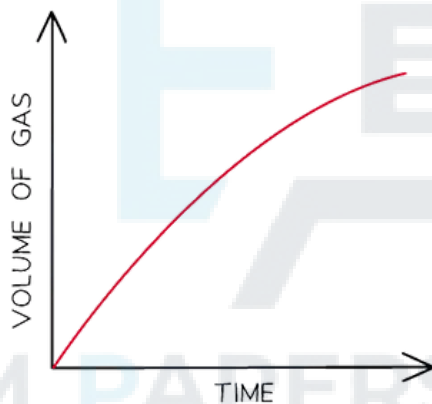
Collecting gases experimental set up

- An alternative gas collection set up involves collecting a gas through water using an inverted measuring cylinder (as long as the gas is not water soluble)



Alternative gas collection set up

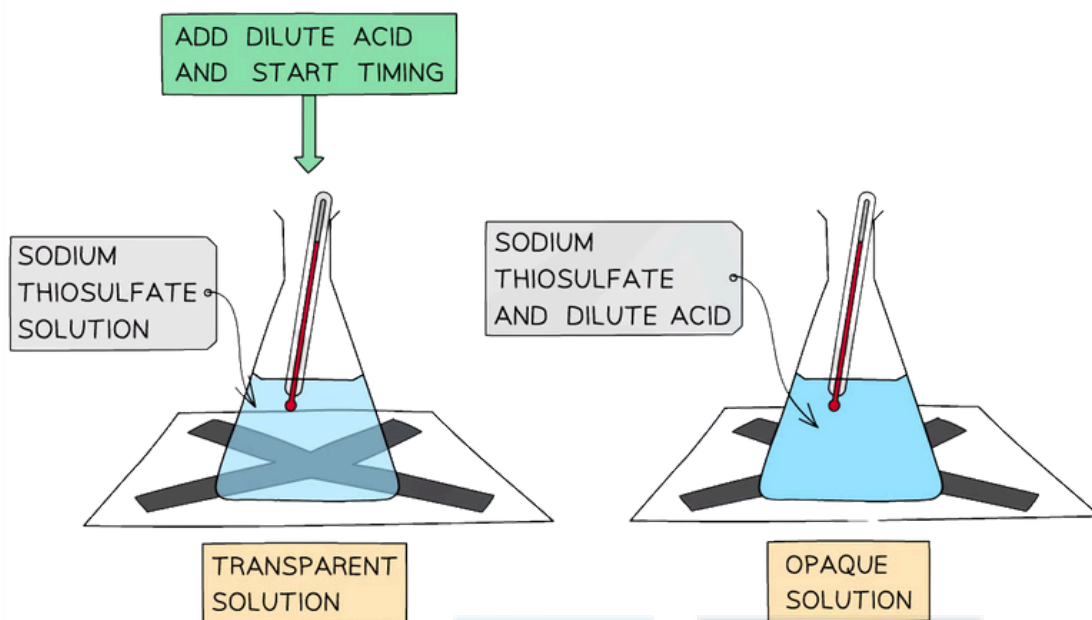
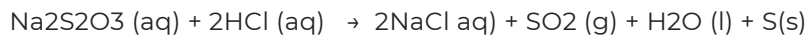
- The volume can be measured every few seconds and plotted to show how the volume of gas varies with time
- The volume provides a measure of the amount of product, so the graph is a graph of amount of product against time



Graph of gas volume evolved against time

Measuring concentration changes

- Measuring concentration changes during a reaction is not easy; the act of taking a sample and analysing it by **titration** can affect the rate of reaction (unless the reaction is deliberately stopped- this is called **quenching**).
- Often it is more convenient to 'stop the clock' when a specific (visible) point in the reaction is reached
 - For example when a piece of magnesium dissolves completely in hydrochloric acid
 - Another common rate experiment is the reaction between sodium thiosulfate and hydrochloric acid which slowly produces a yellow precipitate of sulfur that obscures a cross when viewed through the solution:



The disappearing cross experiment

- The main limitation here is that often it only generates one piece of data for analysis

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☐ Worked Example

Using the results shown below, calculate the initial rate of reaction for the reaction using 2.0 mol dm^{-3} HCl (aq)



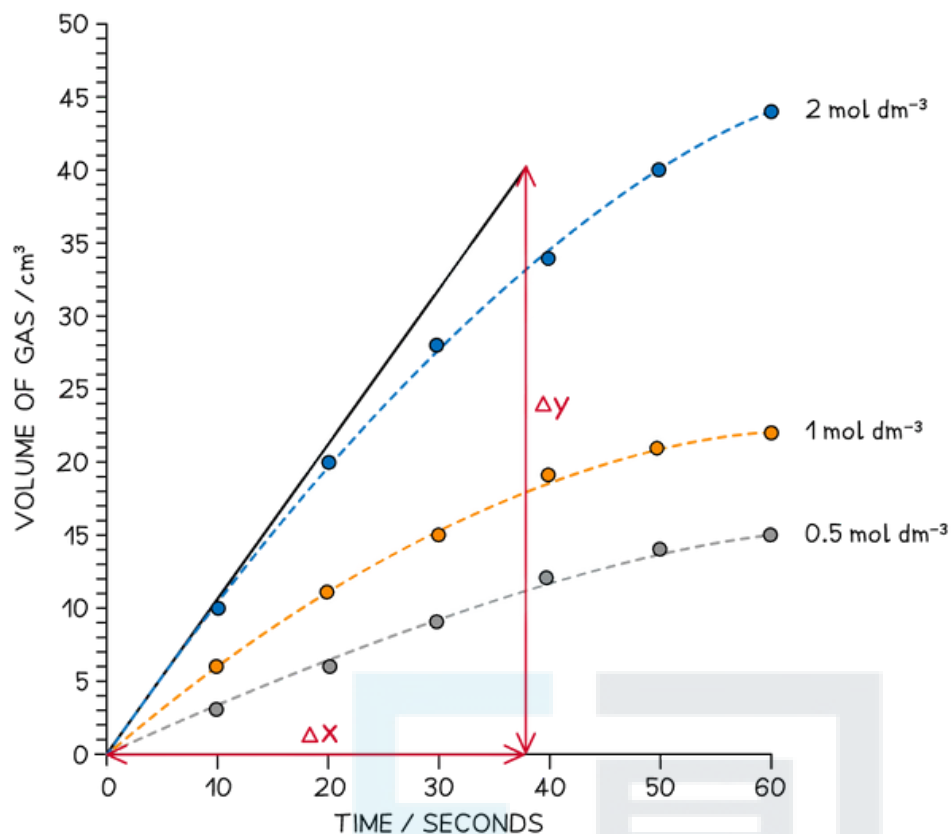
	Volume of gas / cm^3		
Time / seconds	2.0 mol dm^{-3}	1.0 mol dm^{-3}	0.5 mol dm^{-3}
0	0	0	0
10	10	6	3
20	20	11	6
30	28	15	9
40	34	19	12
50	40	21	14
60	44	22	15

Answer

Step 1: Draw a graph of the results

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- The gradient can be used to give the rate of reaction, however, the graph has produced a curve

Step 2: Draw a tangent to the curve at time = 0 seconds

Step 3: Calculate the gradient

◦ Gradient $\frac{\Delta y}{\Delta x} = \frac{40}{38} = 1.05 \text{ mol dm}^{-3} \text{ s}^{-1}$

☐ Exam Tip

You should be familiar with the interpretation of graphs of changes in concentration, volume or mass against time and be able to calculate a rate from a tangent to the graph

1.9.3 Maxwell-Boltzmann Distributions

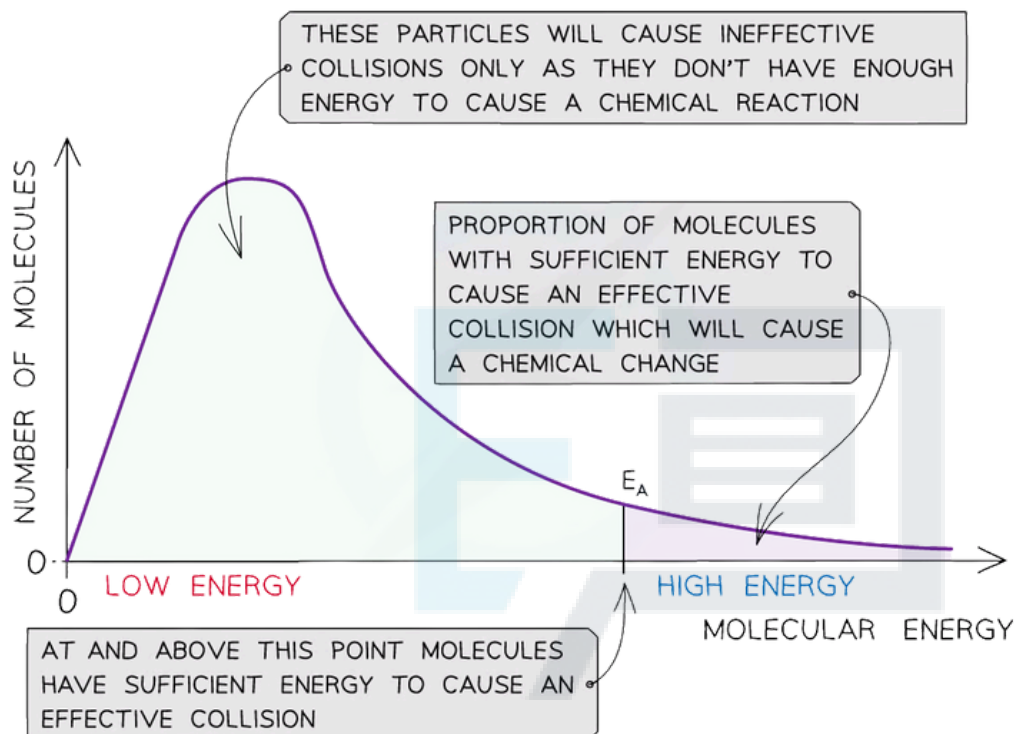
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Temperature Effects

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.



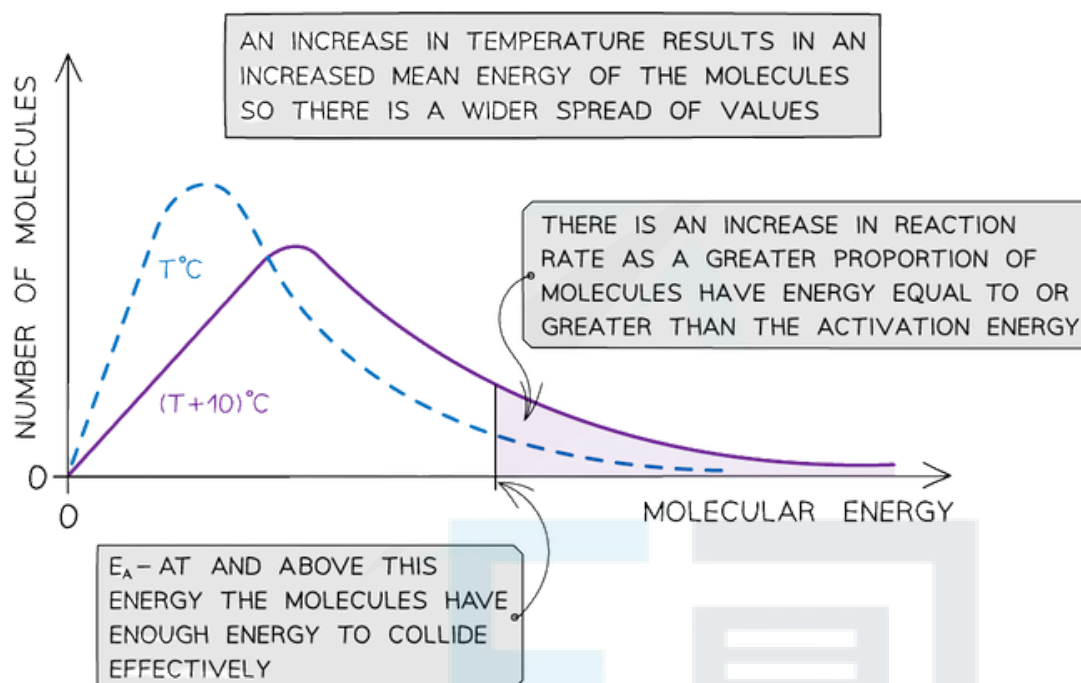
The Maxwell-Boltzmann distribution curve shows the distribution of the energies and the activation energy

- 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 $T^{\circ}\text{C}$ 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

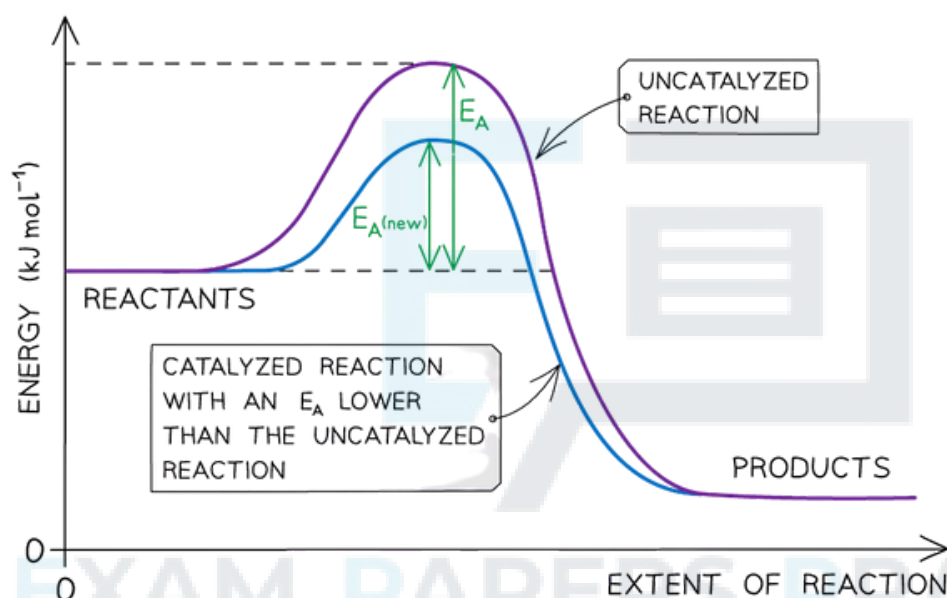
The increase in proportion of molecules having kinetic energy greater than the activation has a greater effect on the rate of reaction than the increase in effective collisions

Effects of Adding a Catalyst

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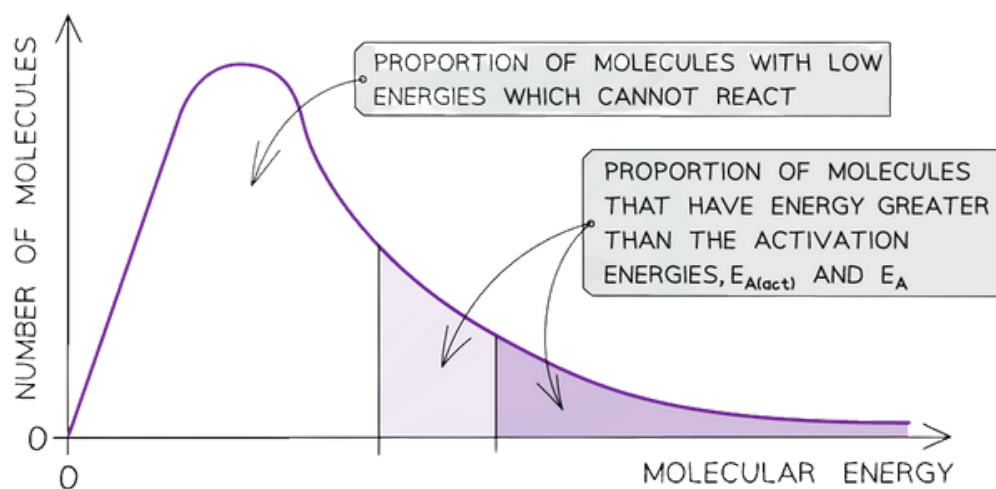
- **Catalysis** is the process in which the rate of a chemical reaction is increased, by adding a **catalyst**
- A catalyst increases the rate of a reaction by providing the reactants with an **alternative reaction pathway** which is **lower in activation energy** than the uncatalysed reaction
- Catalysts 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
- On the graph below, the original number of successfully reacting particles is shown by the dark shaded area
- 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**
- This is shown by the combined number of particles in the light and dark shaded areas
- As a result of this, the rate of the catalysed reaction is increased compared to the uncatalysed reaction



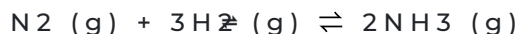
The diagram shows that the total shaded area (both dark and light shading) under the curve shows the number of particles with energy greater than the E_a when a catalyst is present. This area is much larger than the dark shaded area which shows the number of particles with energy greater than the E_a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

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1.9.4 Catalysts in Industry

Catalysts in Industry

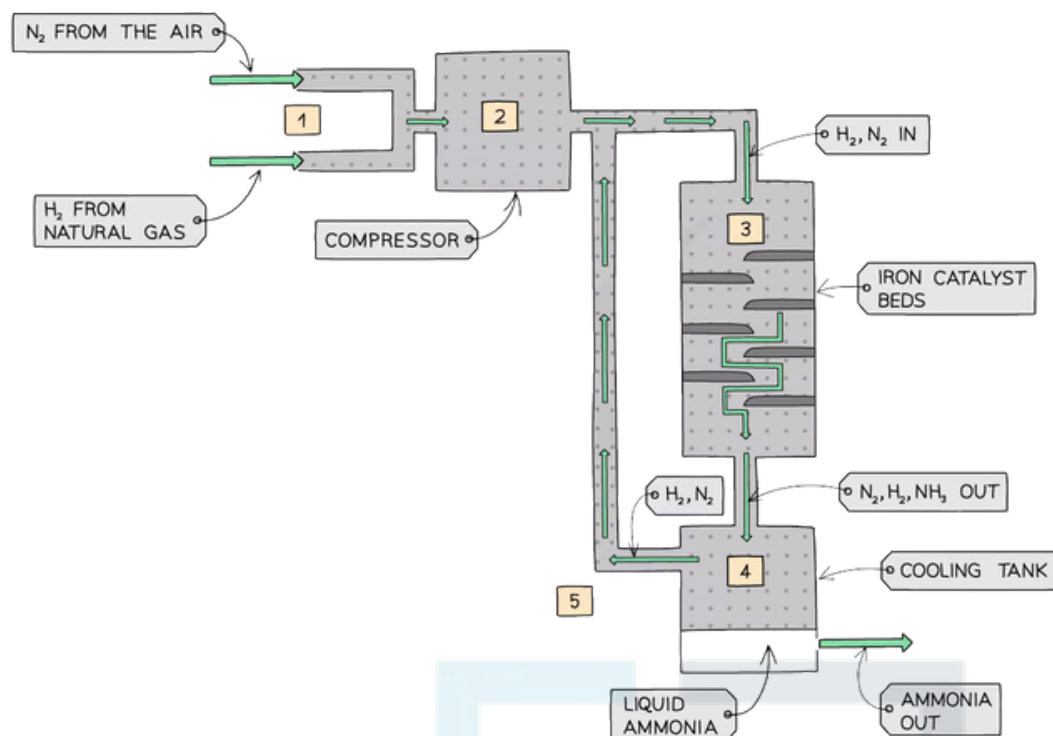
- Catalysts can be divided into two types:
 - Homogeneous catalysts
 - Heterogeneous catalysts
- Homogeneous means that the catalyst is in the **same phase** as the reactants
 - For example, the reactants and the catalysts are all in solution
- Heterogeneous means that the catalyst is in a **different phase** to the reactants
 - For example, the reactants are gases, but the catalyst used is a solid
- Ammonia production via the **Haber Process** is a classic example of the use of a heterogeneous catalyst



- The Haber Process occurs in five stages
 - Hydrogen and nitrogen are obtained from natural gas and air respectively and pumped into the compressor
 - The gases are compressed to about 200 atmospheres
 - The pressurised gases, at around 450 °C, are pumped into a tank containing beds of solid iron which is a heterogeneous catalyst, where some of the hydrogen and nitrogen react to form ammonia
 - Unreacted hydrogen, nitrogen and the ammonia product pass into a cooling tank where the ammonia is liquefied and removed
 - The unreacted hydrogen and nitrogen are recycled back into the system and start over again

YOUR NOTES





The production of ammonia by the Haber Process

Conditions

Temperature: 450°C

- A higher temperature favours the reverse reaction as it is endothermic (takes in heat) so a higher yield of **reactants** would be made
- Lower temperature favours the forward reaction as it is exothermic (releases heat) so a higher yield of **products** will be made
 - However, at a lower temperature the rate of reaction is very slow
- So 450°C is a compromise temperature between having a lower yield of products but being made more quickly

Pressure: Approximately 20 MPa

- Lower pressure favours the reverse reaction as the system will try to increase the pressure by creating more molecules (4 molecules of gaseous reactants) so a higher yield of **reactants** will be made
- Higher pressure favours the forward reaction as it will try to decrease the pressure by creating less molecules (2 molecules of gaseous products) so a higher yield of **products** will be made
- However, high pressures can be dangerous and very expensive equipment is needed

- So, 20 MPa is a **compromise** pressure between a lower yield of products being made **safely** and **economically**

Catalyst

- A catalyst of iron is used to speed up the reaction
- Without a catalyst, the required temperature and pressure for the Haber Process would be much higher, more dangerous, more expensive and less environmentally friendly

Benefits of catalysts

- Catalysts speed up the rate of reaction, meaning the use of a catalyst may mean lower temperatures and pressures can be used
 - This can save energy costs as there is reduced energy demand for providing high temperatures and less electrical pumping costs for producing the high pressures usually required
 - This can mean fewer CO₂ emissions from burning fossil fuels
- Catalysts can also enable different reactions to be used, with better atom economy and with reduced waste, or fewer undesired products or less use of hazardous solvents and reactants
- Catalysts are often enzymes, generating very specific products, and operating effectively close to room temperature and pressure

☐ Exam Tip

You should be able to apply the arguments shown above to any potential reaction with supporting information to explain the overall effects of changing reaction conditions as well as the benefits of using a catalyst

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