AS Chemistry Edexcel

1. Physical Chemistry

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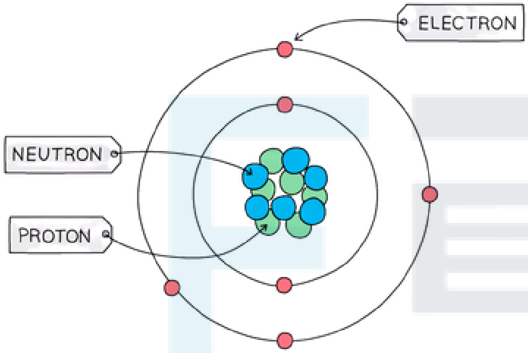
1.1 Atomic Structure

1.1.1 Structure of the Atom

Structure of the Atom

- All matter is composed of **atoms**,whichare thesmallest 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



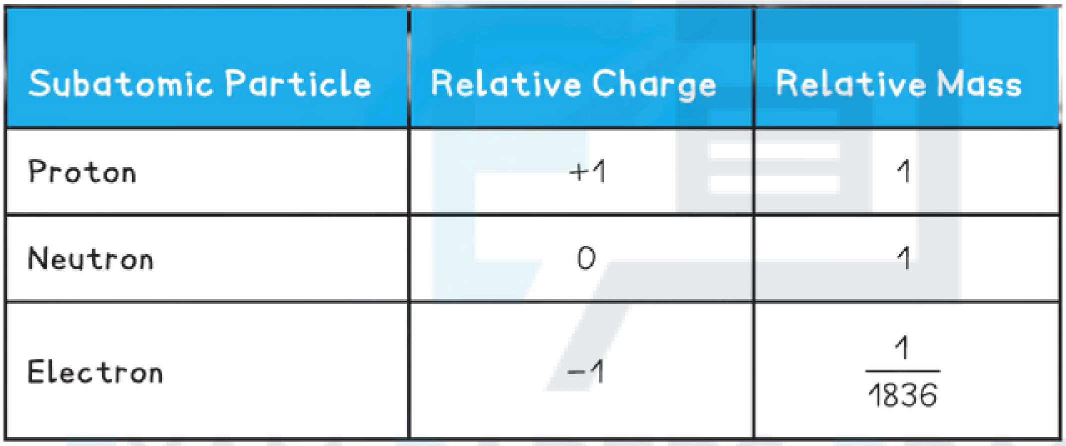
The basic structure of an atom (not to scale)

Subatomic Mass & Charge

- **Subatomic particles** are the particlesan element is madeup 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 x 10-19 coulombs whereas the charge of a **proton** is +1.602 x 10-19 coulombs, however, relative to each other, their charges are -1 and +1 respectively.

Atomic & Mass Numbers

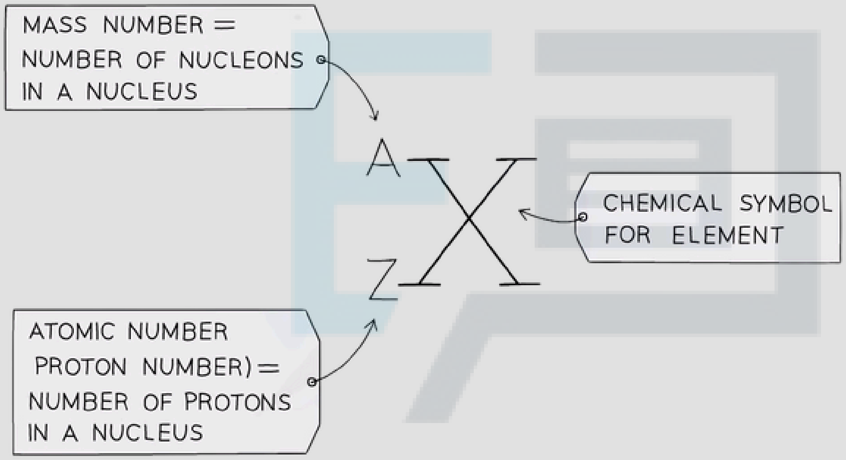
- The **atomic number** (or **proton number**) is the numberofprotons in the nucleus of an atom and has **symbol** *Z*
    - The atomic number is equal to the number of electrons present in a **neutral** atom of an element Eg. the atomic number of lithium is 3 which indicates
    - that the neutral lithium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

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

Number of neutrons = mass number - atomic number

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

☐ Exam Tip



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

1.1.2 Isotopes

Atomic Structure Calculations

- An atom is **neutral** and has nooverallcharge
- Ions on the other hand are formed when atoms either **gain** or **lose** electrons, causing them to become **charged** The number of **subatomic particles** in atoms
- and ions can be determined given their atomic (proton) number, mass (nucleon) number and charge

Protons

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

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

Mass number = number of protons + number of neutrons Number of protons = mass number - number of neutrons

☐ Worked Example

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

1. 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 indicating that the number of protons in the magnesium element is 12

- Therefore the number of protons in a **Mg2+ ion** is also 12

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

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

Number of protons = mass number - number of neutrons Number of protons = 63 - 34 Number of protons = 29

- **Element X** is therefore copper

Electrons

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

☐ Worked Example

Determine thenumber 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)

☐ **Worked Example**

Determine thenumber of neutrons of the following ions and atoms:

1. Mg2+ ion
2. Carbon atom
3. An unknown atom of element X with mass number 63 and 29 protons

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

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

(Z) Number of neutrons = 24 - 12 Number of neutrons = 12

- The **Mg2+ ion** has 12 neutrons in its nucleus

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

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

(Z) Number of neutrons = 12 - 6 Number of neutrons = 6

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

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

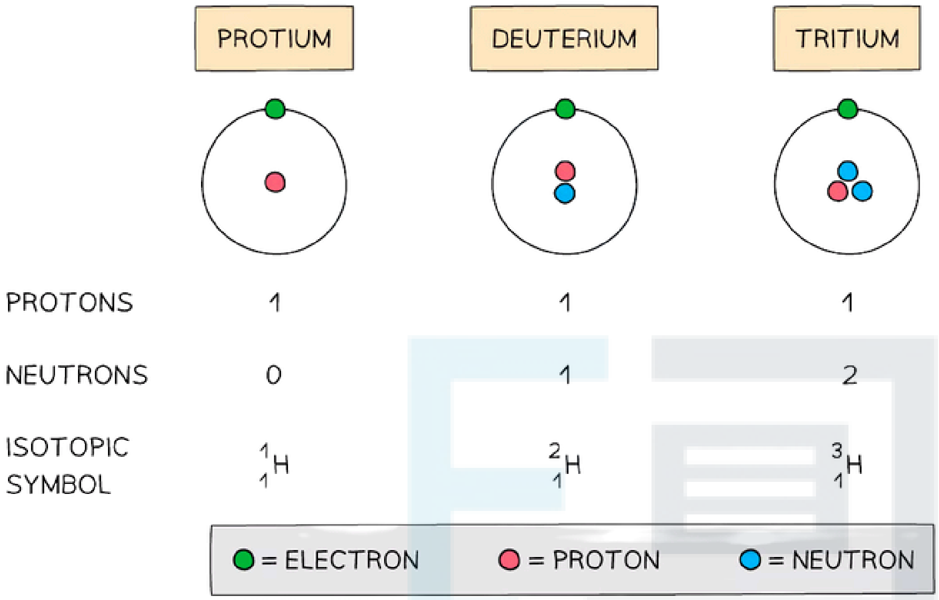
Number of neutrons = mass number (A) - number of protons

(Z) Number of neutrons = 63 - 29 Number of neutrons = 34

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

Defining & Calculating Isotopes

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



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 x 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 112 of a carbon- 12 atom

Relative isotopic mass

- Relative isotopic mass is defined as the mass of an isotope relative to 112 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

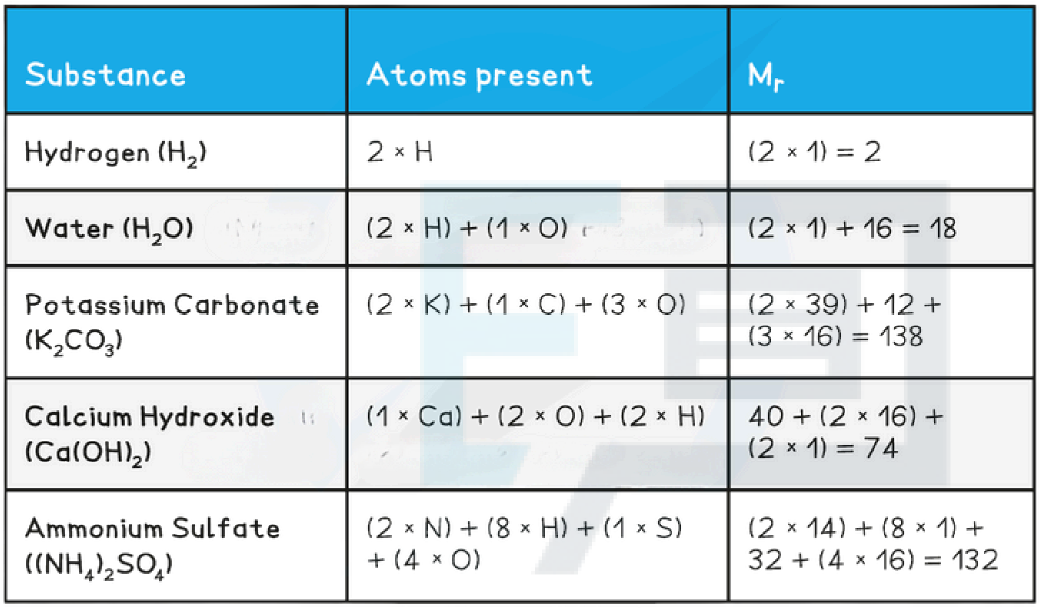
Relative atomic mass

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

Molecular & Formula Mass

- We have seen previously that the symbol for the relative atomic mass is *Ar*
- 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 *Mr* 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 × H	(2 × 1) = 2
Water (H_2O)	(2 × H) + (1 × O)	(2 × 1) + 16 = 18
Potassium Carbonate (K_2CO_3)	(2 × K) + (1 × C) + (3 × O)	(2 × 39) + 12 + (3 × 16) = 138
Calcium Hydroxide ($Ca(OH)_2$)	(1 × Ca) + (2 × O) + (2 × H)	40 + (2 × 16) + (2 × 1) = 74
Ammonium Sulfate ($(NH_4)_2SO_4$)	(2 × N) + (8 × H) + (1 × S) + (4 × O)	(2 × 14) + (8 × 1) + 32 + (4 × 16) = 132

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 x 39.1) + 12.0 + (3 x 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

Interpreting Mass Spectra

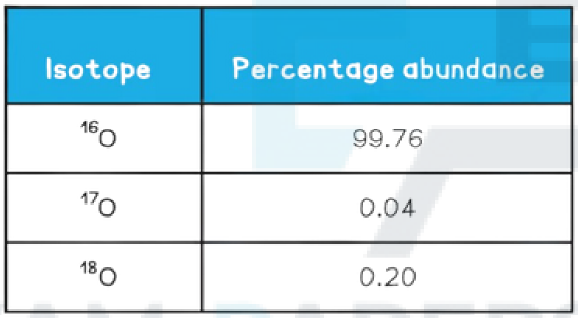
- Isotopes are different atoms of the sameelement thatcontain the same number of protons and electrons but a different number of neutrons
  These are atoms of the same elements but with different mass numbers
- Therefore, the mass of an element is given as relative atomic mass (Ar) by using the average mass of the isotopes
  - The relative atomic mass of an element can be calculated by using the relative abundance values

$$Ar = \frac{(relativeabundance_{isotope\ 1} \times mass_{isotope\ 1}) + (relativeabundance_{isotope\ 2} \times mass_{isotope\ 2})\ etc}{100}$$

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

☐ **Worked Example**

Calculating relative atomic mass of oxygen A sample of oxygen contains the following isotopes:



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

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

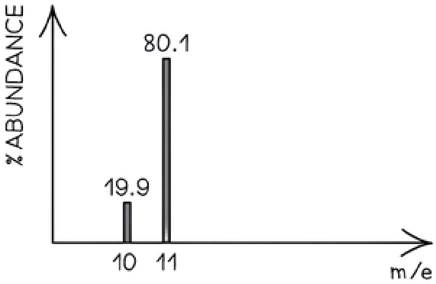
Answer

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

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

Youcan beexpected 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

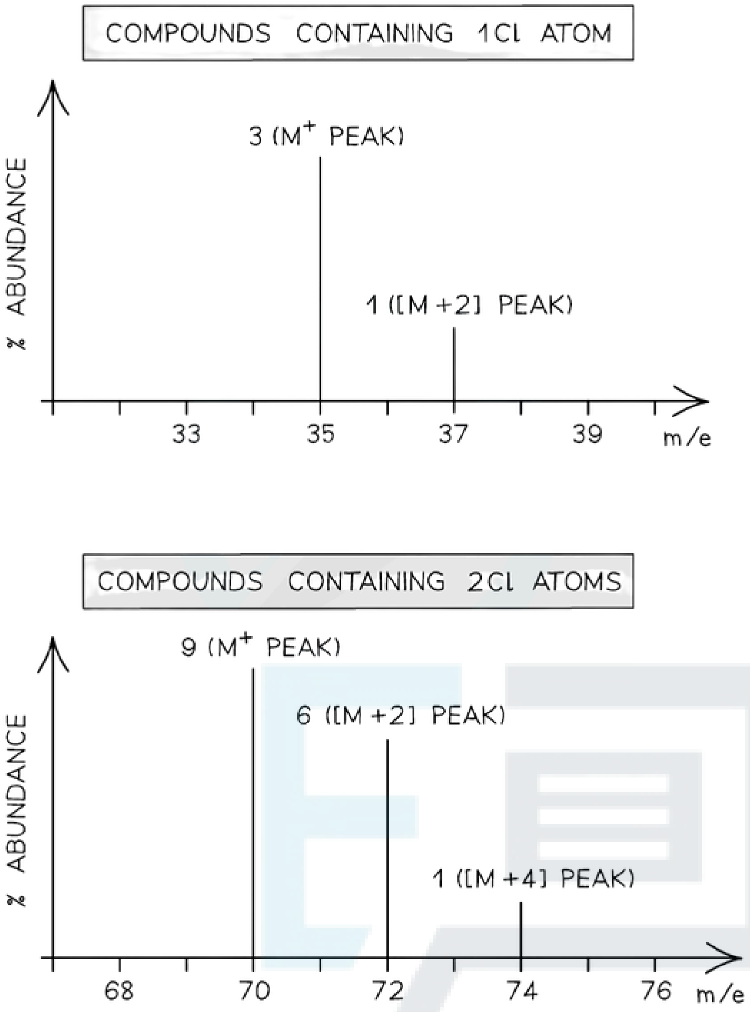
Predicting Mass Spectra

- You can also predict how a mass spectrum might appear for a given compound, e.g. ethanol, CH_3CH_2OH
  - 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, CH_2OH^+, 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}Cl = **M+** peak
  - ^{37}Cl = **[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}Cl + ^{35}Cl = **M+** peak
  - ^{35}Cl + ^{37}Cl = **[M+2]** peak
    - There is an alternative of ^{37}Cl + ^{35}Cl doubling the **[M+2]** peak
  - ^{37}Cl + ^{37}Cl = **[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}Cl + ^{35}Cl = $\frac{3}{4} \times \frac{3}{4} = \frac{9}{16}$
    - ^{35}Cl + ^{37}Cl = $\frac{3}{4} \times \frac{1}{4} = \frac{3}{16}$ but this doubles for the ^{37}Cl + ^{35}Cl option, therefore, $\frac{6}{16}$
    - ^{37}Cl + ^{37}Cl = $\frac{1}{4} \times \frac{1}{4} = \frac{1}{16}$
- The presence of bromine or chlorine atoms in a compound gives rise to a **[M+2]** and possibly **[M+4]** peak

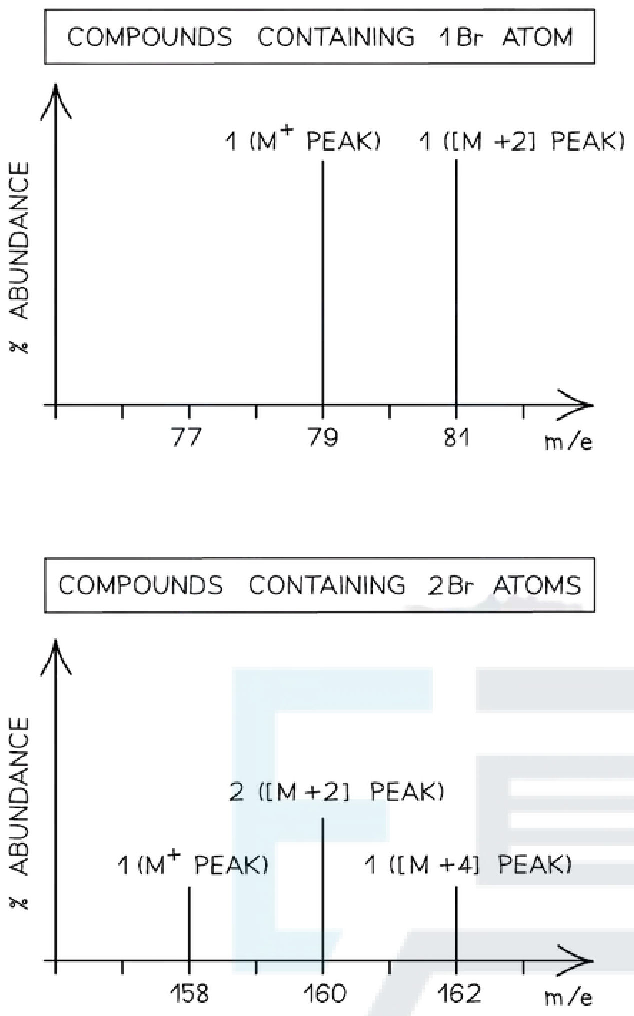


Mass spectrum of compounds containing one chlorine atom (1) and two chlorine atoms (2)

Bromine

- Bromine too exists as two isotopes, 79Br and 81Br A compound containing
- **one** bromine atom will have two molecular ion peaks
    - ^{79}Br = **M+** peak
    - ^{81} Br = **[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}Br + 79Br= **M+** peak
    - ^{79}Br+ 81Br = **[M+2]** peak
    - $_{81}$ Br + 81Br= **[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 analysedin 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:**

$$\text{MOLECULE} \xrightarrow{\text{Electron bombardment}} \underbrace{\text{MOLECULE}^{+\bullet}}_{\text{Molecular ion}} + e^-$$

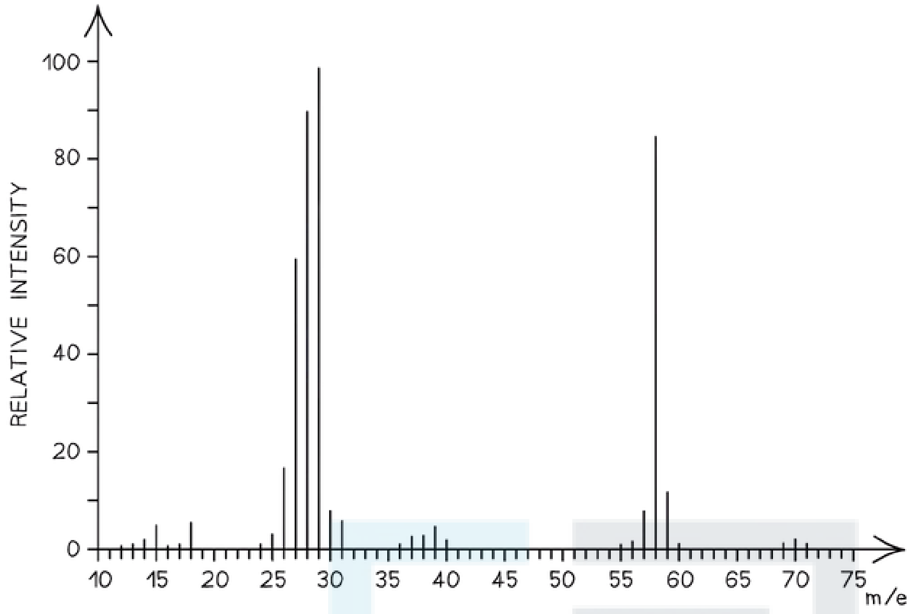
- The relative abundances of the detected ions form a **mass spectrum**: a kind of molecular fingerprint that can be identified by computer using a spectral database
- The peak with the highest ***m/z*** value is the molecular ion (M+) peak which gives information about the **molecular mass** of the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

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 $CH_3CH_2CHO^+$ ion which has a molecular mass of 58
- Butanal arises from the $CH_3CH_2CH_2CHO^+$ 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

1.10.2 Le Chatelier's Principle

Le Chatelier's Principle

Position of the equilibrium

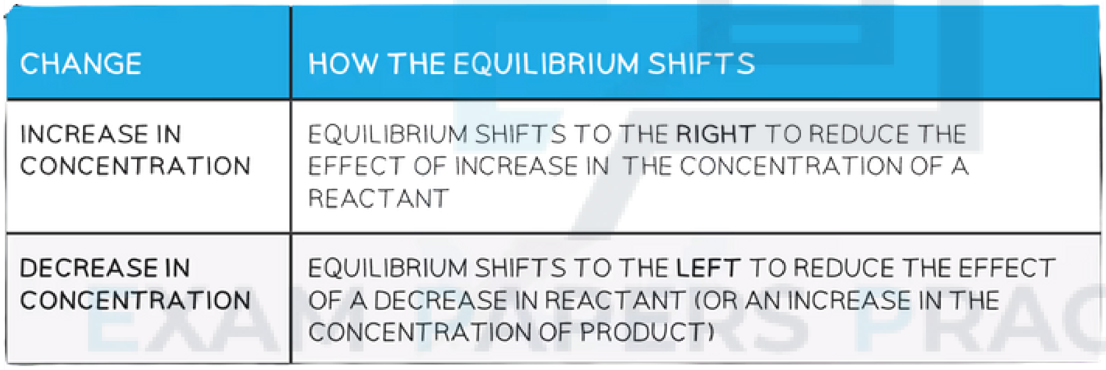
- The **position of the equilibrium** refers to the relative amounts of products and reactants in an equilibrium mixture
- When the position of equilibrium shifts to the **left**, it means the concentration of **reactants** increases
- When the position of equilibrium shifts to the **right**, it means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

CH3COOH (l) + C2H5OH (l) ⇌ CH3COOC2H5 (l) + H2O (l)

Explain what happens to the position of equilibrium when:

1. **More CH3COOC2H5 is added**
2. **Some C2H5OH is removed** Using the reaction below:

Ce4+ (aq) + Fe2+ (aq) ⇌ Ce3+ (aq) + Fe3+ (aq)

Explain what happens to the position of equilibrium when

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

Answer 1:

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

Answer 2:

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

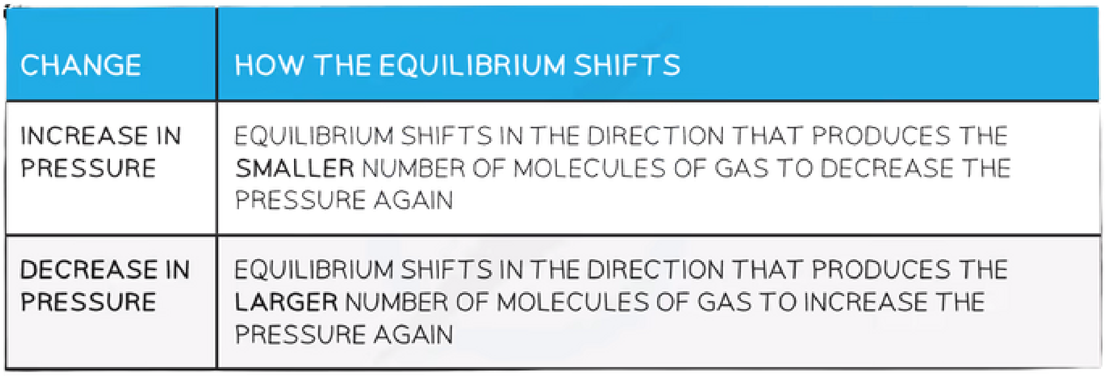
Answer 3:

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

Effects of pressure

- Changesinpressure 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. $\mathrm{N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)}$
2. $\mathrm{CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)}$ Predict the effect of decreasing the pressure on the following reaction:
3. $\mathrm{2NO_2\ (g) \rightleftharpoons 2NO\ (g) + O_2\ (g)}$

Answer 1:

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

Answer 2:

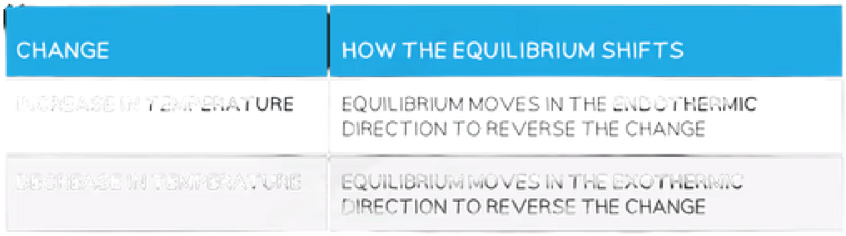
- The equilibrium shifts to the left as there are no gas molecules on the left but there is $\mathrm{CO_2}$ on the right This causes a decrease in pressure

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:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O\ (g) + CO\ (g)$ ΔH = +41.2 kJmol-1

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

Using the reaction below: $Ag_2CO_3\ (s) \rightleftharpoons Ag_2O\ (s) + CO_2\ (g)$

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

Explain your answer

Answer 1:

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

Answer 2:

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

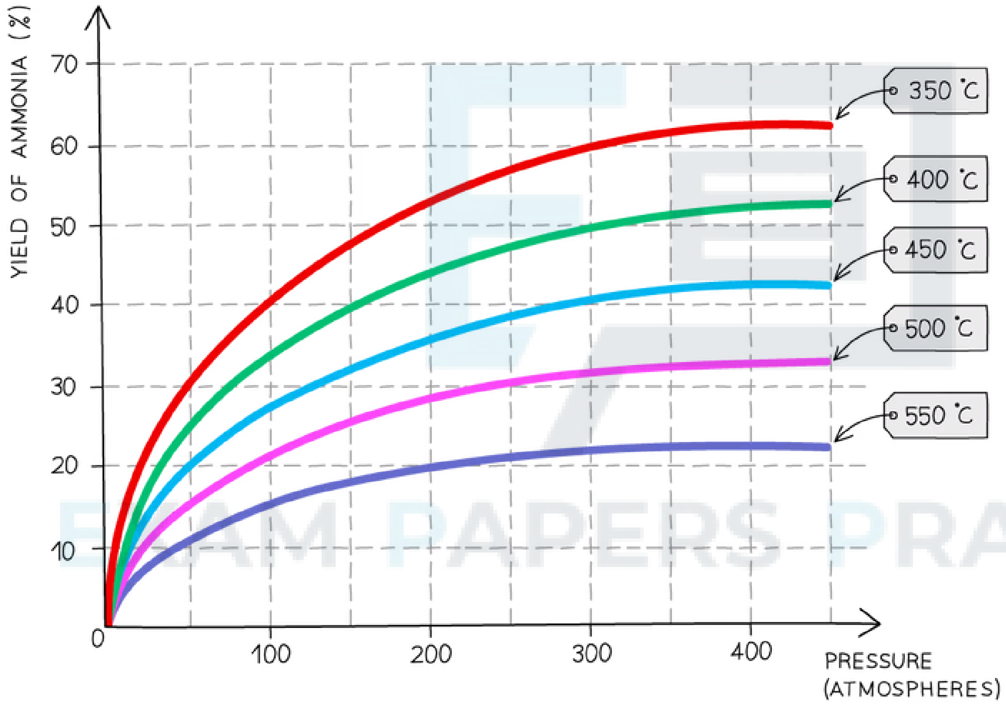
Industrial Compromises

- The Haber Process is, onceagain,agoodexampleoftheneed for a compromise of reaction conditions in industrial processes

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

- 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 oC 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

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 Kc Expressions

Deducing Kc Expressions

Equilibrium expression&constant

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

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

- *Kc* 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 *Kc* of a reaction is specific and only changes if the **temperature** of the reaction changes

Homogeneous systems and K_c

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

$$CH3COOH\ (l) + C2H5OH\ (l) \rightleftharpoons CH3COOC2H5\ (l) + H2O\ (l)$$

- For this reaction, all of the reactants and products are in the same, liquid state / phase and will, therefore, all feature in the *Kc* expression
  - $K_c = \frac{[CH3COOC_2H5]\ [H2O]}{[CH3COOH]\ [C2H5OH]}$

Heterogeneous systems and K_c

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

$$CaCO3\ (s) \rightleftharpoons CaO\ (s) + CO2\ (g)$$

- **Solids** are ignored in equilibrium expressions
  - This leads to a *Kc* expression of *Kc* = [CO2]

Exam Tip

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

Answer 1:

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

Answer 2:

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

Answer 3:

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

1.2 Ions & Electrons

1.2.1 Ionisation Energy

Factors Affecting Ionisation Energy

Ionisation energy

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

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

Successive ionisation energies of an element

- More than oneelectron can be removed form 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** (*IE*2) 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 can be represented as

$$X^{+}(g) \rightarrow X^{2+}(g) + e^{-}$$

OR (for calcium)

$$Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-} \qquad IE_2 = 1145\ kJ\ mol^{-1}$$

- **The third ionisation energy** (*IE*3) *of* an element can be represented as

$$X^{2+}(g) \rightarrow X^{3+}(g) + e^{-}$$

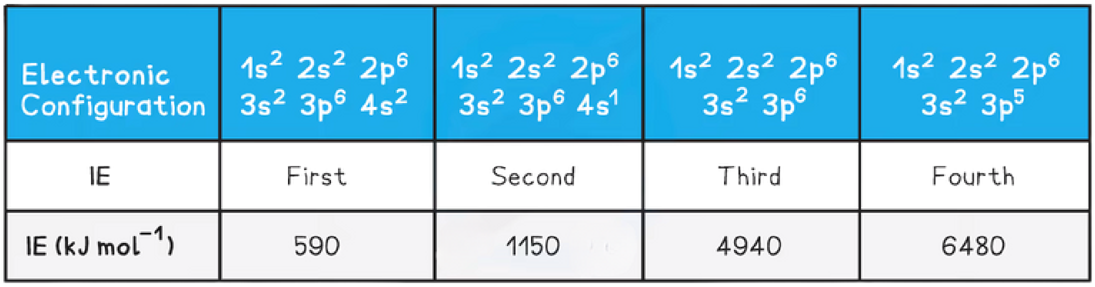
OR (for calcium)

$$Ca^{2+}(g) \rightarrow Ca^{3+}(g) + e^{-} \qquad IE_3 = 4912\ kJ\ mol^{-1}$$

- The **successive** ionisation energies of an element **increase**
- This is because once you have removed the outer electron from an atom, you have formed a **positive ion**
- Removing an electron from a positive ion is **more difficult** than from a neutral atom
- As more electrons are removed, the **attractive forces increase** due to decreasing shielding and an increase in the proton to electron ratio

- The increase in ionisation energy, however, is not constant and is dependent on the atom's electronic configuration
- Taking calcium as an example:

Ionisation Energies of Calcium Table



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

First Ionisation Energy – Period

Trends in Ionisation Energies

- Ionisation energiesshow **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

- Theionisation energy acrossaperiod 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

- Thereis 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 2px orbital of oxygen
  - **Nitrogen** has a first ionisation energy of **1400 kJ mol-1** as its electron configuration is $1s2\ 2s2\ 2p1_x\ 2p1_y\ 2p1_z$
  - **Oxygen** has a first ionisation energy of **1310 kJ mol-1** as its electron configuration is $1s2\ 2s2$ **$2p2_x$** $2p1_y\ 2p1_z$
  - In oxygen, there are 2 electrons in the 2px 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

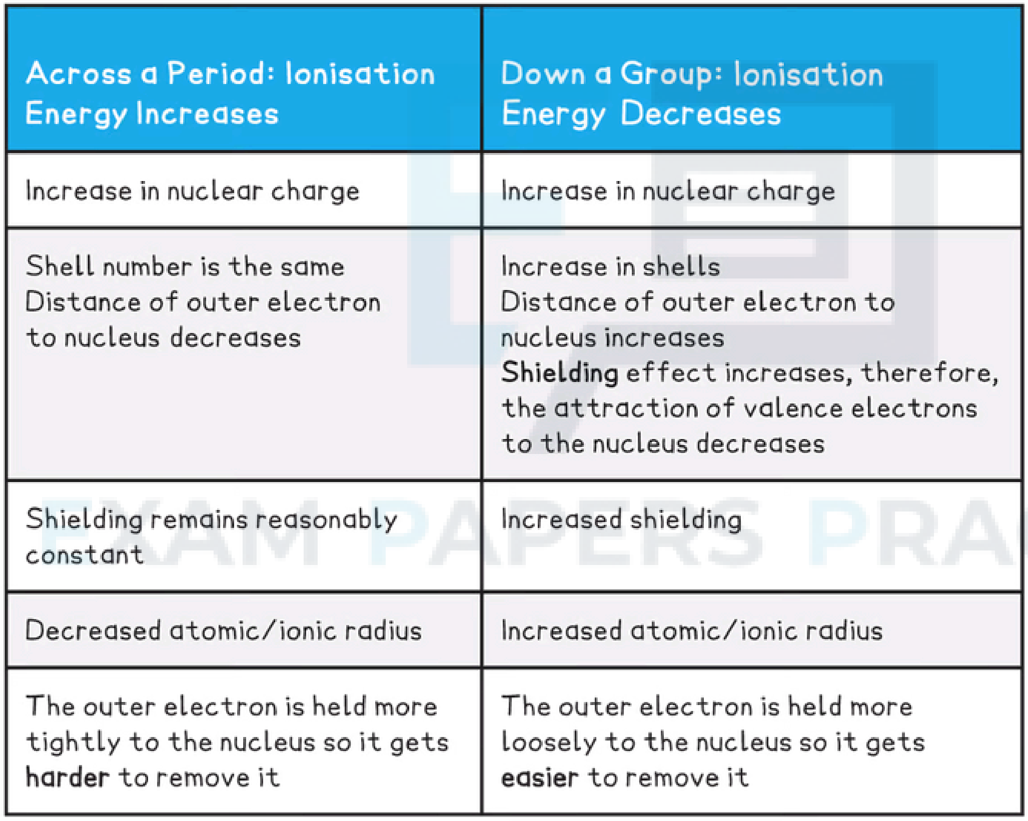
- There is a large **decrease** in ionisation energy between the **last** element in one period, and the **first** element in the next period
- This is because:
    - There is increased **distance** between the nucleus and the outer electrons as you have added a new shell
    - There is increased **shielding**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

First Ionisation Energy – Group

Ionisation energy downagroup

- Theionisationenergydown 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

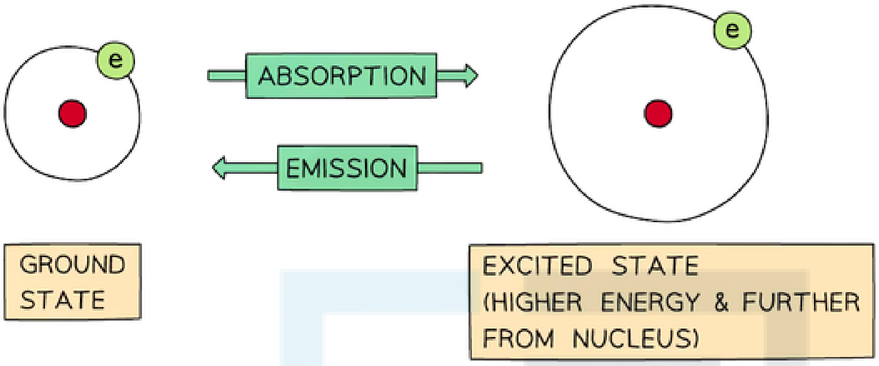


Across a Period: Ionisation Energy Increases	Down a Group: Ionisation Energy Decreases
Increase in nuclear charge	Increase in nuclear charge
Shell number is the same Distance of outer electron to nucleus decreases	Increase in shells Distance of outer electron to nucleus increases **Shielding** effect 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

1.2.2 Quantum Shells

Developing Electronic Configuration

- Electrons move rapidlyaroundthe nucleus inenergy 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

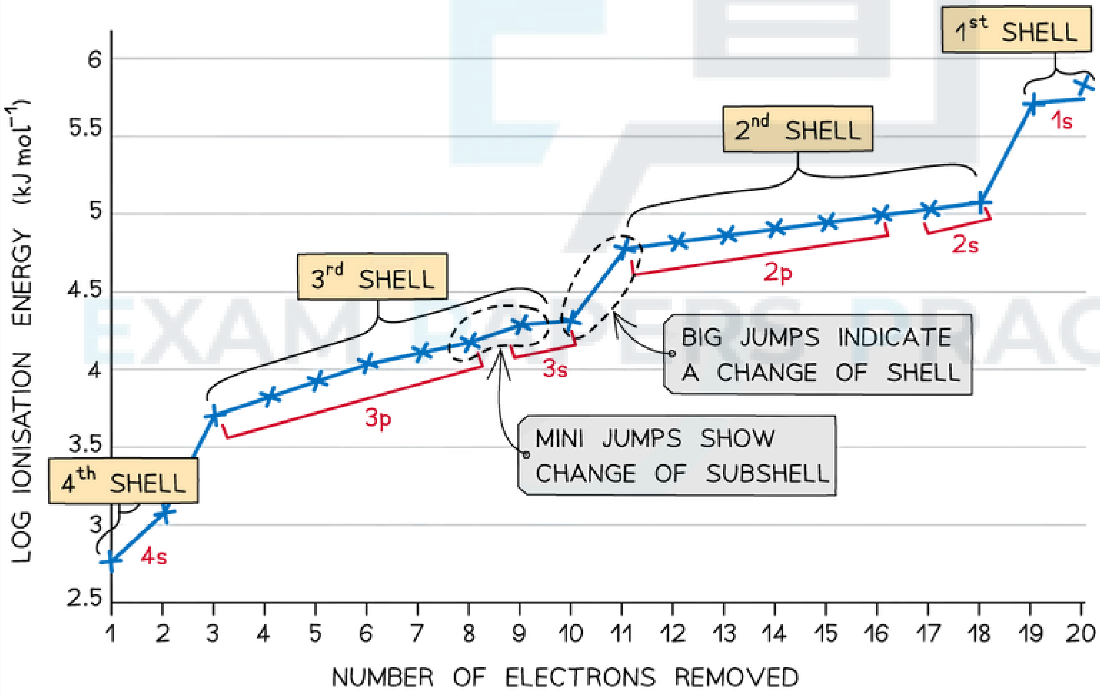
The line emission (visible) spectrum of hydrogen

- 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

- 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 *IE*1 as it is easily removed from the atom due to the spin-pair repulsion of the electrons in the 4s orbital
- The **second** electron is more difficult to remove than the first electron as there is no **spin-pair repulsion**
- The **third** electron is much more difficult to remove than the second one corresponding to the fact that the third electron is in a **principal quantum** shell which is closer to the nucleus (3p)
- Removal of the **fourth** electron is more difficult as the orbital is no longer full, and there is less **spin-pair repulsion**
- The graph shows there is a large increase in successive ionisation energy as the electrons are being removed from an increasingly positive ion
- The big jumps on the graph show the change of **shell** and the small jumps are the change of **subshell**



Successive ionisation energies for the element calcium

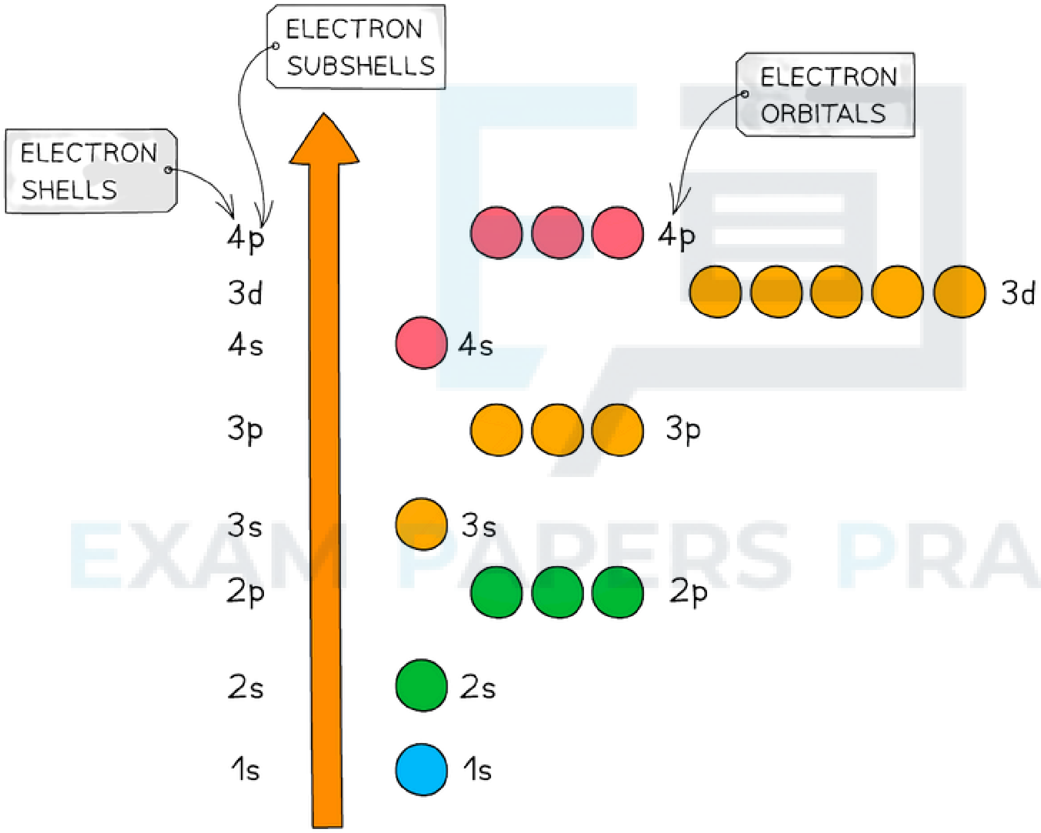
Filling Quantum Shells

Shells

- Thearrangement 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

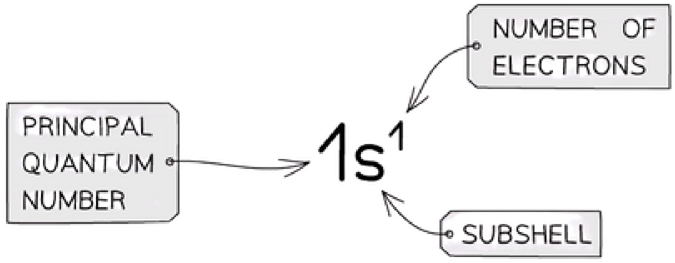
Electronic Configurations of Atoms & Ions

- 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. px, py and pz are all equal in energy



Relative energies of the shells and subshells

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



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

- Writing out the **electron configuration** tells us how the electrons in an atom or ion are arranged in their shells, subshells and orbitals This can be done using
- the **full** electron configuration or the **shorthand** version
  - The **full** electron configuration describes the arrangement of all electrons from the 1s subshell up The **shorthand** electron configuration includes using the
  - symbol of the **nearest preceding noble gas** to account for however many electrons are in that noble gas

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

Full Electron Configurations

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

- Using potassium as an example again:
  - The nearest preceding noble gas to potassium is **argon**
  - This accounts for 18 electrons of the 19 electrons that potassium has
  - The shorthand electron configuration of potassium is **[Ar] 4s1**

Worked Example

Writedownthefulland shorthand electron configuration of the following elements
:

1. Calcium
2. Gallium
3. Ca2+

Answer

Answer 1:

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

  1s2 2s2 2p6 3s2 3p6 4s2

- The 4s orbital is lower in energy than the 3d subshell and is therefore filled first
- The **shorthand** version is [Ar] 4s2 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:

  1s2 2s2 2p6 3s2 3p6 3d10 4s2 4p1

  [Ar] 3d10 4s2 4p1

- 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 Ca2+ ion is identical to that of argon **Ca2+** is 1s2 2s2 2p6 3s2 3p6 **Ar** is also

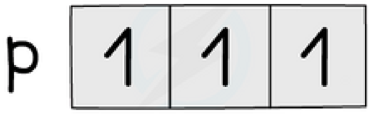
  1s2 2s2 2p6 3s2 3p6

Exceptions

- Chromium and copper have the following electron configurations, which are different to what you may expect:
  - Cr is [Ar] 3d5 4s1 **not** [Ar] 3d4 4s2
  - Cu is [Ar] 3d10 4s1 **not** [Ar] 3d9 4s2
- This is because the [Ar] 3d5 4s1 and [Ar] 3d10 4s1 configurations are **energetically stable**

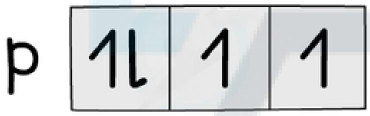
Presenting the Electron Configuration

- 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

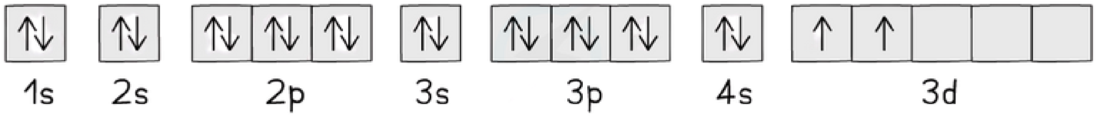
- Electrons are only paired when there are no more empty orbitals available within a subshell, in which case the spins are the **opposite** spins to minimize repulsion E.g. if there are four electrons in a p subshell, one p orbital contains 2 electrons with opposite spin and two orbitals contain one 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

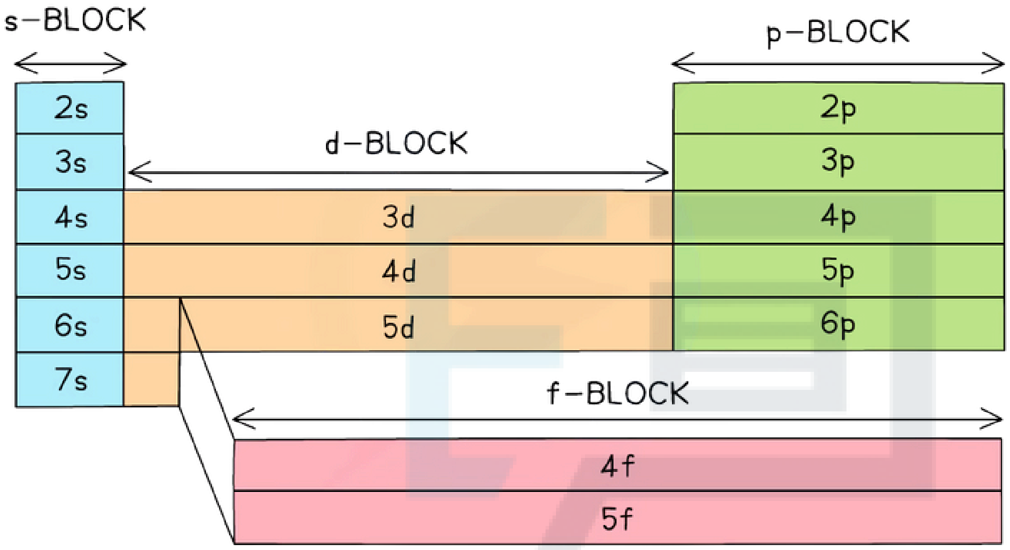
- The **electron configuration** can be represented using the **electrons in boxes** notation
- Each box represents an **atomic orbital**
- The boxes are arranged in order of **increasing** energy from bottom to top
- The electrons are represented by opposite arrows to show the **spin** of the electrons
  - 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



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

Classifying Elements

- The Periodic Table is split up into fourmainblocks 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

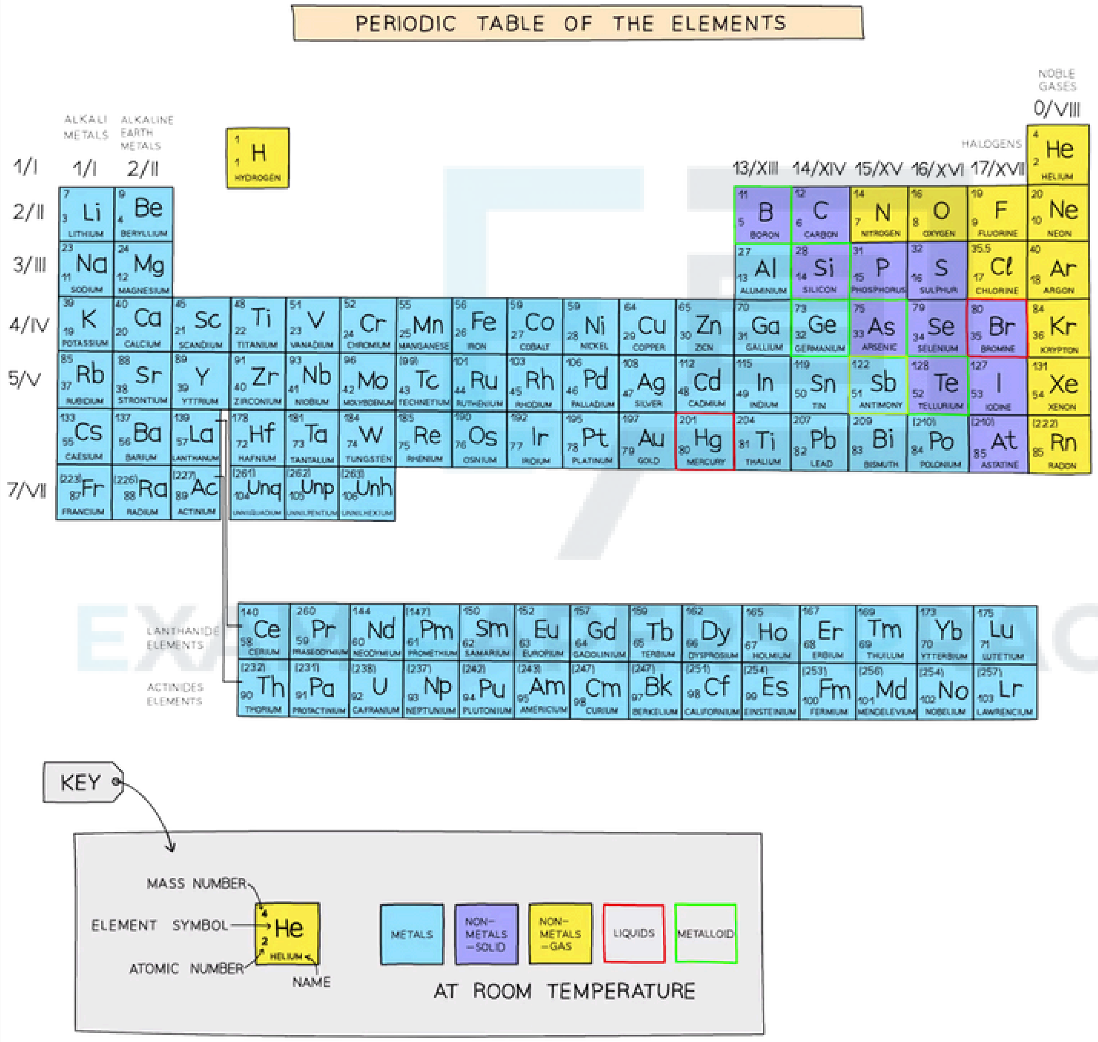
- The way an element reacts with other elements is determinedbyannumber of factors, but in particular the **electronic configuration** of its atoms The
- Periodic Table is arranged in **periods (horizontal)** and **groups (vertical)**
  - All the elements in the same period have the same number of shells (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

1.3 The Periodic Table

1.3.1 Periodicity

Melting & Boiling Point Trends

- Elements in the periodic table are arranged in orderof 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**

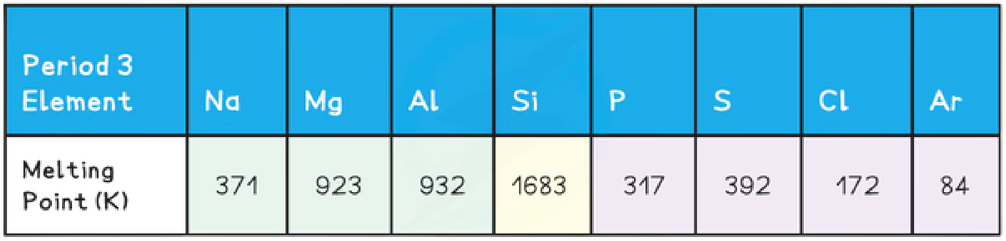


All elements are arranged in the order of increasing atomic number from left to right

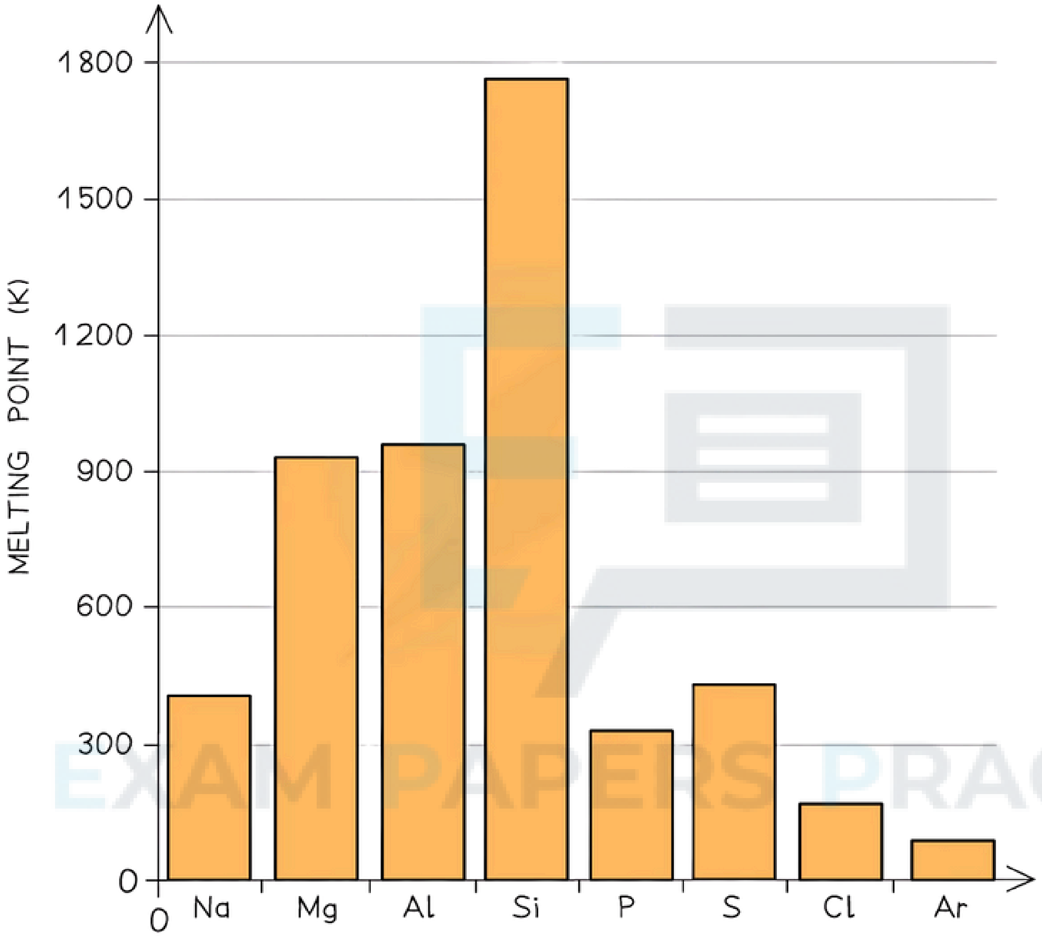
Melting point

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

Melting points of the elements across Period 3 table



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



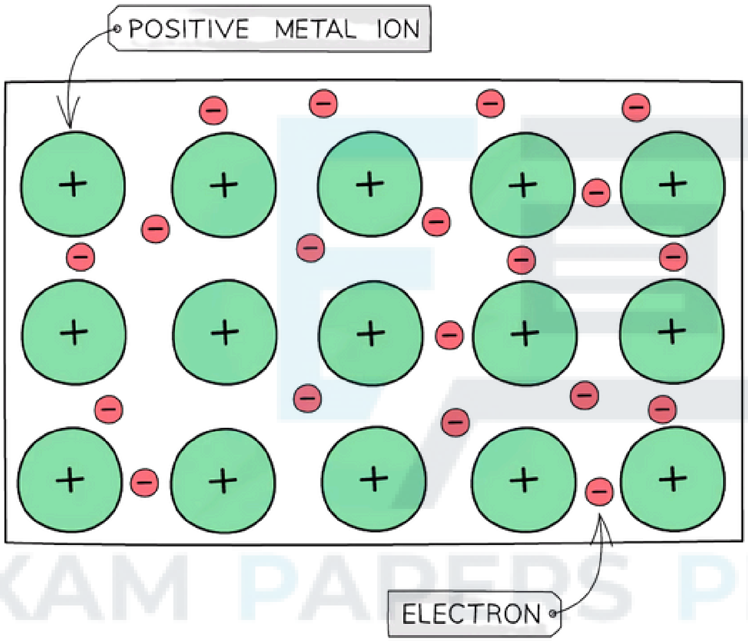
Ions of Period 3 elements with increasing positive charge (metals) and increasing of number of outer electrons across the period

- 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

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)

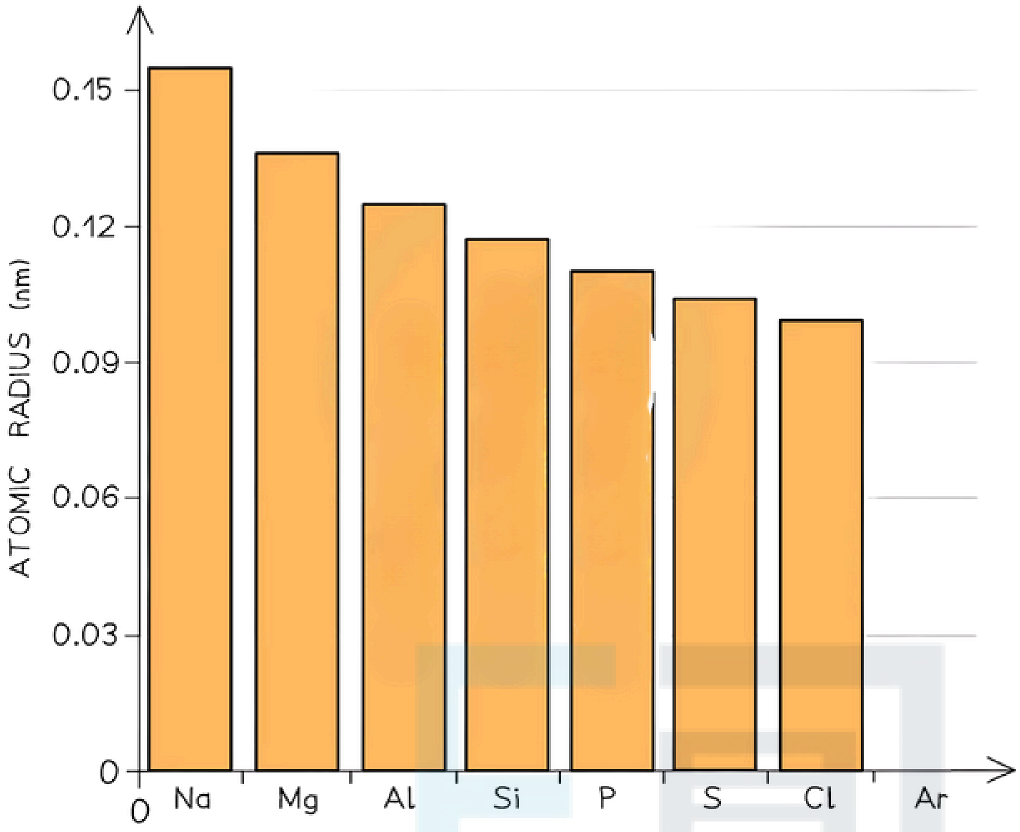
Atomic radius

- 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

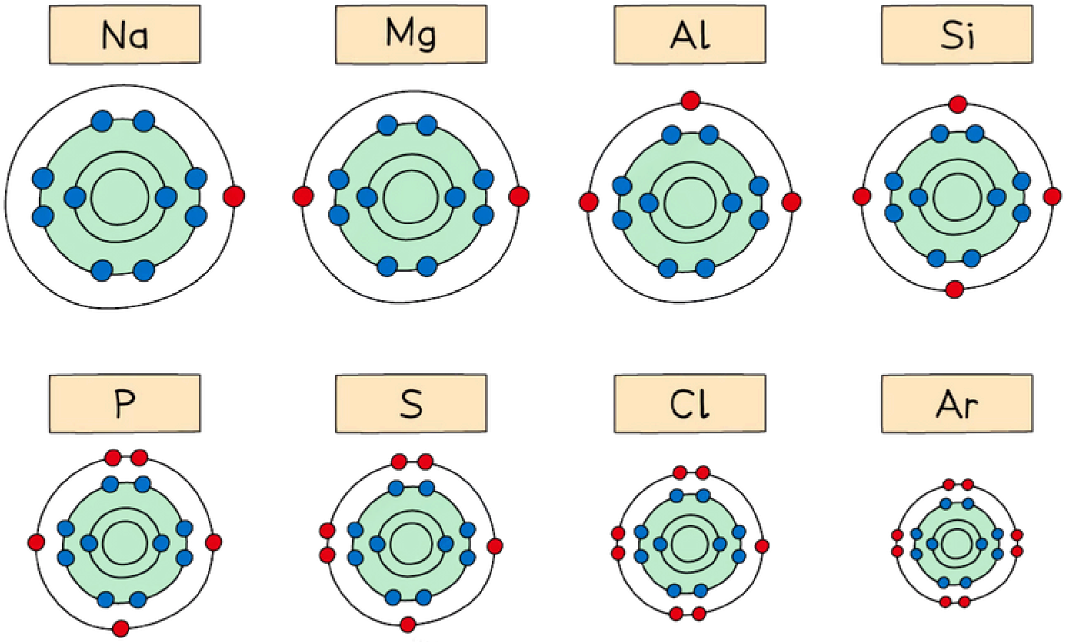
- You can see a clear trend across the period which also **repeated** in period 2

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



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 *IE*1 between **beryllium** and **boron** as the fifth electron in boron is in the 2p subshell, which is further away from the nucleus than the 2s subshell of beryllium
  - Beryllium has a first ionisation energy of 900 kJ mol-1 as its electron configuration is 1s2 2s2
  - Boron has a first ionisation energy of 800 kJ mol-1 as its electron configuration is 1s2 2s2 2p 1x
- There is a slight **decrease** in *IE*1 between **nitrogen** and **oxygen** due to **spin-pair repulsion** in the 3px orbital of oxygen
  - Nitrogen has a first ionisation energy of 1400 kJ mol-1 as its electron configuration is 1s2 2s2 $2p1_x$ $2p1_y$ $2p1_z$
  - Oxygen has a first ionisation energy of 1310 kJ mol-1 as its electron configuration is 1s2 2s2 $2p2_x$ $2p1_y$ $2p1_z$
- In oxygen, there are 2 electrons in the 2px 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

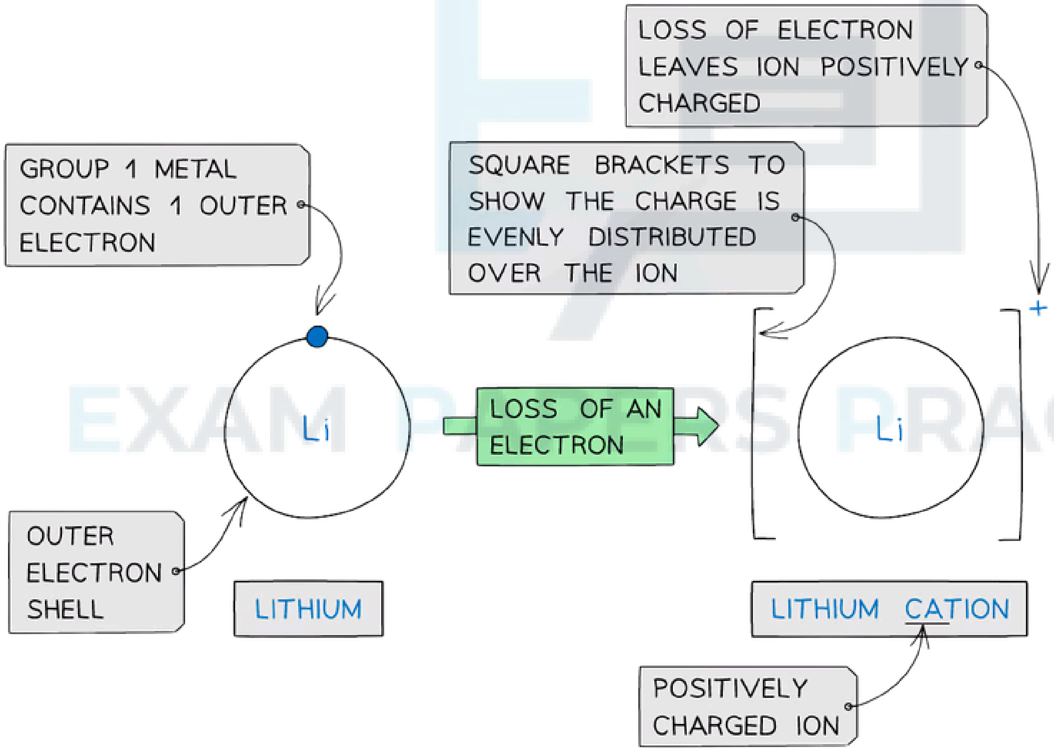
- There is again a slight decrease between **magnesium** and **aluminium** as the thirteenth electron in aluminium is in the 3p subshell, which is further away from the nucleus than the 3s subshell of magnesium
  - Magnesium has a first ionisation energy of 738 kJ mol-1 as its electron configuration 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 3p1x
- There is a slight decrease in *IE*1 between **phosphorus** and **sulfur** due to **spin-pair repulsion** in the 3px orbital of oxygen
  - Phosphorus has a first ionisation energy of 1012 kJ mol-1 as its electron configuration is 1s2 2s2 2p6 3s2 $3p1_x$ $3p1_y$ $3p1_z$
  - Sulfur has a first ionisation energy of 1000 kJ mol-1 as its electron configuration is 1s2 2s2 2p6 3s2 $3p2_x$ $3p1_y$ $3p1_z$
- In sulfur, there are 2 electrons in the 3px orbital, so the repulsion between those electrons makes it slightly easier for one of those electrons to be removed

1.4 Bonding

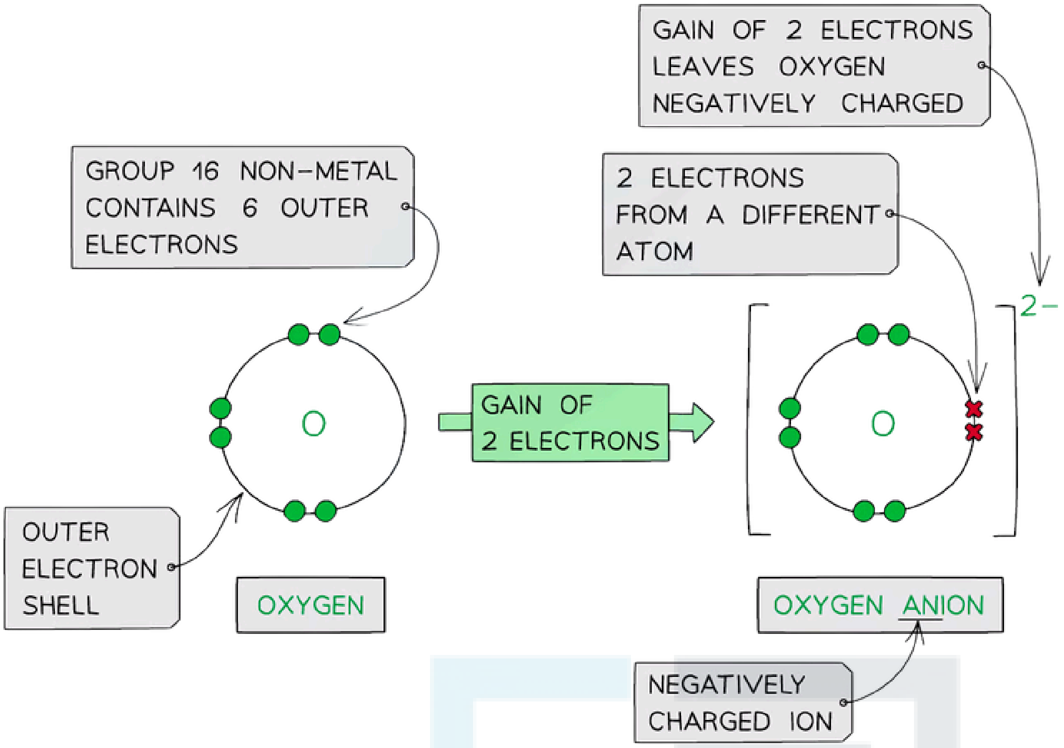
1.4.1 Ionic Bonding Overview

Ionic Bonds

- As a general rule, **metals** are onthe **left**oftheperiodic 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 shells.**
- Metals **lose** electrons from their valence shell, forming **positively charged cations.**
- Non-metal atoms **gain** electrons, forming **negatively charged anions.** Once the atoms become ions, their electronic configurations are the same as a noble gas
    - A potassium ion (K+) has the same electronic configuration as argon: [2,8,8]+
    - A chloride ion (Cl-) also has the same electronic configuration as argon: [2,8,8]-

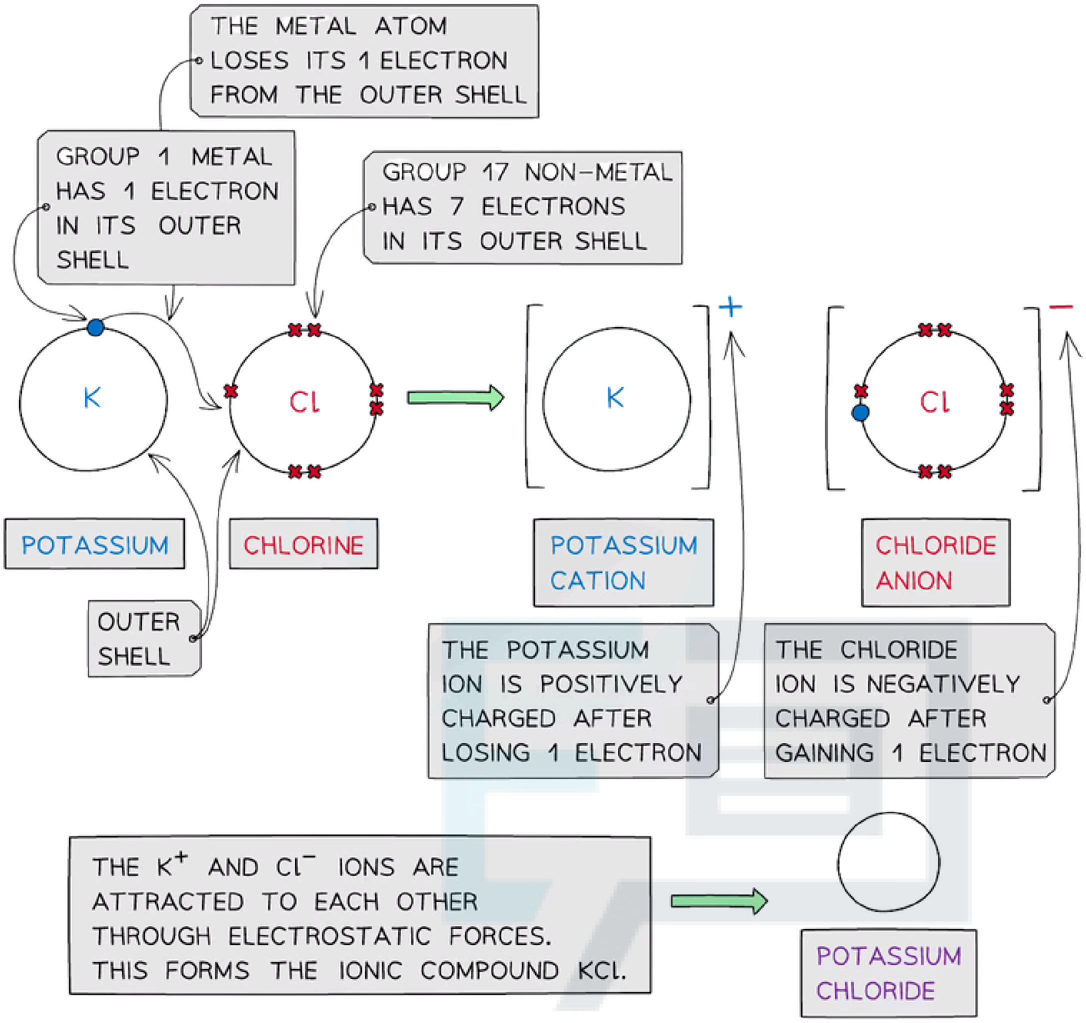


Forming cations by the removal of electrons from metals



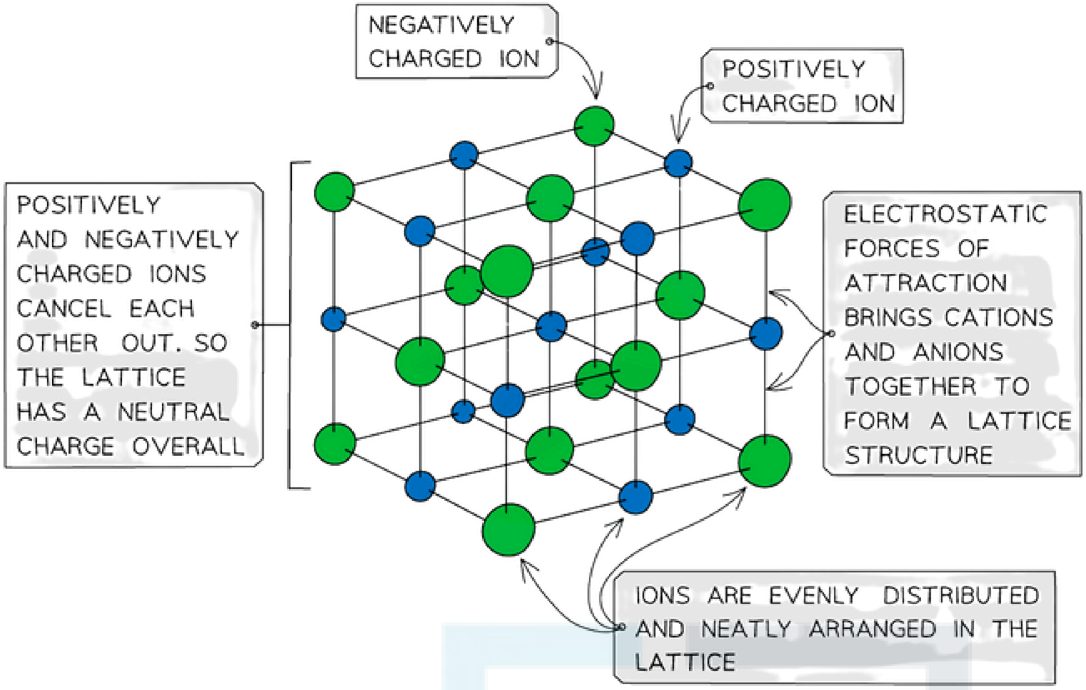
Forming anions by the addition of electrons to nonmetals

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



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

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



Ionic solids are arranged in lattice structures

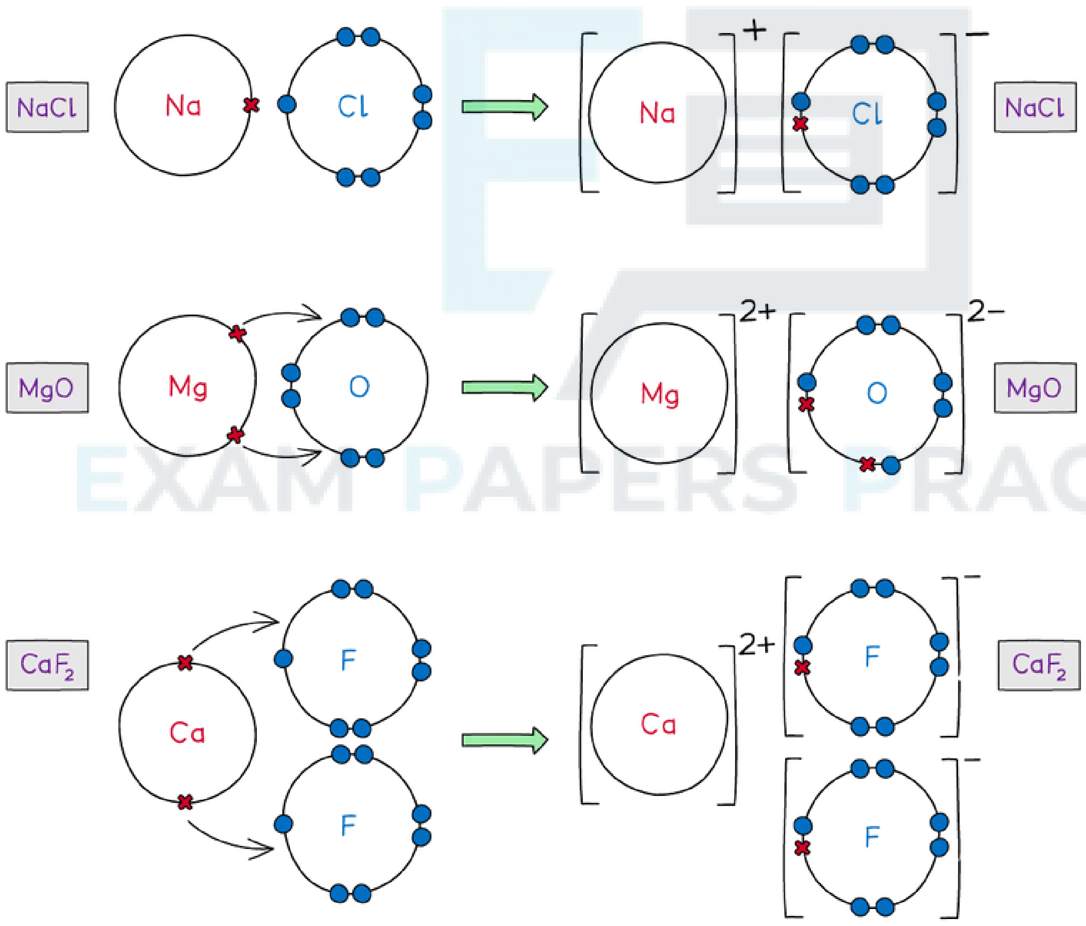
1.4.2 Representing Ionic Bonding

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

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



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

Calcium fluoride

- Calciumis 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

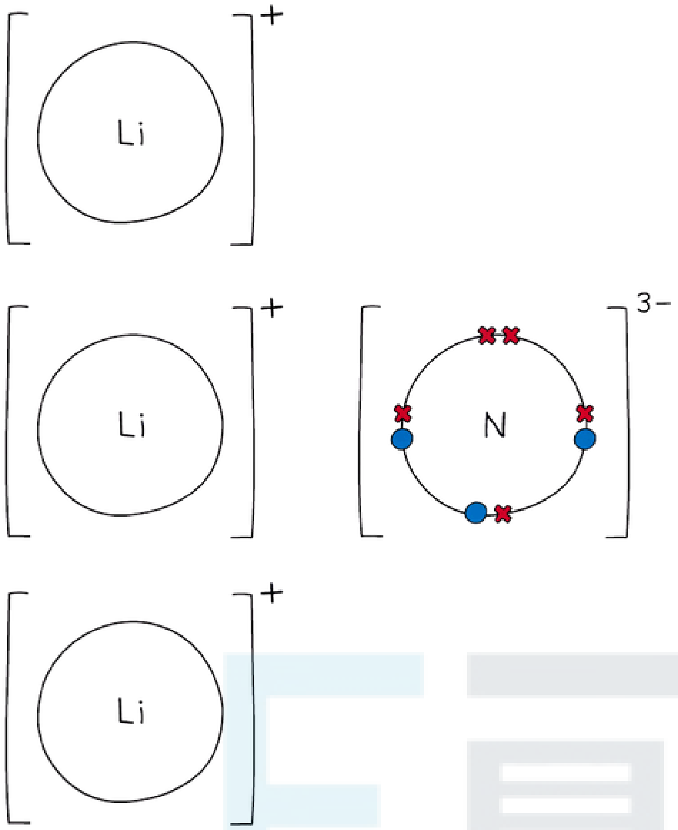
- Calcium fluoride is made when 1 calcium ion and 2 fluoride ions form ionic bonds, CaF_2
- The final ionic solid of CaF_2 is **neutral** in charge

Worked Example

Drawadotcrossdiagram 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



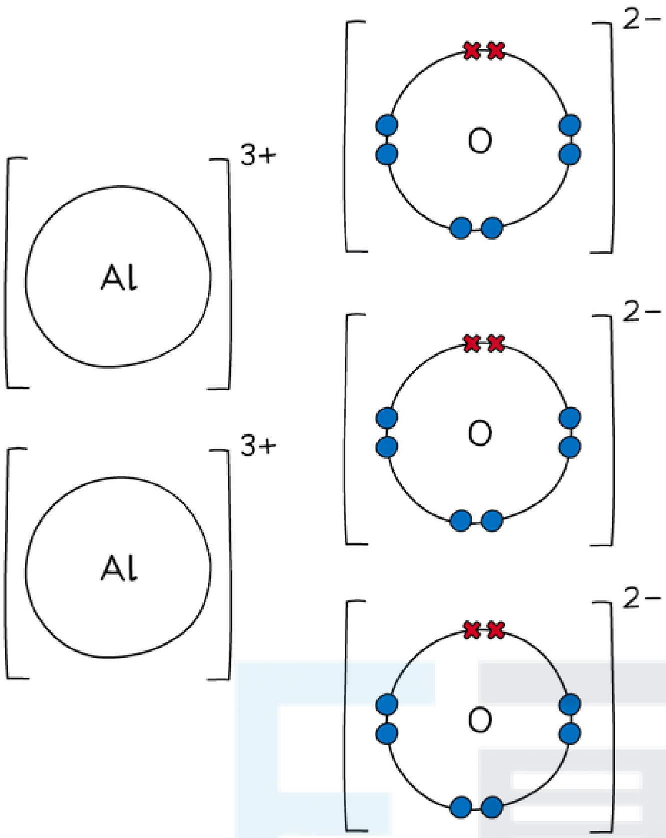
Dot and cross diagram to show the ionic bonding in lithium nitride

Worked Example

Draw a dot 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 (Al3+)
- Oxygen is a Group 6 **non-metal**
- It **gains** 2 electrons to form an oxide ion with a -2 charge (O2-)
- 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 Al2O3 is **neutral** in charge

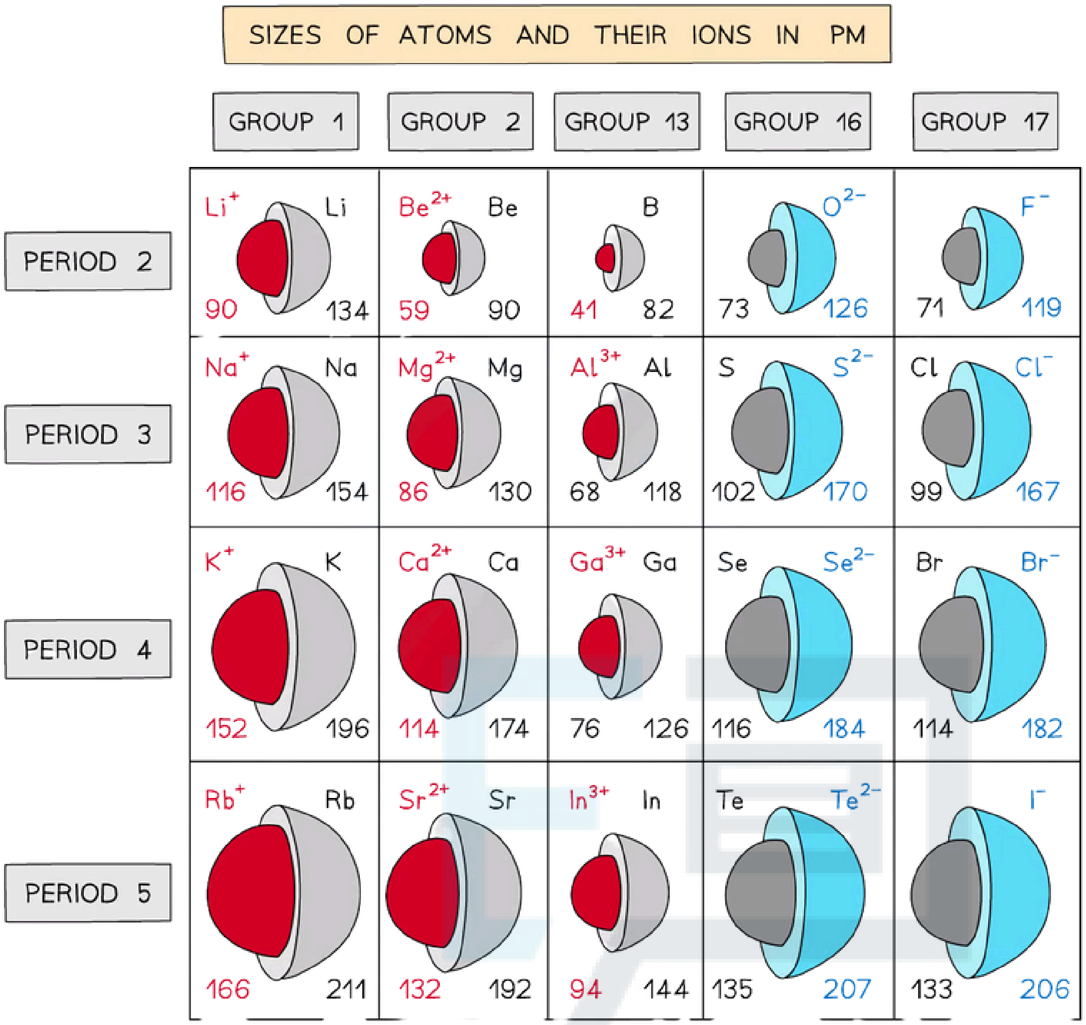


Dot and cross diagram to show the ionic bonding in aluminium oxide

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 charger, the smaller the ionic radius



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

Isoelectronic Ions

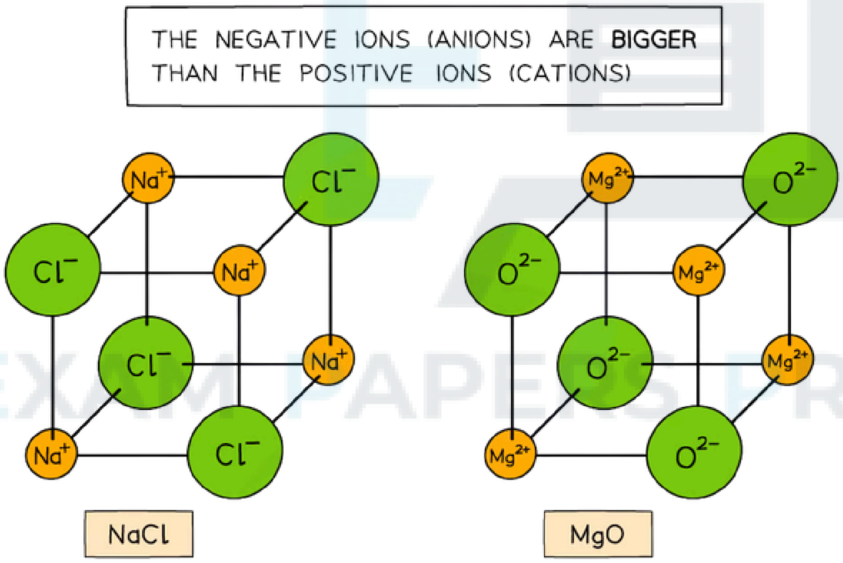
- Theseare ions that have the **same electronic configuration**
- For example the following ions all have the electronic configuration of 1s2 2s2 2p6
- However, they all have different numbers of protons, therefore will have a different ionic radius
    - N3- (7 protons)
    - O2- (8 protons) F-
    - (9 protons) Na+
    - (11 protons) Mg2+
    - (12 protons) Al3+
    - (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
    - N3- has an ionic radius of 0.171 nm and Al3+ has an ionic radius

Physical Properties of Ionic Compounds

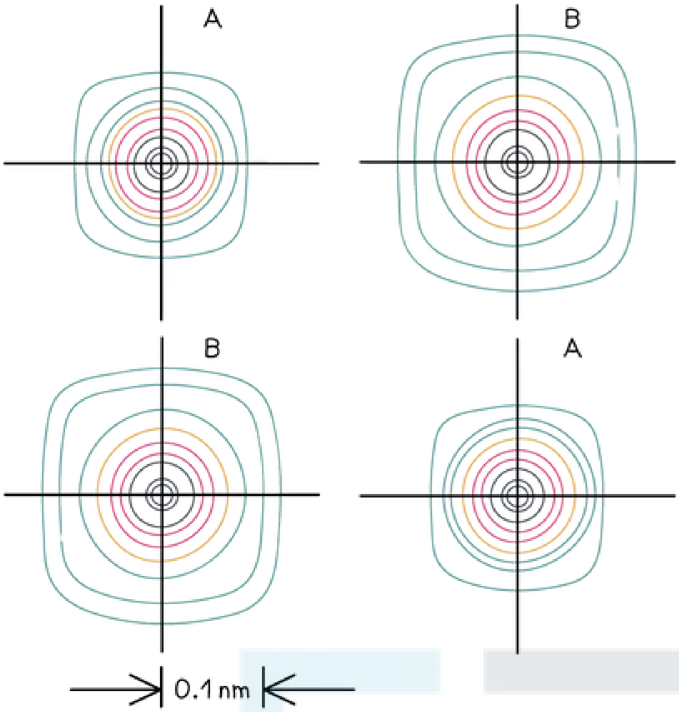
- Most ionic, metallic and covalent solids are **crystalline lattices**
- The ions, atoms or molecules are arranged in a **regular and repeating arrangement**

Giant ionic lattices

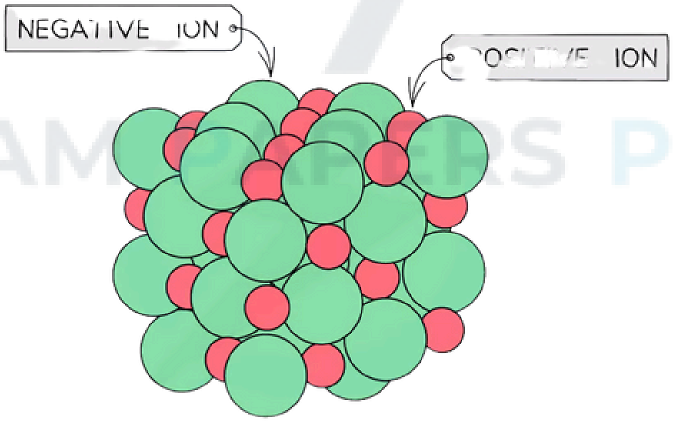
- An **ionic bond** is an electrostatic force of attraction between a positively charged metal (**cation**) ion and a negatively charged non-metal (**anion**) ion
  - The metal becomes positively charged as it transfers electrons to the non-metal which then becomes negatively charged
  - When an ionic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



Ionic lattices of the ionic compounds NaCl and MgO



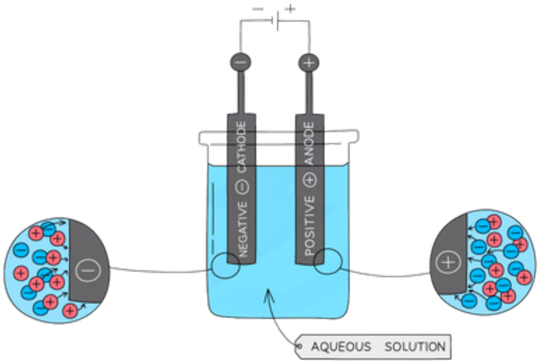
Electron density maps shown above show the likelihood of finding electrons in a region. This shows the electron density map for NaCl. The contours are lines of equal electron density. A = Na+ ions (smaller), B = Cl- ions (larger). Between the ions the electron density falls to zero.



General ionic lattice which shows the actual packing of the ions

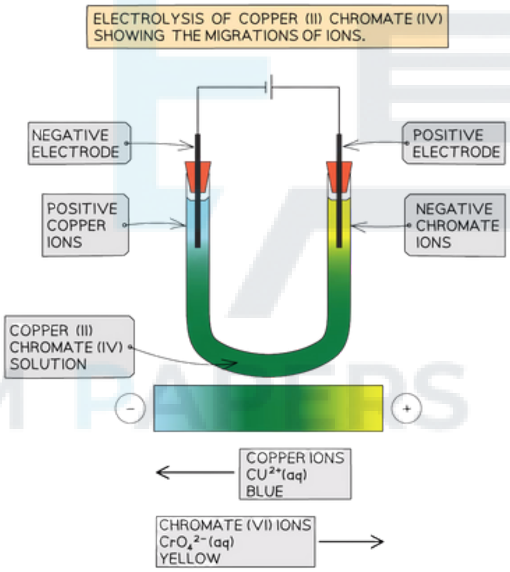
Evidence

- 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), CuCrO4
- The solution contains
    - Cu^{2+} ions (blue)
    - CrO_4^{2-} ions (yellow)

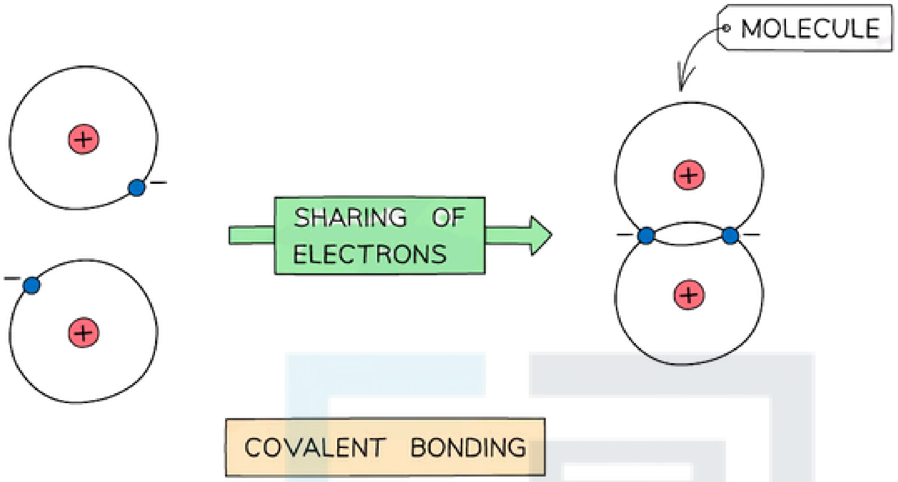


- Overall the solution is an olive green colour, but when the solution undergoes electrolysis a blue colour appears around the negative electrode, and a yellow colour appears around the positive electrode
- This is because the Cu2+ ions are attracted to the negative electrode and their blue colour is observed and the CrO_4^{2-} ions are attracted to the positive electrode and their yellow colour is observed

1.4.5 Covalent Bonding Overview

Covalent Bonding

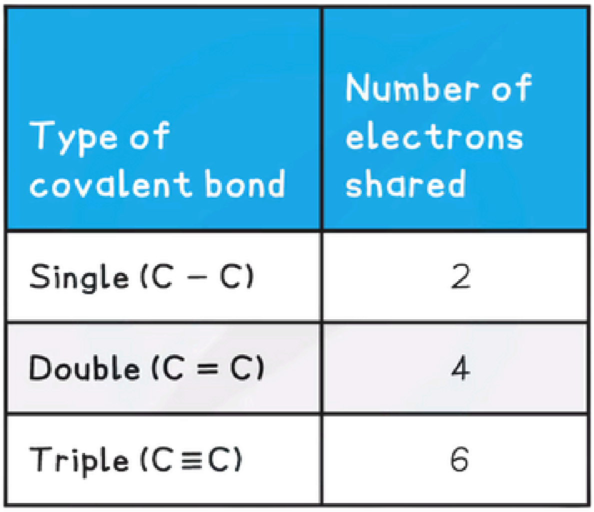
- **Covalent** bonding occurs between two**non-metals**
- A covalent bond involves the **electrostatic attraction** between nuclei of two atoms and the bonding electrons of their outer shells
- **No electrons** are **transferred** but only **shared** in this type of bonding



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



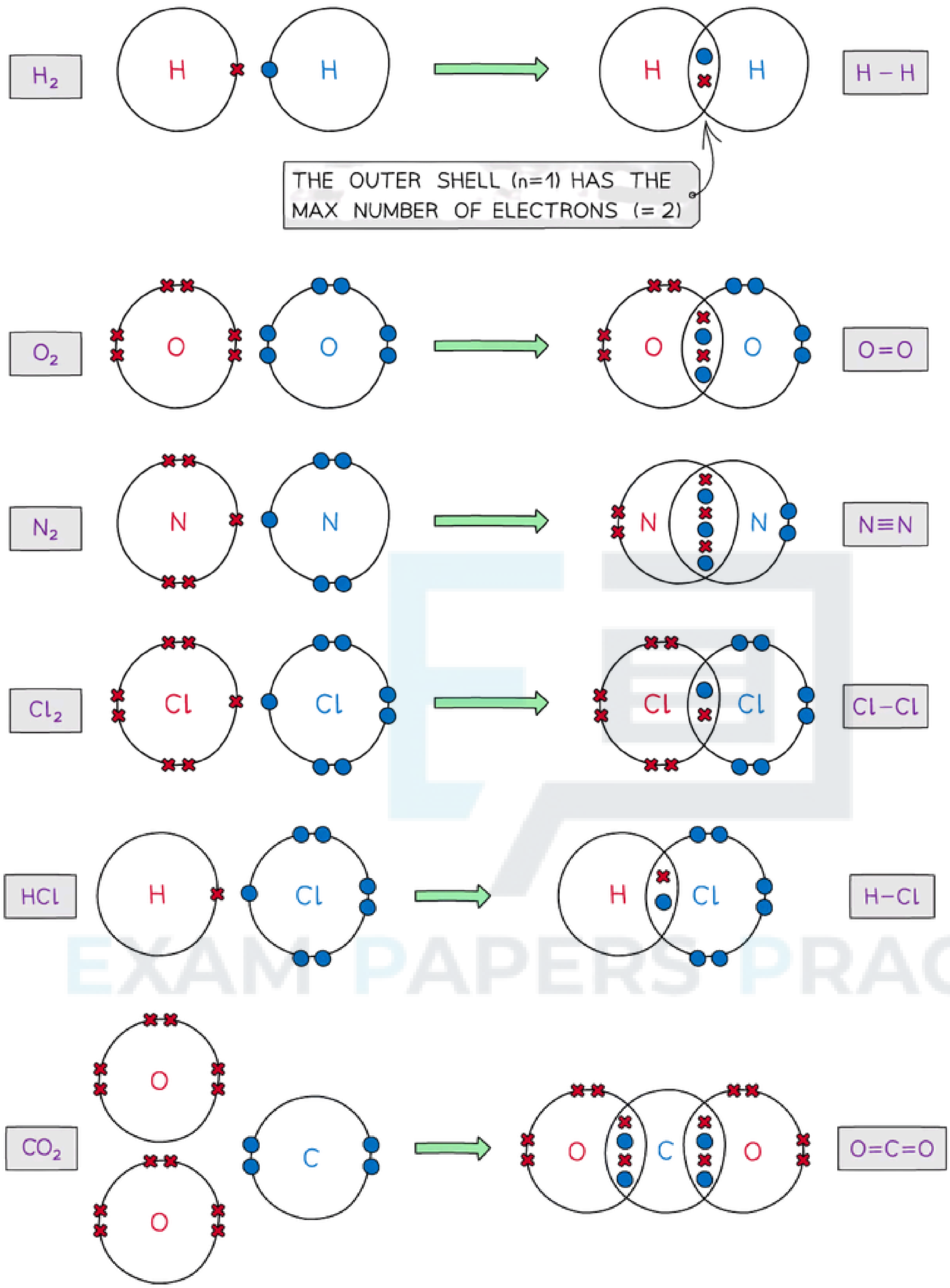
Type of covalent bond	Number of electrons shared
Single (C – C)	2
Double (C = C)	4
Triple (C ≡ C)	6

1.4.6 Covalent Dot-and-Cross Diagrams

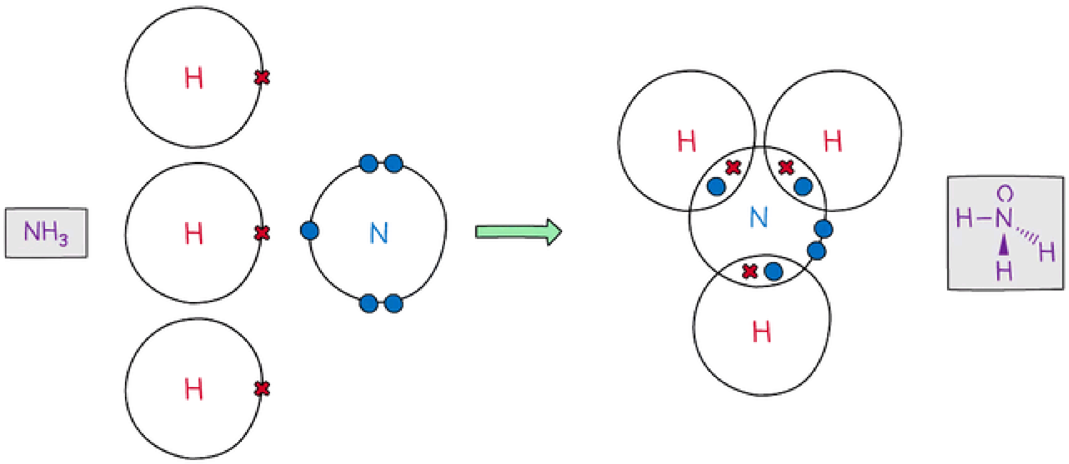
Covalent Dot-and-Cross Diagrams

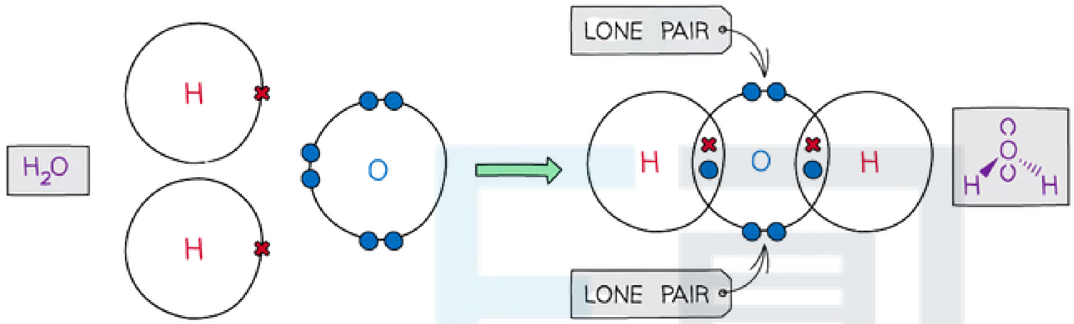
Covalent compounds

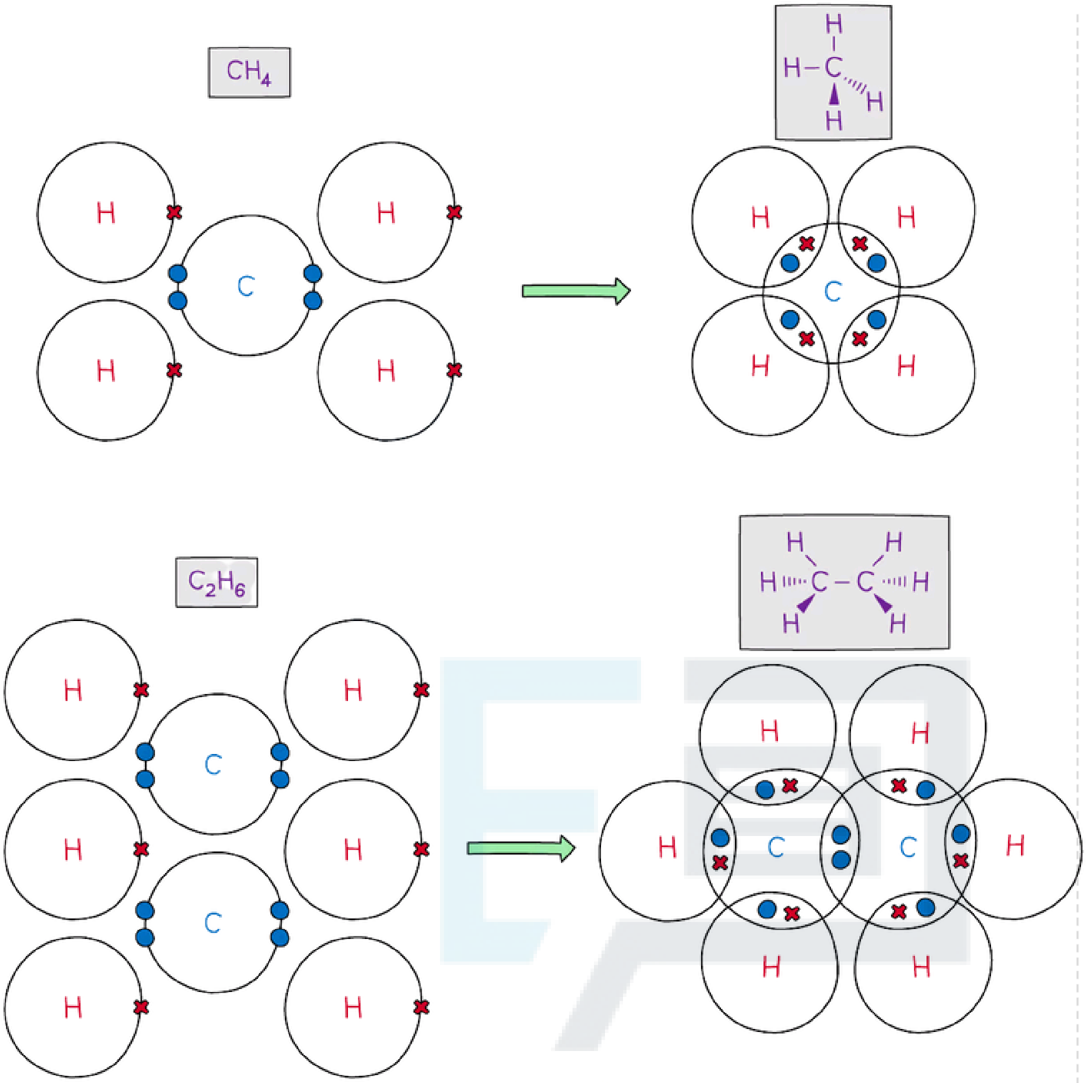
- Theatoms incovalentcompounds will **share** their outer valence electrons to achieve a **noble gas** configuration



THE OUTER SHELL (n=1) HAS THE MAX NUMBER OF ELECTRONS (= 2)


NH3
H
H
H
N
H
H
N
H
H–N
H
H

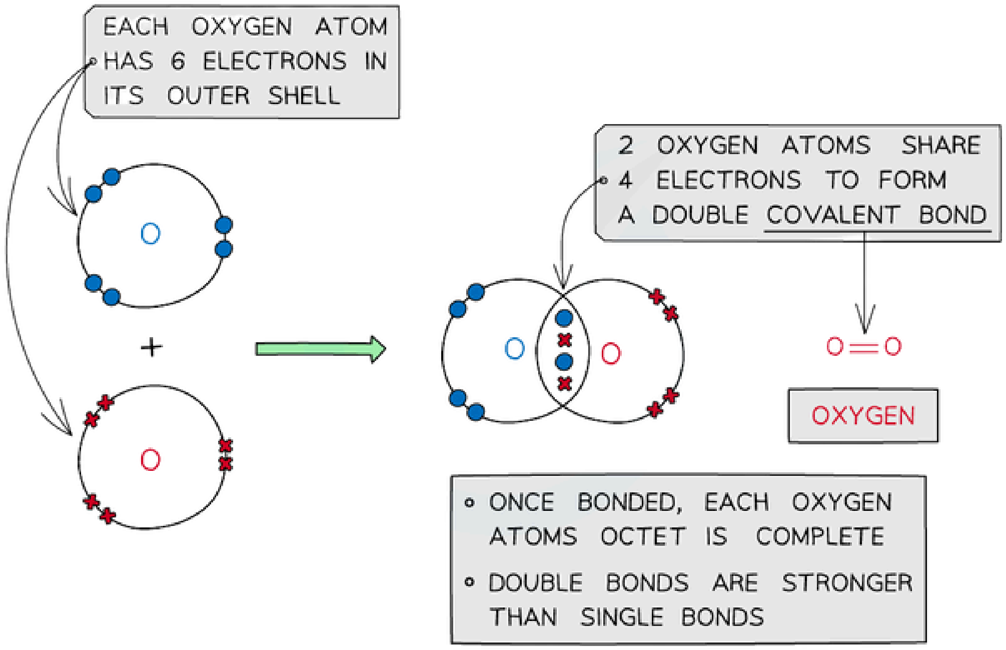

H2O
H
H
O
LONE PAIR
H
O
H
LONE PAIR
O
H
H



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

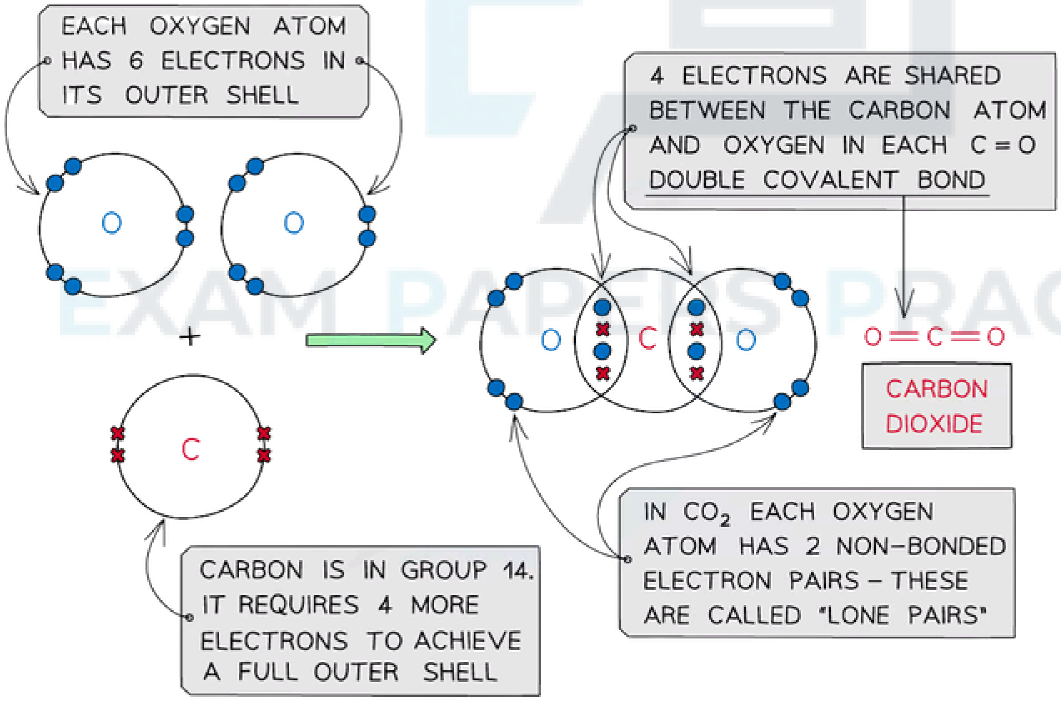
Double covalent bonding

Oxygen, O2



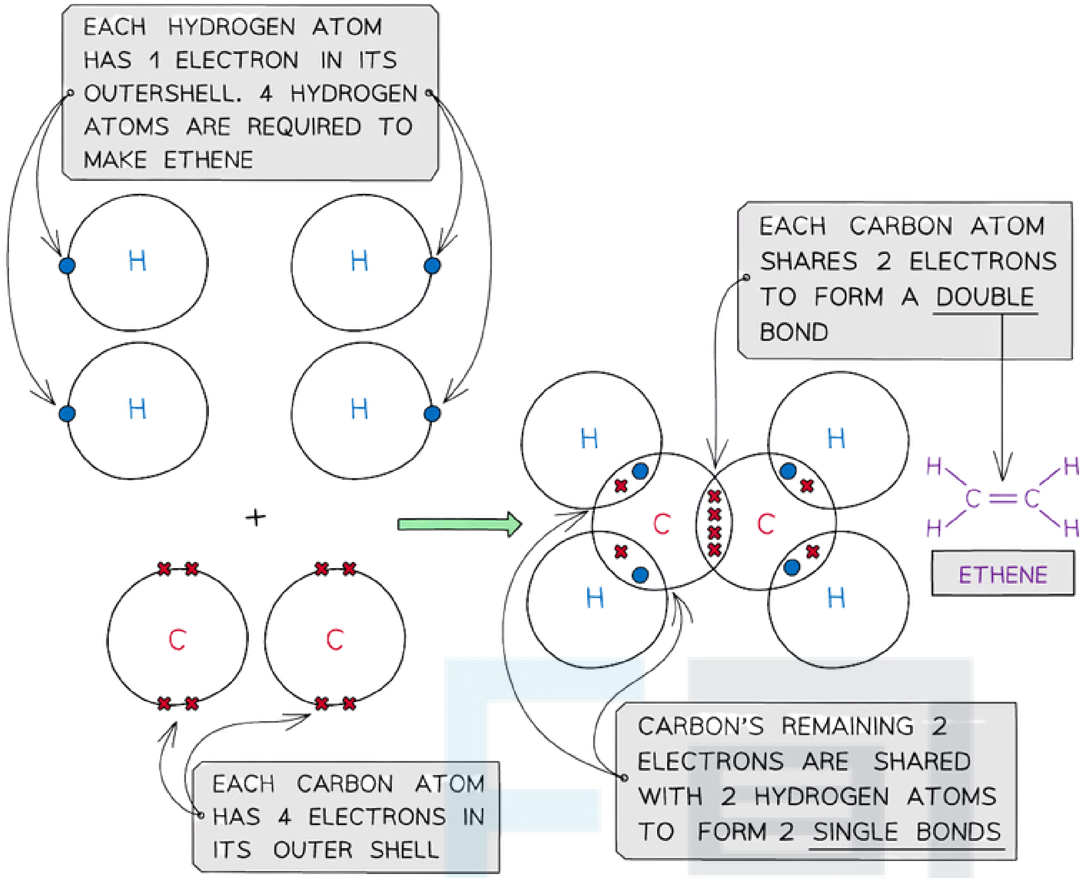
Covalent bonding in oxygen

Carbon dioxide, CO_2



Covalent bonding in carbon dioxide

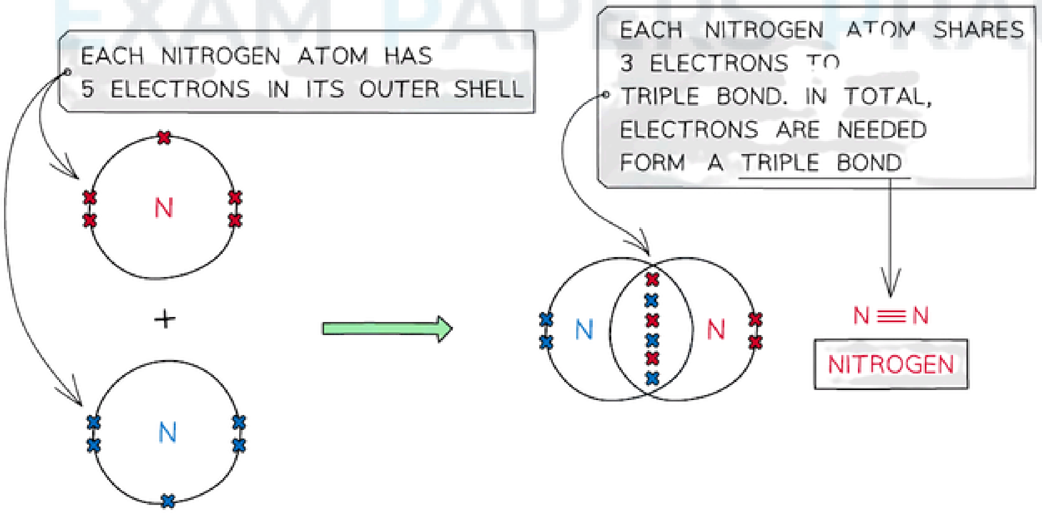
Ethene, C_2H_4



Covalent bonding in ethene

Triple covalent bonding

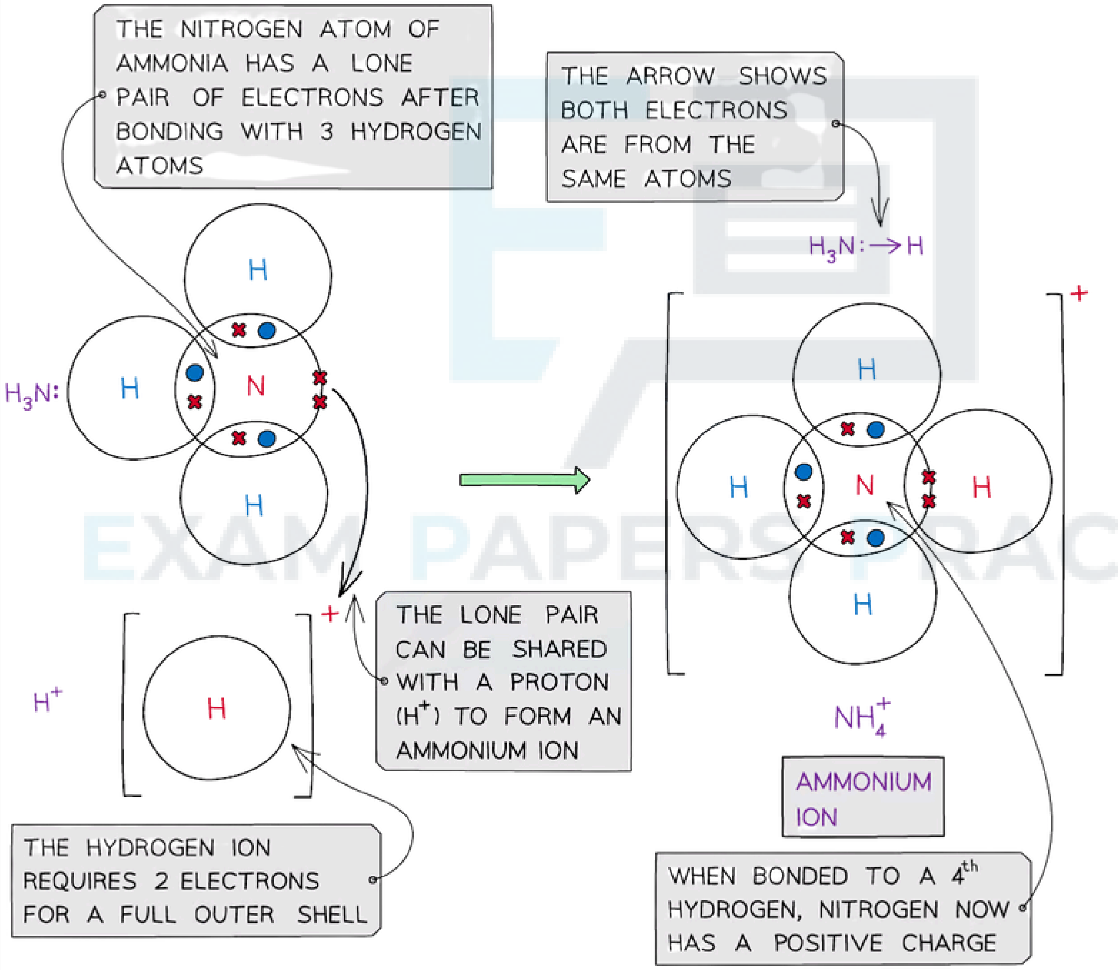
Nitrogen, N_2



Covalent bonding in nitrogen

Dative covalent bonding

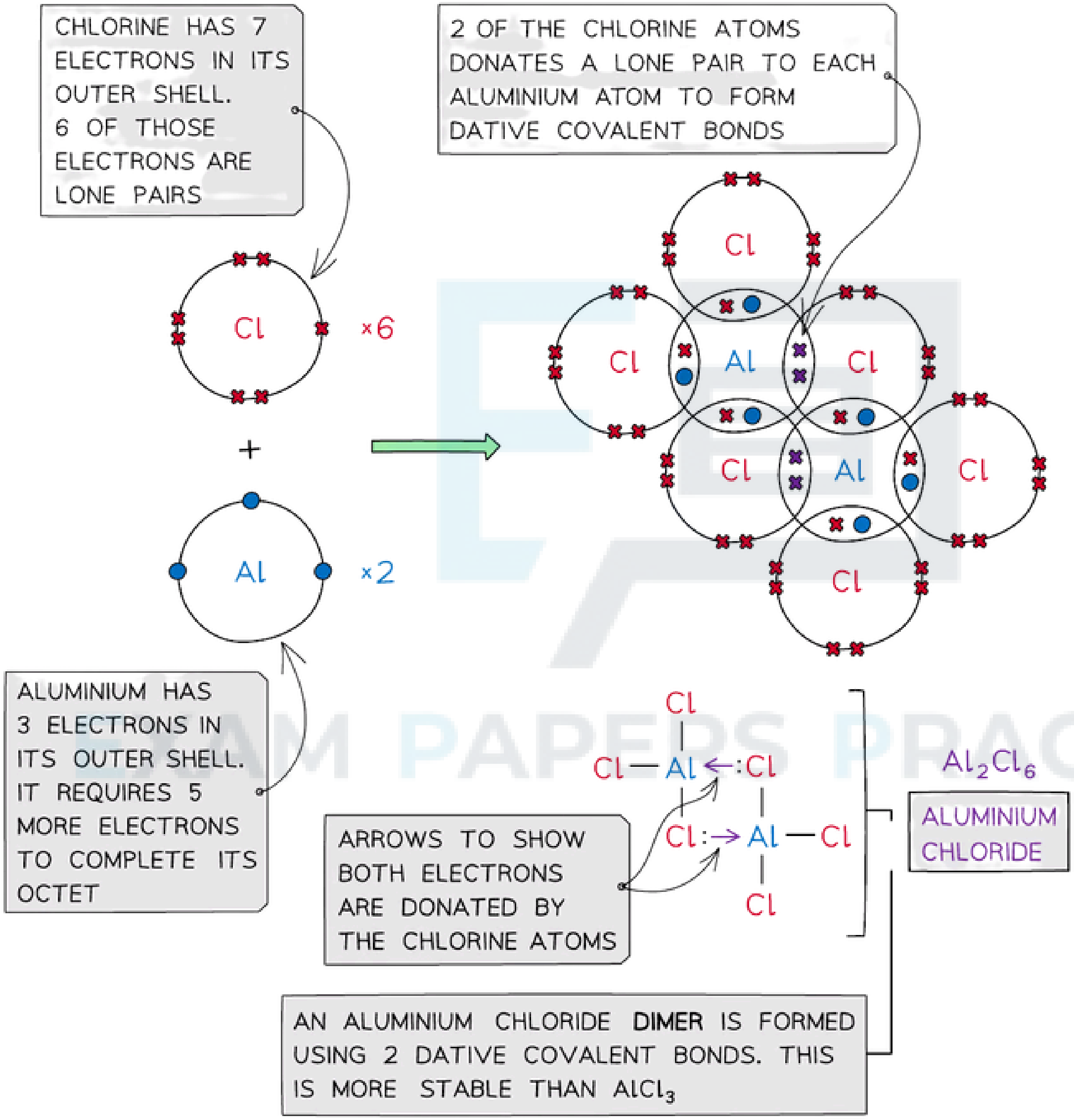
- In **simple covalent bonds**, the two atoms involved share electrons
- Some molecules have a **lone** pair of electrons that can be donated to form a bond with an **electron-deficient** atom
    - An electron-deficient atom is an atom that has an **unfilled outer orbital**
- So **both electrons** are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



Ammonia (NH3) can donate a lone pair to an electron-deficient proton (H+) to form a charged ammonium ion (NH4+)

Aluminium chloride

- **Aluminiumchloride** is also formed using dative covalent bonding
- At **high temperatures** aluminium chloride can exist as a **monomer** ($AlCl3$)
    - The molecule is electron-deficient and needs two electrons to complete the aluminium atom's outer shell
- At **lower temperatures** the two molecules of $AlCl3$ join together to form a dimer ($Al2Cl6$)
    - The molecules combine because lone pairs of electrons on two of the chlorine atoms form **two coordinate bonds** with the aluminium atoms



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

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

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

ARROWS TO SHOW BOTH ELECTRONS ARE DONATED BY THE CHLORINE ATOMS

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

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

Exam Tip

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.

1.4.7 Bond Length & Bond Strength

Bond Length & Bond Strength

Bond energy

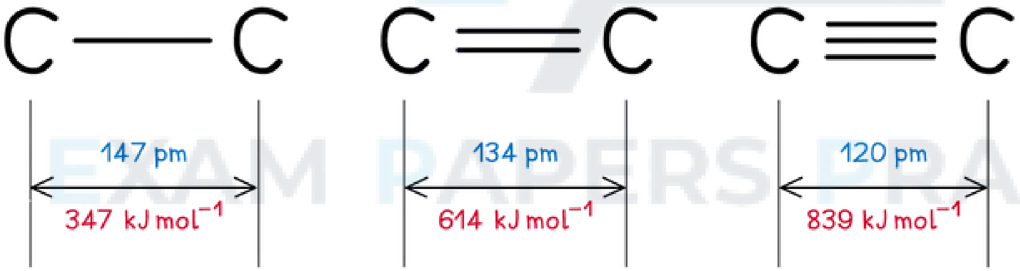
- The **bond energy** is the energy required to **break** one mole of a particular covalent bond in the gaseous states
    - Bond energy has units of kJ mol-1

- The **larger** the bond energy, the **stronger** the covalent bond is

Bond length

- The**bondlength** 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**

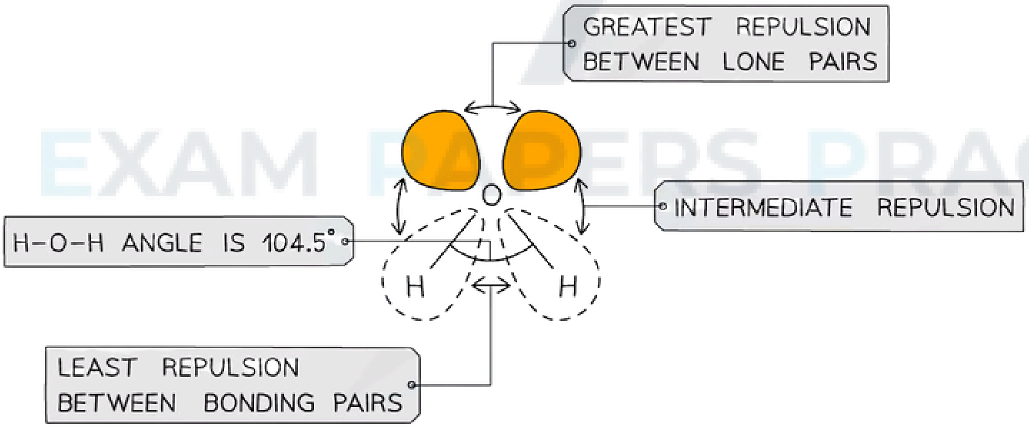


Triple bonds are the shortest covalent bonds and therefore the strongest ones

Electron Pair Repulsion & Shape

- The **valence shell electronpairrepulsion 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

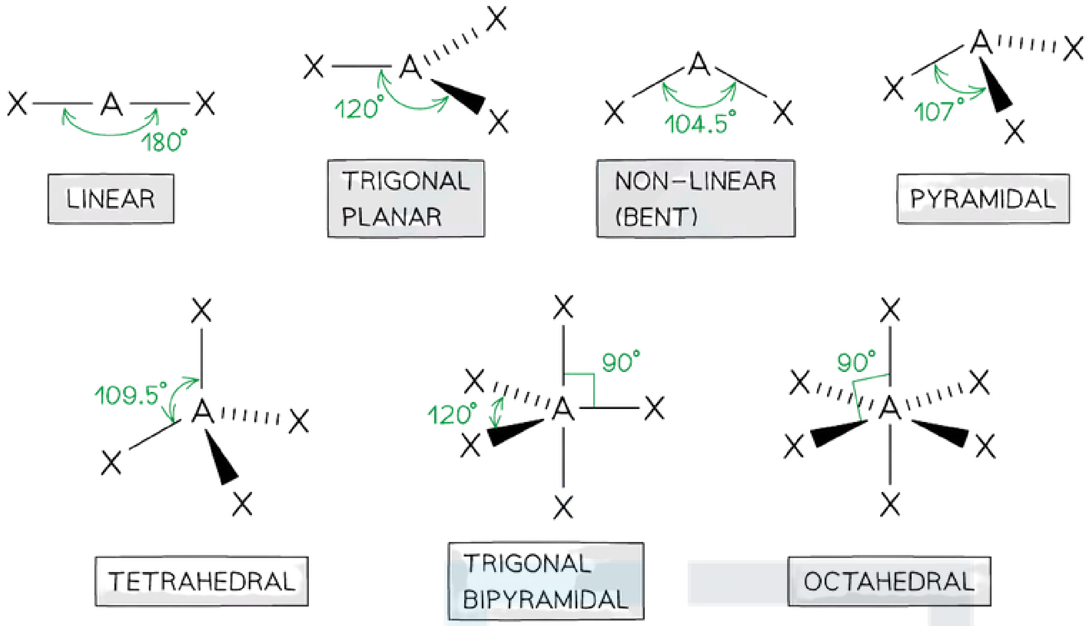
- Different types of electron pairs have different repulsive forces
    - Lone pairs of electrons have a more concentrated electron charge cloud than bonding pairs of electrons
    - The cloud charges are wider and closer to the central atom's nucleus
    - The order of repulsion is therefore: lone pair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

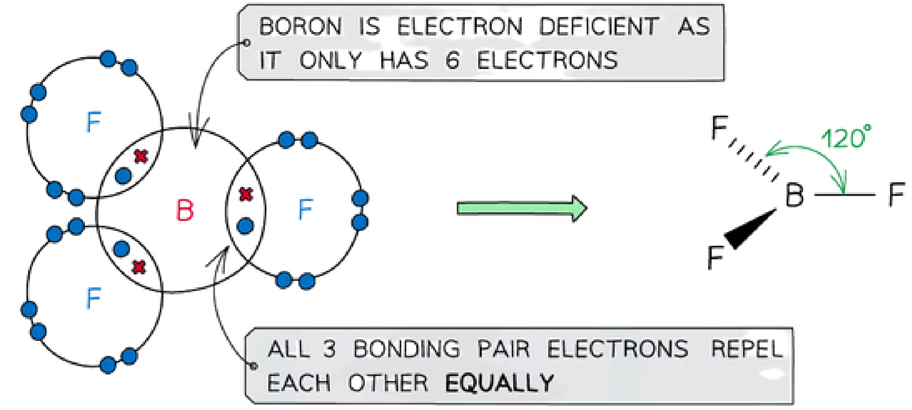


Molecules of different shapes can adapt with their corresponding bond angles

Examples

TRIGONAL PLANAR

BF_3 (120°)

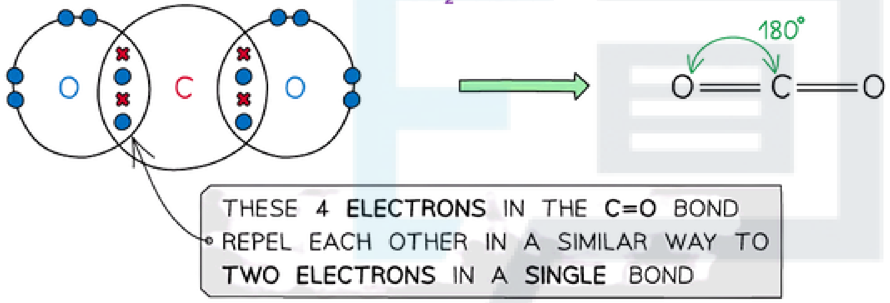


BORON IS ELECTRON DEFICIENT AS IT ONLY HAS 6 ELECTRONS

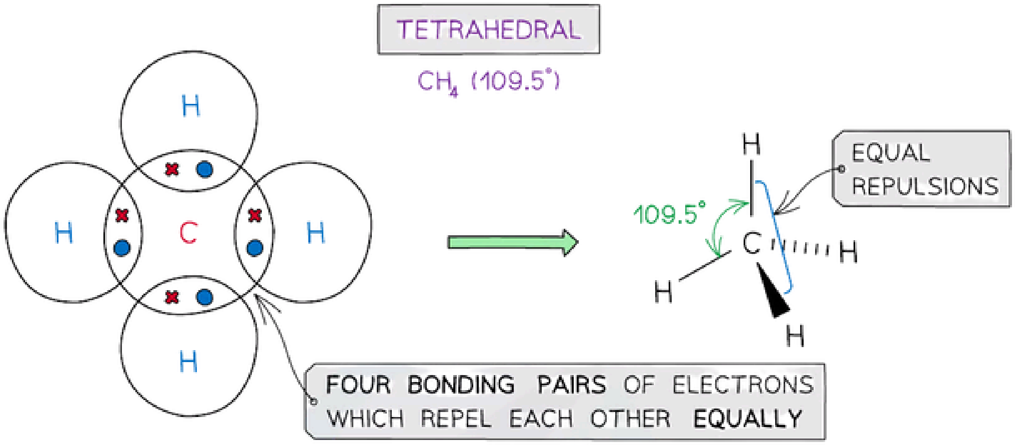
ALL 3 BONDING PAIR ELECTRONS REPEL EACH OTHER **EQUALLY**

LINEAR

CO_2 (180°)



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

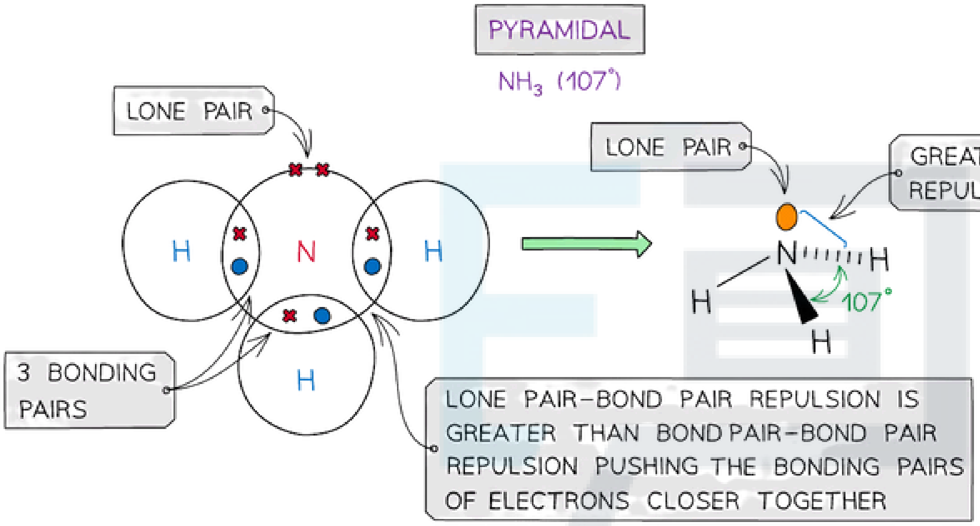


TETRAHEDRAL

CH_4 (109.5°)

EQUAL REPULSIONS

FOUR BONDING PAIRS OF ELECTRONS WHICH REPEL EACH OTHER EQUALLY



PYRAMIDAL

NH_3 (107°)

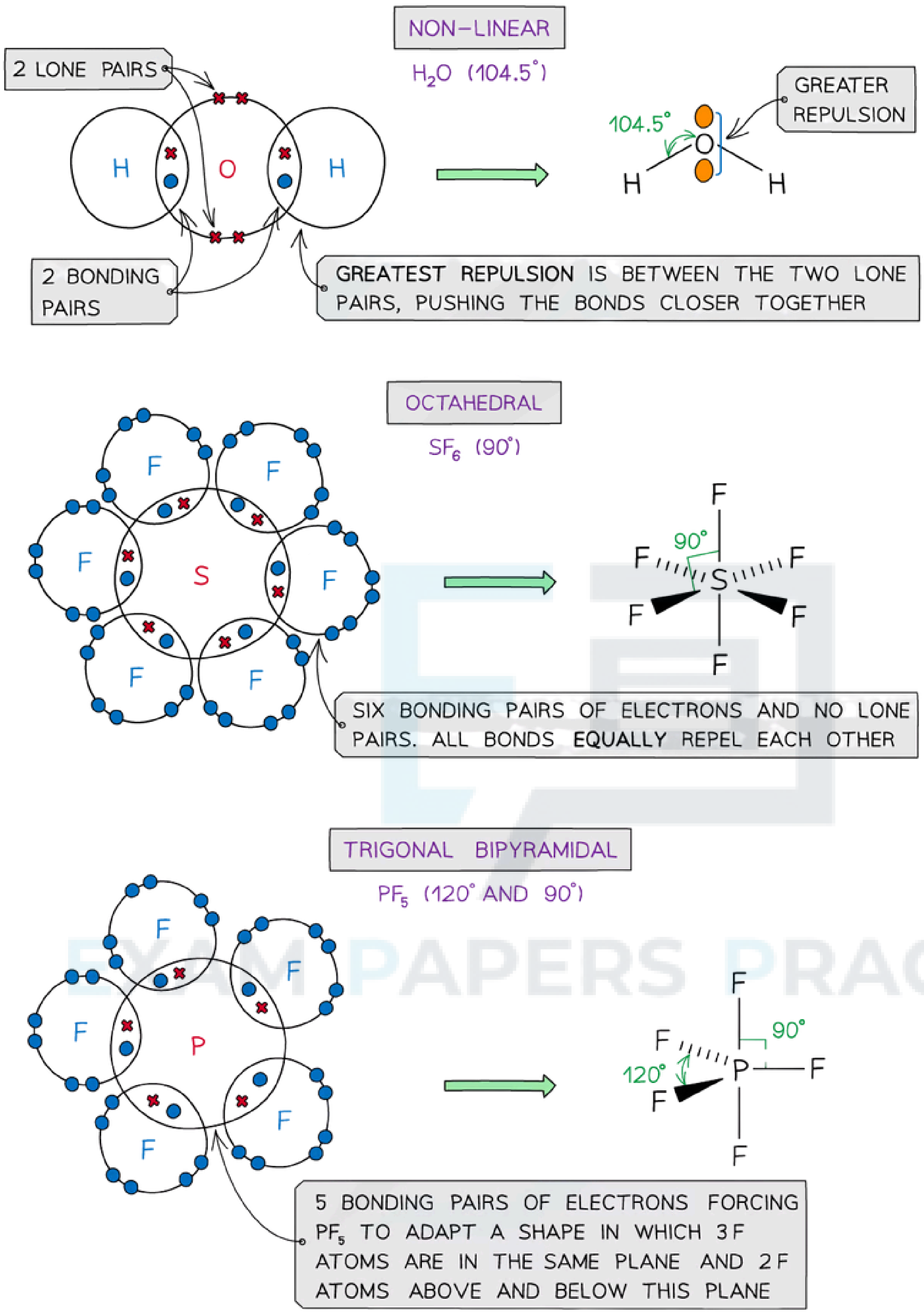
LONE PAIR

LONE PAIR

GREATER REPULSION

3 BONDING PAIRS

LONE PAIR–BOND PAIR REPULSION IS GREATER THAN BOND PAIR–BOND PAIR REPULSION PUSHING THE BONDING PAIRS OF ELECTRONS CLOSER TOGETHER



Examples of molecules with different shapes and bond angles

Worked Example

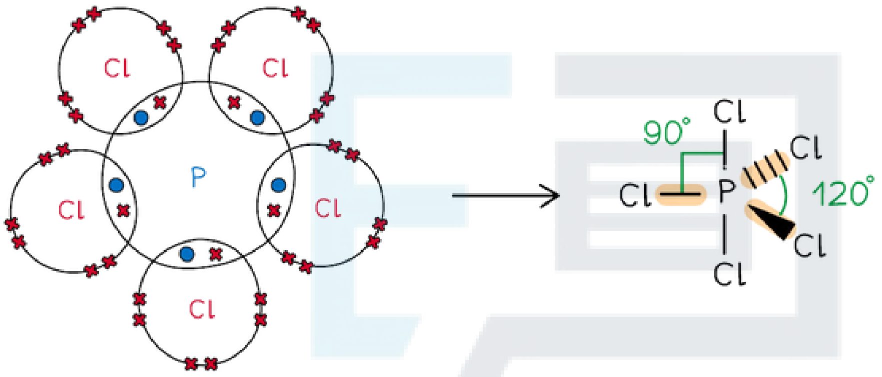
VSEPR & shapes of molecules Draw the

shape of the following molecules:

1. Phosphorus(V) chloride
2. N(CH3)3
3. CCl4

Answer 1:

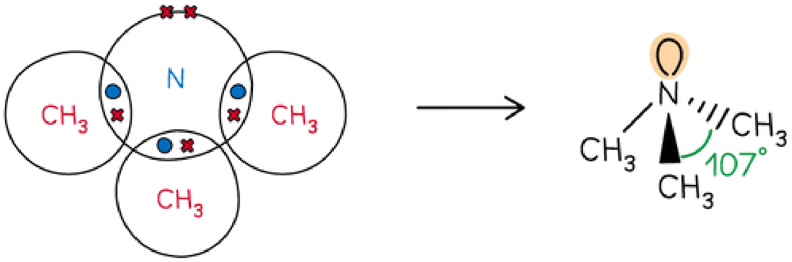
- Phosphorus is in group 15, so has 5 valence electrons; Cl is in group 17, so has 17 valence electrons
- All 5 electrons are used to form covalent bonds with Cl and there are no lone pairs
- This gives a **trigonal** (or **triangular**) **bipyramidal** shape:



Phosphorus pentachloride or phosphorus (V) chloride

Answer 2:

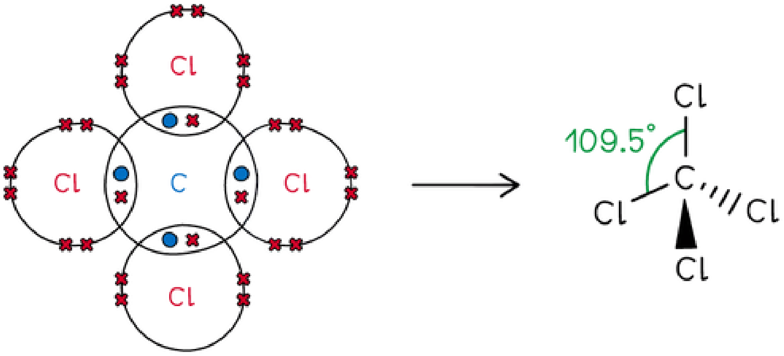
- Nitrogen is in group 15, so has 5 valence electrons; carbon is in group 14, so has 4 valence electrons, 3 of which are already used in the covalent bonds with hydrogen
- Three of the valence electrons in N are used to form bonding pairs, so there is one lone pair left
- N(CH3)3 has a **triangular pyramid** 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 CCl4 is **tetrahedral**



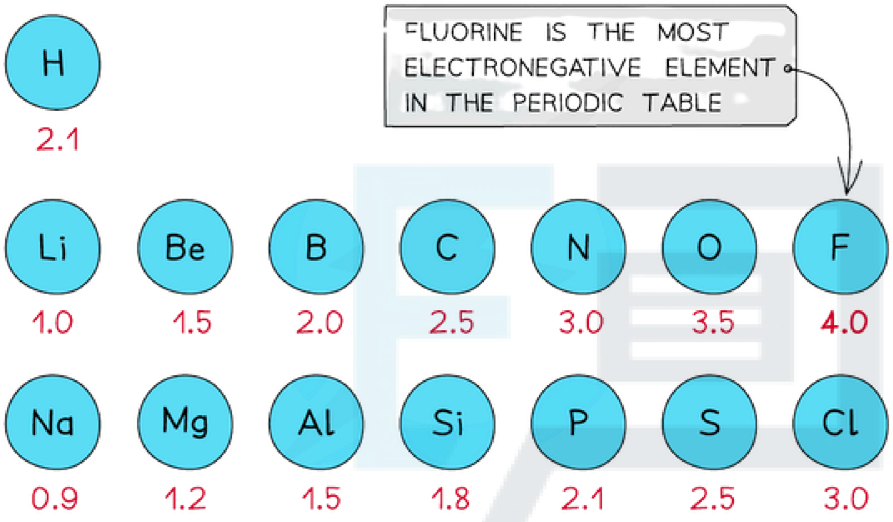
Tetrachloromethane

1.5 Structure

1.5.1 Electronegativity

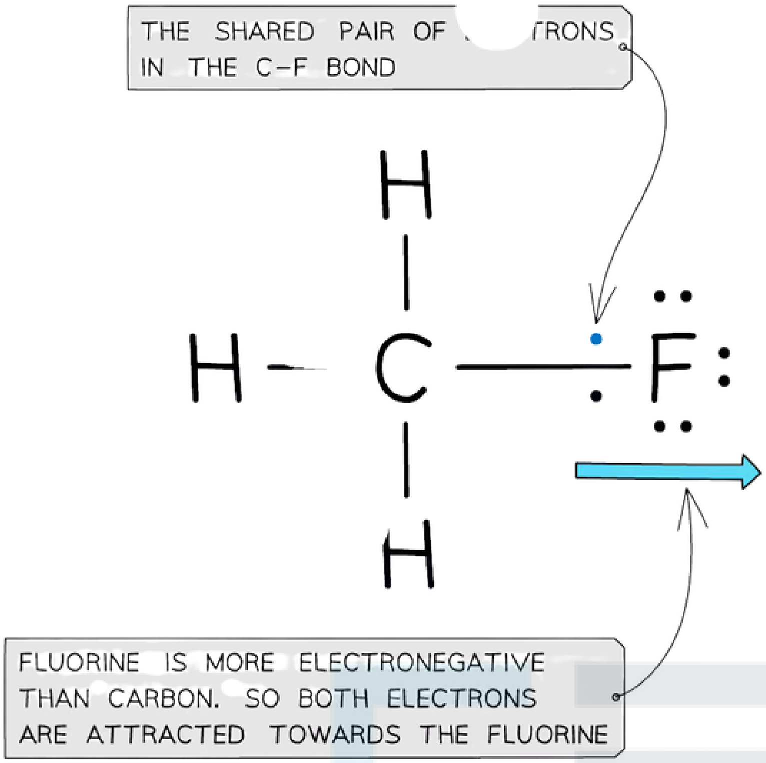
Defining Electronegativity

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



First three rows of the periodic table showing electronegativity values

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



Electron distribution in the C-F bond of fluoromethane

Nuclear charge

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

Atomic radius

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

Shielding

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

less shielding than in caesium

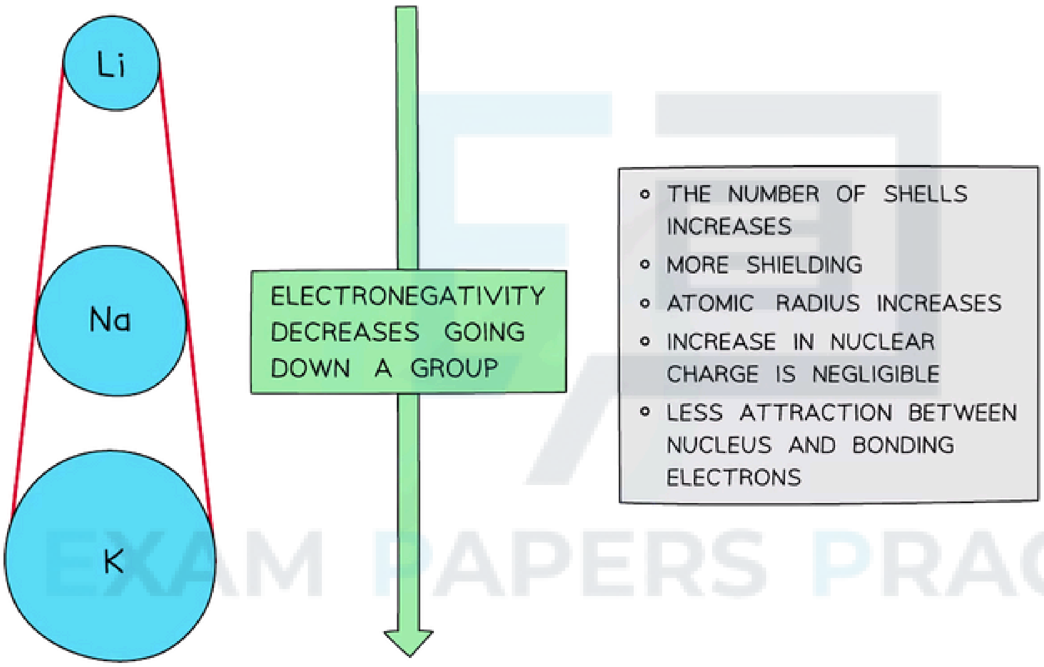
- Thus, an increased number of **inner shells and subshells** will result in a **decreased electronegativity**

Trends in electronegativity

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

Down a group

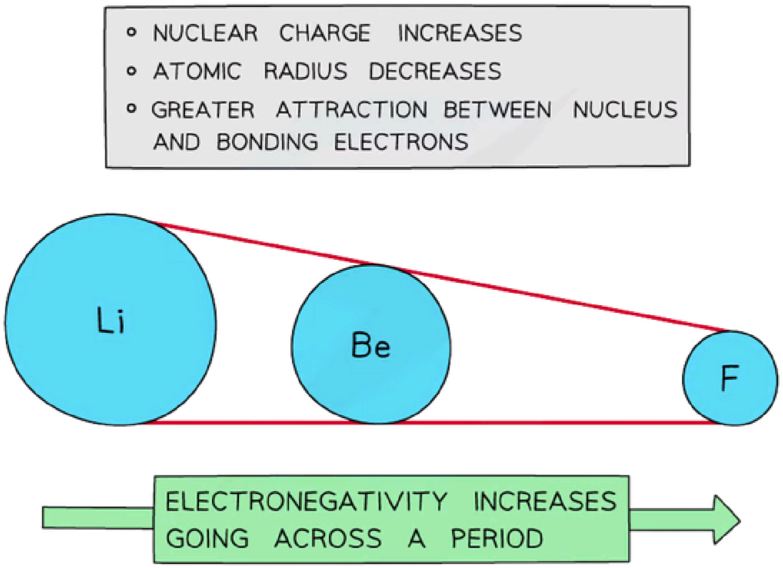
- There is a **decrease** in **electronegativity** going down the group
- The **nuclear charge increases** as more protons are being added to the nucleus
- However, each element has an extra filled electron shell, which increases **shielding**
- The addition of the extra shells increases the distance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



Electronegativity decreases going down the groups of the periodic table

Across a period

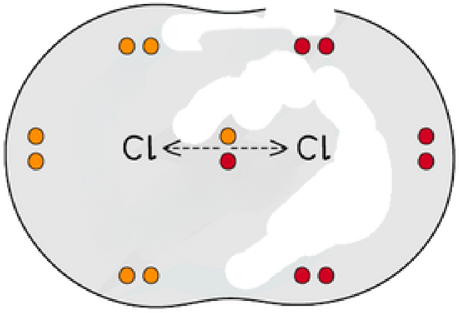
- Electronegativity **increases** across a period
- The **nuclear charge increases** with the addition of protons to the nucleus
- **Shielding** remains relatively **constant** across the period as no new shells are being added to the atoms
- The nucleus has an increasingly strong attraction for the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



Electronegativity increases going across the periods of the Periodic Table

Bond Polarity

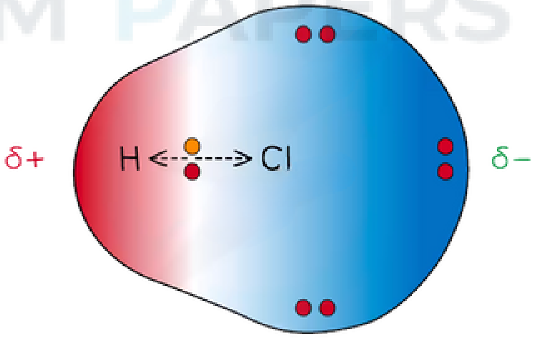
- When two atoms in a covalentbondhavethe**same electronegativity** the covalent bond is **nonpolar**



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

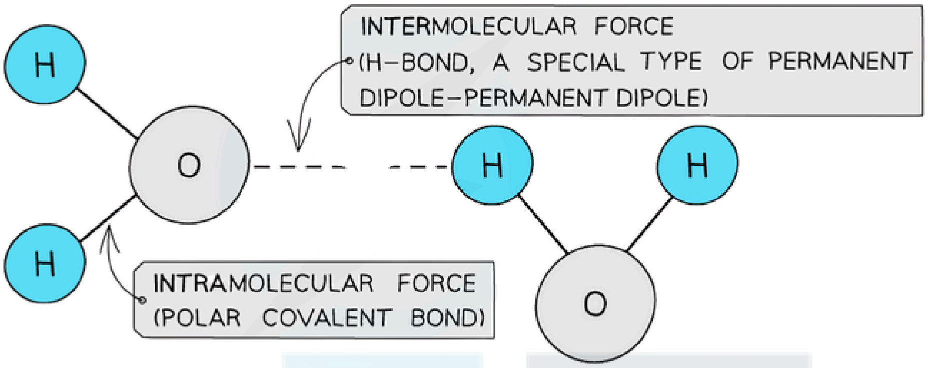


Cl has a greater electronegativity than H causing the electrons to be more attracted towards the Cl atom which becomes delta negative and the H delta positive

Intermolecular Forces

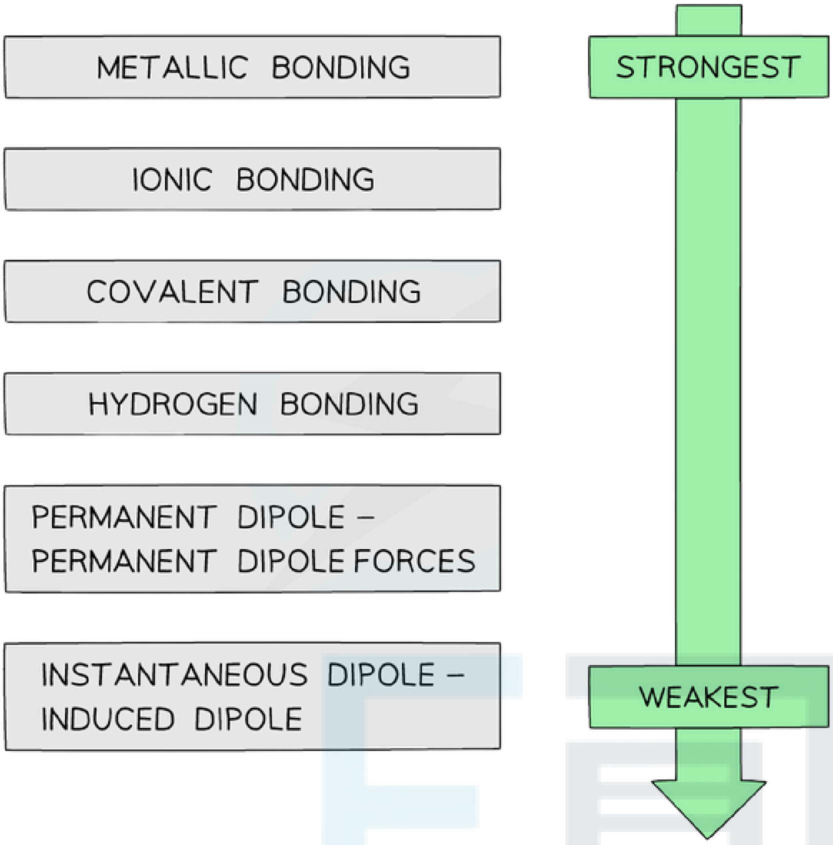
Intramolecular forces

- **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:

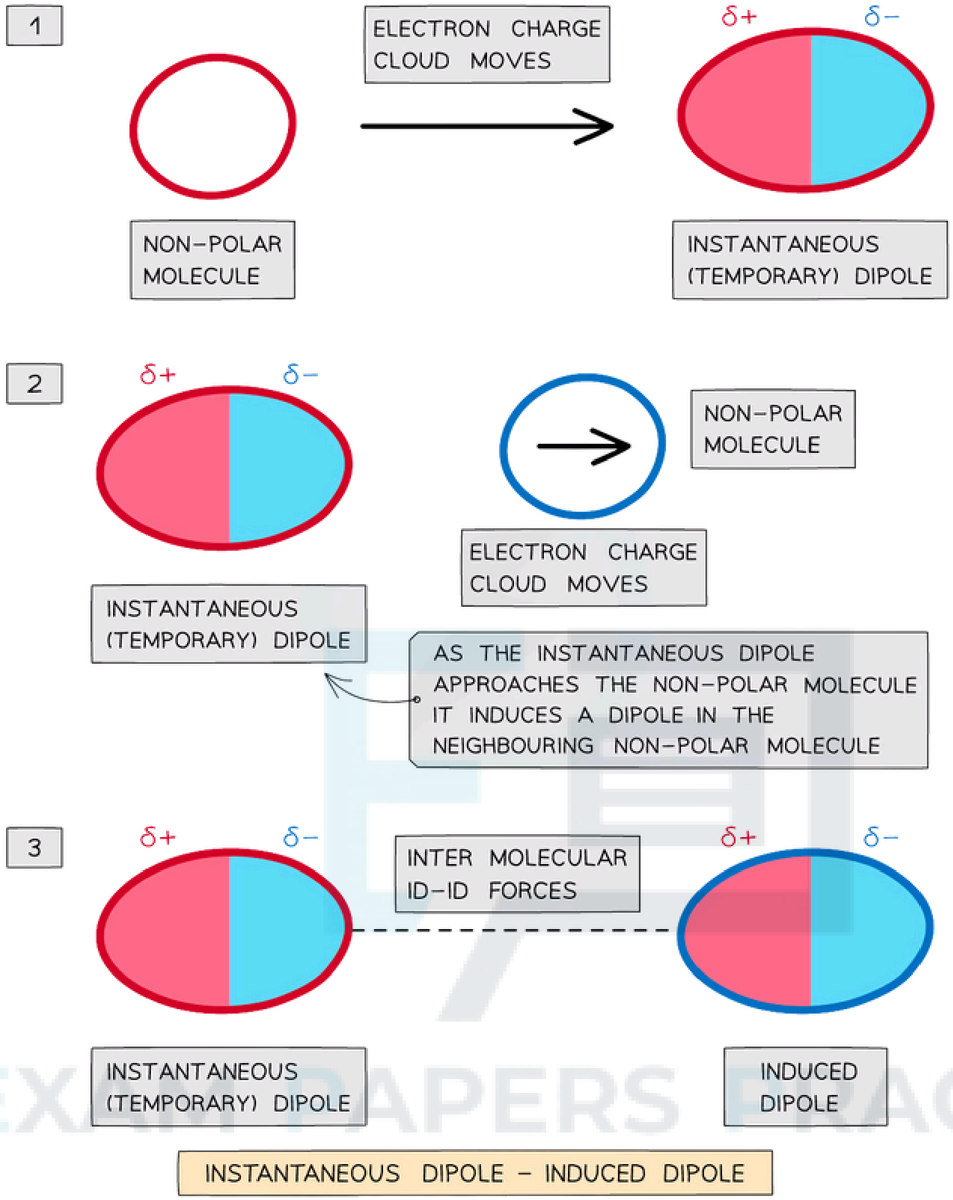


The varying strengths of different types of bonds

Induced dipole-dipole forces:

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

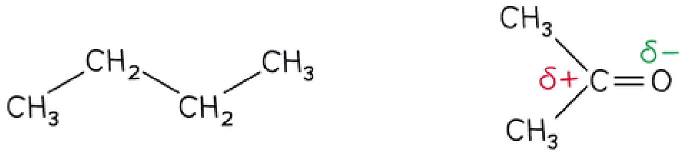
- They are also known as **London dispersion forces**



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

Relative strength

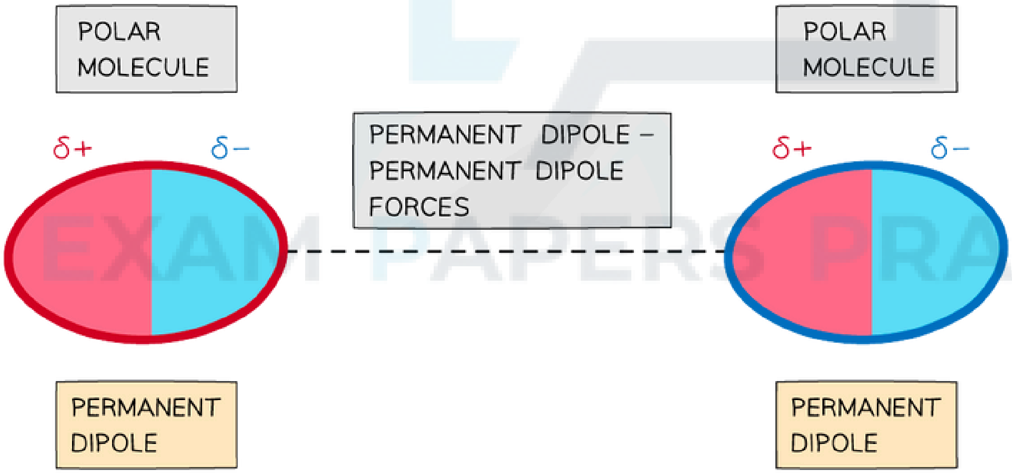
- For small molecules with **the same number of electrons,** permanent dipoles are **stronger** than induced dipoles
  - Butane and propanone have the same number of electrons
  - Butane is a nonpolar molecule and will have induced dipole forces
  - Propanone is a polar molecule and will have permanent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



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

Permanent dipole - dipole forces:

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



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

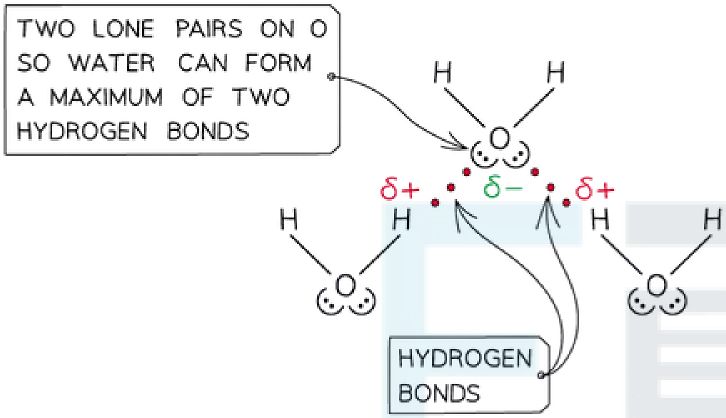
Hydrogen bonding

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

  - Hydrogen bonding is a type of **permanent dipole – permanent dipole** bonding

- For hydrogen bonding to take place the following is needed:
  - A species which has an **O, N or F** (very **electronegative**) atom bonded to a hydrogen

- When hydrogen is covalently bonded to an **O**, **N** or **F**, the bond becomes highly **polarised**
- The H becomes so **δ+** charged that it can form a bond with the **lone pair** of an **O**, **N** or **F** atom in another molecule
- For example, in water
  - Water can form two hydrogen bonds, because the O has two lone pairs



Hydrogen bonding in water

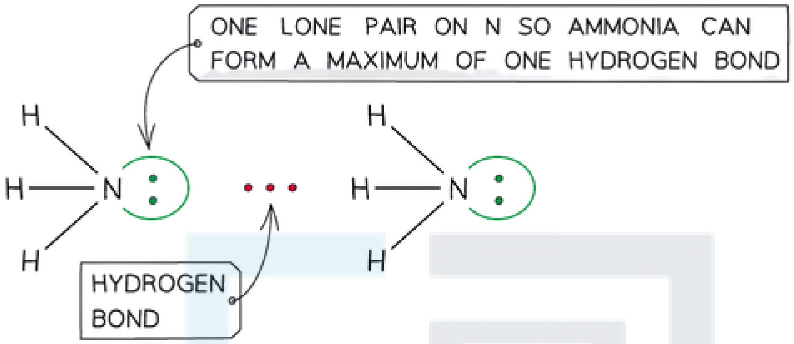
☐ Exam Tip

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

Hydrogen Bonding Interactions

Examples of compounds that can form hydrogenbondsare:

- 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

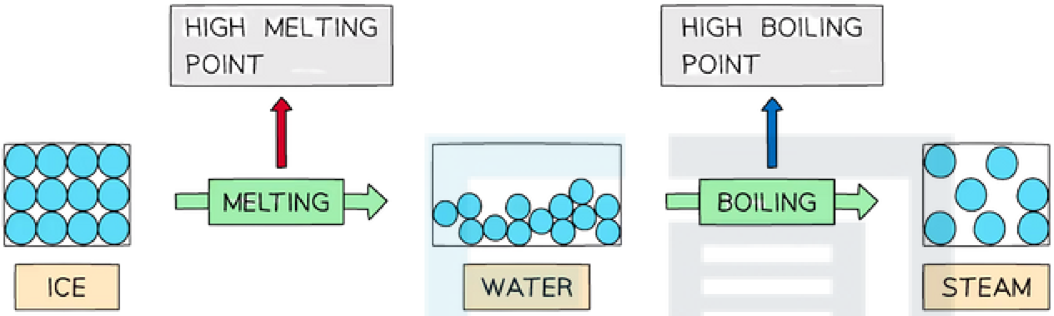
Anomalous Properties of Water

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

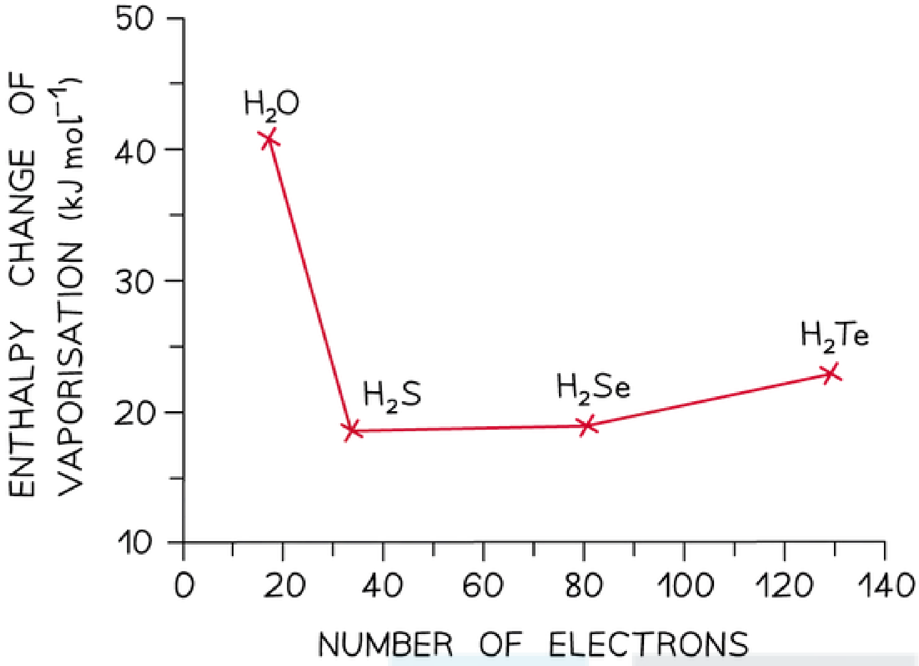
High melting & boiling points

- Water has high**melting**and **boiling points** due to the 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

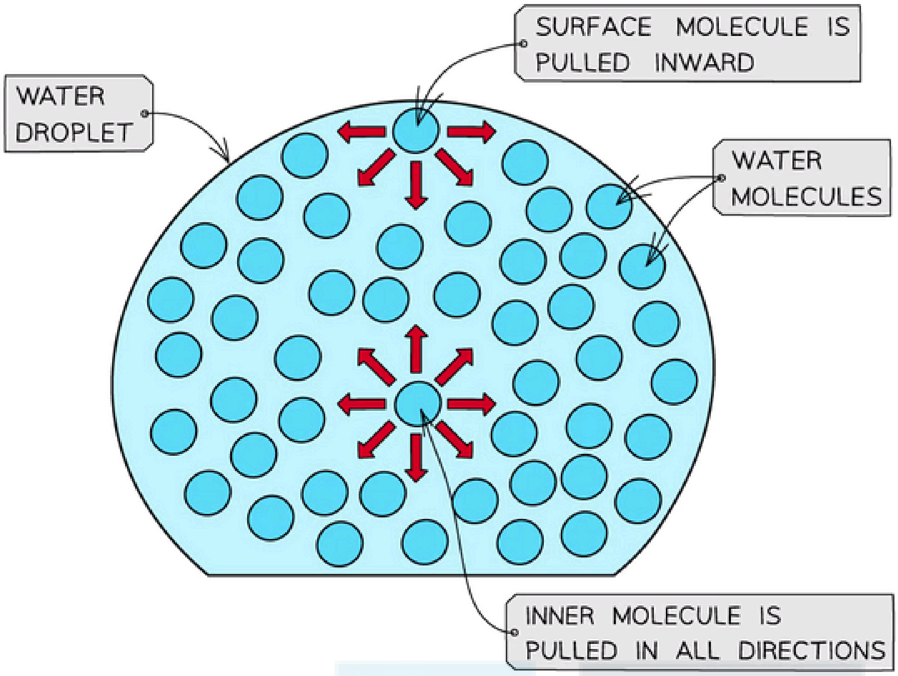
- The graph below compares the **enthalpy of vaporisation** (energy required to boil a substance) of different hydrides
- The enthalpy changes **increase** going from H2S to H2Te due to the increased number of electrons in the Group 16 elements
- This causes an increase in the **instantaneous dipole - induced dipole forces (dispersion forces)** as the molecules become larger
- Based on this, H_2O should h aveamuchlowerenthalpychange(around17kJmol $^{-1}$)
- However, the enthalpy change of vaporisation is almost 3 times **larger** which is caused by the **hydrogen bonds** present in water but not in the other hydrides



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

High surface tension

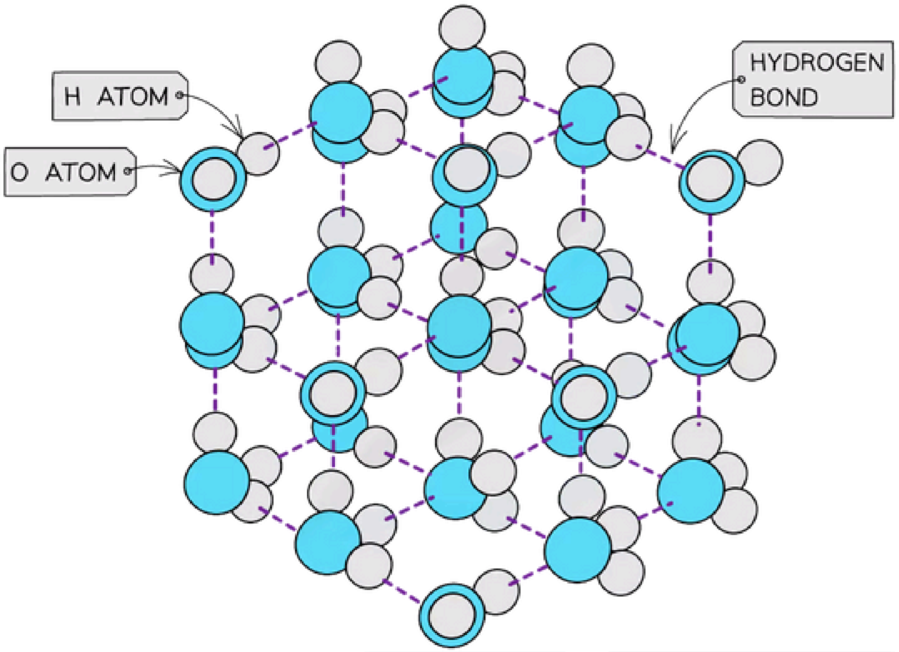
- Water hasa**high surface tension**
- **Surface tension** is the ability of a **liquid surface** to resist any **external forces** (i.e. to stay unaffected by forces acting on the surface)
- The water molecules at the **surface** of liquid are bonded to other water molecules through **hydrogen bonds**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

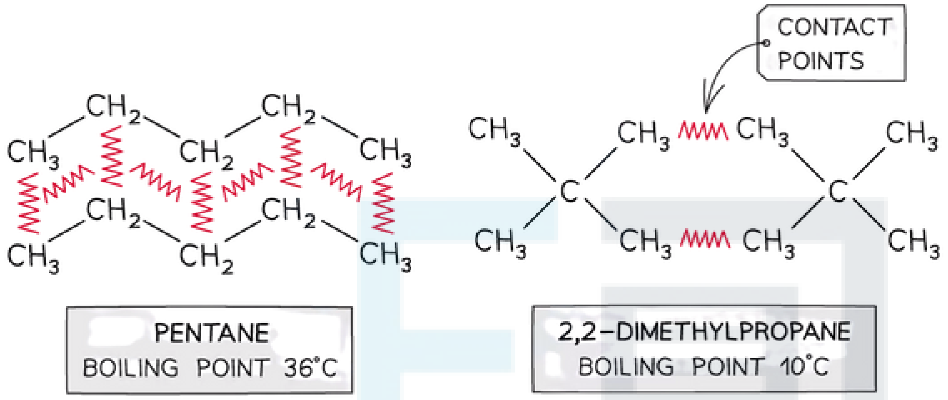


The m‘ore open 'structure of molecules in ice causes it to have a lower density than liquid water

Intermolecular Forces & Physical Properties

Branching

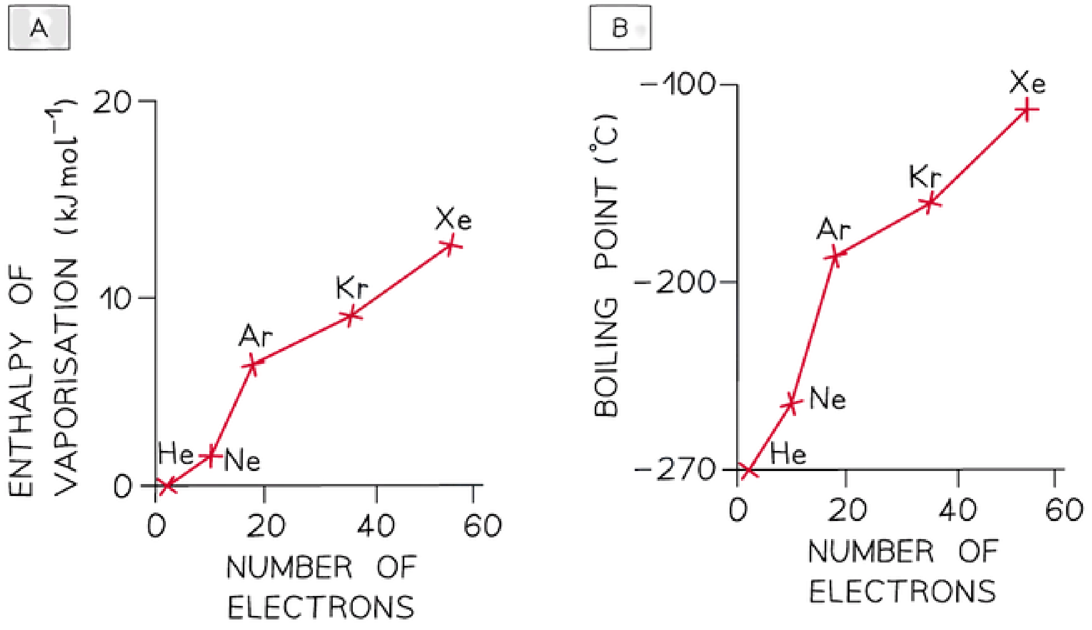
- The larger the surface area of a molecule, the more contact it will have with adjacent molecules
- The surface area of a molecule is **reduced by branching**
- The greater its ability to induce a dipole in an adjacent molecule, the greater the **London (dispersion) forces** and the higher the melting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



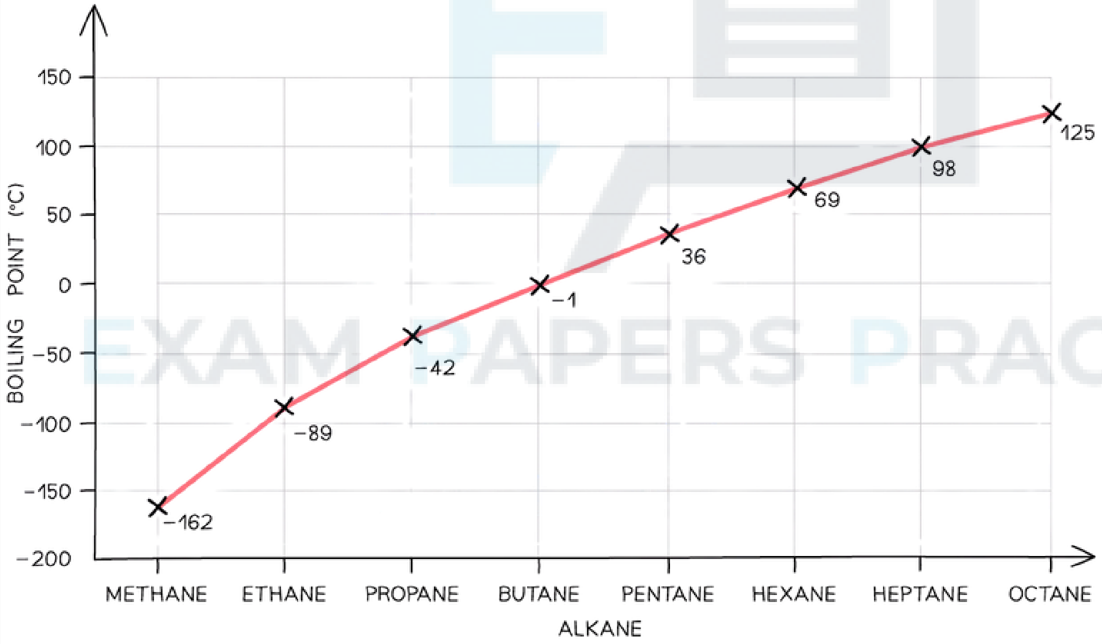
Boiling points of molecules with the same numbers of electrons but different surface areas

Number of electrons

- Thegreaterthe 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

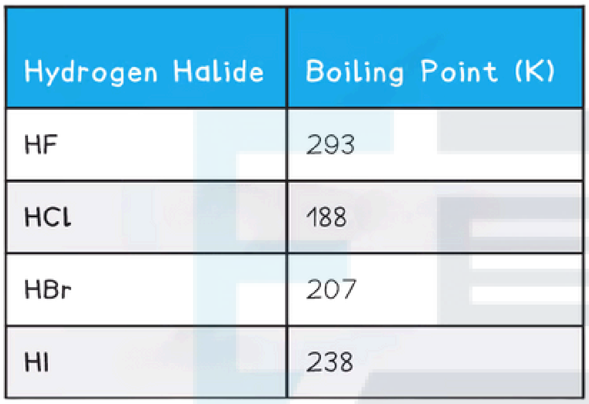
Alcohols

- 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 ($\delta+$ 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 oC and the boiling point of propanol is 97 oC

Hydrogen Halides

- The boiling points of the hydrogen halides are as follows



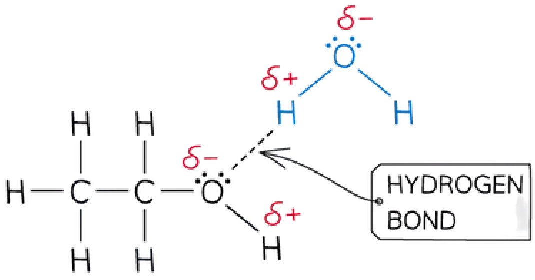
Hydrogen Halide	Boiling Point (K)
HF	293
HCl	188
HBr	207
HI	238

- 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

- Thegeneral 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:

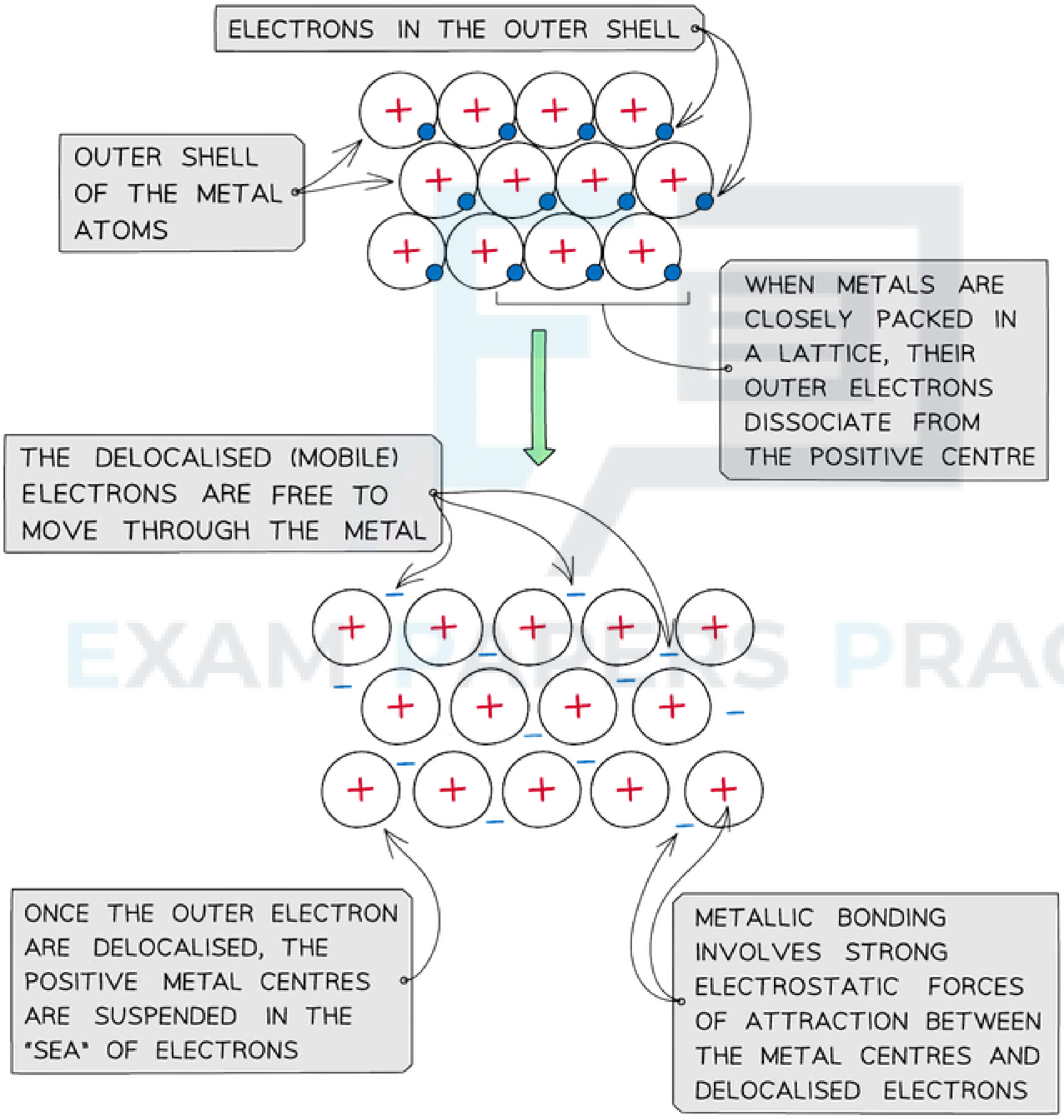


Hydrogen bonds form between ethanol and water

- 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, $C2H5OH$, is readily soluble but hexanol, $C6H13OH$, 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

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

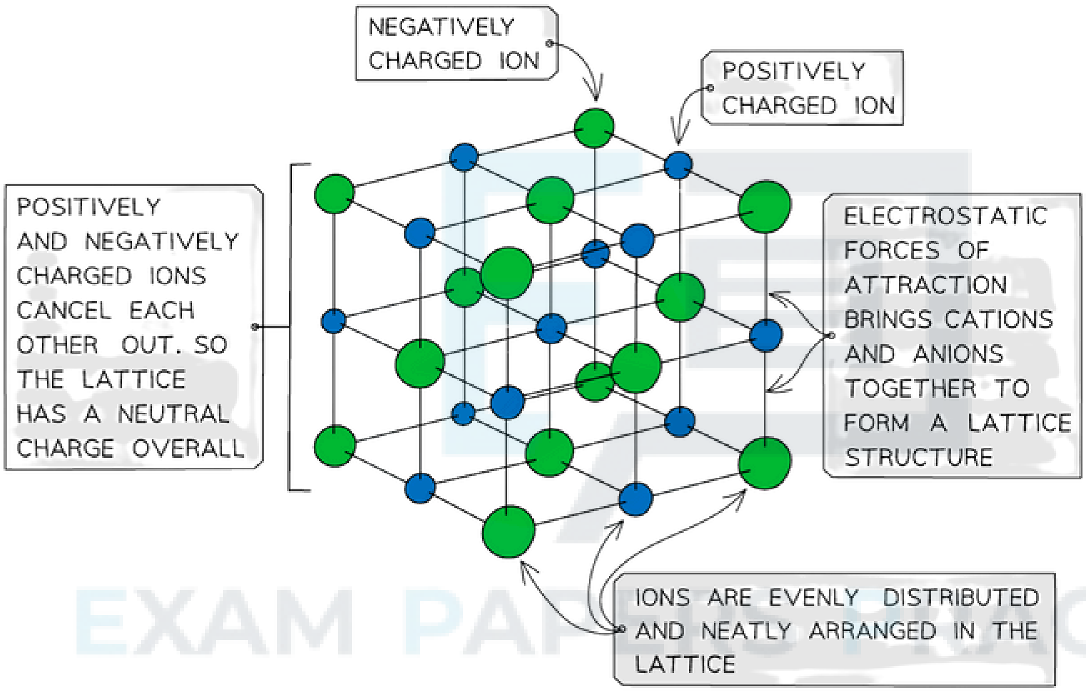


The positive metal centres are suspended in a s‘ea 'of delocalised electrons

Giant Lattices

Ionic Lattices

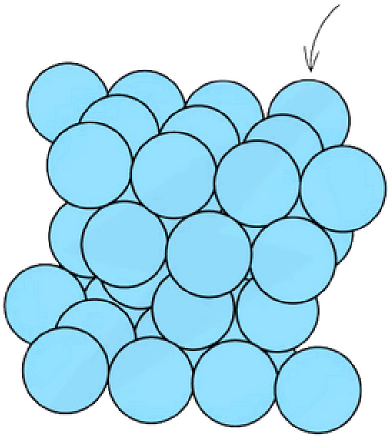
- The ions form a **lattice structure** which is an evenly distributed **crystalline** structure
- Ions in a lattice are arranged in a **regular repeating pattern** so that positive charges cancel out negative charges
- The attraction between the cations and anions is occurring in all directions
- Each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

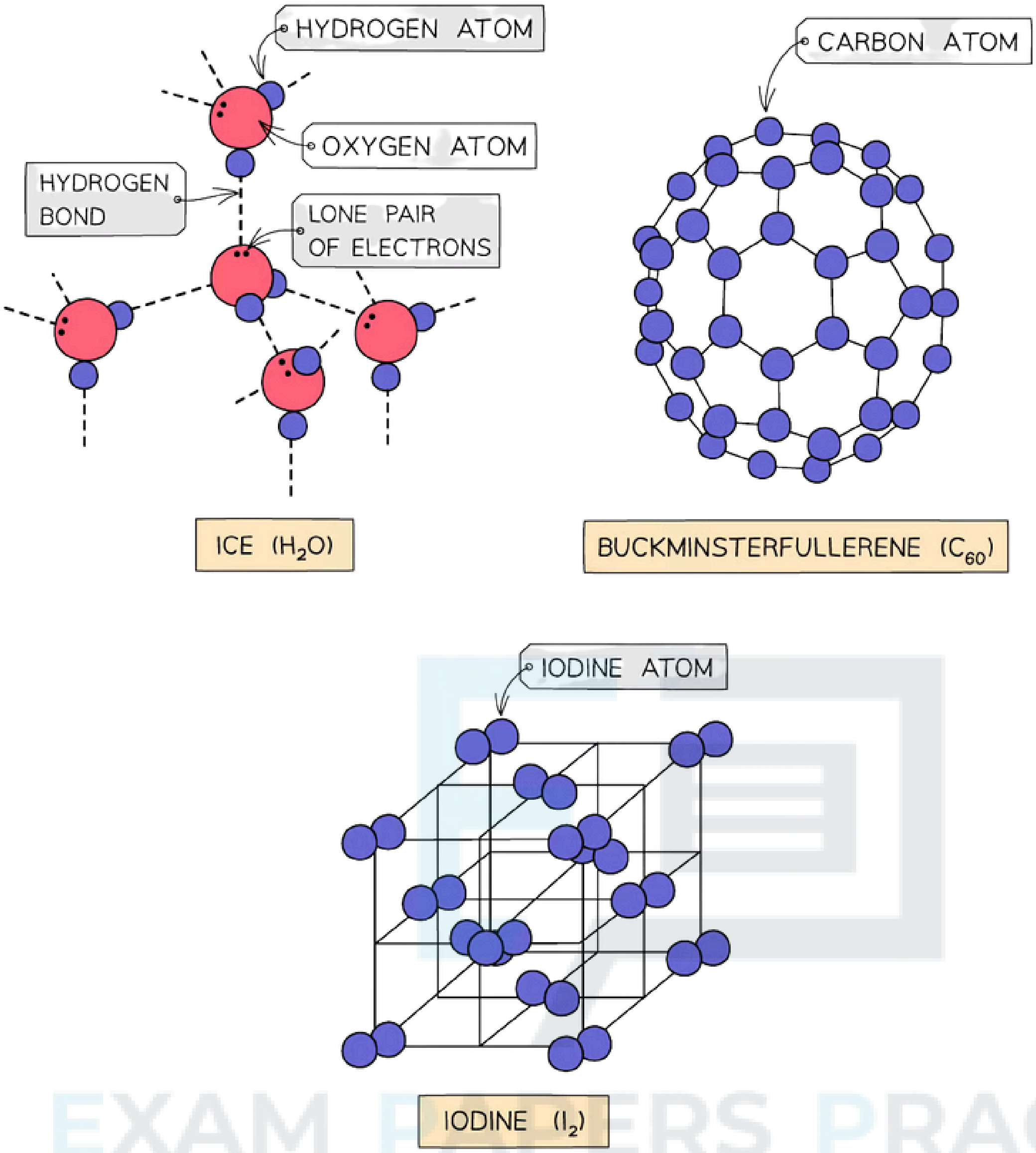
- Metals form **giant metallic lattices** in which the metal ions are surrounded by a 'sea' of **delocalised** electrons
- The metal ions are often packed in **hexagonal layers** or in a **cubic arrangement**
- This layered structure with the delocalised electrons gives a metal its key properties



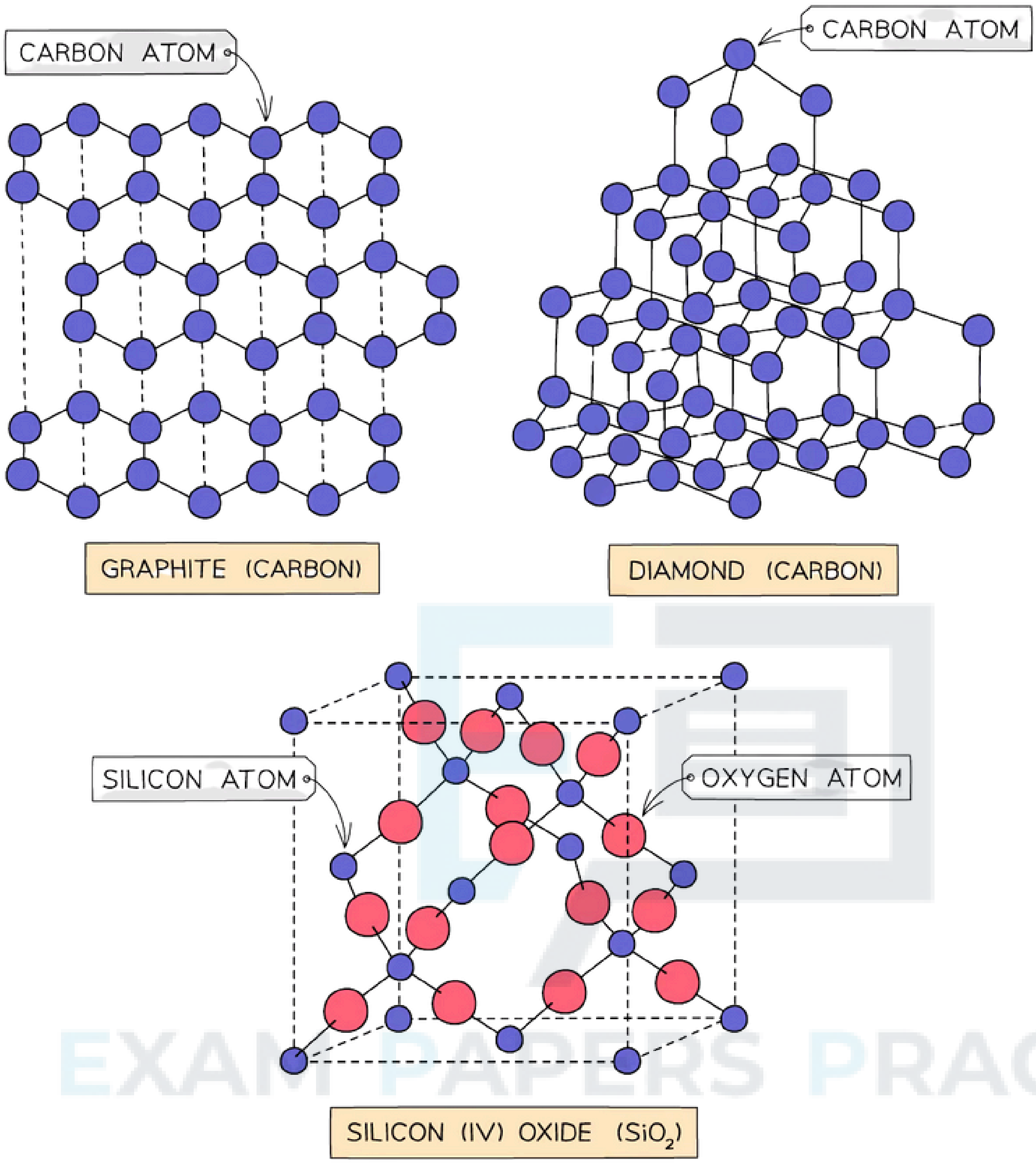
Layers of copper ions (the delocalised electrons are not shown in the diagram)

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



Simple molecular lattices



Giant molecular lattices

☐ Exam Tip

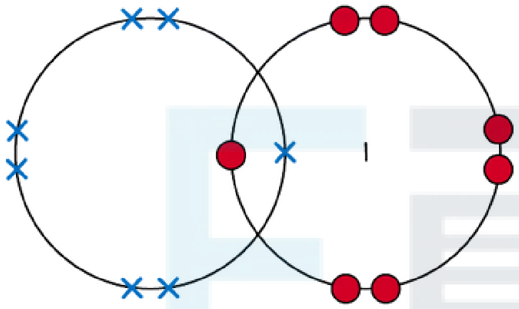
Graphite, diamond and buckminsterfullerene are all **allotropes** of carbon; they are different **structural forms** of the same element (which is carbon).

1.5.7 Covalent Structures

Simple Molecular Compounds

Simple Molecular Compounds

- Covalentsubstancestend to have small molecular structures, such as Cl2, H2O or CO2
- These small molecules are known as **simple molecules**
- Hydrogen (H2), chlorine (Cl2), oxygen (O2), nitrogen (N2), hydrogen chloride (HCl), water (H2O), ammonia (NH3) and methane (CH4) 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

Carbon Allotropes

Covalent bonding & giant covalent lattice structures

- **Giant covalent lattices** have **very highmelting** 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**

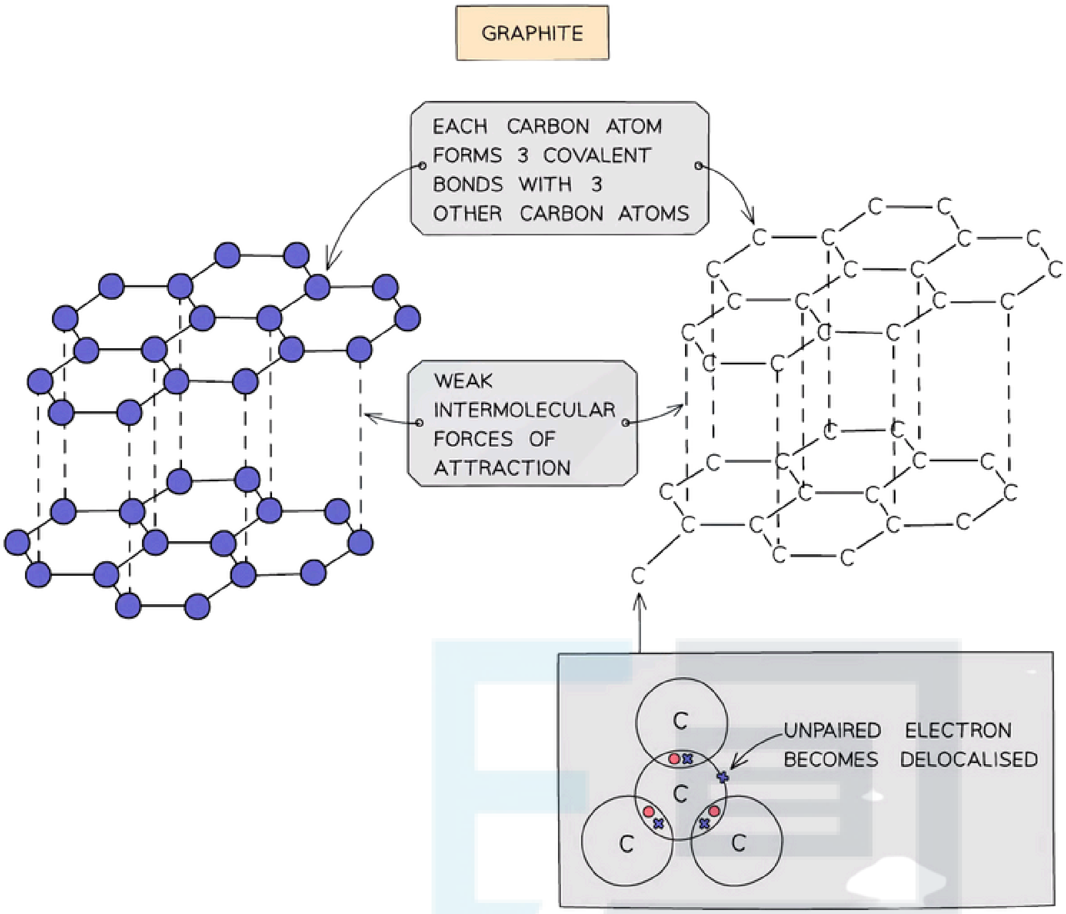


Diagram showing the structure and bonding arrangement in graphite

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**

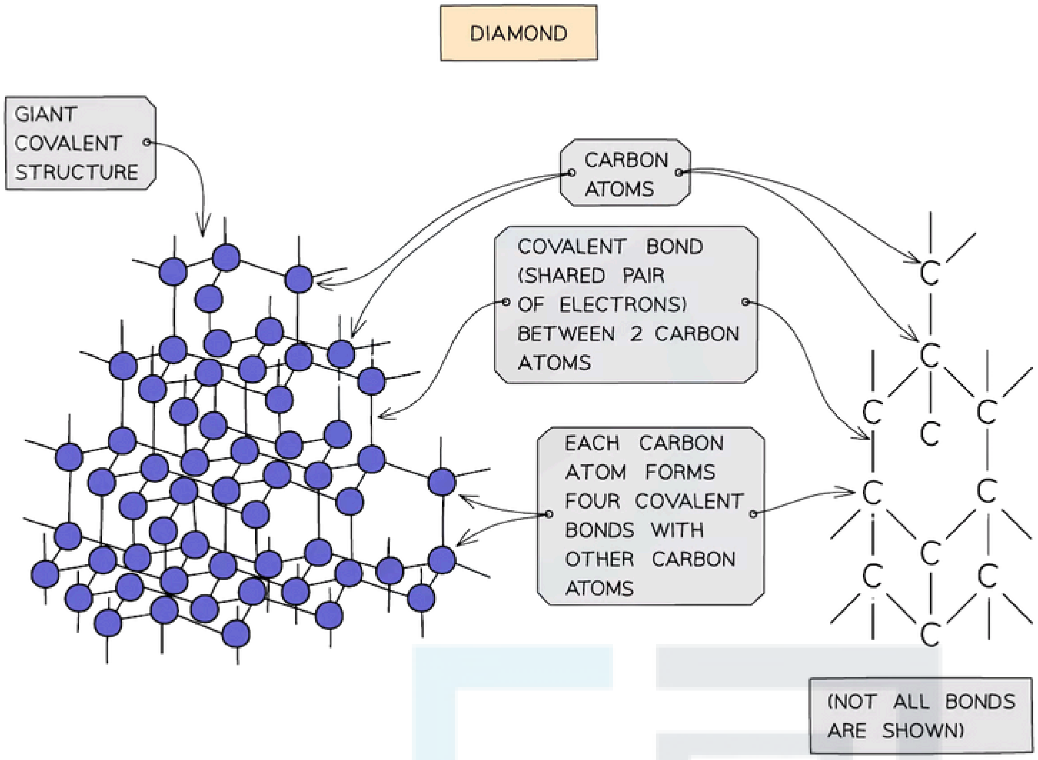
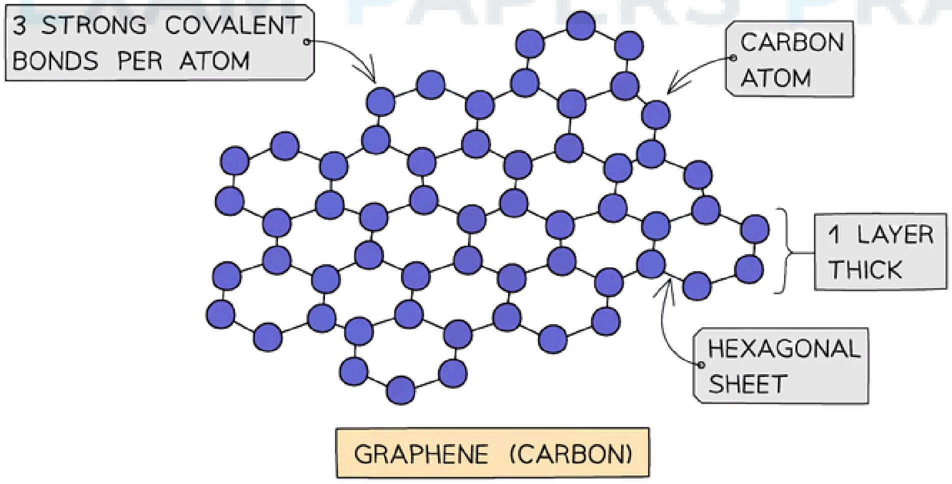


Diagram showing the structure and bonding arrangement in diamond

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**

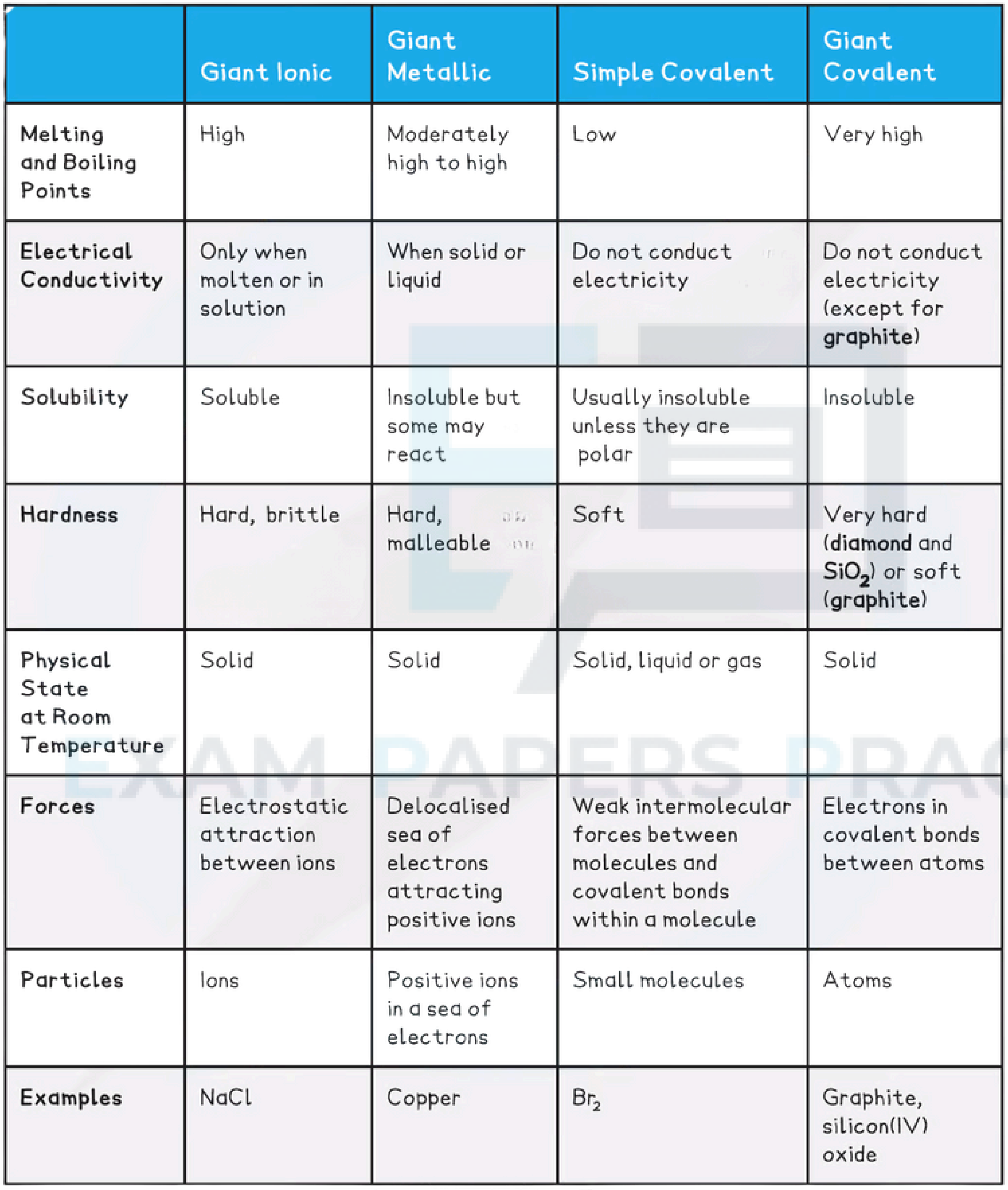


Graphene is a truly remarkable material that has some unexpected properties

Predicting Structure & Bonding

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

Characteristics of Different Compound Structure Types Table

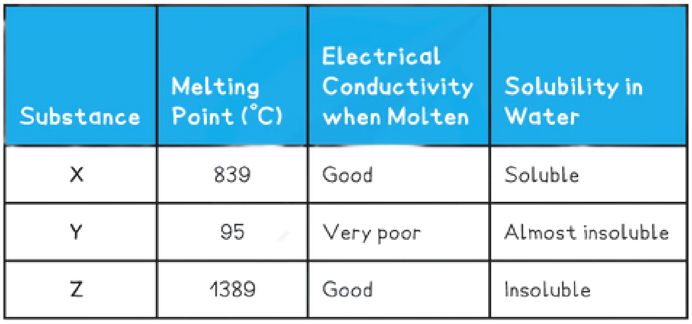


	Giant Ionic	Giant Metallic	Simple Covalent	Giant Covalent
Melting and Boiling Points	High	Moderately high to high	Low	Very high
Electrical Conductivity	Only when molten or in solution	When solid or liquid	Do not conduct electricity	Do not conduct electricity (except for **graphite**)
Solubility	Soluble	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

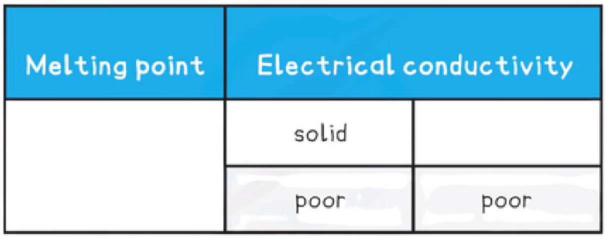
Answer

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.**

Worked Example

Bonding & structure Compound X has the following properties:



Melting point	Electrical conductivity	
	solid	
	poor	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

1.6 Formulae, Equations & Avogadro

1.6.1 Empirical & Molecular Formulae

Empirical & Molecular Formula Definitions

- The **molecularformula** isthe formulathat shows the**number**and**type** of each atom in a molecule
  - E.g. the molecular formula of ethanoic acid is $C2H4O2$
- 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 $CH2O$

Empirical & Molecular Formula Calculations

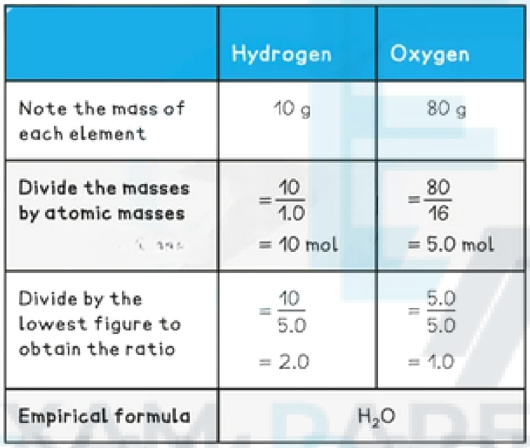
Empirical formula

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

Worked Example

Empirical formula from mass

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



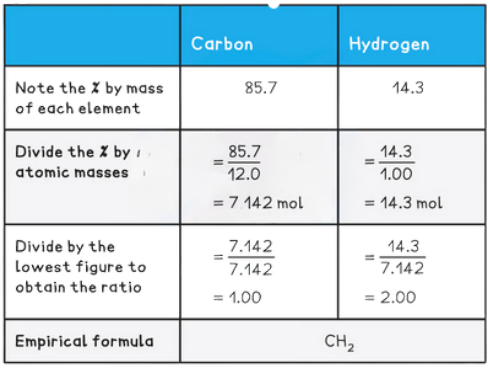
	Hydrogen	Oxygen
Note the mass of each element	10 g	80 g
Divide the masses by atomic masses	$= \frac{10}{1.0}$ $= 10$ mol	$= \frac{80}{16}$ $= 5.0$ mol
Divide by the lowest figure to obtain the ratio	$= \frac{10}{5.0}$ $= 2.0$	$= \frac{5.0}{5.0}$ $= 1.0$
Empirical formula	H_2O	

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

Worked Example

Empirical formula from %

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



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

Molecular formula

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

□

Worked Example

Calculating molecular formula

The empirical formula of X is C4H10S and the relative molecular mass of X is 180.2

What is the molecular formula of X?

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

Answer Step 1: Calculate relative mass of the empirical

formula

- Relative empirical mass = (C x 4) + (H x 10) + (S x 1)
- Relative empirical mass = (12.0 x 4) + (1.0 x 10) + (32.1 x 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 x 2) + (H10 x 2) + (S x 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 J mol^{-1} 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

☐ **Worked Example**

Anunknown 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 oC 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: $\frac{(100 - 66.7 - 11.1)}{160}$ = 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: $\frac{1.3875}{1.3875}$ = 1

Step 3: State the empirical formula

- The empirical formula is C4H8O

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

- $n = \frac{PV}{RT} = \frac{(101\times103)\times(56.0\times10-6)}{8.31\times(90+273)} = 1.875 \times 10^{-3}$ moles

Step 5: Calculate the molar mass

- Molar mass $= \frac{0.135}{1.875\times10^{-3}} = 72$

Step 6: Deduce the molecular formula

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

1.6.4 The Mole & the Avogadro Constant

The Mole & Avogadro

- The **Avogadro constant** (N_A or L) is the numberofparticles 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 **6.02×10^{23} $g\,mol^{-1}$**
- 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:

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

- 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 x 1 + 16) = 18 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, $H_2O = (2 \times 1.0) + 16.0 = 18.0\ g\,mol^{-1}$
2. Moles = $\frac{mass}{molar\ mass} = \frac{100}{18.0} = 5.56$ moles (to 3 s.f.)
3. Number of molecules = number of moles x Avogadro's constant = 5.56 x (6.02×10^{23}) = 3.35×10^{24} 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:

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

Mass = moles x molar mass = (8.31 x10-16) x 195.1 = 1.62 x 10-13 g (lots of atoms, a tiny mass)

Answer 2: Molar mass of ethanol, C_2H_5OH = (2 x 12.0) + (5 x 1.0) +16.0 +1.0=46.0gmol^{-1}

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

Mass = moles x molar mass = 0.0218 x 46.0 = 1.00 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 x 1023 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

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 oC 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 oC and 101.3 kPa respectively
- The equation to calculate the number of moles for any volume of gas is:

$$\text{Number of moles} = \frac{\text{Volume of gas}\,(\text{dm3})}{\text{Molargasvolume}\,(\text{dm3})}$$

☐ 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. $\text{Number of moles} = \frac{\text{Volume of gas}\,(\text{dm3})}{\text{Molar gas volume}\,(\text{dm3})} = \frac{4.5}{24} = 0.1875 \text{ moles}$
2. $\text{Number of moles} = \frac{\text{Volume of gas}\,(\text{dm3})}{\text{Molargasvolume}\,(\text{dm3})} = \frac{4.5}{22.4} = 0.201 \text{ moles (to 3 s.f.)}$

- 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

☐ 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

- 2Na (s) + H2O (l) → 2NaOH (aq) + H2 (g)

Step 2: Calculate the number of moles of sodium

- Number of moles = $\frac{\text{mass (g)}}{\text{molarmass (gmol}^{-1})} = \frac{1.5}{23.0}$ = 0.0652 moles (to 3s.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 $\frac{0.065}{2\ 2}$ = 0.0326 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 x 22.4 = 0.730 dm3 (to 3s.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

- C3H8 (g) + 5O2 (g) → 3CO2 (g) + 4H2O (g)

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 x 6.50 dm3 of gas = 45.5 dm3 gas

Ideal Gases

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**idealgas 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 (m3)
- n = number of moles of gas (mol)
- R= gas constant (8.31 J K-1 mol-1)
- T = temperature (kelvin, K)

☐ Worked Example

Calculating the volume of a gas Calculate the volume occupied by 0.781

mol of oxygen at a pressure of 220
kPa and a temperature of 21 °C

Answer Step 1: Rearrange the ideal gas equation to find

volume of gas

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

Step 2: Calculate the volume the oxygen gas occupies

- P = 220 kPa = 220 000 Pa
- n = 0.781 mol
- R = 8.31 J K-1 mol-1
- T = 21 oC = 294 K

$$V = \frac{0.781 \times 8.31 \times 294}{220000} = 0.00867 \text{ m3} = 8.67 \text{ dm3}$$

☐ ## 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 kPa = 300 000 Pa
- V = 1000 cm3 = 1 dm3 = 0.001 m3
- R = 8.31 J K-1 mol-1
- T = 23 oC = 296 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

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

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

☐ ## Exam Tip

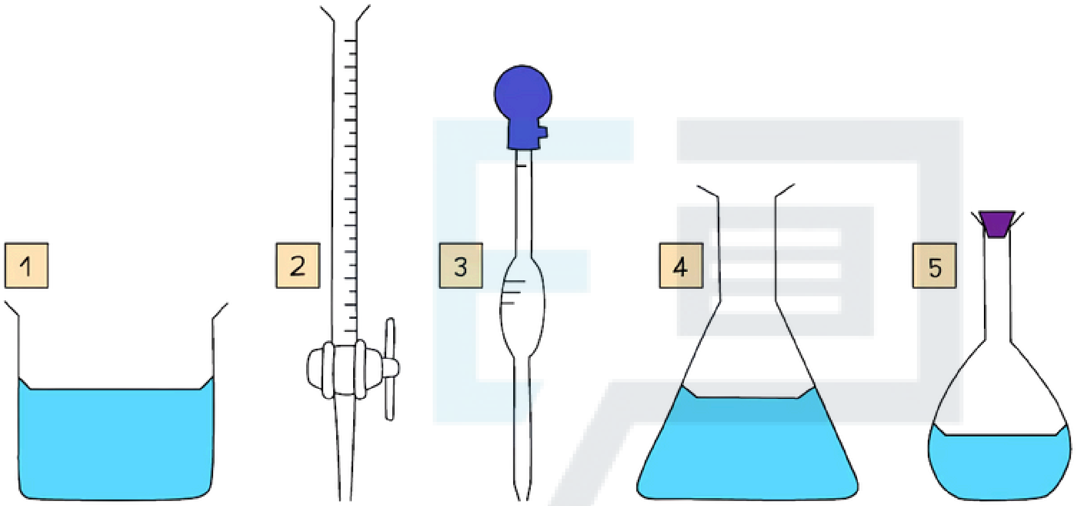
To calculate the temperature in **Kelvin**, add 273 to the Celsius temperature, e.g. 100 oC is 373 Kelvin.

You must be able to rearrange the ideal gas equation to work out all parts of it.
The **units** are incredibly important in this equation - make sure you know what units you should use, and do the necessary conversions when doing your calculations!

Titration Calculations

Volumetric Analysis

- Volumetricanalysisis 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

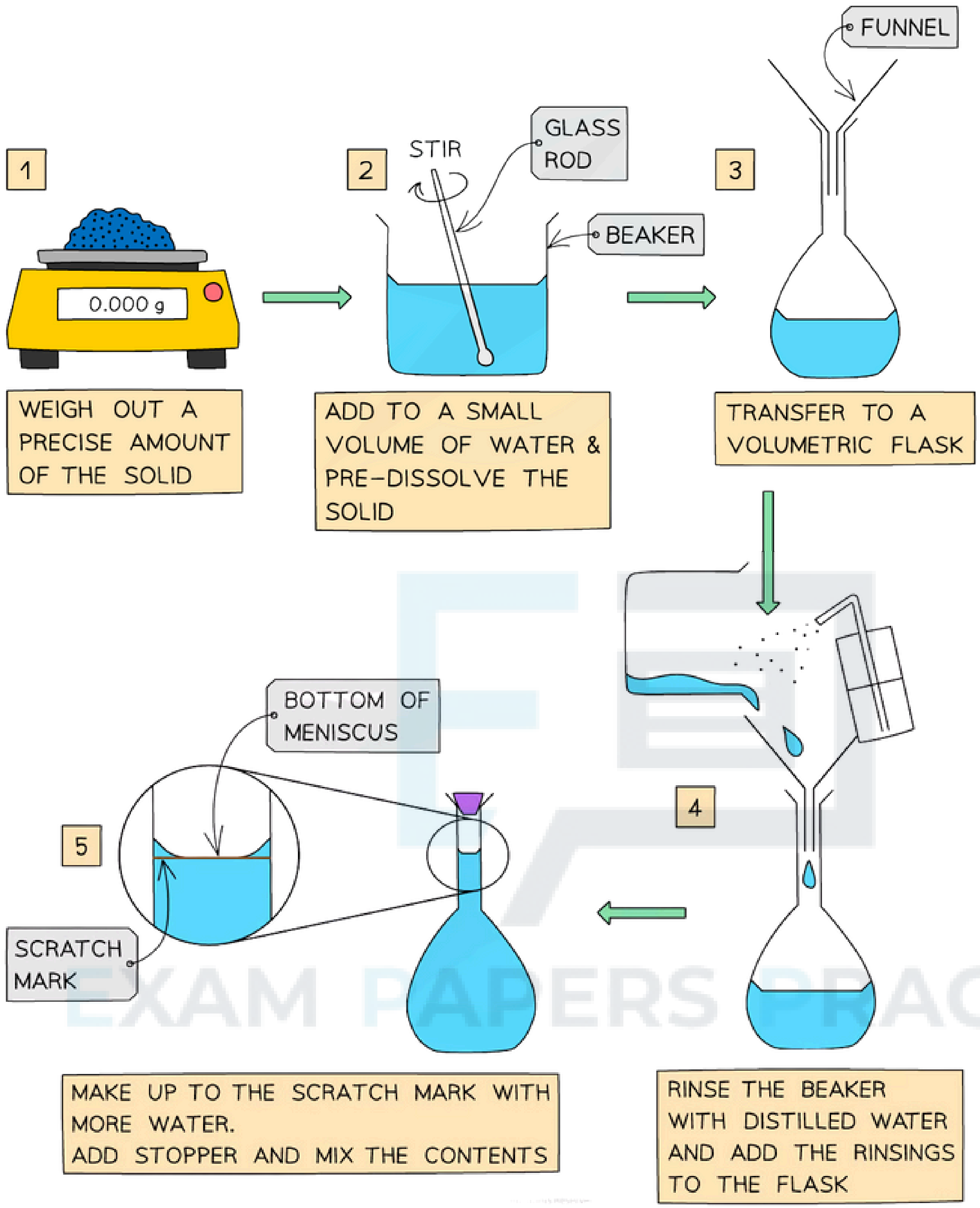


Some key pieces of apparatus used toprepare a volumetric solution and perform a simpletitration

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

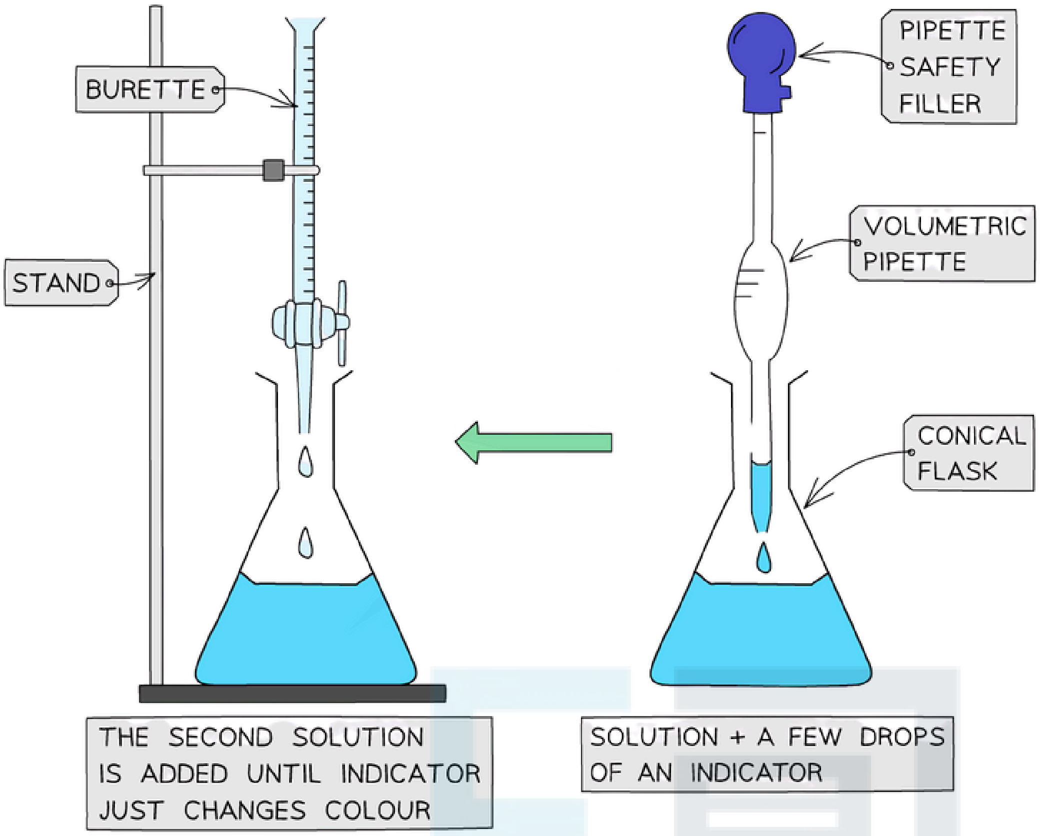
Making a Standard Solution

- 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:



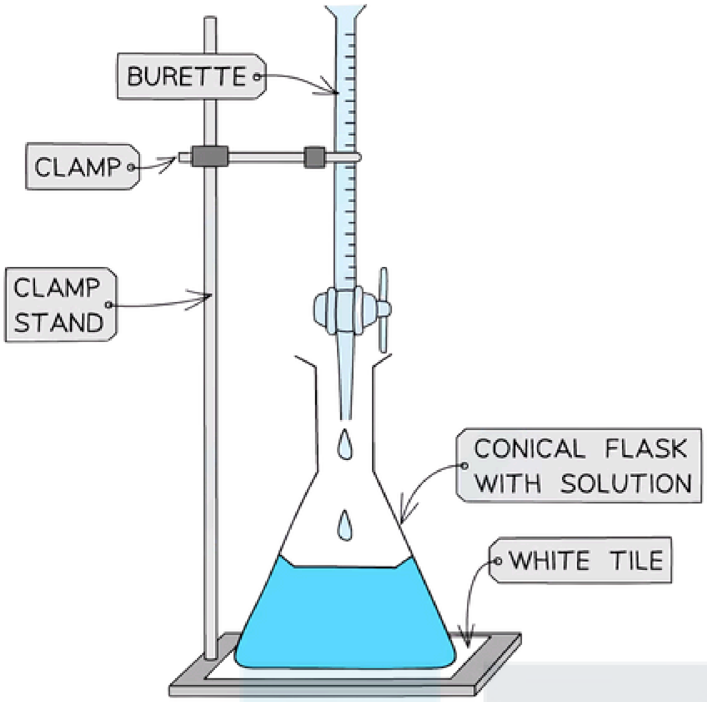
Performing the Titration

- Thekey 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**



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

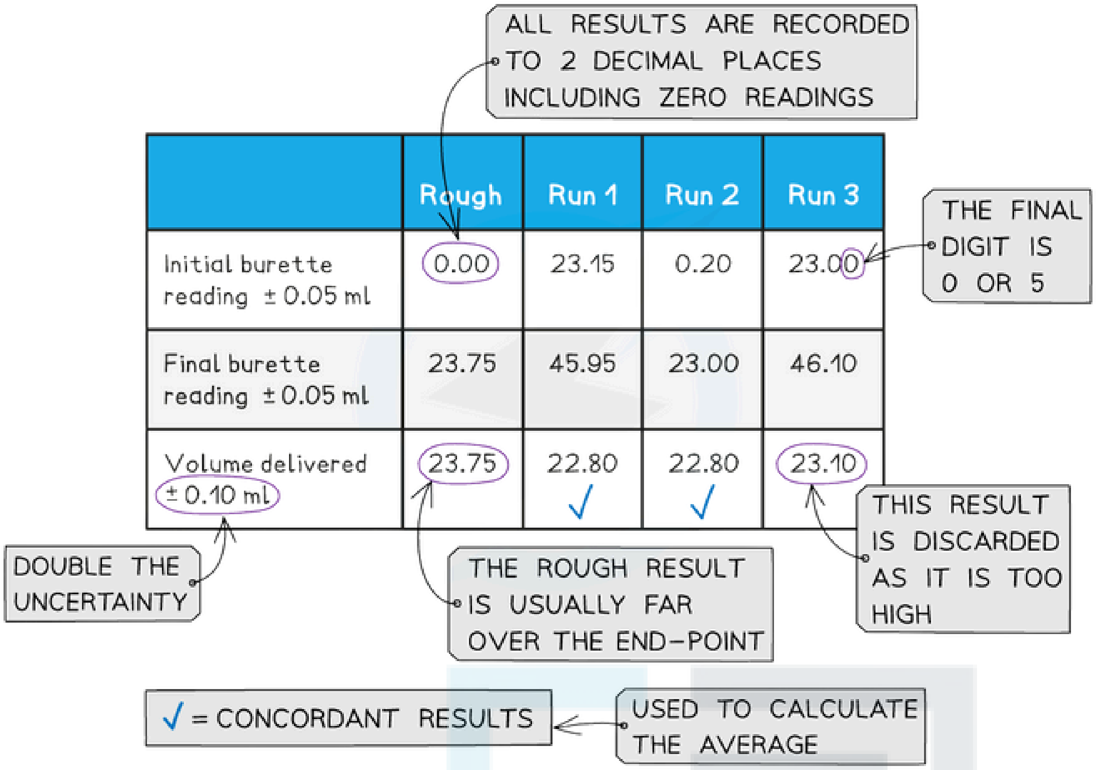


The steps in a titration

- 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



	Rough	Run 1	Run 2	Run 3
Initial burette reading ± 0.05 ml	0.00	23.15	0.20	23.00
Final burette reading ± 0.05 ml	23.75	45.95	23.00	46.10
Volume delivered ± 0.10 ml	23.75	22.80 ✓	22.80 ✓	23.10

ALL RESULTS ARE RECORDED TO 2 DECIMAL PLACES INCLUDING ZERO READINGS

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 ±0.10 cm3
    - The uncertainty is doubled, because two burette readings are made to obtain the titre (V final – V 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 dm3 of **solution**
    - The solute is the substance that dissolves in a solvent to form a solution
    - The solvent is often water

$$\text{Concentration (mol dm-3)} = \frac{\text{numberofmolesofsolute (mol)}}{\text{volumeofsolution (dm3)}}$$

- A **concentrated** solution is a solution that has a **high** concentration of solute A
- **dilute** solution is a solution with a **low** concentration of solute When carrying
- out calculations involve concentrations in mol dm-3 the following points need to be considered:
    - Change mass in grams to **moles**
    - Change cm3 to dm3

- To calculate the **mass** of a substance present in solution of known **concentration and volume**:
  - Rearrange the concentration equation

number of moles (mol) = concentration (mol dm-3) x volume (dm3)

- Multiply the moles of solute by its molar mass

mass of solute (g) = number of moles (mol) x molar mass (g mol-1)

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

Na2CO3 + 2HCl → 2NaCl + H2O + CO2

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

- Amount (Na_2CO_3) = 0.025 dm3 x 0.050 mol dm-3 = 0.00125 mol

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

- 1 mol of 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

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

1.7.3 Error & Uncertainty

Error & Uncertainty

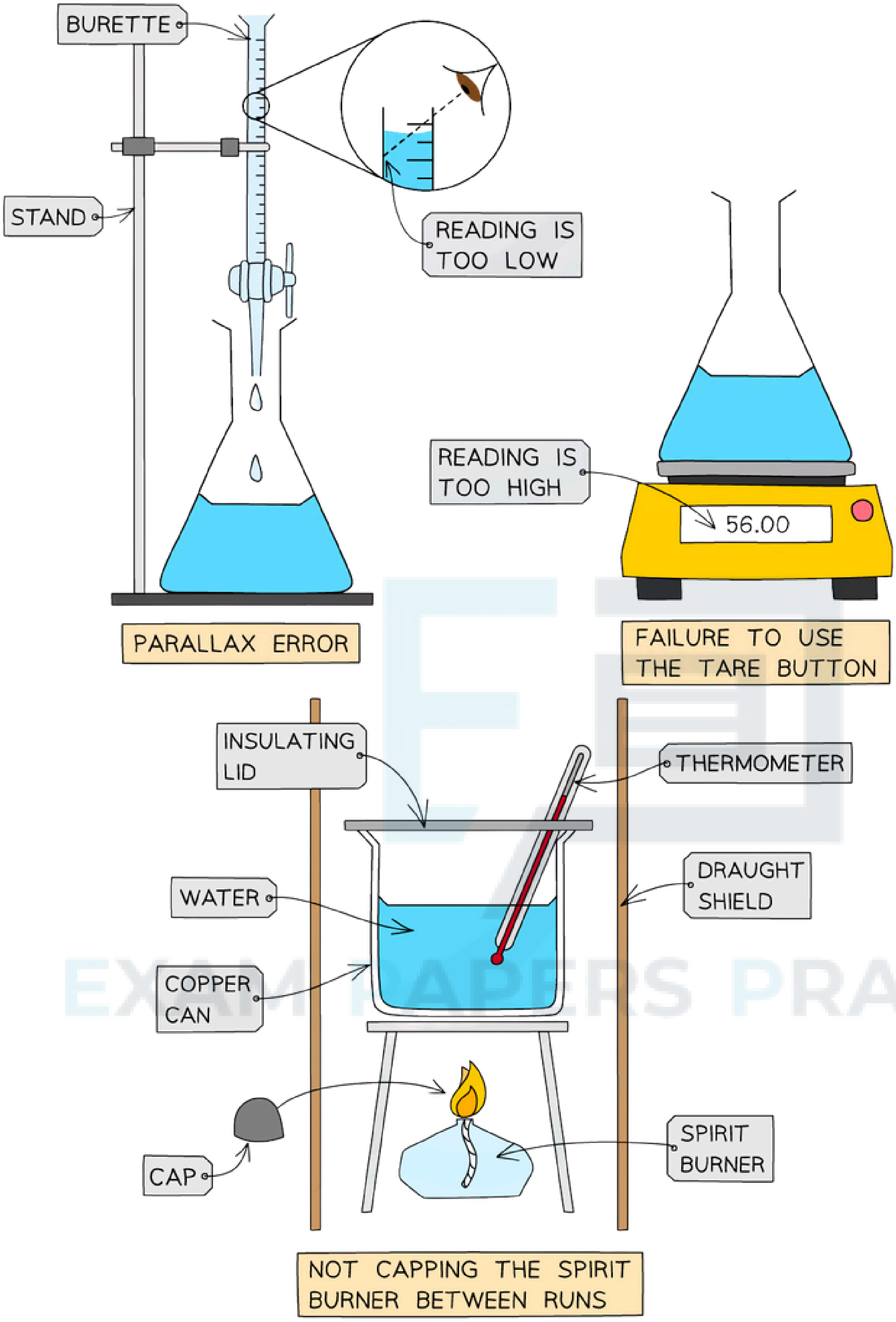
- An error is the differencebetween a value or quantityobtained in an experiment and an accepted or literature value for an experiment There are two types of
- errors in experiments, **random errors** and **systematic errors**

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** are 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



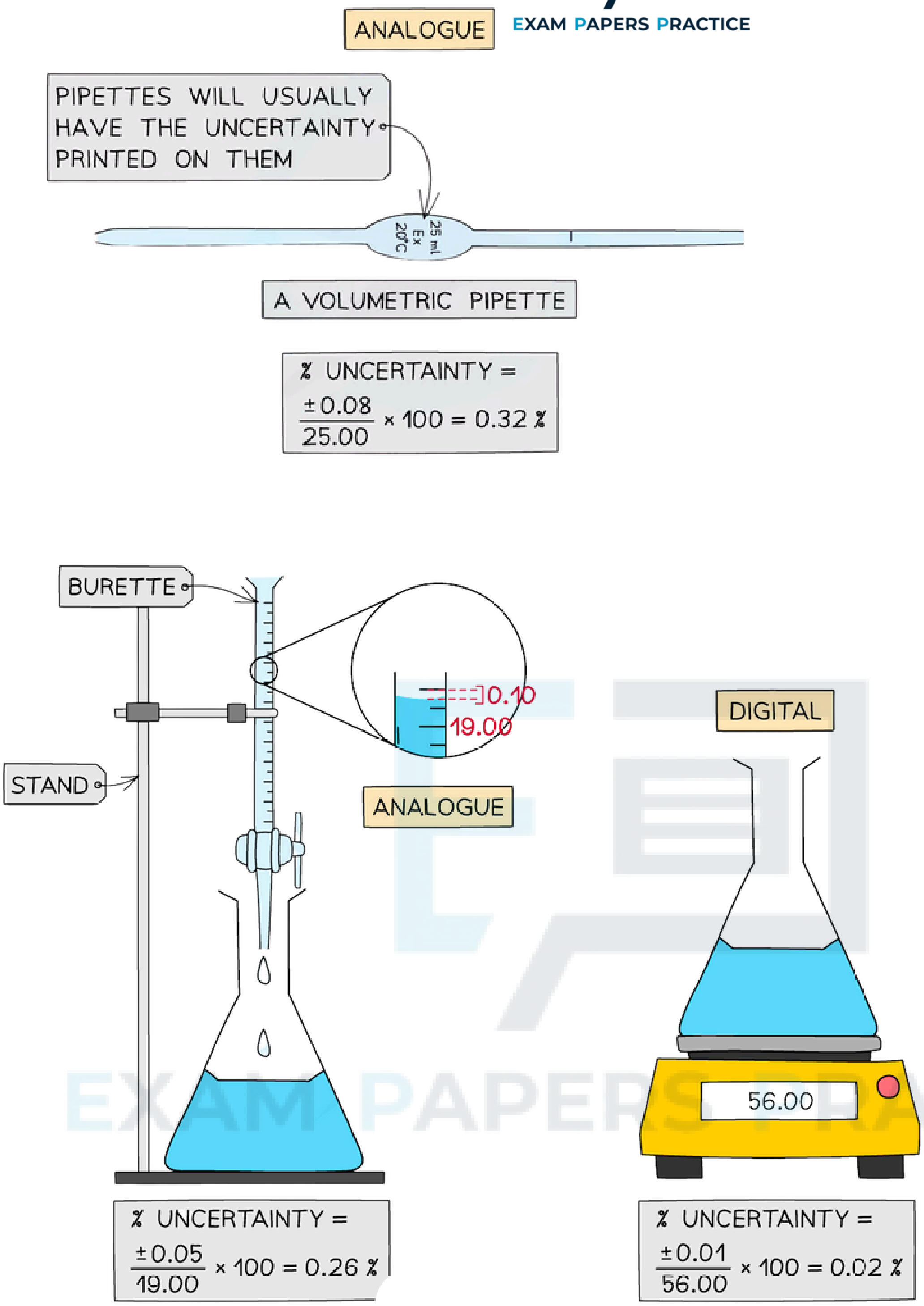
Systematic errors

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:

$$\text{Percentage uncertainty} = \frac{\text{absoluteuncertainty}}{\text{measuredvalue}} \times 100$$

- Some examples of percentage uncertainty calculations for common laboratory apparatus:



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 you 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

Yield & Atom Economy

Percentage yield

- Inalot 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:

$$\textit{percentage yield} = \frac{\textit{actualyield}}{\textit{theoreticalyield}} \times 10$$

0

  - 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**

Inan experiment todisplace 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:

Zn (s) + $CuSO4$ (aq) → $ZnSO4$ (aq) + Cu (s)

Step 2: Calculate the amount of zinc reacted in moles

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

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

Sincetheratio of Zn(s) to Cu(s) is 1:1 a maximum of 0.10molescanbeproduced

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

mass = mol x M
mass = 0.10 mol x 63.55 g mol^{-1}
mass = 6.4 g (2 sig figs)

Step 5: Calculate the percentage yield of copper

$$percentage\ yield = \frac{4.8\ g}{6.4\ g} \times 100 = 75\%$$

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 *Mr* of the desired product

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

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

CH_2=CH_2 + Br_2 → CH_2BrCH_2Br

- The atom economy could also be calculatedusing mass, instead or *Mr*
    - In this case, you would divide the massofthe desired product formed by the total mass of all reactants, and then multiply by 100
- Questions about atom economy often ask inqualitative or quantitative terms

☐ Worked Example

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

Hydration of ethene: $C_2H_4 + H_2O \rightarrow C_2H_5OH$

Substitution of bromoethane: $C_2H_5Br + NaOH \rightarrow C_2H_5OH + NaBr$

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.

Fe2O3 + 3CO → 2Fe + 3CO2

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

(*Ar* / *Mr* data: Fe2O3 = 159.6, CO = 28.0, Fe = 55.8, CO2 = 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

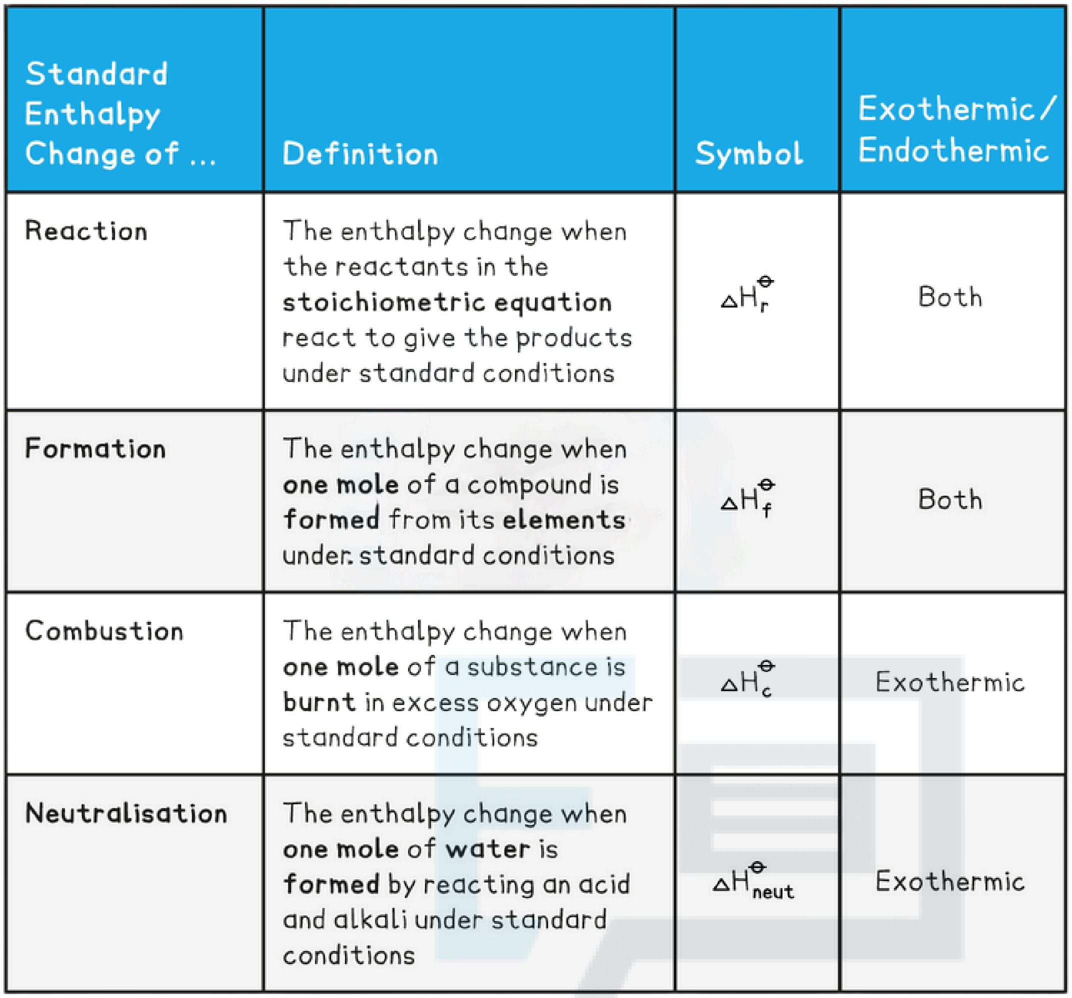
Enthalpy Change Definitions

- To be able to comparethe changes in enthalpy betweenreactions, 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 oC)
  - Each substance involved in the reaction is in its **standard physical state** (solid, liquid or gas)

- To show that a reaction has been carried out under standard conditions, the symbol   is used
  - ΔH = the standard enthalpy change

- There are a number of key definitions relating to enthalpy changes that you need to know

Enthalpy Definitions Table



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

☐ Exam Tip

Youwillseevarious enthalpy change symbols used with subtle changes, e.g.

ΔH^c or ΔcH for enthalpy of combustion

Whichever symbol you use must have the following basic points:

- Δ to represent change
- *H* to represent enthlalpy
- to respresent 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

$H_2(g) + ½O_2(g) \rightarrow H_2O (l)$ $\Delta H r = -286 \text{ kJ mol}^{-1}$

Calculate $\Delta H\ r$ for the reaction below:

2H2 (g) + O2 (g) → 2H2O (l)

A n s w e r

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

☐ Worked Example

Calculating the enthalpy change Calculate ΔH_f for the reaction below, giventhat ΔHf [Fe2O3(s)] = -824.2 kJ mol^{-1}

4Fe(s) + 3 O2(g) → 2 Fe2O3(s)

A n s w e r

- Since two moles of Fe2O3 (s) are formed the total change in enthalpy for the reaction above is:
- ΔH_f = 2 x (-824.2 kJ mol-1) = - 1648 kJ

☐ Worked Example

Calculating enthalpy changes

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

1. MgCO3 (s) → MgO (s) + CO2 (g)
2. C (graphite) + O2 (g) → CO2 (g)
3. HCl (aq) + NaOH (aq) → NaCl (aq) + H2O (l)

Answer

Answer 1: *ΔH r*

Answer 2: *ΔH f* as one mole of CO2 is formed from its elements in standard state *and ΔH c* as one mole of carbon is burnt in oxygen

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

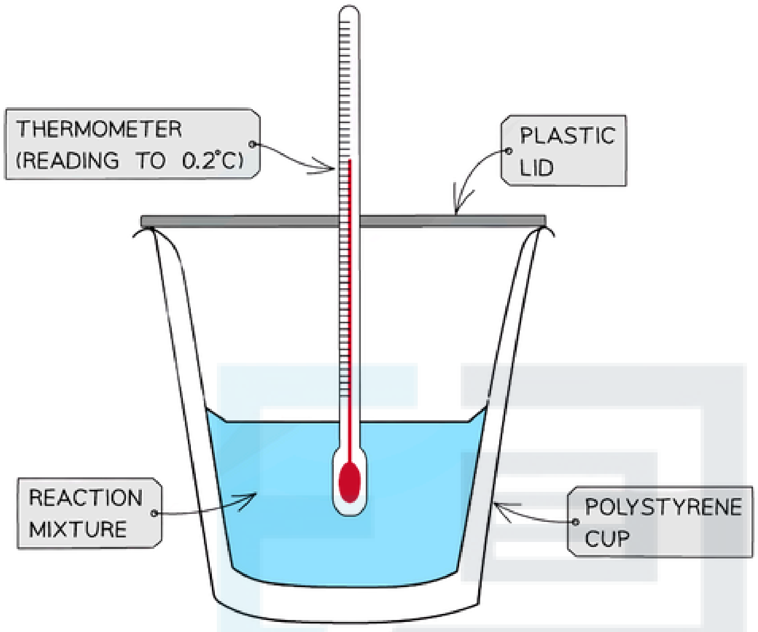
Exam Tip

The ΔH_f of an **element** in its standard state is zero. For example, ΔH_f of $O_2(g)$ is 0 kJ^{1}mol

Calculating Energy Transferred, Q

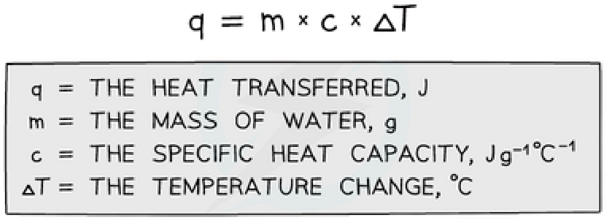
Measuring enthalpychanges

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



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 oC 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:



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* x *c* x
- Δ*T* *m* (of water) = 500 g
- *c* (of water) = 4.18 J g-1 °C-1
- Δ*T* (of water) = 68 oC - 25 oC = 43 oC

Step 2:

- *q* = 500 x 4.18 x 43 = 89 870

Step 3:J

- This is only 30% of the total energy released by methane
- Total energy x 0.3 = 89 870 J
- Total energy = 299 567 J

Step 4:

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

Calculating Enthalpy Changes

- Aqueous solutions of acid, alkalis and saltsare 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 n

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

- 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 (*Mr* = 58.0) underwent complete combustion.
The heat formed raised the temperature of 100 g of water from 20 oC to 75 oC.

Calculate the enthalpy of combustion for the organic liquid

Answer Step 1: Calculate the energy released by the

organic liquid

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

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

- Number of moles $\frac{mass}{molarmass} = \frac{150}{580} = 0.0259$ moles (to 3s.f.)

Step 3: Calculate the enthalpy change of combustion

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

1.8.4 Hess Cycles

Constructing Hess Cycles

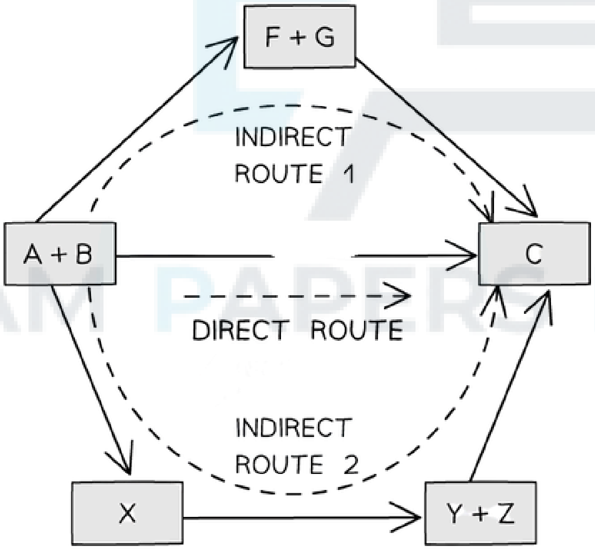
- In 1840, the Russian chemistGermain Hess formulatedalaw which went on to be known as **Hess's Law**
- This went on to form the basis of one of the laws of thermodynamics. The first law of thermodynamics relates to the **Law of Conservation of Energy**
- It is sometimes expressed in the following form:

> *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

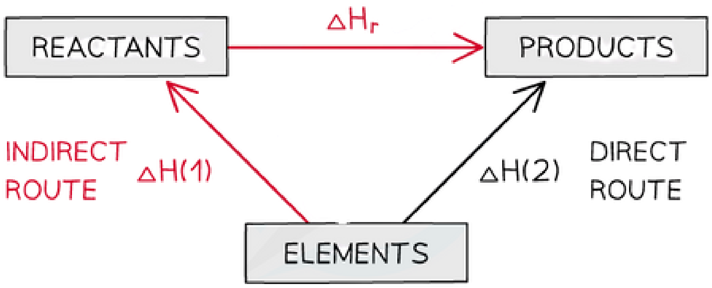
- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using **calorimetry**, e.g.:

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$$

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

Calculating $\Delta_r H$ 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

Hess Cycle Calculations

- Hess cycles can be usedto calculate various enthalpychanges as long as sufficient information about the other sides of the cycle is known

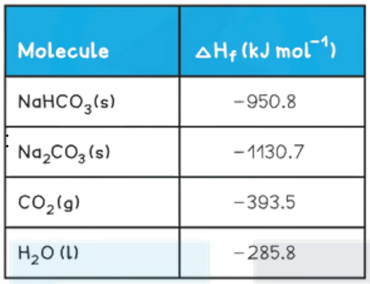
☐ Worked Example

Calculating the enthalpy change of reaction

Calculate the ΔHf for the following reaction:

$2NaHCO3 (s) \rightarrow Na2CO3 (s) + CO2 (g) + O(l)$

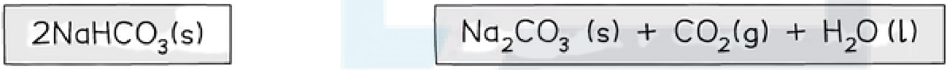
The table below shows the standard enthalpy of formations (ΔH_f) relevant to this reaction:



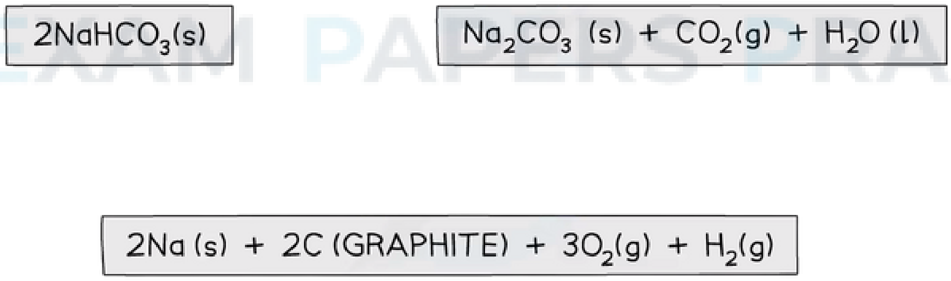
Molecule	ΔH_f (kJ mol^{-1})
$NaHCO_3(s)$	−950.8
$Na_2CO_3(s)$	−1130.7
$CO_2(g)$	−393.5
$H_2O(l)$	−285.8

Answer

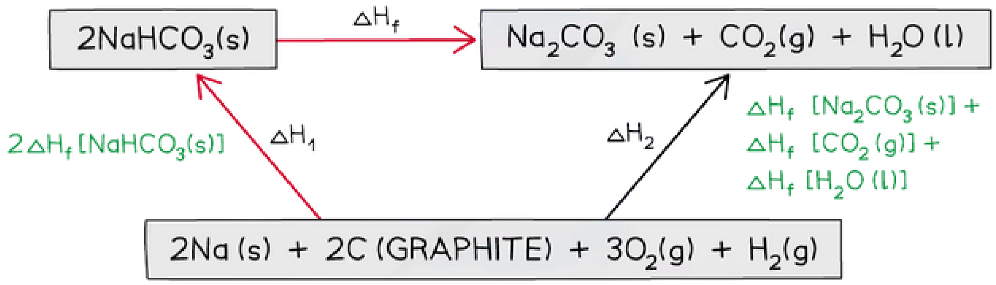
Step 1: Write the balanced equation at the top



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



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



Step 4: Apply Hess's Law

- ΔrH = ΔH2 - ΔH1
    - It is minus ΔH1 because you have to go in the opposite direction of the arrow
- ΔH2 is ΔfH [Na2CO3 (s)] + ΔfH [CO2 (g)] + ΔfH [H2O (l)] 1
- Δ is 2 x ΔfH [NaHCO3 (s)]
- ΔrH = (ΔfH [Na2CO3 (s)] + ΔfH [CO2 (g)] + ΔfH [H2O (l)]) - (2ΔfH [NaHCO3 (s)])
- ΔrH = ((-1130.7) + (-393.5) + (-285.8)) - (2 x (-950.8))
- ΔrH = +91.6 kJmol-1

☐ **Exam Tip**

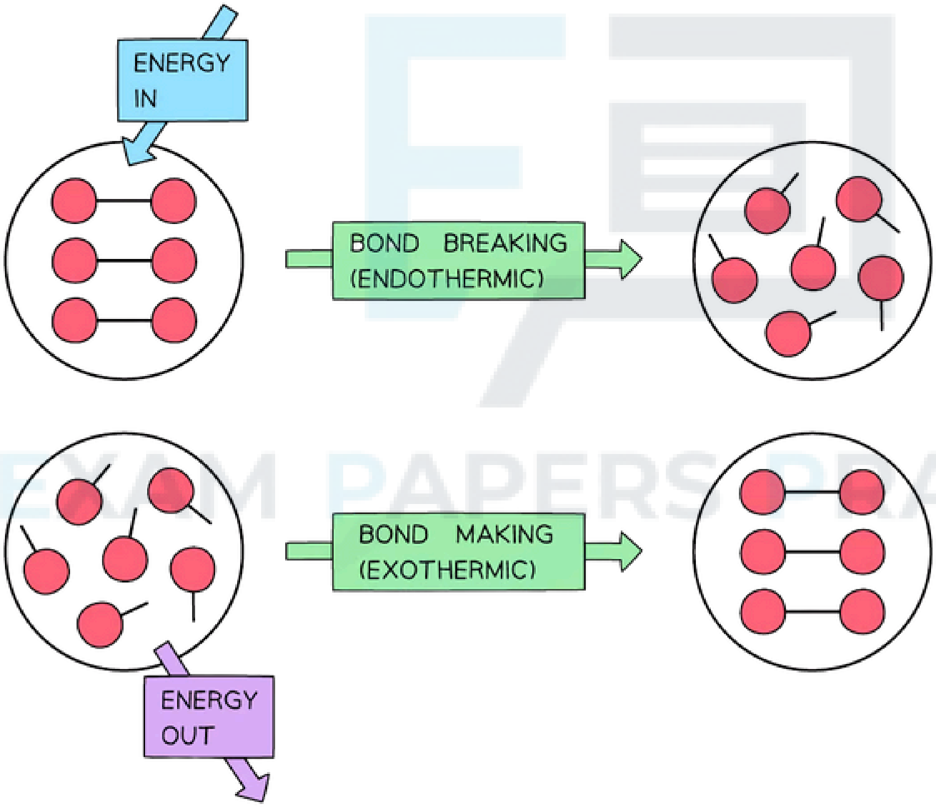
Keep your enthalpy values inside their own brackets so that you don't accidentally lose a minus sign

1.8.5 Bond Enthalpy

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

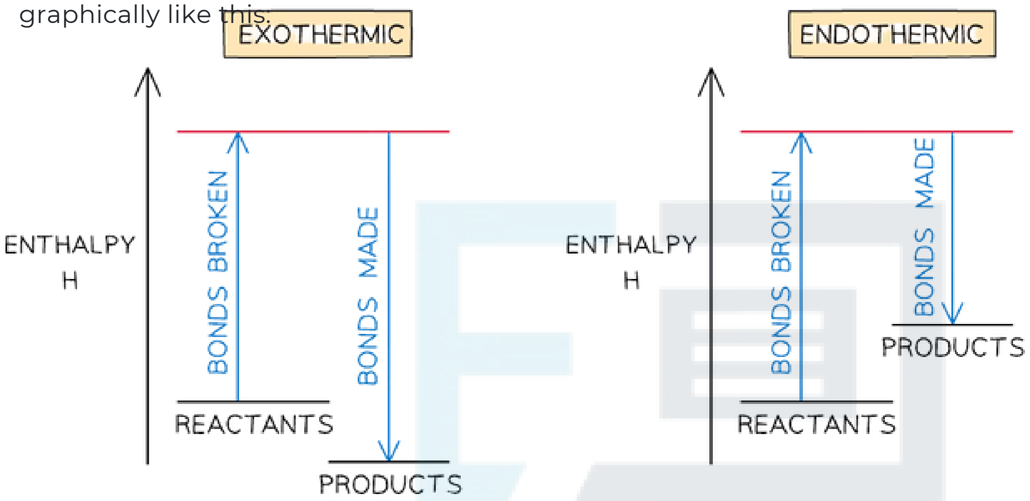


To break bonds energy is required from the surroundings and to make new bonds energy is released from the reaction to the surroundings

- 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:

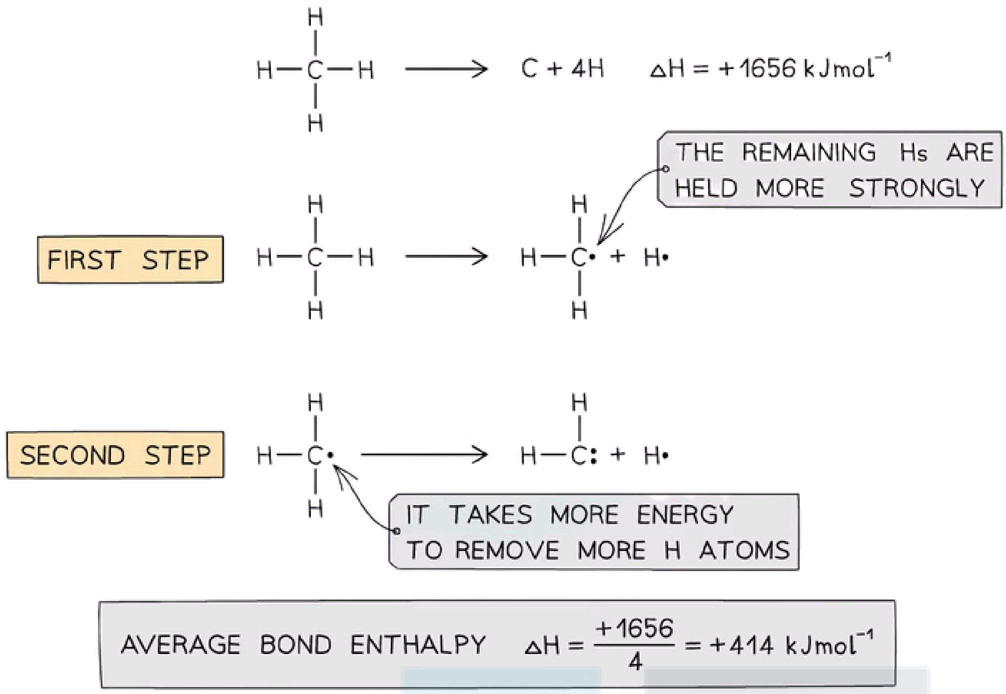


Bond enthalpy profiles

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'**



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'**

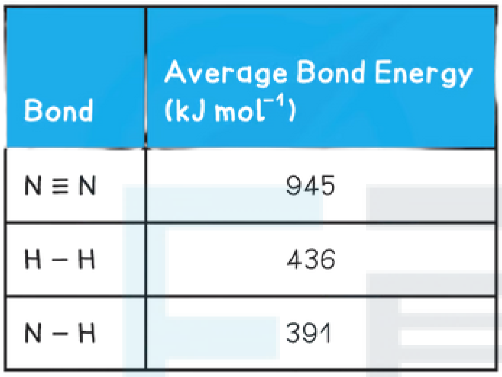
Calculating Bond Enthalpies

- ΔH_r of a reaction whenthis cannot be done
  Bond energies are usedtofind the experimentally
- The process is a step-by-step summation of the bond enthalpies of the all the molecules present finishing with this formula:

  $\Delta H\theta_{r}$ = enthalpy change for bonds broken + 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:

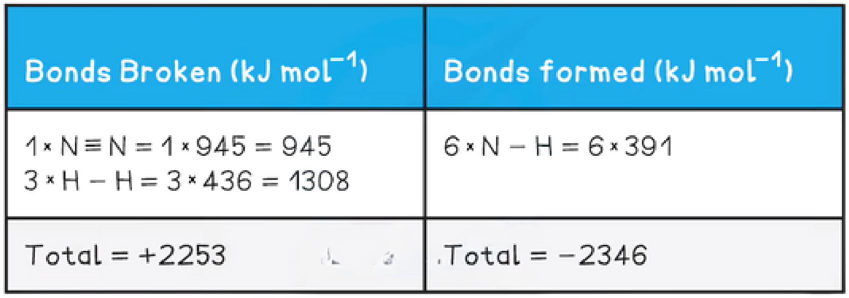


Bond	Average Bond Energy (kJ mol^{-1})
N ≡ N	945
H – H	436
N – H	391

Answer : **Step 1:** The chemical equation for the Haber process is: N2 (g) + 3H2 (g) ⇌ 2NH3 (g)

N≡N ⇌ 3 H-H ≡ 6 N-H

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



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

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

Step 3: Calculate the standard enthalpy of reaction

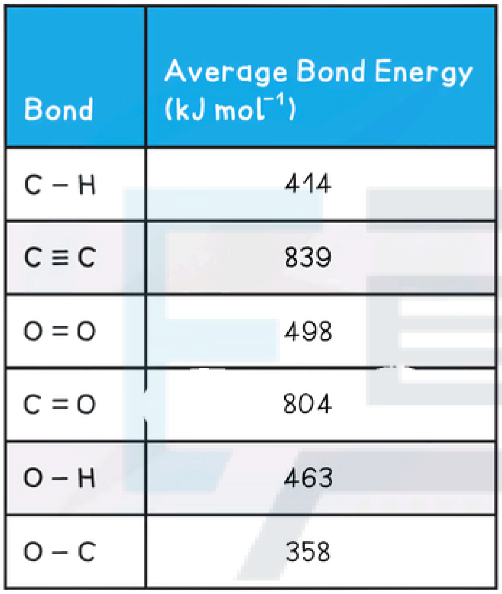
- $\Delta r H^\theta$ = enthalpy change for bonds broken + enthalpy change for bonds formed
- $\Delta_f H\theta$=(+2253kJmol-1)+(-2346 kJmol-1)
- $\Delta_r H\theta$ = -93 kJ mol^{-1}

☐ Worked Example

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

$$2C_2H_2\,(g) + 5\,O_2\,(g) \rightarrow 2H_2O\,(g) + 4CO_2\,(g)$$

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



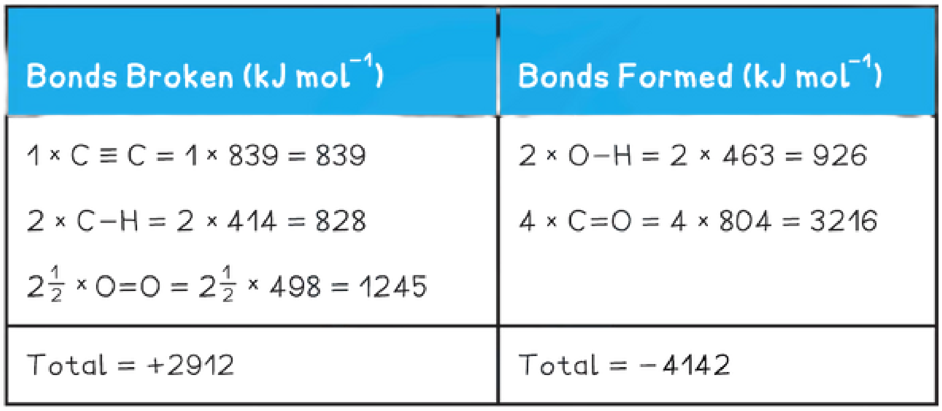
Bond	Average Bond Energy (kJ mol^{-1})
C – H	414
C ≡ C	839
O = O	498
C = O	804
O – H	463
O – C	358

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:

$$H\text{-}C{\equiv}C\text{-}H + 2\tfrac{1}{2}\,O{=}O \rightarrow H\text{-}O\text{-}H + 2O{=}C{=}O$$

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



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

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

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

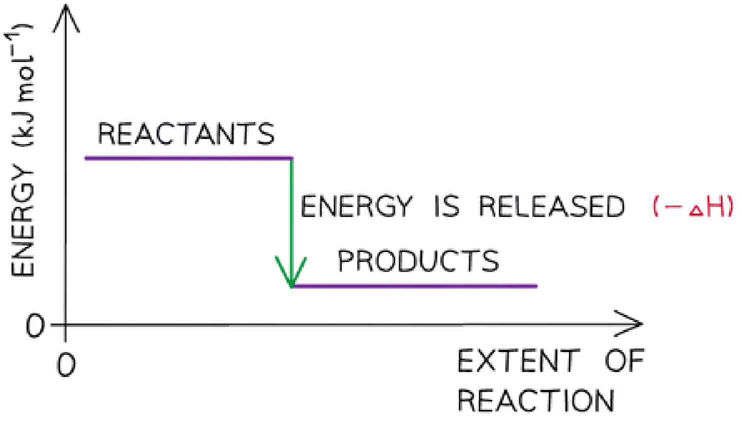
☐ Exam Tip

Activation energy is not shown in enthalpy level diagrams

Activation is shown in reaction profile diagrams

Exothermic reactions

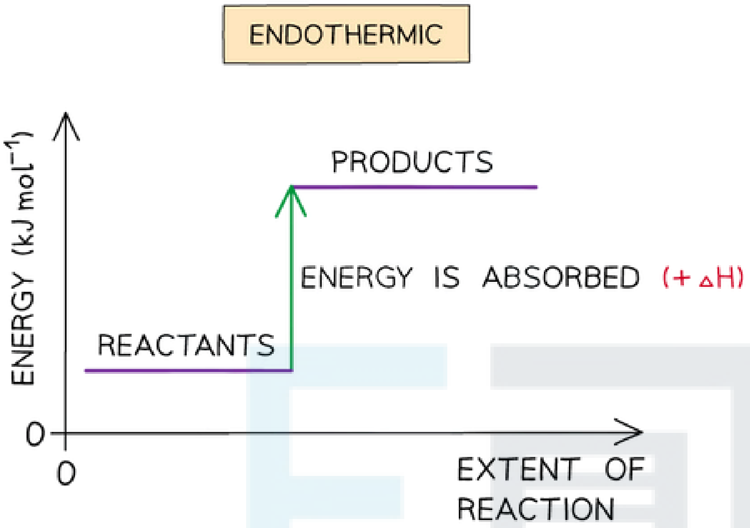
- A reaction is exothermic when the products have less energy than the reactants
- Heat energy is **given off** by the reaction **to the surroundings**
    - The **temperature** of the **environment increases** - this can be measured with a thermometer
    - The **energy** of the **system decreases**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

- Areactionis 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 Δ*H* is positive



The enthalpy change during an endothermic reaction

Exam Tip

Itis 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:

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

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

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

1.9 Kinetics

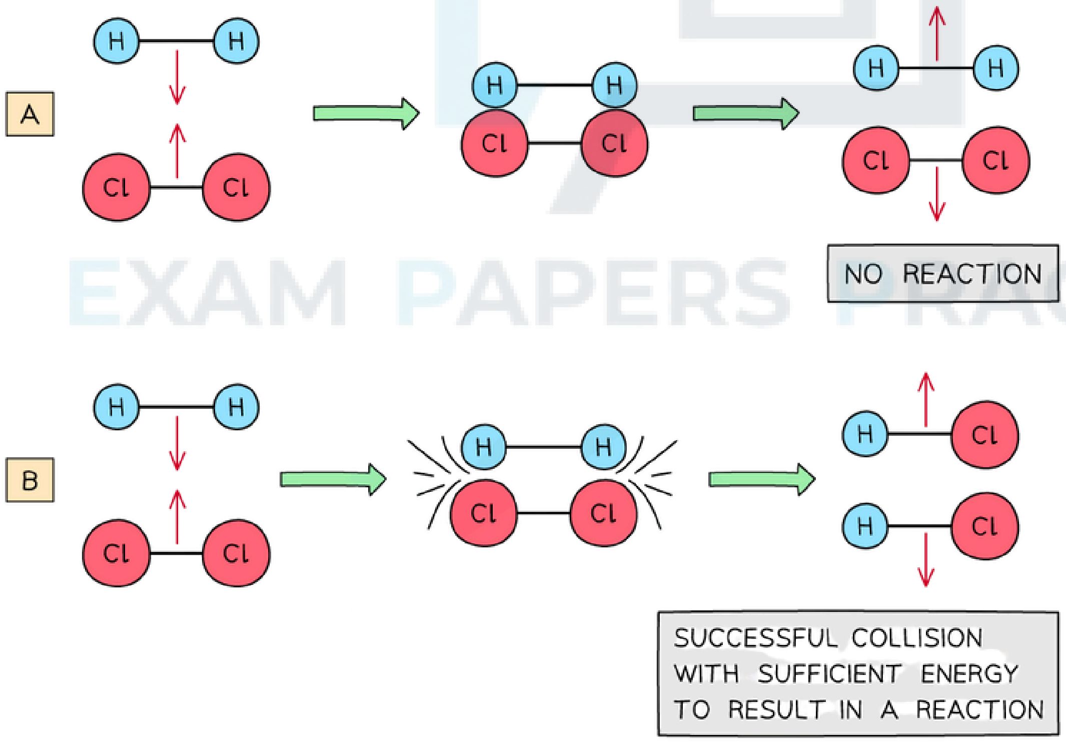
1.9.1 Collision Theory & Rates

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



(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

- Ifa 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

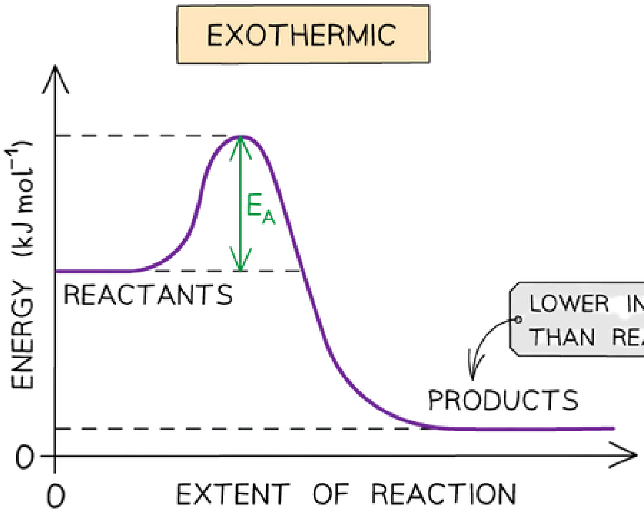
Collision energy

- Notallcollisions 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**

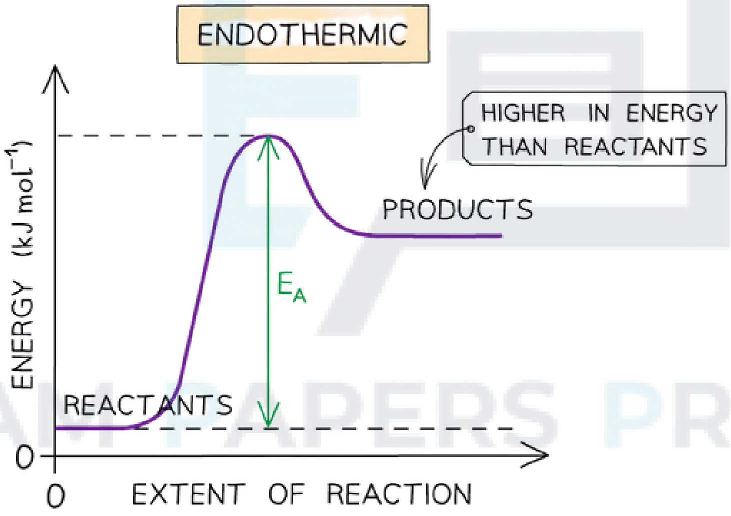
- **Unsuccessful collisions** happen when the colliding species do not have enough energy to break the necessary bonds
- If they do not have sufficient energy, the collision will not result in a chemical reaction
- If they have sufficient energy, they will react, and the collision will be successful

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 *Ea* 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 *Ea* 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 *Ea* 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

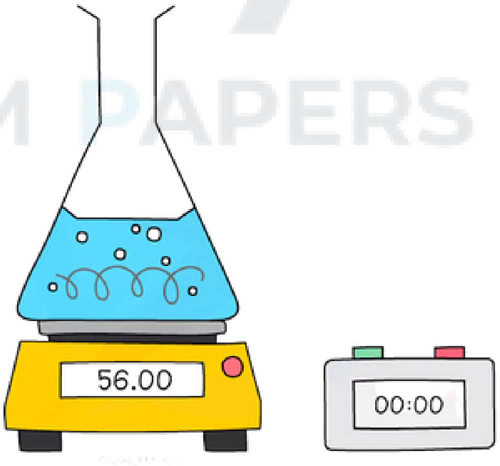
1.9.2 Calculating Rates of Reaction

Calculating Rates of Reaction

- To measure the **rate of a reaction**, weneed to be abletomeasure 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**

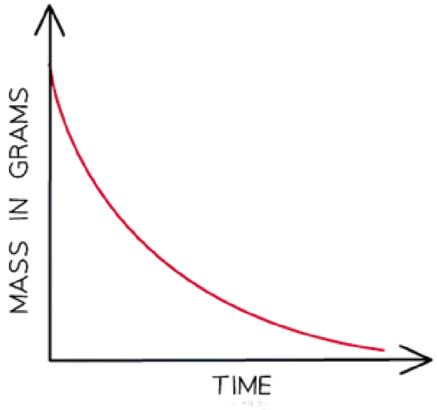
Changes in mass

- 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 CO2
  - The mass is measured every few seconds and change in mass over time is plotted as the CO2 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



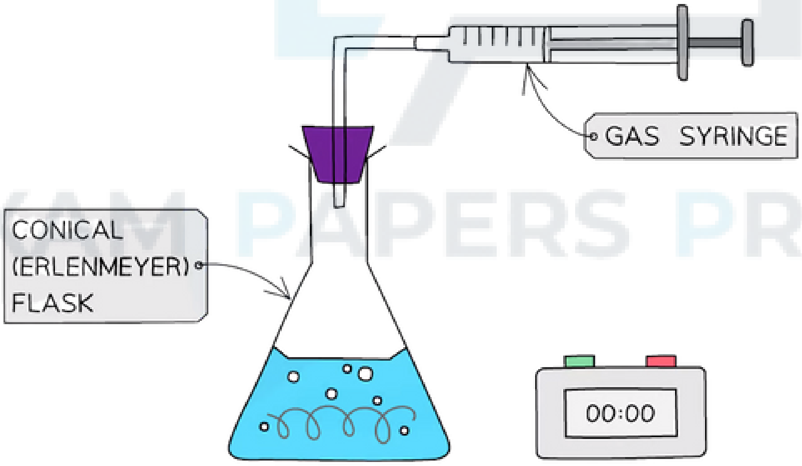
Mass loss of a product against time

- 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)

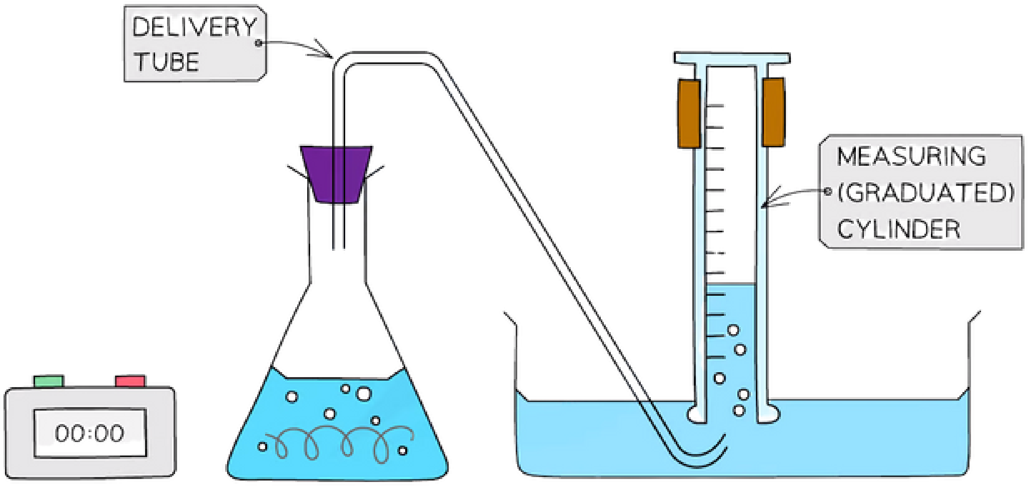
Volumes of gases

- 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



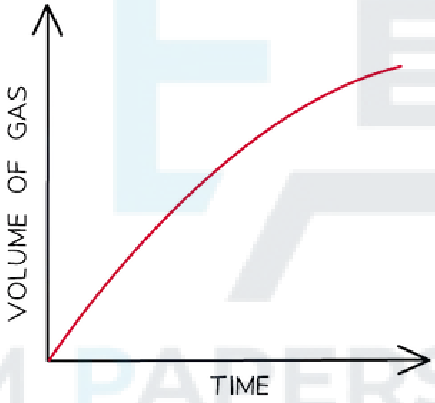
Collecting gases experimental set up

- 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

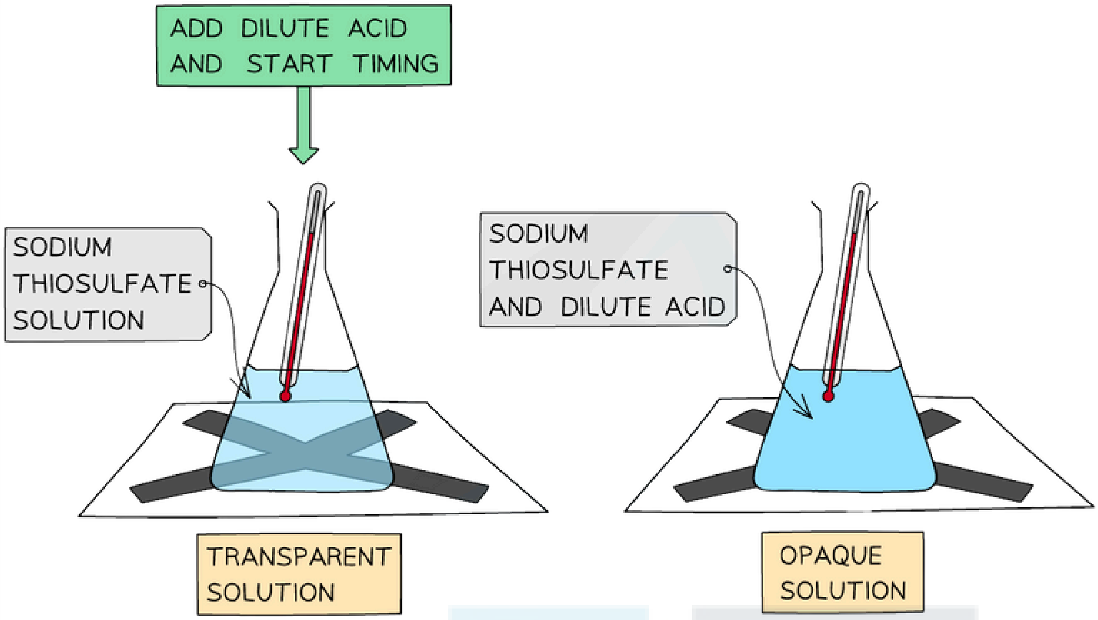


Graph of gas volume evolved against time

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:

$Na_2S_2O_3 (aq) + 2HCl (aq) \rightarrow 2NaCl (aq) + SO_2 (g) + H_2O (l) + S(s)$



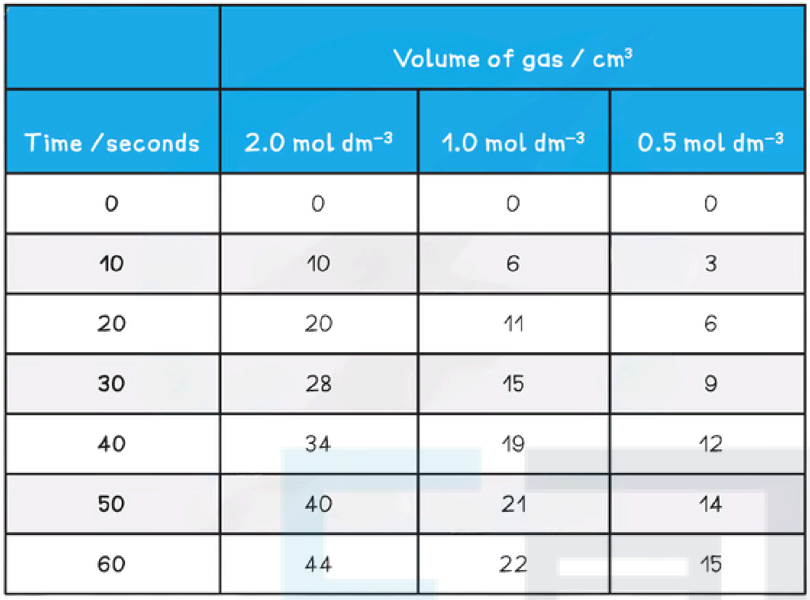
The disappearing cross experiment

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

Worked Example

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

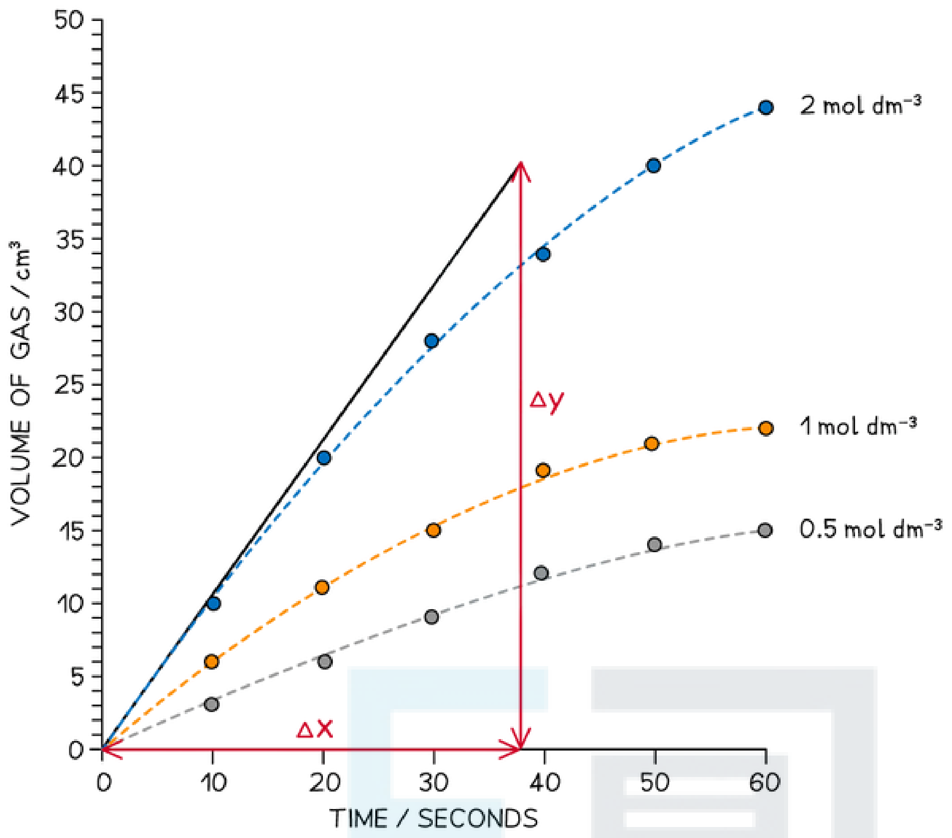
Mg (s) + 2HCl (aq) → MgCl2 (aq) + H2 (g)



	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



- 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 mol dm-3 s-1

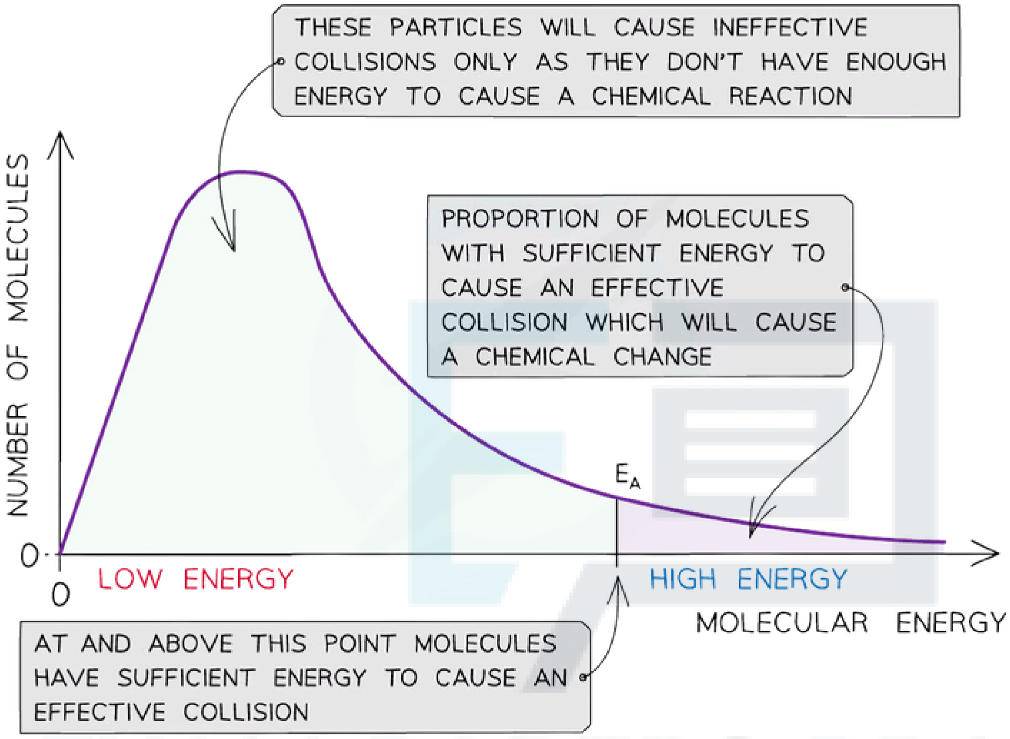
☐ Exam Tip

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

Temperature Effects

Maxwell-Boltzmann distributioncurve

- 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



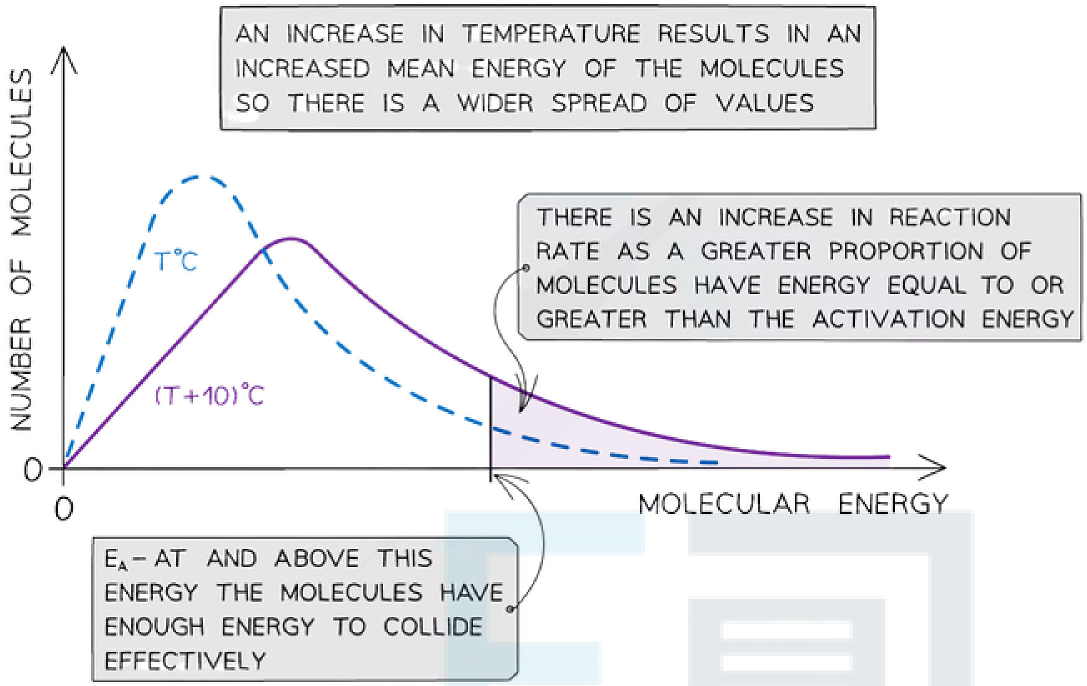
The Maxwell-Boltzmann distribution curve shows the distribution of the energies and the activation energy

- 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 thetemperatureof 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 oC and when the temperature is increased by 10 oC

- 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

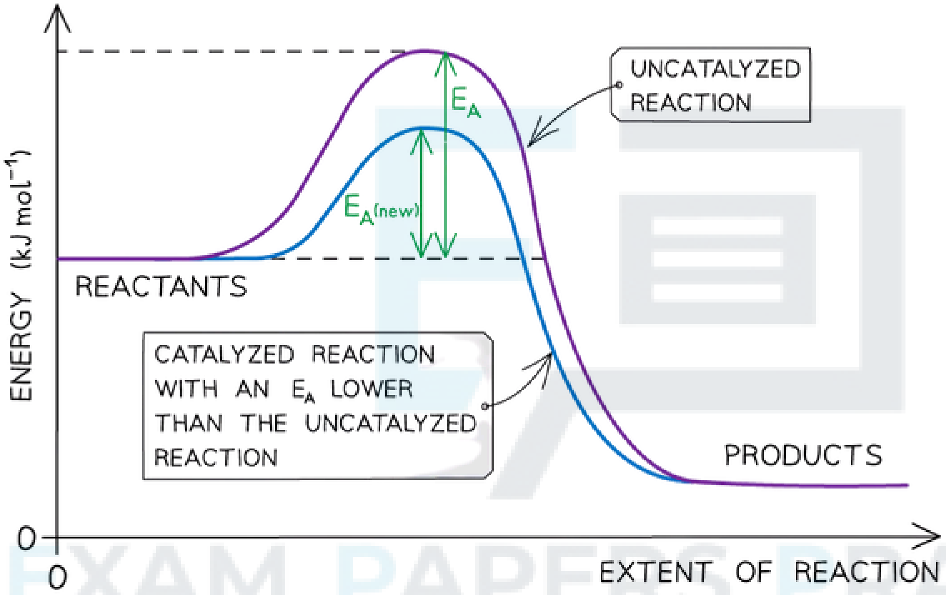
The increase in proportion of molecules having kinetic energy greater than the activation has a greater effect on the rate of reaction than the increase in effective collisions

Effects of Adding a Catalyst

- **Catalysis** is the process in which therate 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 s

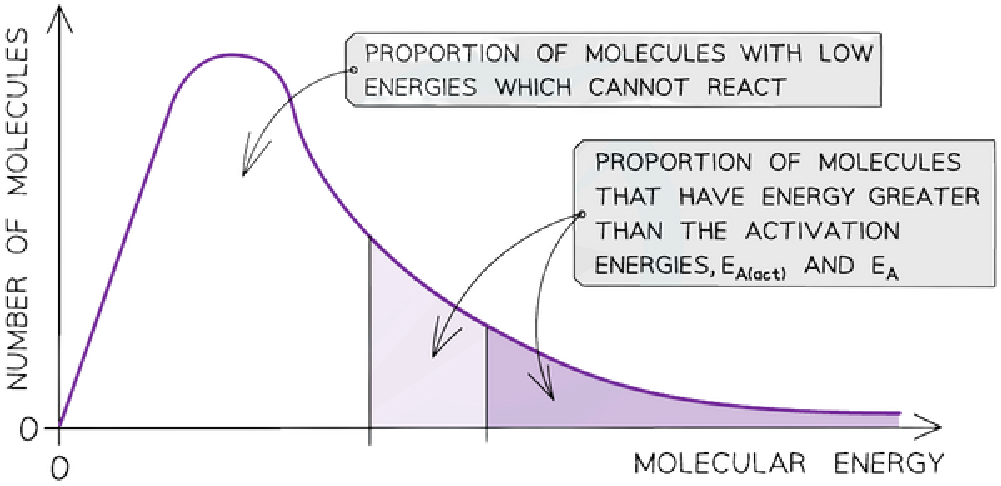


The diagram shows that the catalyst allows the reaction to take place through a different mechanism, which has a lower activation energy than the original reaction

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 *Ea,* 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 Ea 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 Ea without a catalyst

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

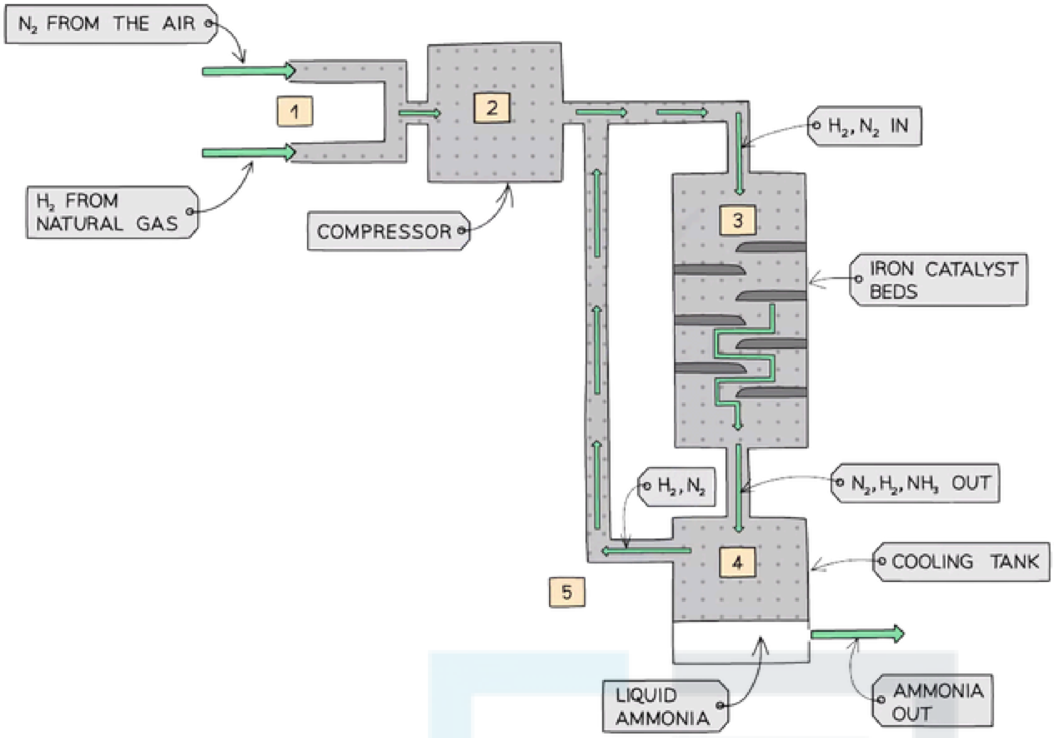
- **Heterogeneous** means that the catalyst is in a **different phase** to the reactants
  - For example, the reactants are gases, but the catalyst used is a solid

- Ammonia production via the **Haber Process** is a classic example of the use of a **heterogeneous catalyst**

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

- The Haber Process occurs in five stages

1. Hydrogen and nitrogen are obtained from natural gas and air respectively and pumped into the compressor
2. The gases are compressed to about 200 atmospheres
3. The pressurised gases, at around 450 oC, 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
4. Unreacted hydrogen, nitrogen and the ammonia product pass into a cooling tank where the ammonia is liquefied and removed
5. The unreacted hydrogen and nitrogen are recycled back into the system and start over again



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