A Level Chemistry OCR

3. Periodic Table & Energy

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CONTENTS

3.1 Periodicity

3.1.1 Periodicity

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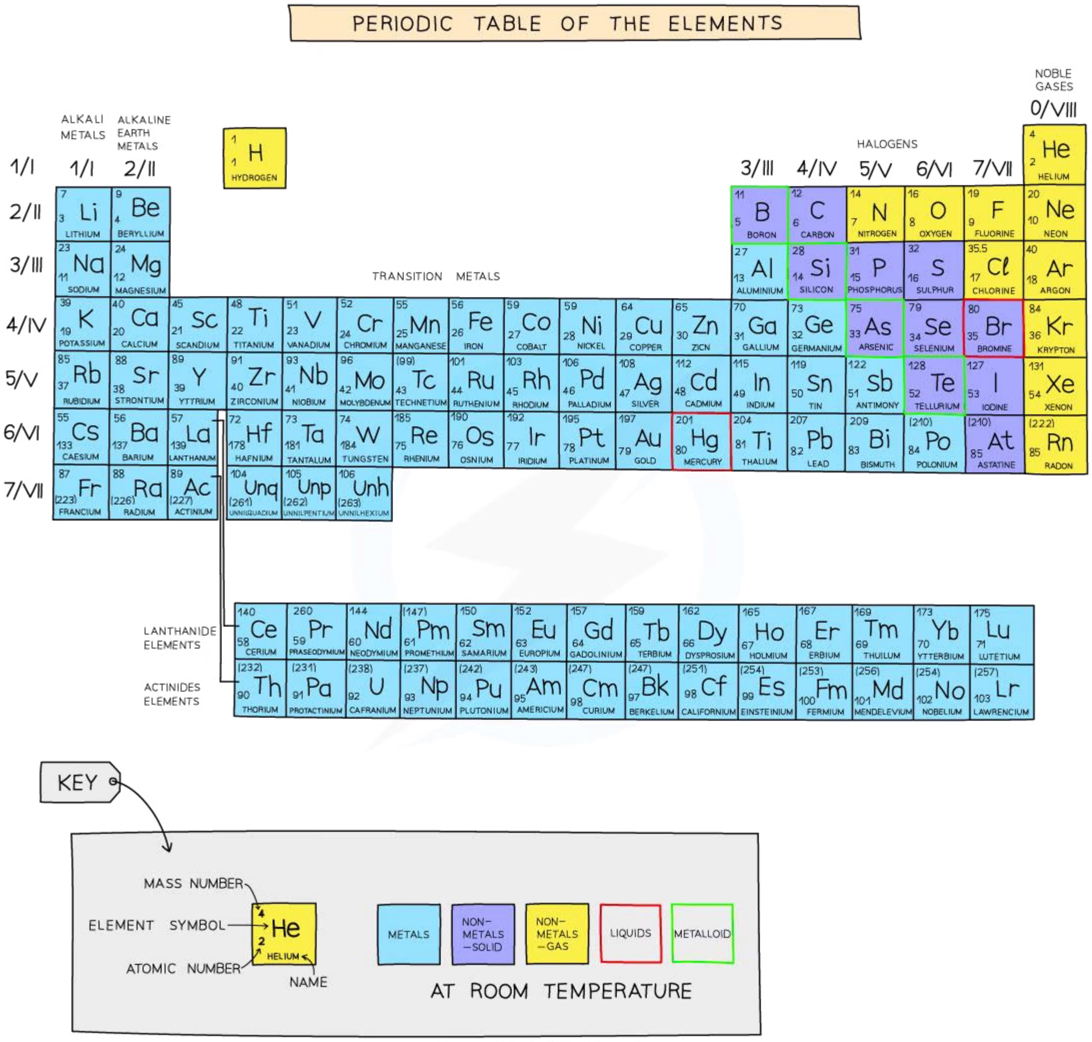
Structure of the Periodic Table

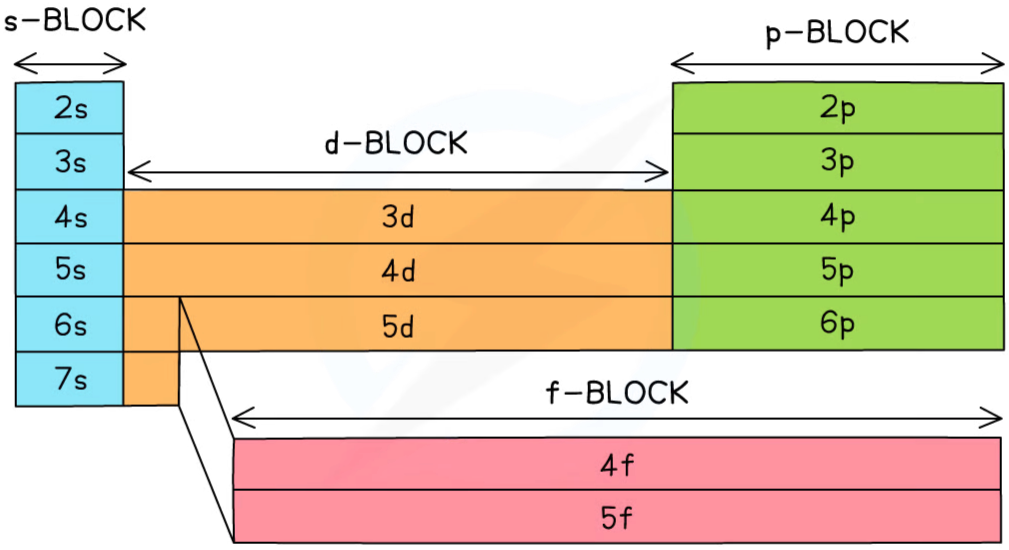
- The **Periodic Table** is a list of all known elements arranged in order of **increasing atomic number,** from 1 to 118.
- In addition to this, the elements are arranged so that atoms with the same number of shells are placed together, and atoms with similar electronic configurations in the outer shell are also placed together. This is achieved as follows:
    - The elements are arranged in rows and columns.
    - Elements with **one** shell are placed in the **first row** (i.e. H and He)
    - Elements with **two** shells are placed in the **second row** (Li to Ne) and so on.
- A row of elements thus arranged is called a **period**. The period number, **n**, is the outer energy level occupied by electrons.
- In addition, the elements are aligned vertically (in columns) with other elements in different rows, if they share a similar outer-shell electronic configuration
    - The outer electrons are known as the **valence** electrons.
- A column of elements thus arranged is called a **group**



- Since the electronic configurations of **H** and **He** are unusual, they do not fit comfortably into any group. They are thus allocated a group based on similarities in physical and chemical properties with other members of the group
- **He** is placed in **group 0** on this basis, but hydrogen does not behave like any other element and so is placed in a group of its own
- The physical and chemical properties of elements in the periodic table show clear patterns related to the position of each element in the table
  - Elements in the same group show similar properties
  - Properties change gradually as you go across a period
- As atomic number increases, the properties of the elements show trends that repeat themselves in each period of the periodic table
  - These trends are known as **periodic trends**, and the study of these trends is known as **periodicity**

Periodic Trends in Electron Configuration

- All elements belong to one of **four** main blocks: the s-block, the p-block, the d-block and the f-block
  - The **s–block** elements are all those with only s electrons in the outer shell
  - The **p–block** elements are all those with at least one p-electron in the outer shell
  - The **d–block** elements are all those with at least one d-electron and at least one s-electron but no f or p electrons in the outer shell (up to 5d)
  - The **f–block** elements are all those with at least one f-electron and at least one s-electron but no d or p electrons in the outer shell



The blocks of the periodic table

Trends across a period

- Each period starts with an electron in a new highest energy shell.
  - Across period 2, the 2s sub-shell fills with two electrons, followed by the 2p sub-shell with six electrons.
  - Across period 3, the same pattern of filling is repeated for the 3s and 3p sub-shells,
- For each period, the s and p sub-shells are filled in the same way - a periodic pattern.

Periodic Trends In Ionisation Energy

- The **first ionisation energy (*IE_1*)** is the energy required to **remove** one mole of electrons from one mole of atoms of an element in the **gaseous state** to form one mole of **gaseous ions**
  - E.g. the first ionisation energy of Na is:

$Na (g) \rightarrow Na^+ (g) + e^-$ First ionisation energy = +496 kJ mol^{-1}

Factors affecting ionisation energy

- Ionisation energies show **periodicity**
- The **first ionisation** energy **increases** across a period and **decreases** down a group and is caused by three factors that influence the ionisation energy:
  1. **Atomic radius:** electrons in shells that are further away from the nucleus are less attracted to the nucleus so the further the outer electron shell is from the nucleus, the **lower** the ionisation energy
  2. **Nuclear charge:** the nuclear charge increases with increasing atomic number, which means that there are greater **attractive forces** between the nucleus and outer electrons, so more energy is required to overcome these attractive forces when removing an electron
  3. **Electron shielding:** the **shielding effect** is when the electrons in full inner shells repel electrons in outer shells preventing them to feel the **full nuclear charge** so the greater the shielding of outer electrons by inner electron shells, the lower the ionisation energy
- These three factors affect the attraction between the nucleus and the outer electrons of an atom, and therefore, the ionisation energy.

Trend in first ionisation energy down a group

- As you move down a group, the nuclear charge **increases** but the ionisation energy **decreases**
- This is due to the following factors:
  - The atomic radius increases
  - The shielding (by inner shell electrons) increases
  - Therefore, the attraction between the nucleus and the outer electrons decreases

Trend in first ionisation energy across a period

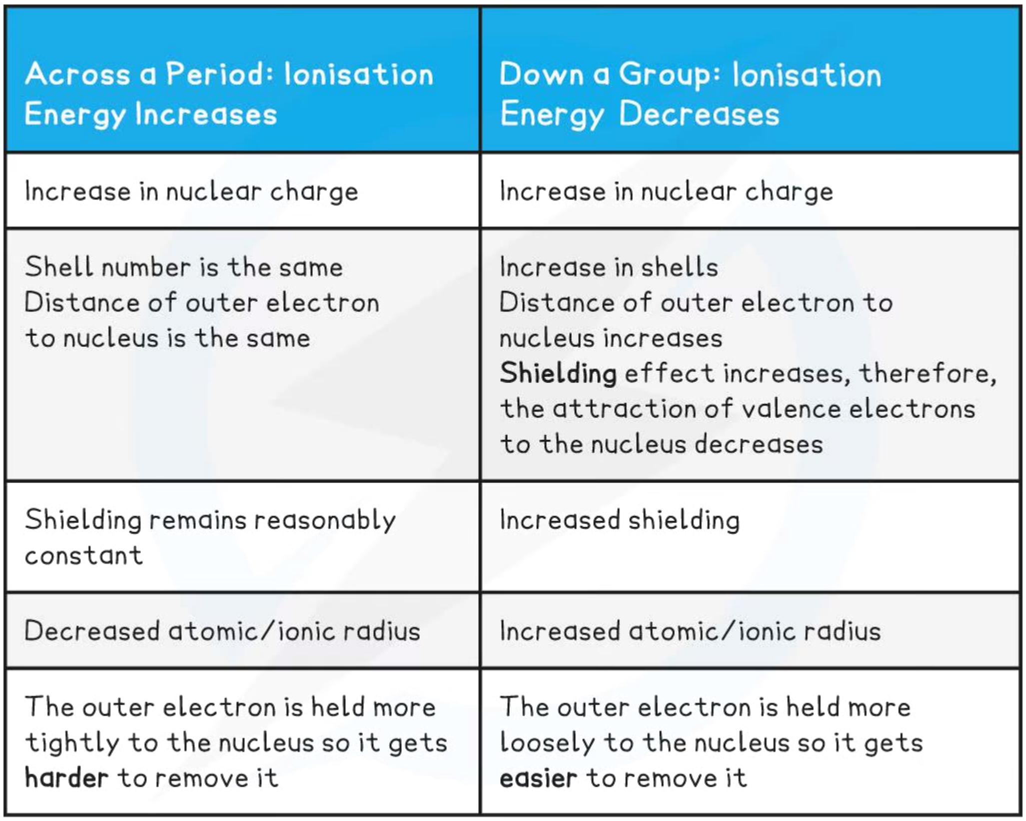
- The ionisation energy across a period increases due to the following factors:
  - Across a period, the **nuclear charge** increases
  - The **distance** between the nucleus and outer electron remains reasonably **constant** (no significant change in **atomic radius**)
  - The **shielding** by inner shell electrons remains the same
- There is a rapid **decrease** in ionisation energy between the **last** element in one period and the **first** element in the next period caused by:
  - The increased **distance** between the nucleus and the outer electrons
  - The increased **shielding** by inner electrons

  - These two factors outweigh the increased **nuclear charge**

- There is a slight **decrease** in first ionisation energy between **beryllium** and **boron** as the fifth electron in boron is in the 2p subshell, which is further away from the nucleus than the 2s subshell of beryllium
  - **Beryllium** has a first ionisation energy of **900 kJ mol^{-1}** as its electron configuration is **$1s^2$ $2s^2$**
  - **Boron** has a first ionisation energy of **801 kJ mol^{-1}** as its electron configuration is **$1s^2$ $2s^2$ $2p^1$**

- There is a slight **decrease** in first ionisation energy between **nitrogen** and **oxygen** as the paired electrons in the 2p subshell of oxygen repel each other, making it easier to remove an electron in oxygen than nitrogen.
  - **Nitrogen** has a first ionisation energy of **1402 kJ mol^{-1}** as its electron configuration is $1s^2$ $2s^2$ $2p^3$
  - **Oxygen** has a first ionisation energy of **1314 kJ mol^{-1}** as its electron configuration is $1s^2$ $2s^2$ $2p^4$

Table explaining the Ionisation Energy Trends Across a Period & Down a Group



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 is the same	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

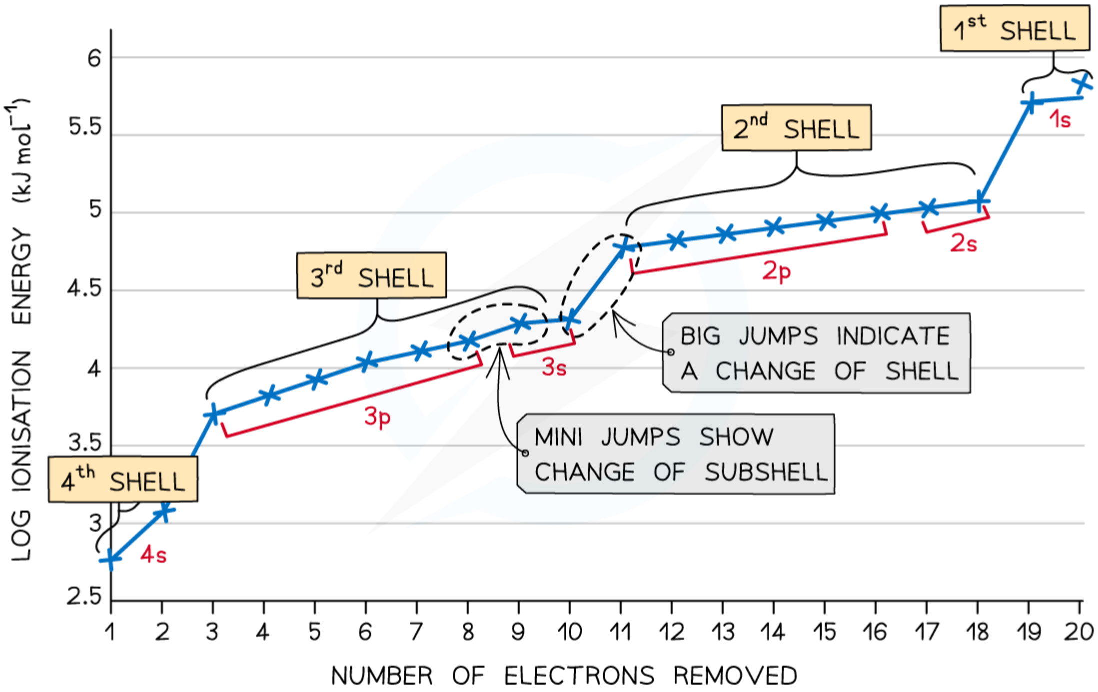
Predicting Ionisation Energy

- The **successive** ionisation energies of an element **increase** as 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
- Take calcium as an example:

Ionisation Energies of Calcium Table

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

- The values become very large and difficult to represent meaningfully, so it is more convenient to show the logarithm of the ionisation energies
- This helps us to see significant jumps in ionisation energies



Successive ionisation energies for the element calcium

- The **first** electron removed has a low ionisation energy as it is easily removed from the atom due to the repulsion of the paired electrons in the 4s orbital

- The **second** electron is a little more difficult to remove than the first electron as you are removing an electron from a positively charged ion
- The **third** electron is much more difficult to remove than the second one corresponding to the fact that the third electron is in a shell that is closer to the nucleus (3p)
- 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 **sub-shell**

Exam Tip

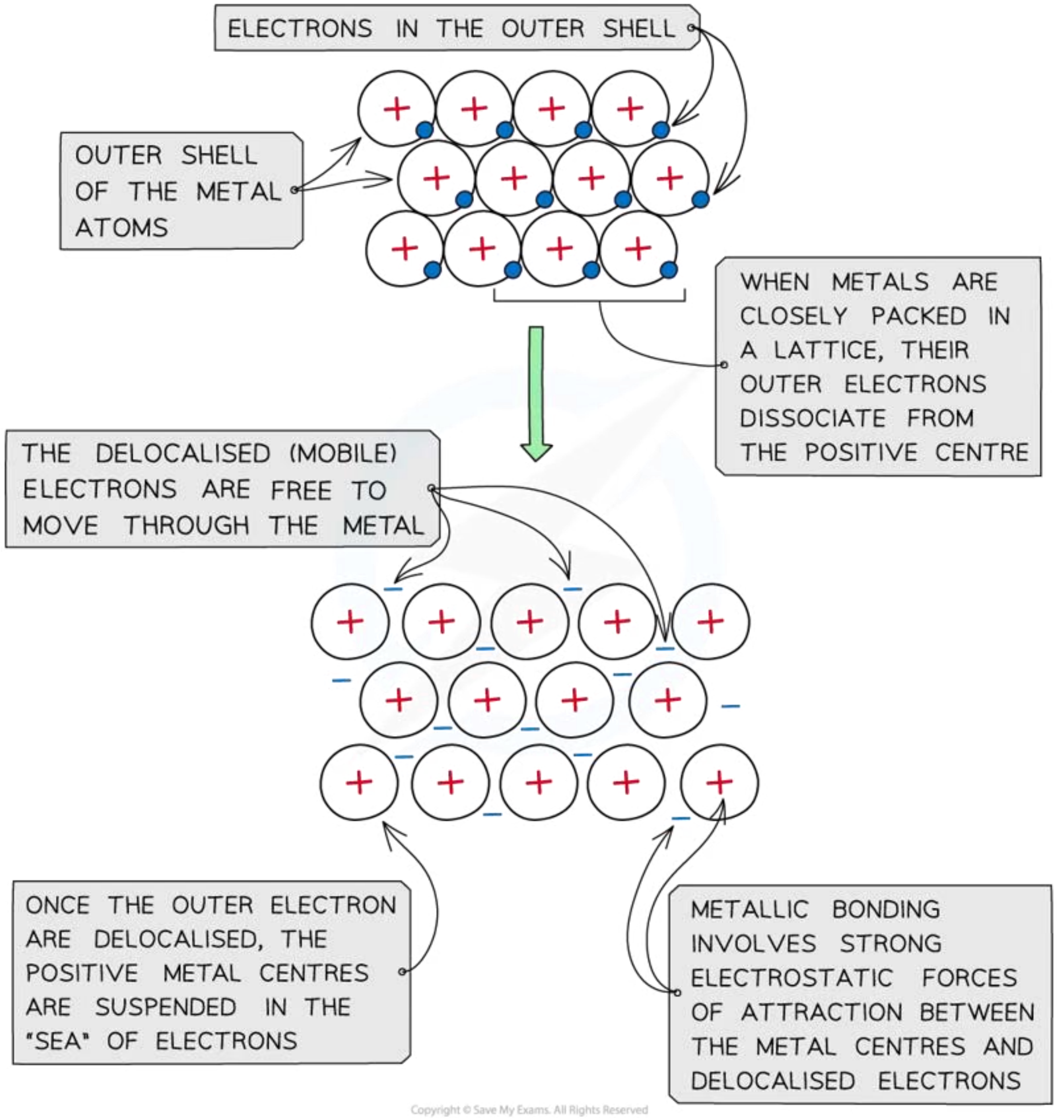
Be careful with how you interpret successive ionisation energy graphs as it is common for students to read them the wrong way around and count outer electrons from right to left instead of left to right so they get the jumps in the wrong place.

This happens particularly when you are given only a partial successive ionisation energy graph and have to deduce which group the element comes from.

It's a good idea if you see an ionisation energy graph in an exam question to label the shells and subshells so you are less likely to make this mistake!

Metallic Bonding & Structure

- **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 ions
- The positive charges **repel** each other and keep the neatly arranged lattice in place
- There are very strong **forces** between the positive metal centres and the 'sea' of delocalised electrons



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

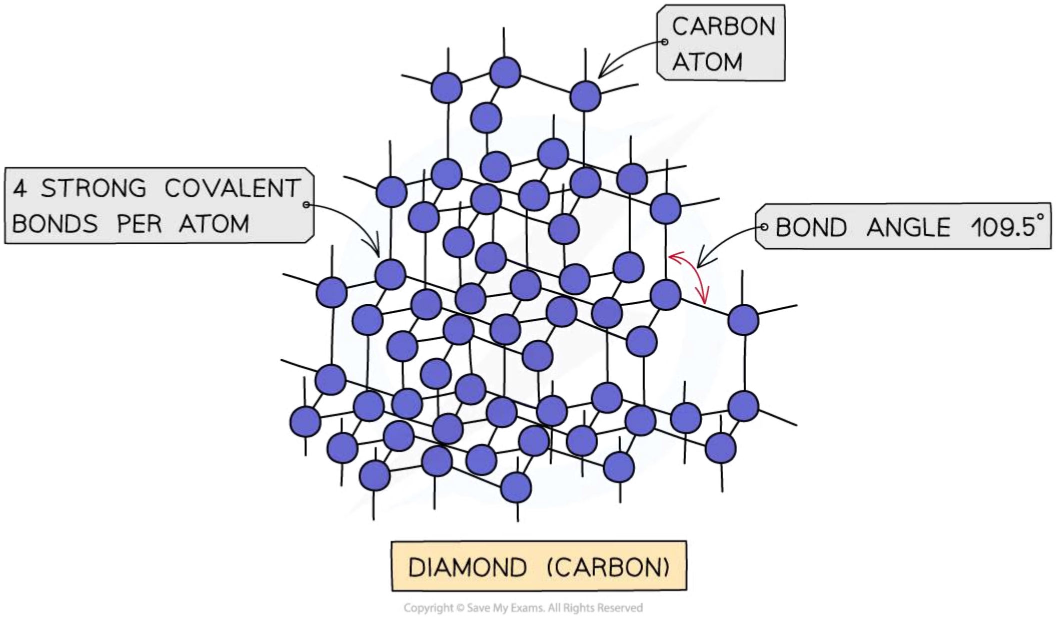
Giant Covalent Lattices

Covalent lattices

- **Covalent bonds** are bonds between nonmetals where there is a **shared** pair of electrons between the atoms
- In some cases, it is not possible to satisfy the bonding capacity of a substance in the form of a molecule
    - The bonds between atoms continue indefinitely, and a large lattice is formed
    - There are no individual molecules and covalent bonding exists between all adjacent atoms
- Such substances are called **giant covalent substances**
- The most important examples are the carbon allotropes graphite, diamond and graphene as well as silicon(IV) oxide

Diamond

- Diamond is a giant covalent lattice (or macromolecule) of carbon atoms
- Each carbon is covalently bonded to four others in a tetrahedral arrangement with a bond angle of 109.5°
- The result is a giant lattice structure with strong bonds in all directions
- Diamond is the hardest substance known
    - For this reason, it is used in drills and glass-cutting tools

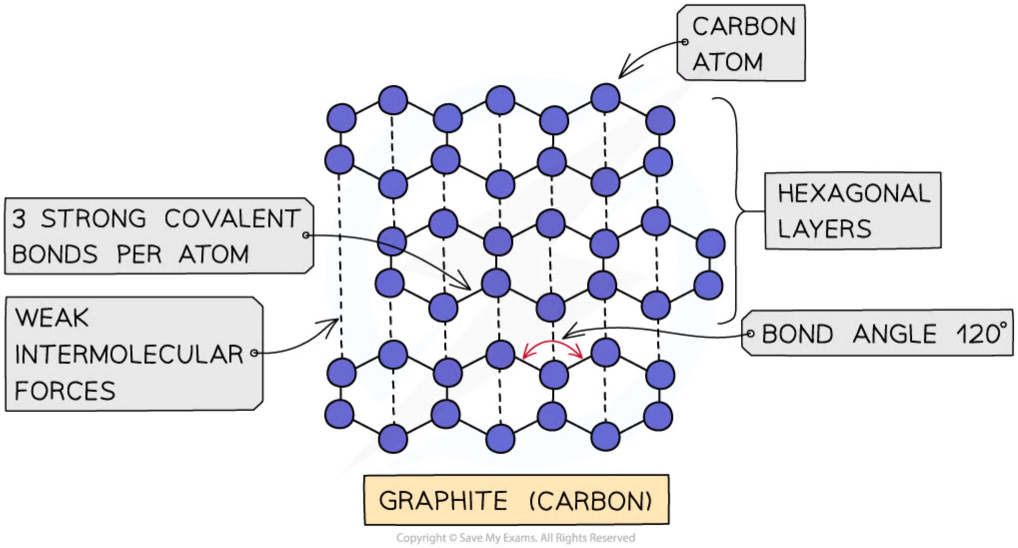


The structure of diamond

Graphite

- In graphite, each carbon atom is bonded to three others in a layered structure
- The layers are made of hexagons with a bond angle of 120°
- The spare electrons are delocalised and occupy the space between the layers
- All atoms in the same layer are held together by strong covalent bonds
- However, the layers are held together by weak intermolecular forces

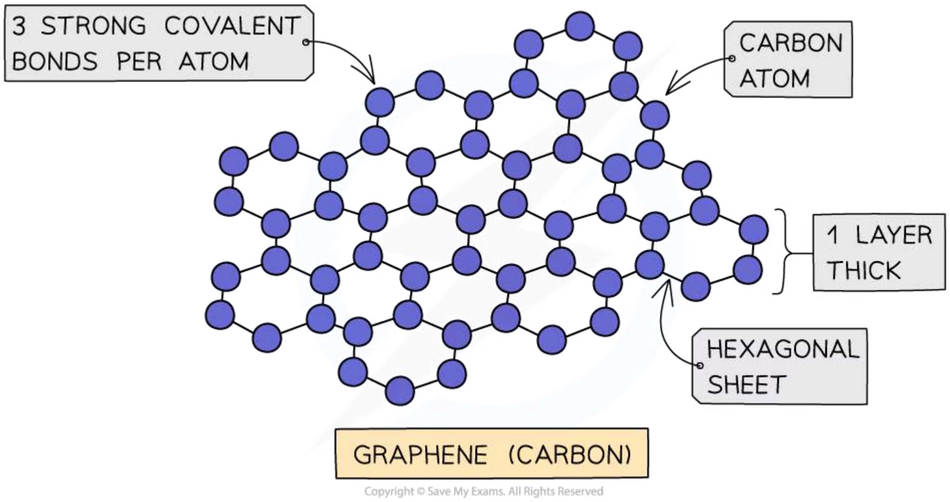
  - These weak intermolecular forces allow the layers to slide over each other



The structure of graphite

Graphene

- Some substances contain an infinite lattice of covalently bonded atoms in two dimensions only to form layers.
  - Graphene is an example
- Graphene is made of a single layer of carbon atoms that are bonded together in a repeating pattern of hexagons
- Graphene is one million times thinner than paper; so thin that it is actually considered two dimensional

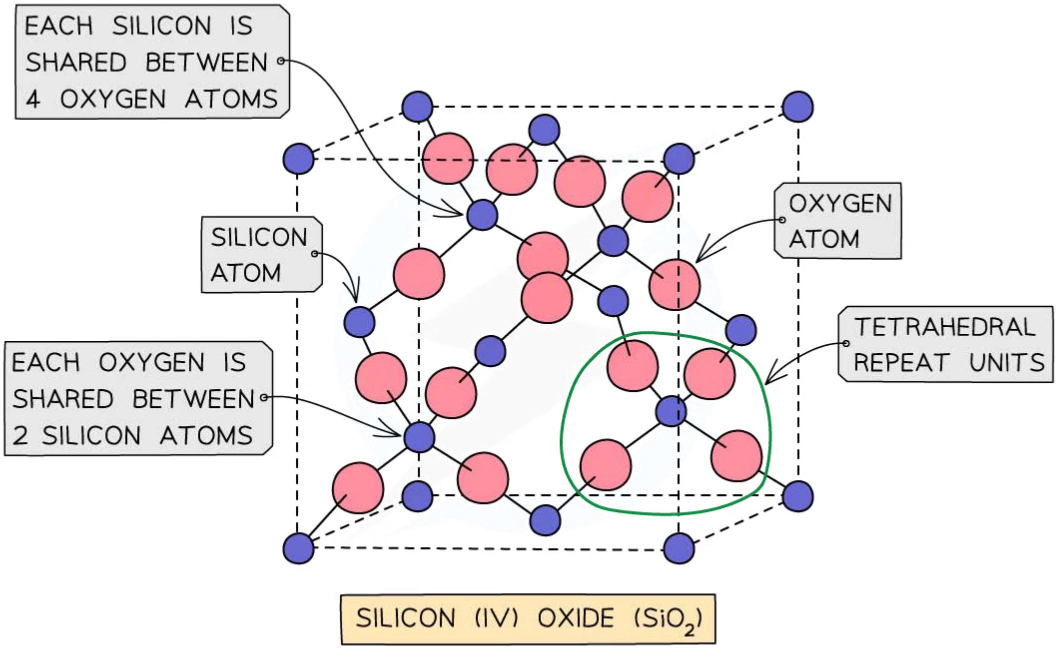


The structure of graphene

Silicon(IV) oxide

- Silicon(IV) oxide is also known as silicon dioxide, but you will be more familiar with it as the white stuff on beaches!

- Silicon(IV) oxide adopts the same structure as diamond - a giant covalent lattice / macromolecular structure made of tetrahedral units all bonded by strong covalent bonds
- Each silicon is shared by four oxygens and each oxygen is shared by two silicons
- This gives an empirical formula of SiO_2



The structure of silicon dioxide

Periodic Trends in Physical Properties

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

Properties of metallic substances

- Due to the delocalised ‘sea’ of electrons, metallic structures have some **characteristic properties:**
- **High melting and boiling point:** as a lot of energy is required to overcome the strong electrostatic forces of attraction between positive ions and the 'sea' of delocalised electrons
- **Solubility:** metals do not dissolve. There is some interaction between polar solvents and charges in the metallic lattice but these lead to reactions, rather than dissolving e.g. sodium and water
- **Electrical conductivity:** conduct electricity in both solid and liquid states. This is due to the delocalised electrons which are free to move / carry charge around the structure

Properties of giant covalent substances

- **Giant covalent lattices** have very high **melting** and **boiling points**
    - These compounds have a large number of **covalent bonds** linking the whole structure
    - A lot of energy is required to break the lattice

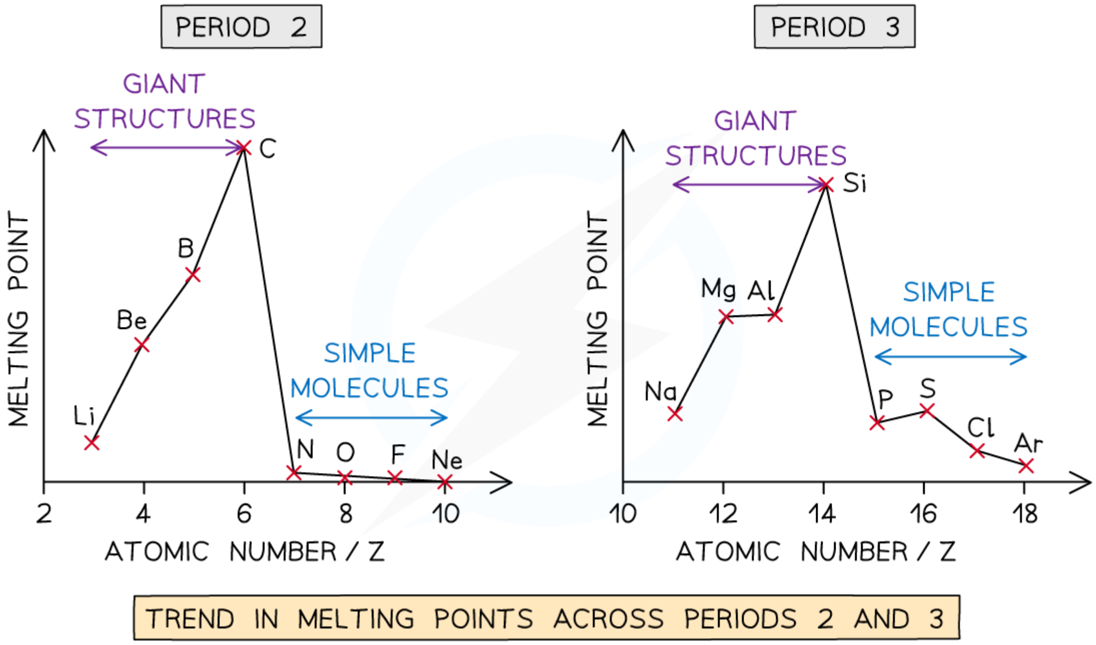
- The compounds can be **hard** or **soft**
    - Graphite is **soft** as the intermolecular forces between the carbon layers are weak
    - Diamond and silicon(IV) oxide are **hard** as it is difficult to break their 3D network of strong covalent bonds
    - Graphene is strong, flexible and transparent, which makes it potentially a very useful material

- Most compounds are insoluble with water
- Most covalent substances do not **conduct electricity**
    - For example, diamond and silicon(IV) oxide do not conduct electricity as all four outer electrons on every carbon atom is involved in a **covalent bond** , so there are no free electrons available
- There are some covalent substances that are exceptions because they do conduct electricity
    - Graphite has **delocalised** electrons between the carbon layers, which can move along the layers when a voltage is applied
    - Graphene is an excellent conductor of electricity due to the **delocalised** electrons

Periodic trend in melting points

- Across Period 2 and Period 3,

- Melting point increases from Group 1 to Group 4 (14)
    - Groups 1 to 3 (13) have metallic bonding which increases in strength due to increased forces of attraction between more electrons in the outer shell that are released to the sea of electrons and a smaller positive ion
    - Group 4 (14) has a giant covalent structure with many strong covalent bonds requiring a lot of energy to overcome
- A sharp decrease in melting point from Group 4 (14) to Group 5 (15)
    - Groups 5 (15) to 0 (18) have simple molecular structures with weak London forces between molecules requiring little energy to overcome



Trend in melting points across Periods 2 and 3

3.2 Group 2

3.2.1 Group 2 Elements

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Structure & Ions

- All elements in Group 2 (also called **alkali earth metals)** have two electrons in their outermost shell in the **s sub-shell** (s^2 electron configuration)
- Redox reactions are the most common reaction of the Group 2 elements
- Each metal atom is oxidised, losing its two valence electrons to form a 2+ ion witha noble gas configuration

$$\mathbf{Ca \rightarrow Ca^{2+} + 2e^-}$$

  - The calcium changes from an electron configuration of $[Ar]4s^2$ to $[Ar]$
- Another species will gain the two electrons lost
  - This species will therefore be reduced
- The Group 2 element can be referred to as a **reducing agent** as it has reduced another species

Relative Reactivity

- The reactivity of Group 2 elements increases down the group.
    - As the atomic radii increase there is more shielding
    - The nuclear attraction decreases and it is easier to remove outer electrons
    - Cations form more easily

Reactions with water and oxygen

- The reaction of group 2 metals with oxygen follows the following general equation:

$$2M\ (s) + O_2\ (g) \rightarrow 2MO\ (s)$$

Where M is any metal in group 2

- We can see this is a redox reaction by looking at the changes in oxidation number of the metal, M, and oxygen
    - M = 0 → +2 so the metal has been oxidised
    - O = 0 → -2 so the oxygen has been reduced
- The reaction of all group 2 metals with water follows the following general equation:

$$M\ (s) + 2H_2O\ (l) \rightarrow M(OH)_2\ (s) + H_2\ (g)$$

- We can again see this is a redox reaction by taking a look at changes in the oxidation number of each element in the reaction
    - M = 0 → +2 so the metal has been oxidised
    - H = +1 → 0 so the hydrogen has been reduced
    - No change in oxidation number for oxygen
- The solubility of the hydroxides increases down the group

Reactions of Group 2 metals with acid

- The Group 2 metals will react with dilute acids to form **metal salts**
    - For example, they will form metal chlorides if reacted with hydrochloric acid, HCl

- When metals react with an acid, the by-product of this reaction is hydrogen gasThe
    - reaction of the metals with dilute HCl follows the following general equation:

$$M\ (s) + 2HCl\ (aq) \rightarrow MCl_2\ (aq) + H_2\ (g)$$

- We can again see this is a redox reaction by taking a look at changes in the oxidation number of each element in the reaction
    - M = 0 → +2 so the metal has been oxidised
    - H = +1 → 0 so the hydrogen has been reduced
    - No change in oxidation number of chlorine

- The reaction of the metals with dilute sulfuric acid, H_2SO_4, follows the following general equation:

$$\mathbf{M\ (s) + H_2SO_4\ (aq) \rightarrow MSO_4\ (aq) + H_2\ (g)}$$

- When some of Group 2 metals react with sulfuric acid rather than hydrochloric, an insoluble sulfate forms
- Going down the group, the Group 2 sulfates become less and less soluble
    - Calcium sulfate is sparingly soluble, but strontium sulfate and barium sulfate are insoluble

Trends in Ionisation Energy

- We can think about the increasing reactivity moving down Group 2 in terms of ionisation energies
- The atoms of Group 2 elements react by losing electrons to form +2 ions
- The formation of +2 ions from gaseous atoms requires two ionisation energies

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

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

- Both the first and second ionisation energies decrease down the group as
  - The attraction between the nucleus and outer electrons decreases
  - Atomic radius increases, and there is increased shielding
- Despite other energy changes taking place when Group 2 elements react, the first and second ionisation energies make up most of the energy input
- Therefore, as the total energy input from ionisation energies to form 2+ ions decreases down the group, the elements become more reactive and stronger reducing agents

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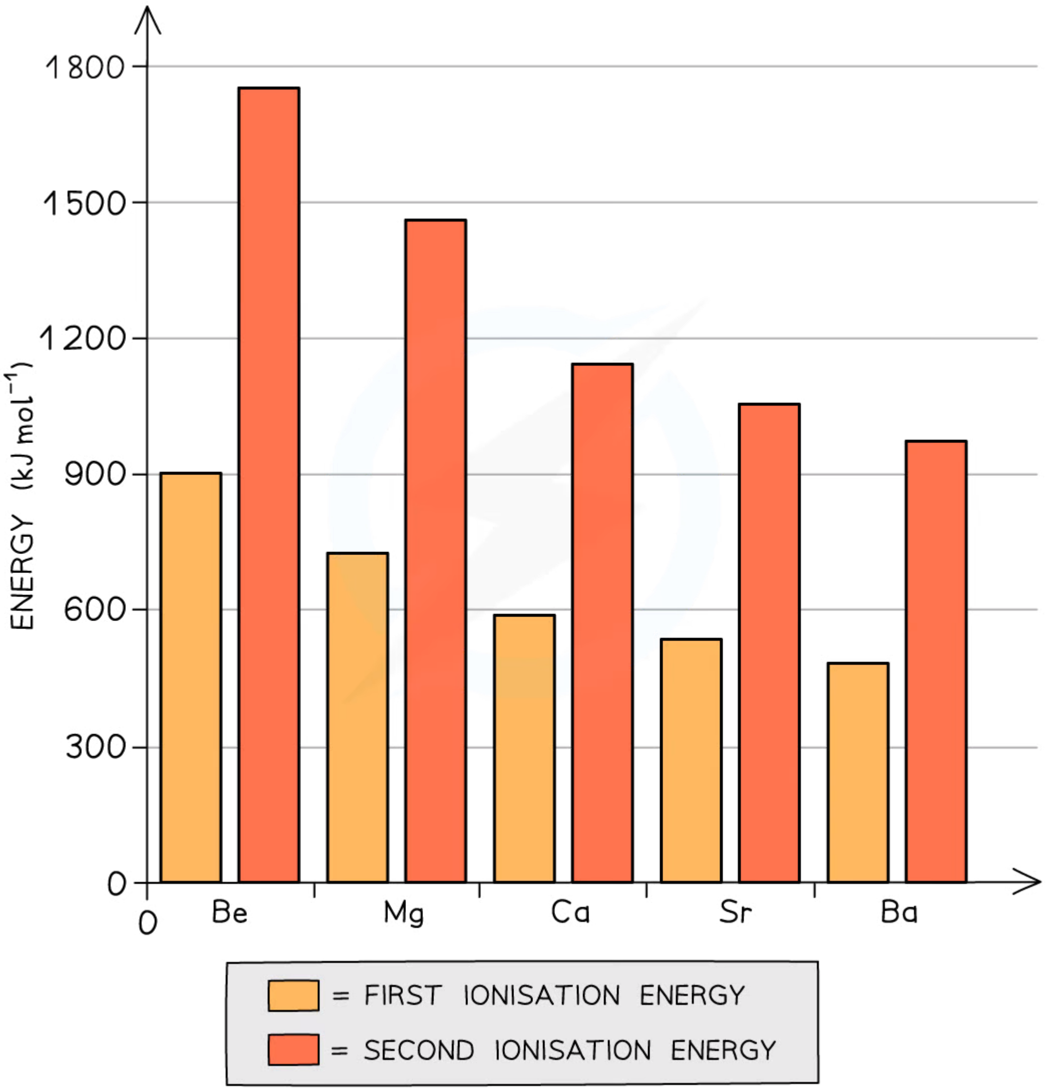


First and second ionisation energies of Group 2 elements

Group 2 Oxides & Water

- Group 2 oxides react with water, releasing hydroxide ions, to form **alkaline** solutions:

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca^{2+}\ (aq) + 2OH^-\ (aq)$$

- These solutions get more **alkaline** going down the group
    - This is due to increasing solubility meaning the resulting solutions formed contain more OH^- ions
- When the solution becomes saturated any further metal and hydroxide ions will form a precipitate:

$$Ca^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Ca(OH)_2\ (s)$$

- Solid magnesium hydroxide, $Mg(OH)_2$ (s), is only slightly soluble in water
    - The solution has a low OH^-(aq) concentration and a pH ≅ 10
- Barium hydroxide, $Ba(OH)_2$ (s), is much more soluble in water
    - The solution has a greater OH^-(aq) concentration and a pH ≅ 13

Uses of Group 2 Compounds

- Due to their basic properties and ability to neutralise acids, Group 2 oxides, hydroxides and carbonates have many uses

Group 2 compounds in agriculture

- Calcium hydroxide, $Ca(OH)_2$, is reasonably soluble in water and is used in agriculture to neutralise acidic soils

$$Ca(OH)_2\ (s) + 2H^+\ (aq) \rightarrow Ca^{2+}\ (aq) + 2H_2O\ (l)$$

- It is important to regulate how much is added as If too much is added then this will result in soil becoming too alkaline to sustain crop growth

Group 2 compounds in medicine

- Magnesium hydroxide, $Mg(OH)_2$, is partially soluble in water and is used in suspension (known as 'milk of magnesia') to neutralise excess acid in the stomach and treat constipation

$$Mg(OH)_2\ (s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + 2H_2O\ (l)$$

- It is safe to use as the magnesium hydroxide is only partially soluble making the solution only slightly alkaline (pH ≅ 10) due to the low OH^- concentration

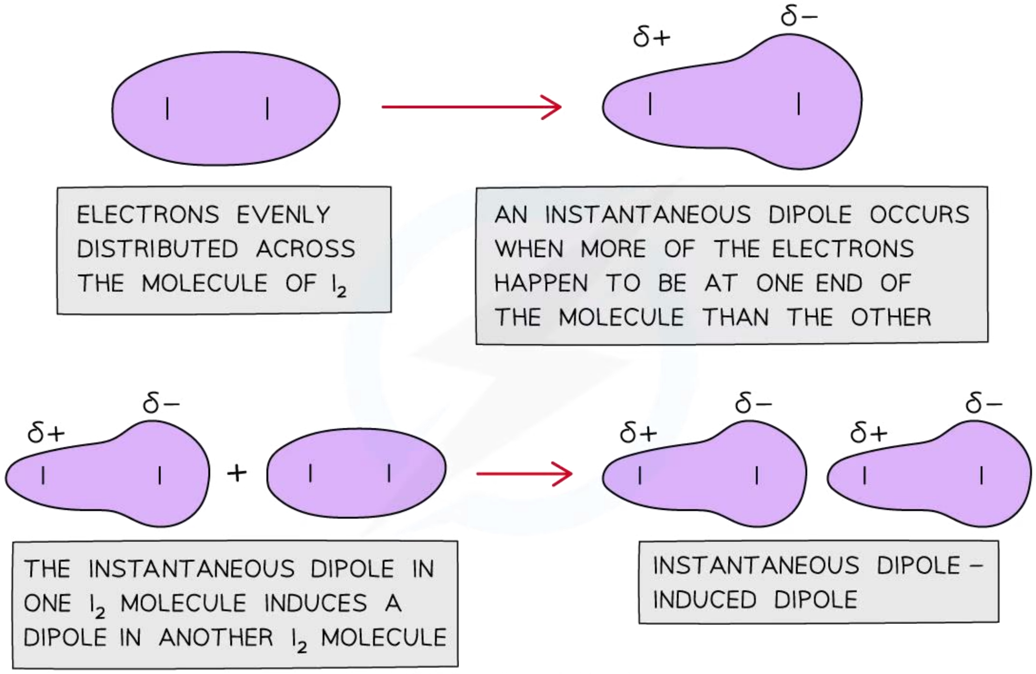
3.3 The Halogens

3.3.1 The Halogens

Physical Properties of the Halogens

Trend in boiling points

- Boiling point increases down the group
- We can explain this trend by looking at the forces between the molecules
- Halogens are non-metals and are **diatomic molecules** at room temperature
- This means that they exist as molecules that are made up of two similar atoms, such as F_2
- The halogens are **simple molecular structures** with **weak London forces** between the diatomic molecules caused by instantaneous dipole-induced dipole forces



The diagram shows that a sudden imbalance of electrons in a nonpolar molecule can cause an instantaneous dipole. When this molecule gets close to another non-polar molecule it can induce a dipole as the cloud of electrons repel the electrons in the neighbouring molecule to the other side

- The more **electrons** there are in a molecule, the greater the instantaneous dipole-induced dipole forces
- Therefore, the **larger** the molecule the **stronger** the London forces between molecules
- This is why as you go down the group, it gets more difficult to separate the molecules and the **boiling point** increases

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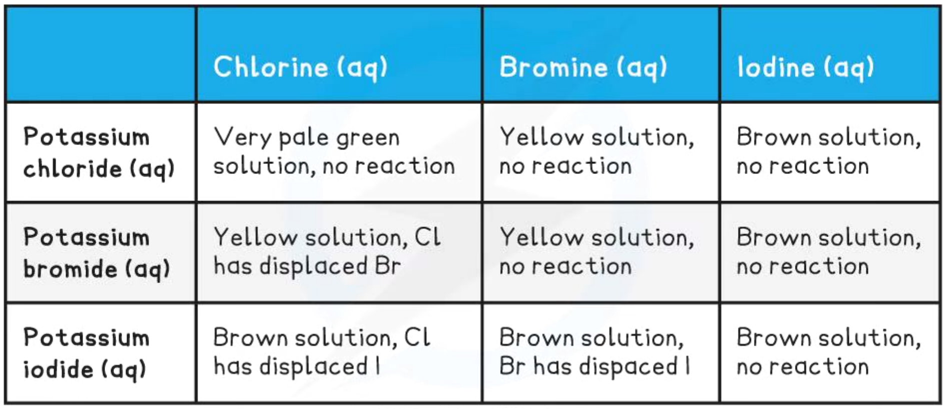
Reactivity of the Halogens

Reaction of the halogens with halide ions in displacement reactions

- A halogen **displacement** occurs when a **more r**eactive halogen displaces a **less** reactive halogen from an aqueous solution of its halide
- The reactivity of Group 7 non-metals increases as you move up the group
- Out of the 3 halogens, chlorine, bromine and iodine, chlorine is the most reactive and iodine is the least reactive

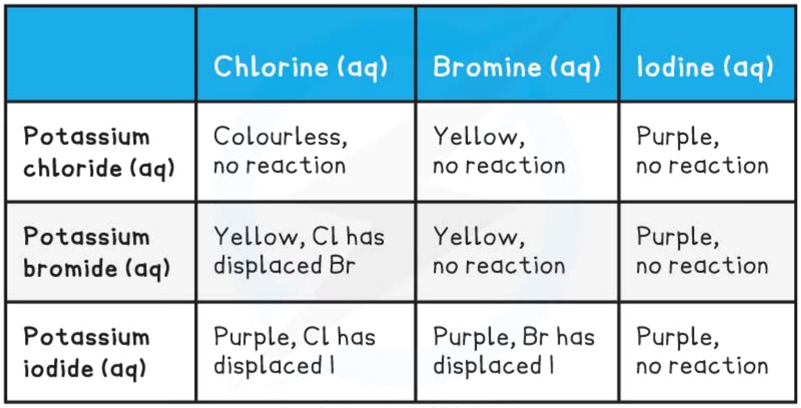
Observations in aqueous solution



	Chlorine (aq)	Bromine (aq)	Iodine (aq)
Potassium chloride (aq)	Very pale green solution, no reaction	Yellow solution, no reaction	Brown solution, no reaction
Potassium bromide (aq)	Yellow solution, Cl has displaced Br	Yellow solution, no reaction	Brown solution, no reaction
Potassium iodide (aq)	Brown solution, Cl has displaced I	Brown solution, Br has dispaced I	Brown solution, no reaction

- The colour of the solution in the test tube shows which free halogen is present in solution.
    - Chlorine = very pale green solution (often colourless),
    - Bromine = yellow solution
    - Iodine = brown solution(sometimes black solid present)
- The colour of the organic solvent layer in the test tube shows which free halogen is present in solution
    - Chlorine = colourless
    - Bromine = yellow
    - Iodine = purple

Observations with an organic solvent



	Chlorine (aq)	Bromine (aq)	Iodine (aq)
Potassium chloride (aq)	Colourless, no reaction	Yellow, no reaction	Purple, no reaction
Potassium bromide (aq)	Yellow, Cl has displaced Br	Yellow, no reaction	Purple, no reaction
Potassium iodide (aq)	Purple, Cl has displaced I	Purple, Br has displaced I	Purple, no reaction

Reaction of bromide ions and chlorine

- Chlorine is **above** bromine in Group 7 so it is more reactive
- Chlorine will therefore **displace** bromine from an aqueous solution of a metal bromide

$$2KBr\ (aq) + Cl_2\ (aq) \rightarrow 2KCl\ (aq) + Br_2\ (aq)$$

- We can again see this is a redox reaction by taking a look at changes in the oxidation number of each element in the reaction
  - Br = -1 → 0 so the bromine has been oxidised
  - Cl = 0 → -1 so the chlorine has been reduced
  - No change in oxidation number for the potassium
- Rather than writing the full equation we can also write the ionic equation by removing the potassium spectator ion

$$2Br^-\ (aq) + Cl_2\ (aq) \rightarrow 2Cl^-\ (aq) + Br_2\ (aq)$$

Trend in Reactivity

- The **oxidising power** of the halogens **decreases** going **down the group** (the halogens get less reactive)
- This can be explained as follows:
  - Atomic radius increases
  - There are more inner shells so shielding increases
  - There is less nuclear attraction to attract an electron from another species

Redox Reactions of the Halogens

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- Each halogen has 7 electrons in their outer shell with two electrons in the outer s sub-shell and 5 in the outer p sub-shell
    - **__s^2__p^5**
- Halogens react with metals by accepting an electron from the metal atom to become an ion with 1- charge
    - For example:

$$\mathbf{Ca\ (s) + Cl_2\ (g) \rightarrow CaCl_2\ (s)}$$

consisting of **Ca^{2+}** and **$2Cl^-$ ions**

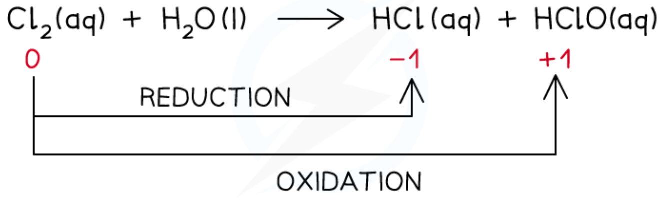
- Halogens are therefore **oxidising agents**:
    - Halogens **oxidise** the metal by removing an electron from the metal (the oxidation number of the metal increases)
    - Halogens become **reduced** as they gain an extra electron from the metal atom (the oxidation number of the halogen decreases)

Reactions of Chlorine

- A **disproportionation reaction** is a reaction in which the same species is both oxidised and reduced
- The reaction of chlorine with **water** and **cold, dilute aqueous alkali** are examples of disproportionation reactions
- In these reactions, the chlorine gets oxidised and reduced at the same time

The reaction of chlorine with water

- Chlorine can be used to clean water and make it drinkable
- The reaction of chlorine in water is a **disproportionation reaction** in which the chlorine gets both **oxidised** and **reduced**



The disproportionation reaction of chlorine with water in which chlorine gets reduced to HCl and oxidised to HClO

- Chloric(I) acid (HClO) sterilises water by killing bacteria
- Chloric acid can further dissociate in water to form ClO^- (aq):

$$HClO\ (aq) \rightarrow H^+\ (aq) + ClO^-\ (aq)$$

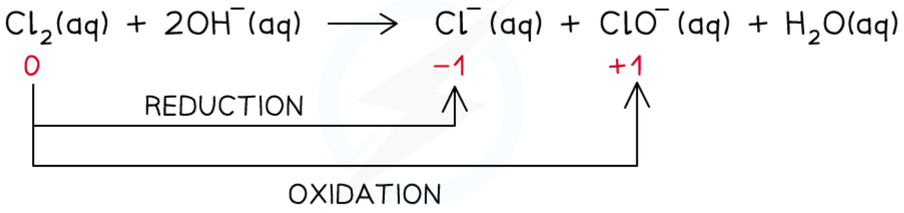
- ClO-(aq) also acts as a sterilising agent cleaning the water
- If some universal indicator is added to the solution it will first turn red due to the acidity of both reaction products. It will then turn colourless as the HClO bleaches the colour.

The reaction of chlorine with cold, dilute aqueous sodium hydroxide

- The reaction that takes place is:

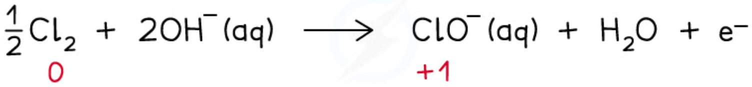
$$Cl_2(aq) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$$

- The ionic equation is:



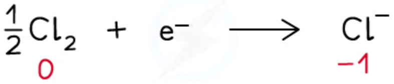
$$\underset{0}{Cl_2(aq)} + 2OH^-(aq) \longrightarrow \underset{-1}{Cl^-(aq)} + \underset{+1}{ClO^-(aq)} + H_2O(aq)$$

- The ionic equation shows that the chlorine gets both oxidised and reduced
- Chlorine gets oxidised as there is an increase in ox. no. from 0 to +1 in $ClO^-(aq)$
  - The half-equation for the oxidation reaction is:



$$\underset{0}{\tfrac{1}{2}Cl_2} + 2OH^-(aq) \longrightarrow \underset{+1}{ClO^-(aq)} + H_2O + e^-$$

- Chlorine gets reduced as there is a decrease in ox. no. from 0 to -1 in $Cl^-(aq)$
  - The half-equation for the reduction reaction is:



$$\underset{0}{\tfrac{1}{2}Cl_2} + e^- \longrightarrow \underset{-1}{Cl^-}$$

- The mixture of NaCl and NaClO (sodium chlorate (I)) is used as Bleach and to disinfect/ kill bacteria

Treating Water

- Adding chlorine to a water supply is an effective way to make the water safe to drink
  - The chlorine reacts to form the sterilising agent HClO
  - The HClO in turn dissociates in water into another sterilising agent, ClO^- (aq)
- Chlorine is used in water treatment to kill bacteria
  - It has been used to treat drinking water and the water in swimming pools
  - The benefits to health of water treatment by chlorine by its killing of bacteria outweigh its risks of toxic effects and possible risks from the formation of chlorinated hydrocarbons

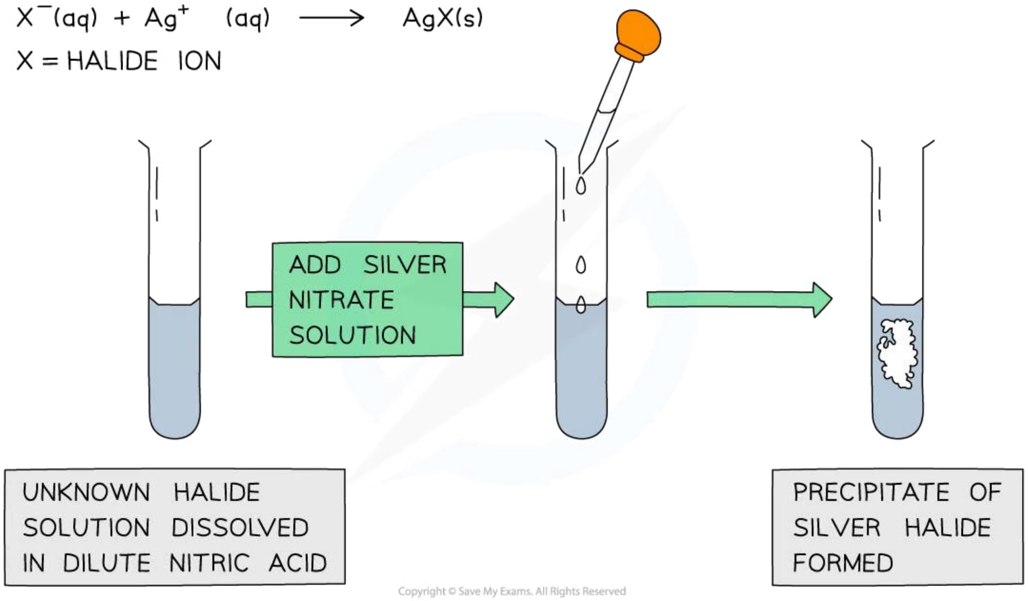
Halide Ions

- Halide ions can be identified in an **unknown solution** by dissolving the solution in **nitric acid** and then adding **silver nitrate solution dropwise**
- The nitric acid is to prevent any false positive results from carbonate ions precipitating out with silver ions
- The halide ions will react with the silver nitrate solution as follows:

$$\mathbf{Ag^+ (aq) + X^- (aq) \rightarrow AgX (s)}$$

(ionic equation)

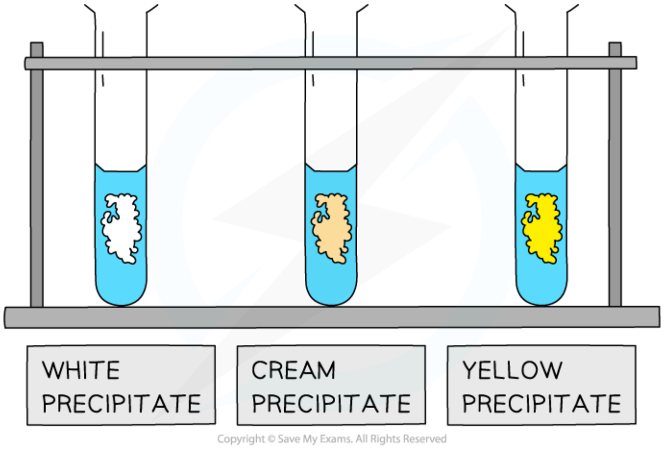
  - Where X^- is the halide ion
- The state symbols are key in this equation
- If the unknown solution contains halide ions, a **precipitate** of the silver halide will be formed (AgX)



A silver halide precipitate is formed upon addition of silver nitrate solution to halide ion solution

- Silver chloride (AgCl) is a white precipitate
- Silver bromide (AgBr) is a cream precipitate

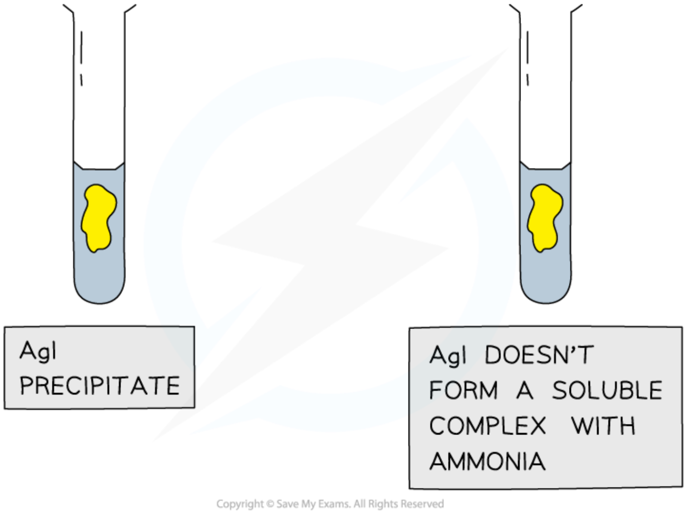
- Silver iodide (AgI) is a yellow precipitate



The silver halide precipitates are dense and characteristically coloured

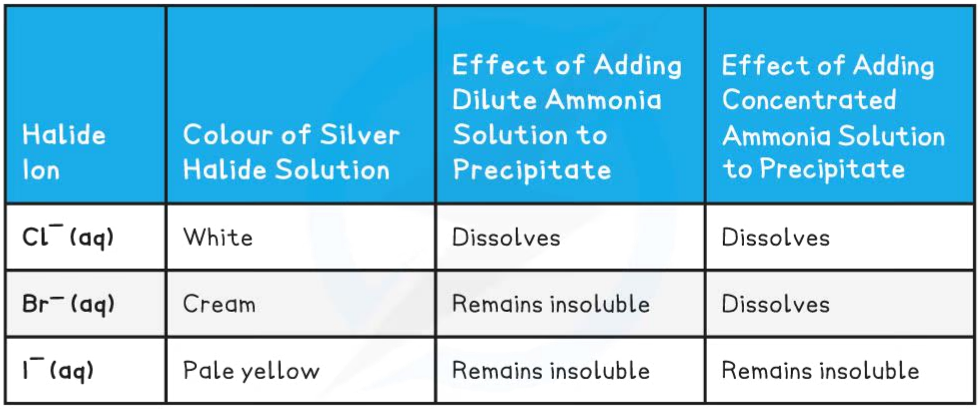
Adding ammonia

- Because the white, cream and yellow precipitates could look very similar in colour, ammonia is often used as a follow up test to determine which halide ion is present
- **Dilute** followed by **concentrated ammonia** is added to the silver halide solution to identify the halide ion
- If the precipitate dissolves in **dilute** ammonia the unknown halide is **chloride**
- If the precipitate does not dissolve in dilute, but does dissolve in **concentrated** ammonia the unknown halide is **bromide**
- If the precipitate does not dissolve in **dilute** or **concentrated** ammonia, then the unknown halide is iodide



Silver chloride and silver bromide precipitates dissolve on addition of ammonia solution whereas silver iodide is insoluble in ammonia

Reaction of Halide Ions with Silver Nitrate & Ammonia Solutions



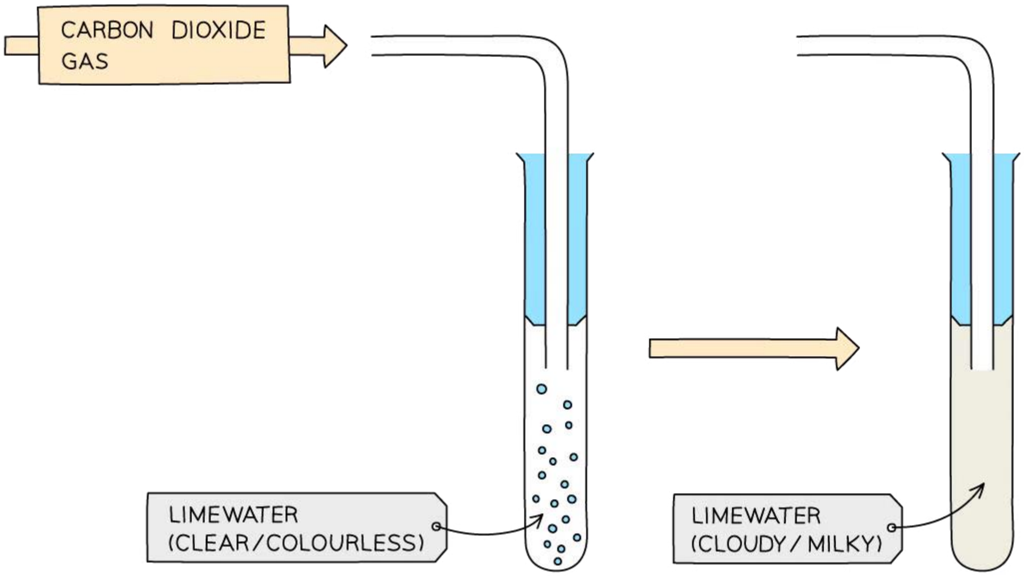
Halide Ion	Colour of Silver Halide Solution	Effect of Adding Dilute Ammonia Solution to Precipitate	Effect of Adding Concentrated Ammonia Solution to Precipitate
Cl^{-} (aq)	White	Dissolves	Dissolves
Br^{-} (aq)	Cream	Remains insoluble	Dissolves
I^{-} (aq)	Pale yellow	Remains insoluble	Remains insoluble

Qualitative Analysis of Ions

Test for Carbonates

- A small amount (around 1 cm^3) of dilute hydrochloric acid should be added to a test tube using a pipette
- An equal amount of sodium carbonate solution should then be added to the test tube using a clean pipette
- As soon as the sodium carbonate solution is added, a bung with a delivery tube should be attached to the test tube
    - The delivery tube should transfer the gas which is formed into a different test tube that contains a small amount of limewater (calcium hydroxide solution)
- If a carbonate compound is present then effervescence should be seen and the gas produced is CO_2 which forms a white precipitate of calcium carbonate when bubbled through limewater:

$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$
$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$$



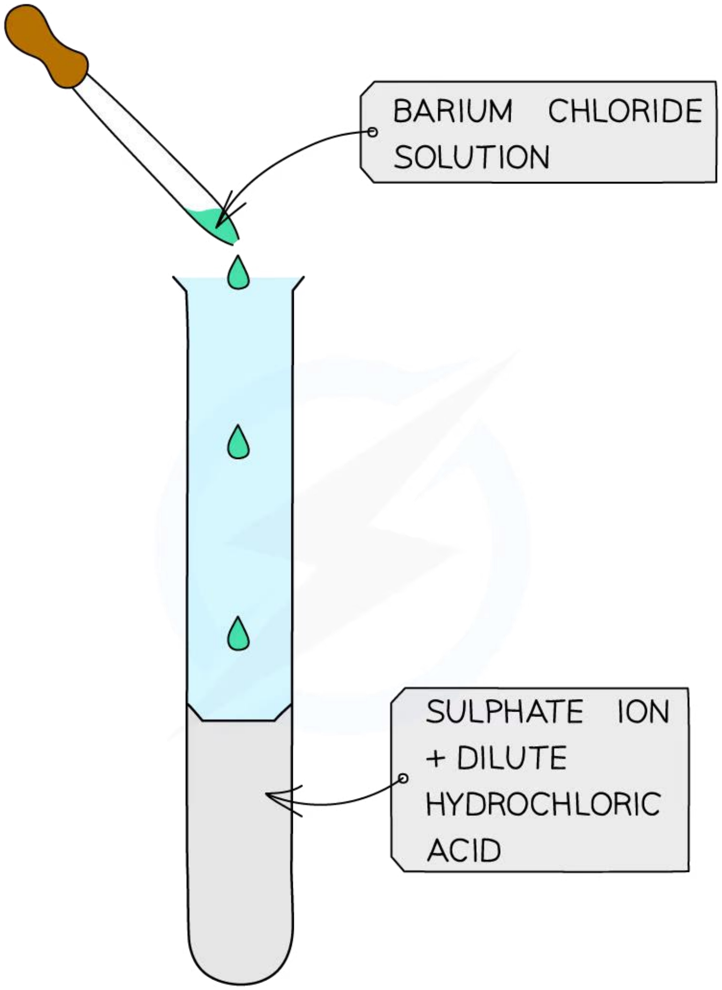
Limewater turns milky in the presence of CO_2 caused by formation of insoluble calcium carbonate

Test for Sulfates

- Acidify the sample with dilute hydrochloric acid and then add a few drops of aqueous barium chloride
- If a sulfate is present then a **white** precipitate of barium sulfate is formed:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

- The test can also be carried out with barium nitrate solution



A white precipitate of barium sulfate is a positive result for the presence of sulfate ions

Testing for ammonium ions

- We can test for the presence of ammonium ions, NH_4^+, by reacting with warm aqueous sodium hydroxide forming ammonia gas

$$NH_4^+ (aq) + OH^- (aq) \rightarrow NH_3(g) + H_2O (l)$$

- Ammonia gas is produced. You are unlikely to see gas bubbles as ammonia is very soluble in water
- Ammonia gas can be identified by its pungent smell or by turning red litmus paper blue

3.4 Enthalpy Changes

3.4.1 Enthalpy Changes

YOUR NOTES
↓

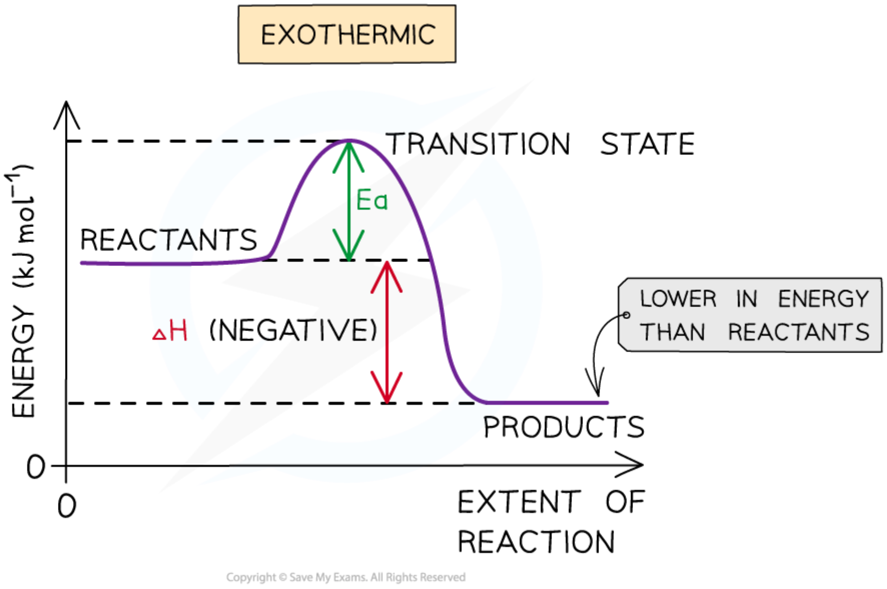
Endothermic & Exothermic Enthalpy Changes

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

Exothermic reactions

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

- There is an enthalpy decrease during the reaction so ΔH is negative
- Exothermic reactions are **thermodynamically** possible (because the enthalpy of the reactants is **higher** than that of the products)
- However, if the rate is too slow, the reaction may not occur
    - In this case the reaction is **kinetically** controlled

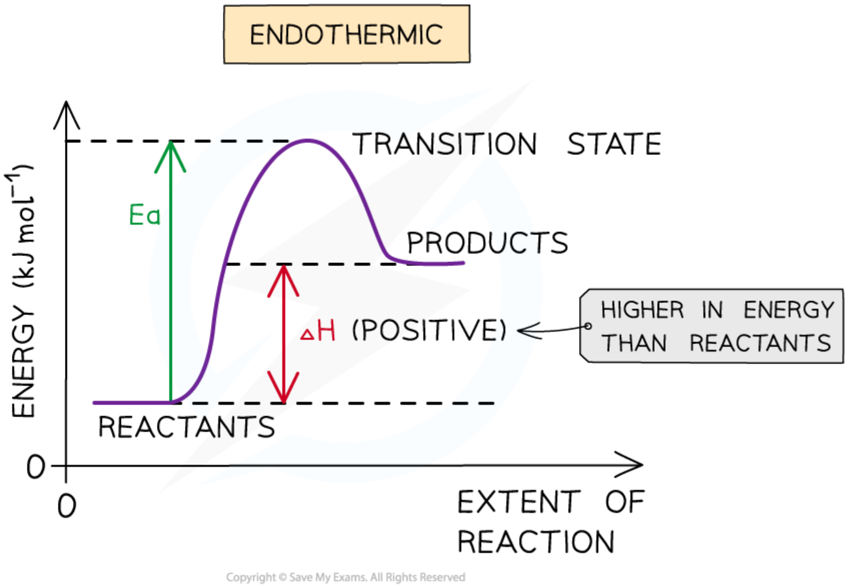


The enthalpy changes during an exothermic reaction

Endothermic reactions

- A reaction is endothermic when the products have more energy than the reactants

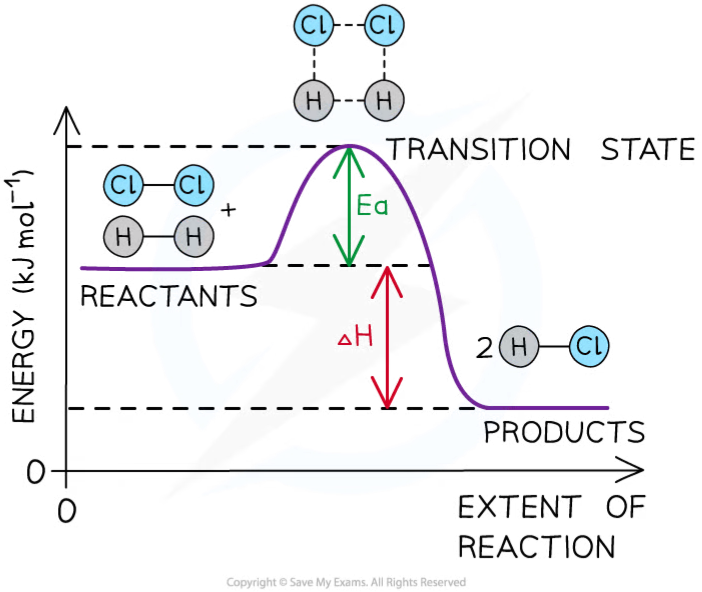
- Heat energy is **absorbed by** the reaction **from** the **surroundings**
  - The **temperature** of the **environment decreases** - this can be measured with a thermometer
  - The **energy** of the **system increases**
- There is an enthalpy increase during the reaction so ΔH is positive



The enthalpy changes during an endothermic reaction

Enthalpy Profile Diagrams

- An energy level diagram is a diagram that shows:
  - The energy level of the reactants
  - The transition state(s) - an unstable intermediate in the reaction which cannot be isolated and is higher in energy than the reactants and products
  - The energy level of the products
  - The **activation energy (*E*$_a$)**
    - The minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction
  - The enthalpy change for the reaction (ΔH)
    - This can be describes as the overall energy taken in from / given out to the surroundings OR the energy difference from reactants to products



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

Exam Tip

You do not need to know or label the specific term transition state on diagrams

Worked Example

Drawing energy level diagrams of the combustion of methane

The activation energy, *E*a, and enthalpy change, ΔH, for the complete combustion of methane are +2653 kJ mol^{-1} and -890 kJ mol^{-1} respectively.

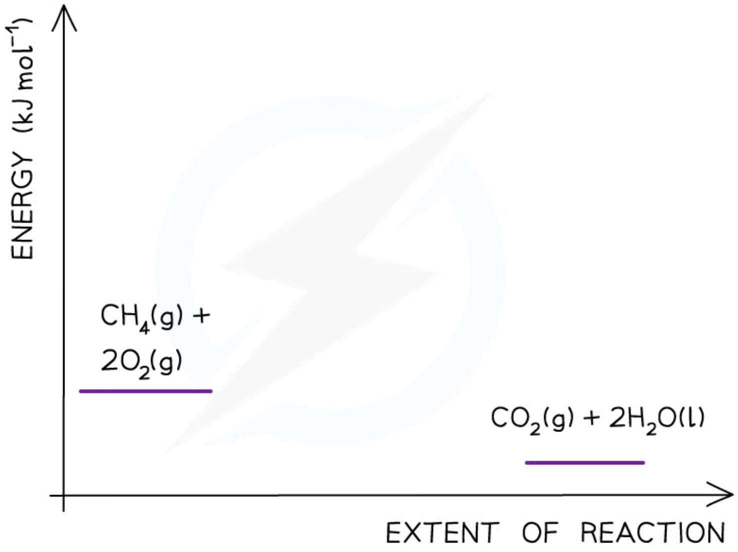
Draw the energy level diagram for this reaction.

Answer

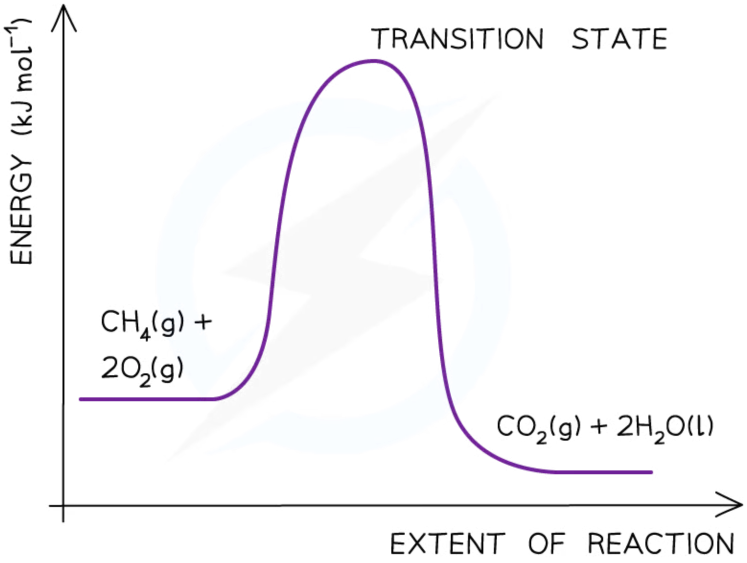
Step 1: The chemical equation for the complete combustion of methane is:

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

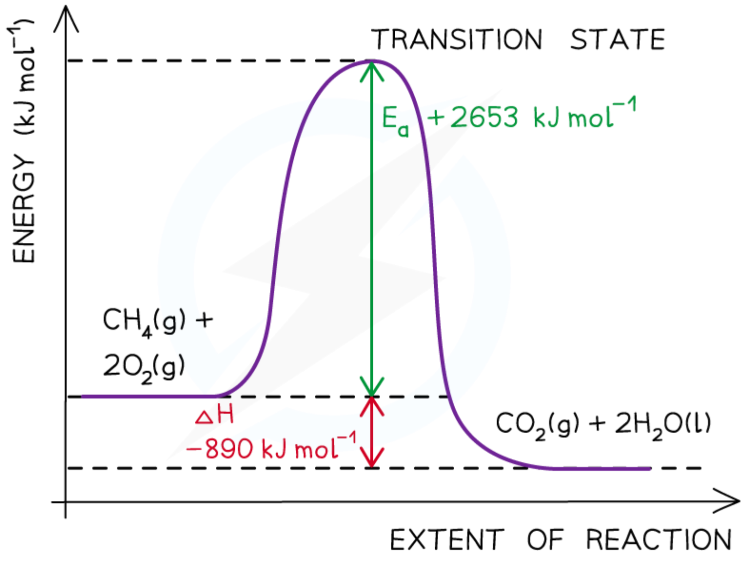
Step 2: Combustion reactions are always exothermic (∆*H* is negative) so the reactants should be drawn higher in energy than the products



Step 3: Draw the curve in the energy level diagram



Step 4: Draw arrows to show the E_a and ∆*H* including their values



Exam Tip

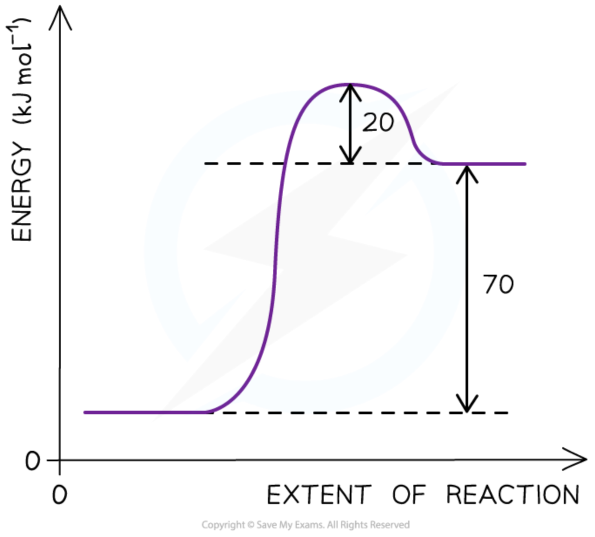
Remember to label the axes of the energy level diagrams!

Worked Example

Determining the activation energy

ΔH for a reaction is +70 kJ mol^{-1} and E_a for the reverse reaction is +20 kJ mol^{-1}.

Use the reaction pathway diagram below to determine the E_a for the forward reaction.



The reaction pathway diagram for a reversible reaction

Answer

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

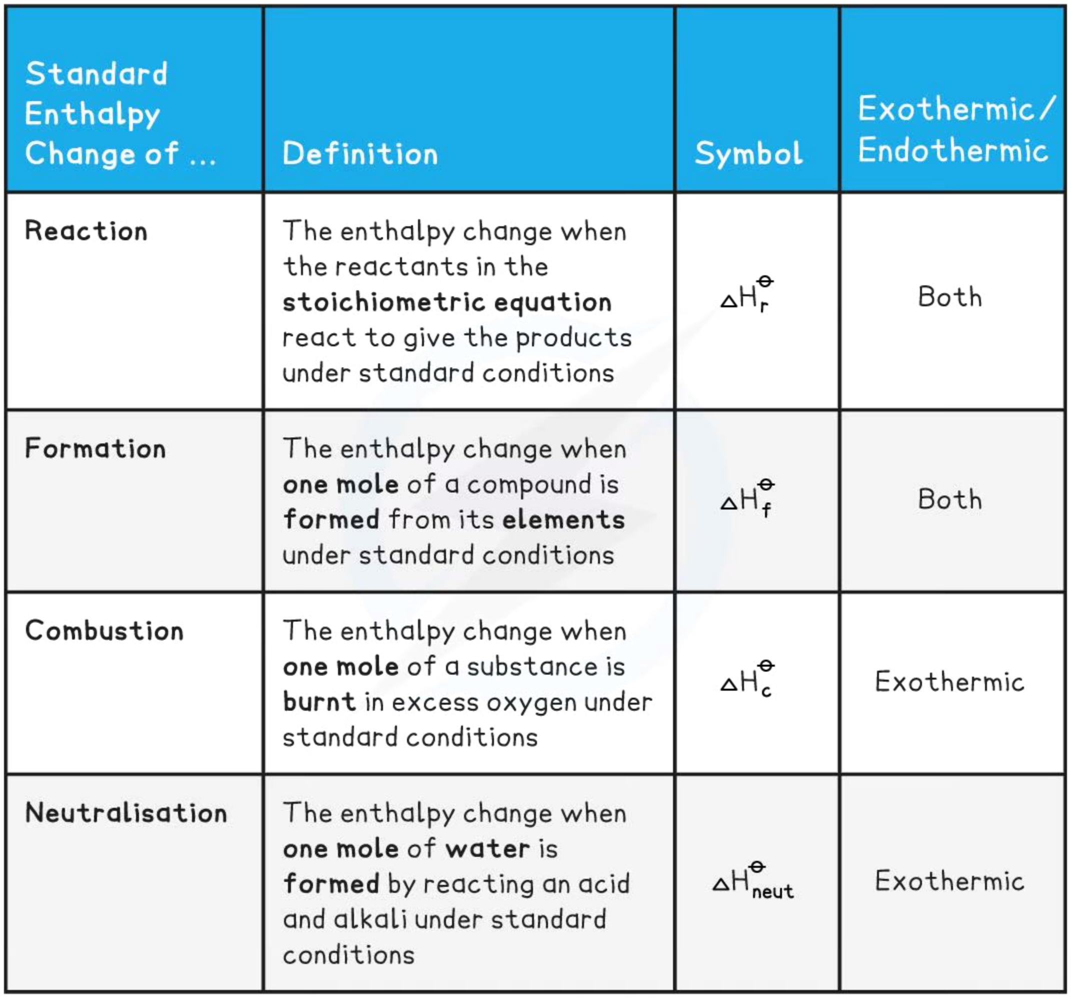
Standard Enthalpy Definitions

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

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

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

Enthalpy Definitions Table



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

Worked Example

Calculating the enthalpy change of reaction

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

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

Calculate ΔH_r for the reaction below:

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

Answer

- Since two moles of water molecules are formed in the question above, the energy released is simply:
  - ΔH_r = 2 mol x (-286 kJ mol^{-1})
  - ΔH_r = -572 kJ mol^{-1}

Worked Example

Calculating the enthalpy change

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

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

Answer

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

Worked Example

Calculating enthalpy changes

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

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

Answers

Answer 1: ΔH_r

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

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

Exam Tip

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

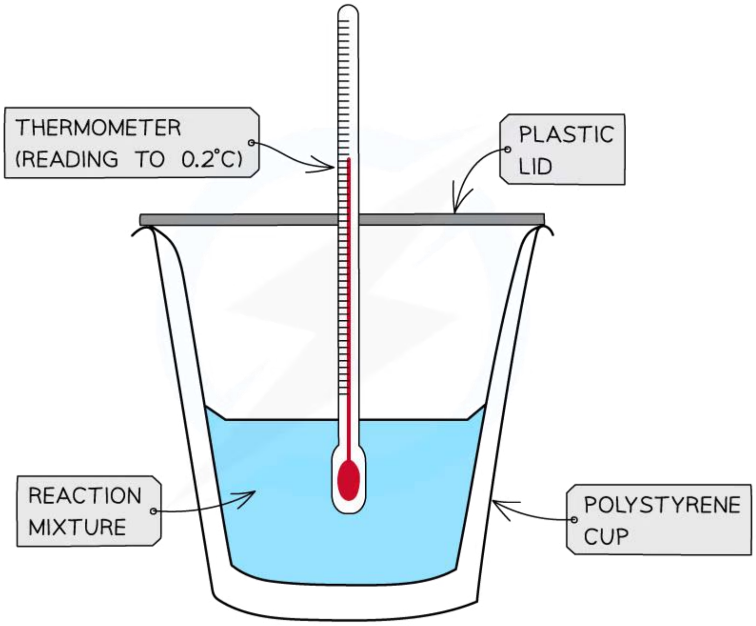
For example, ΔH_f of $O_2(g)$ is 0 kJ mol^{-1}

3.4.2 Calorimetry

Calorimetry & Specific Heat Capacity

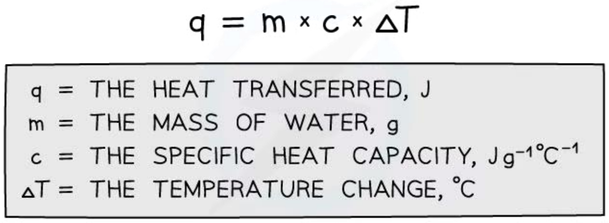
Measuring enthalpy changes

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



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

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



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

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

Equation for calculating energy transferred in a calorimeter

Worked Example

Specific heat capacity calculations

In a calorimetry experiment 2.50 g of methane is burnt in excess oxygen.

30% of the energy released during the combustion is absorbed by 500 g of water, the temperature of which rises from 25 °C to 68 °C.

The specific heat capacity of water is 4.18 J g^{-1} K^{-1}

What is the total energy released per gram of methane burnt?

Answer

Step 1

- $q = m \times c \times \Delta T$
- m (of water) = 500 g
- c (of water) = 4.18 J g^{-1} $°C^{-1}$
- ΔT (of water) = 68 °C - 25 °C = 43 °C

Step 2:

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

Step 3:

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

Step 4:

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

Exam Tip

Aqueous solutions of acid, alkalis and salts are assumed to be largely water so you can just use the m and c values of water when calculating the energy transferred.

To calculate any changes in enthalpy per mole of a reactant or product the following relationship can be used:

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

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

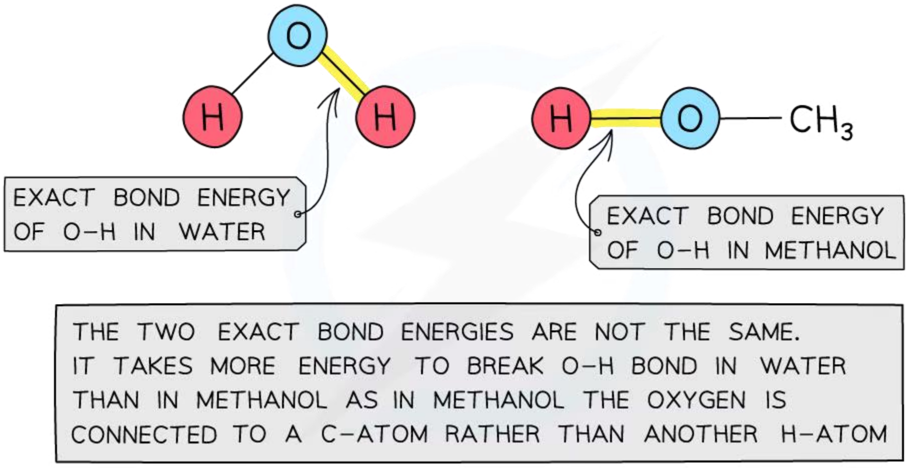
- This means that your value should be positive for an endothermic reaction

Bond Enthalpy Explanations

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

Average bond energy

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



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

Calculating enthalpy change from bond energies

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

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

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

- As energy is required to break bonds, bond breaking is endothermic
    - ΔH is positive
- As energy is released making new bonds, bond forming is exothermic
    - ΔH is negative
- The difference between the energy required for bond breaking and the energy released by bond making determines whether an overall reaction is exothermic or endothermic

Exam Tip

It is important to be aware that the actual bond enthalpy value may differ from the average value

Bond Enthalpy Calculations

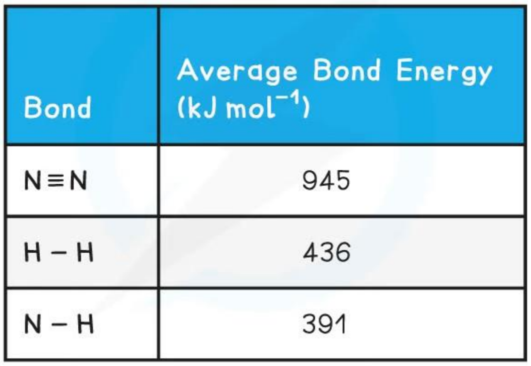
Worked Example

Calculating the enthalpy change in the Haber process

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

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

The relevant bond energies are given in the table below:

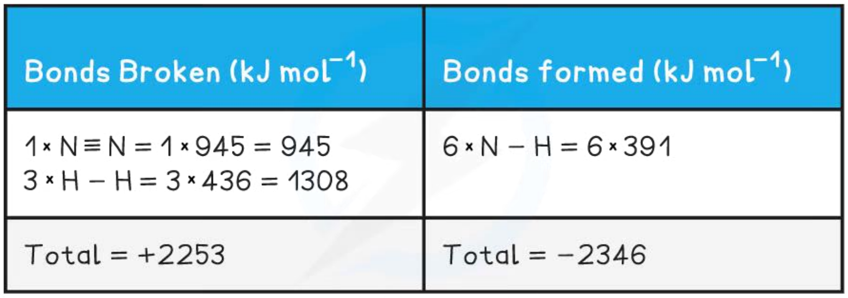


Bond	Average Bond Energy (kJ mol^{-1})
N≡N	945
H – H	436
N – H	391

Answer

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

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



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

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

Step 2: Calculate the standard enthalpy of reaction

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

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

= -93 kJ mol^{-1}

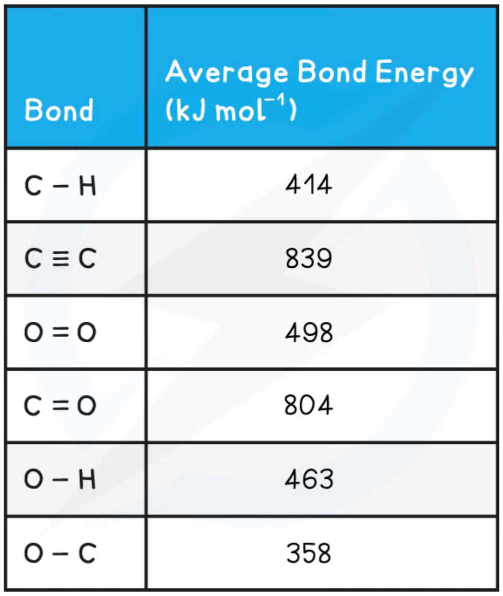
Worked Example

Calculating the enthalpy of combustion using bond enthalpies

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

$$\mathrm{2H{-}C{\equiv}C{-}H + 5O{=}O \rightarrow 2H{-}O{-}H + 4O{=}C{=}O}$$

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



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

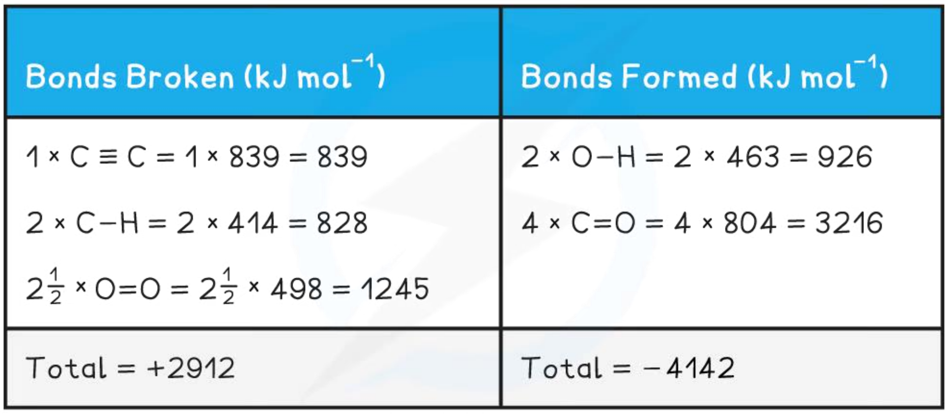
Answer

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:

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

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



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

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

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

= -1230 kJ mol^{-1}

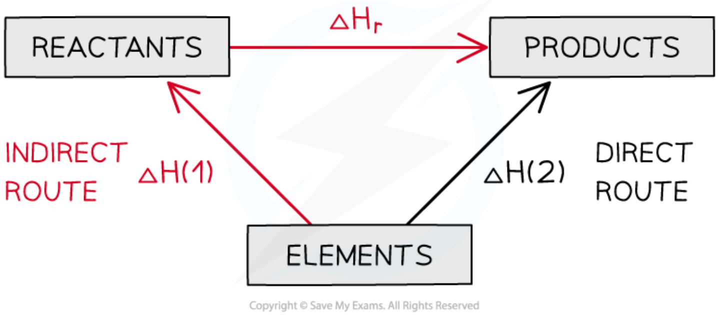
Hess' Law & Enthalpy Cycles

Calculating ΔH_r from ΔH_f using Hess's Law energy cycles

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

OR

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



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

- **Equation**

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

Therefore,

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

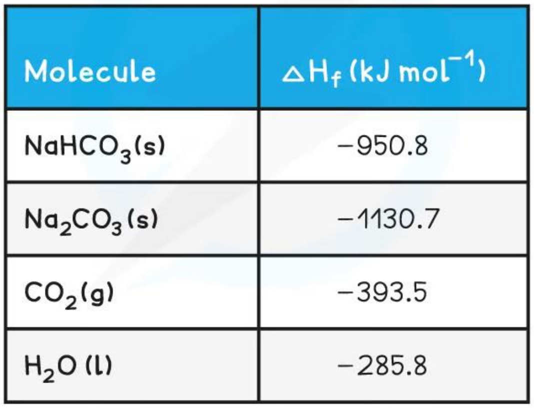
Worked Example

Calculating the enthalpy change of reaction

Calculate the ΔH_f for the following reaction:

$2NaHCO_3\ (s) \rightarrow Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (l)$

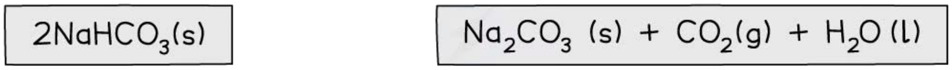
The table below shows the standard enthalpy of formations (ΔH_f) relevant to this reaction:



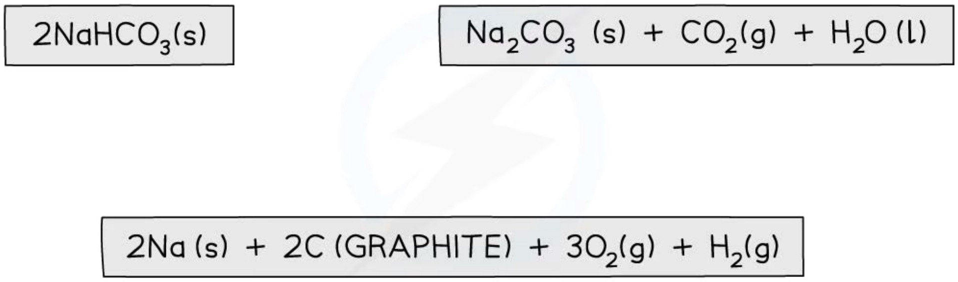
Molecule	ΔH_f (kJ mol^{-1})
$NaHCO_3(s)$	−950.8
$Na_2CO_3\ (s)$	−1130.7
$CO_2(g)$	−393.5
$H_2O\ (l)$	−285.8

Answer

Step 1: Write the balanced equation at the top



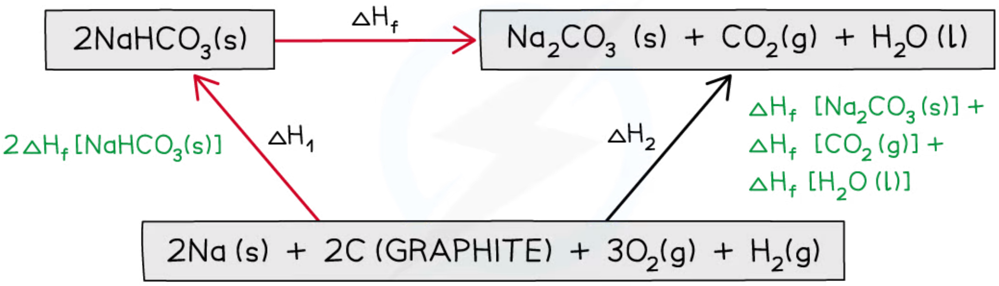
Step 2: Draw the cycle with the elements at the bottom



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

- $\Delta H_r = \Delta H_2 - \Delta H_1$
  - $\Delta H_2 = \Delta H_f\ [Na_2CO_3\ (s)] + \Delta H_f\ [CO_2\ (g)] + \Delta H_f\ [H_2O\ (l)]$
  - $\Delta H_1 = 2 \times \Delta H_f\ [NaHCO_3\ (s)]$
- $\Delta H_r = ((-1130.7) + (-393.5) + (-285.8)) - (2 \times (-950.8))$
- $\Delta H_r = +91.6$ kJ mol^{-1}



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

Worked Example

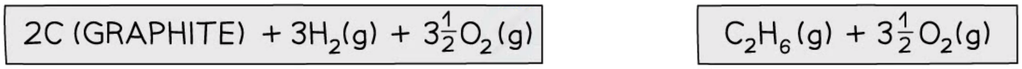
Calculating the enthalpy change of formation of ethane

Calculate ΔH_f [ethane]. The relevant change in standard enthalpy of combustion (ΔH_c) values are shown in the table below:

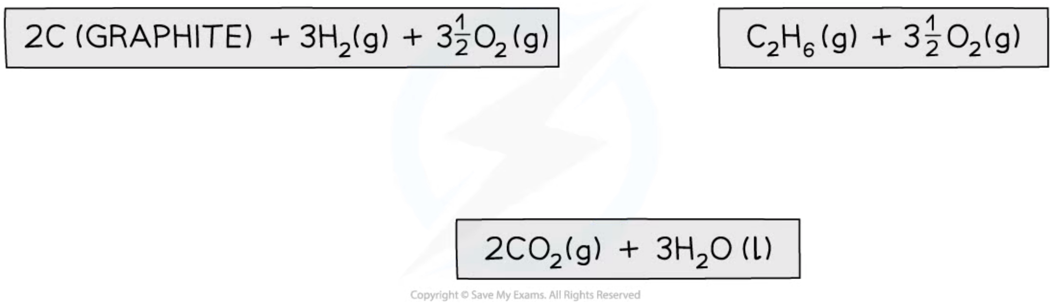
Reaction	ΔH_c (kJ mol^{-1})
$C(graphite) + O_2(g) \longrightarrow CO_2(g)$	−393.5
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
$C_2H_6(g) + 3\frac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1559.7

Answer

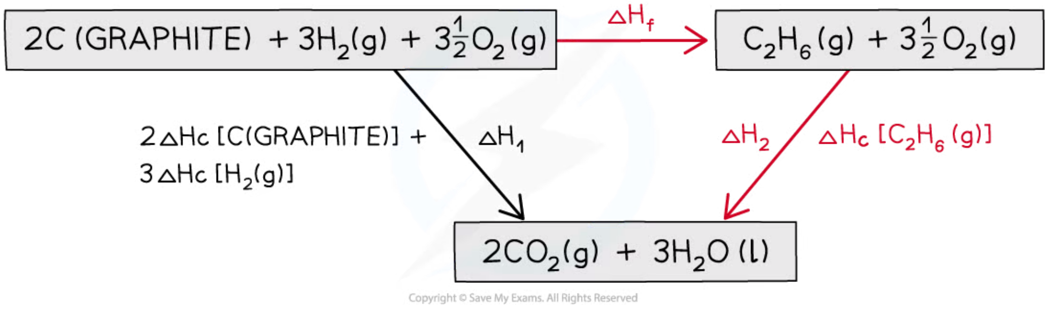
Step 1: Write the equation for enthalpy change of formation at the top and add oxygen on both sides



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



Step 3: Draw all arrows in the correct direction



Step 4: Apply Hess's Law

- $\Delta H_f = \Delta H_1 - \Delta H_2$
  - $\Delta H_2 = \Delta H_c$ [C_2H_6 (g)]
  - ΔH_1 = 2 x ΔH_c [$C_{graphite}$ (s)] + 3 x ΔH_c [H_2 (g)]ΔH_r
- = (2 x (-393.5) + 3 x (-285.8)) - (-1559.7)
- ΔH_r = -84.7 kJ mol^{-1}

Exam Tip

There are two rules that you can use to help with your calculations using enthalpy changes of formation and combustion

- Using enthalpy changes of formation, ΔH_f
  - $\Delta_r H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$
- Using enthalpy changes of combustion, ΔH_c
  - $\Delta_r H = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$

3.5 Reaction Rates

3.5.1 Simple Collision Theory

Effect of Concentration

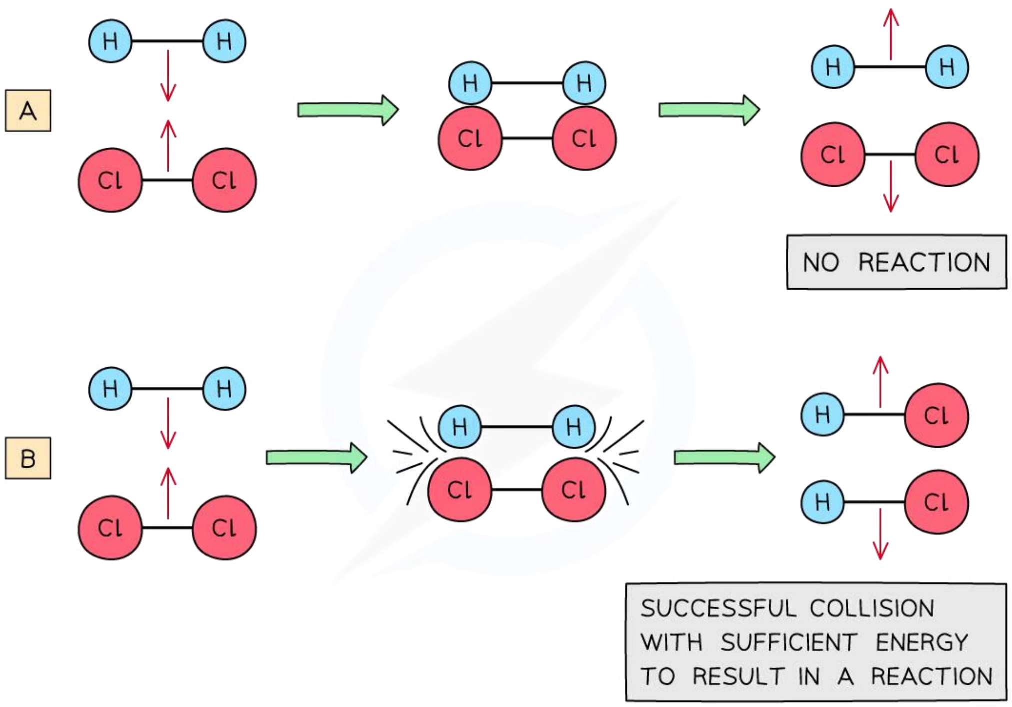
Collision theory

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

Collision Theory Table

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

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



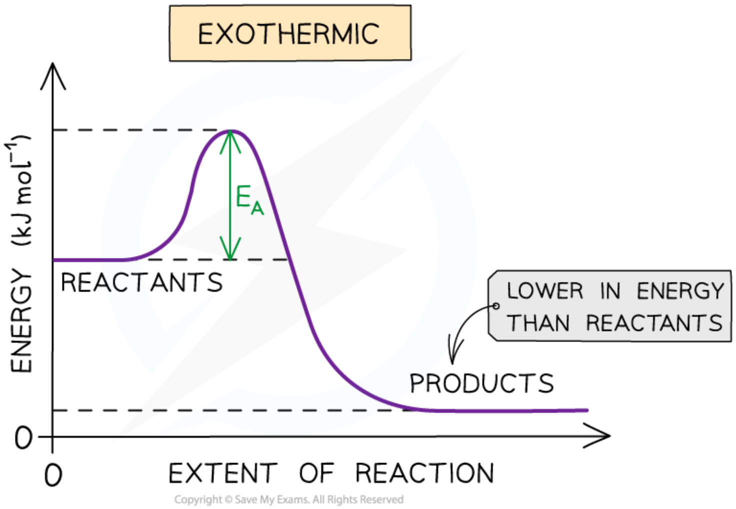
(a) shows an ineffective collision due to the particles not having enough energy whereas (b) shows an effective collision where the particles have the correct orientation and enough energy for a chemical reaction to take place

Increase in reaction rate

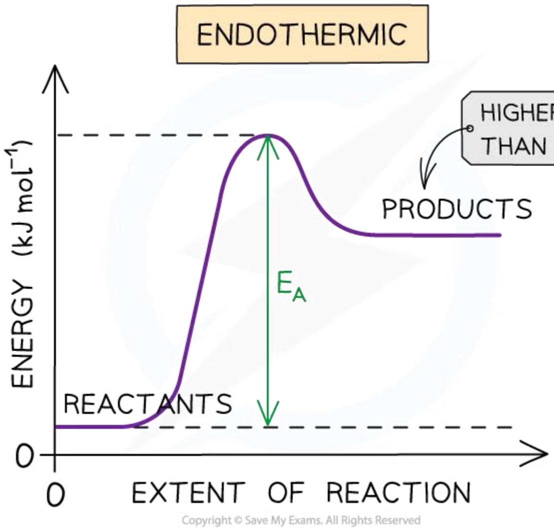
- The **collision frequency** is the number of collisions per unit time
- When more collisions per unit time take place, the number of particles with energy greater than the E_a increases
- This causes an **increase** in the **rate of reaction**

Activation Energy

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



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

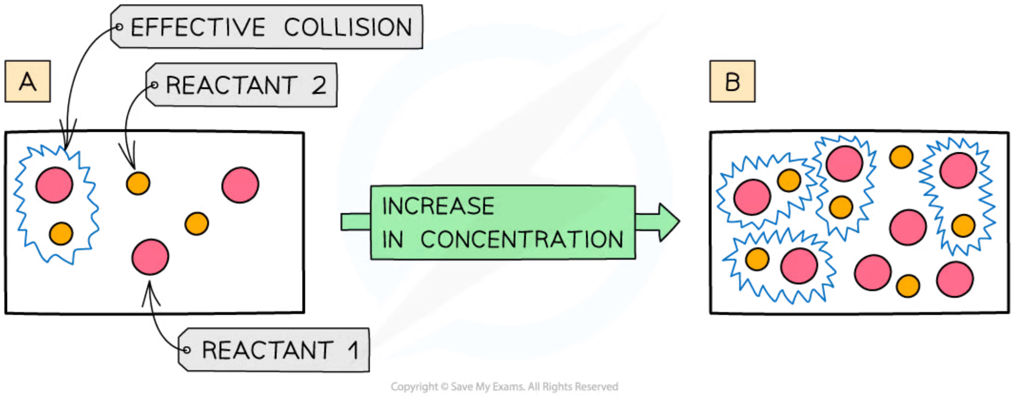


The diagram shows that the reactants are lower in energy than the products in the endothermic reaction, so the energy needed for the reactants to go over the energy barrier is relatively large

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

Effect of concentration

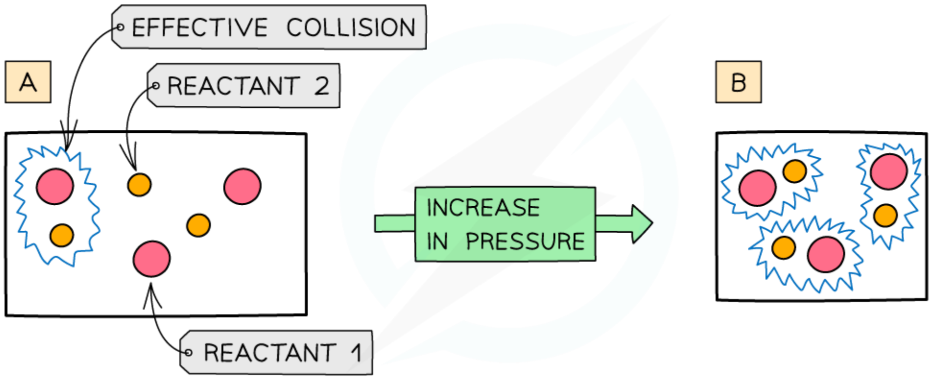
- The more **concentrated** a solution is, the **greater** the number of **particles** in a given volume of solvent
- An increase in **concentration** causes in an increased **collision frequency** and therefore an increased **rate of reaction**



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

Effect of pressure

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



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

Exam Tip

When questions mention a doubling of concentration make sure you mention double the number of particles per unit volume and double the frequency of effective collisions

Calculating Rates

Reaction rate

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

$$\text{Rate of reaction} = \frac{\text{change in amount of reactants or products (mol dm}^{-3}\text{)}}{\text{time (s)}}$$

Worked Example

Calculating the rate of reaction

Calculate the rate of reaction, in mol dm^{-3} s^{-1}, when 0.0440 g of ethyl ethanoate, $CH_3COOC_2H_5$, (M_r = 88.0 g mol^{-1}) is formed in 1.00 minute froma reaction mixture of total volume 400 cm^3

Answer

Step 1: Calculate the number of moles of ethyl ethanoate:

- Number of moles = $\frac{mass}{molar\ mass}$
- Number of moles = $\frac{0.0440}{88.0} = 0.0005 \text{ mol}$

Step 2: Calculate the concentration of the product:

- Concentration of ethyl ethanoate (mol dm^{-3}) = $\frac{\text{number of moles of solute}}{\text{volume of solution}}$
- Concentration of ethyl ethanoate (mol dm^{-3}) = $\frac{0.0005}{0.400} = 0.00125 \text{ mol dm}^{-3}$

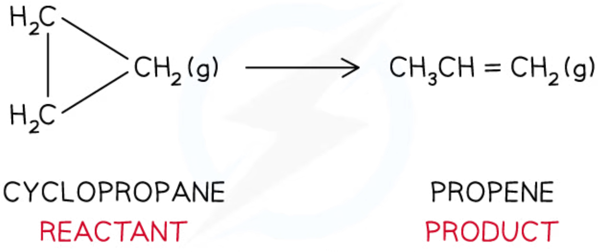
Step 3: Calculate the rate:

- Rate of reaction = $\frac{\text{change in amount of reactants or products (mol dm}^{-3}\text{)}}{\text{time (s)}}$
- Rate of reaction = $\frac{0.00125}{60} = 2.08 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

Measuring a rate from a graph

- During a reaction, the **reactants** are used up and changed into **products**
- This means that as the reaction proceeds, the concentration of the reactants is **decreasing** and the concentration of the products is **increasing**
- Therefore, the **rate of the reaction** is not the same throughout the reaction but **changes**
- The rate of reaction during the reaction can be calculated from a **concentration–time graph**

- The **isomerisation of cyclopropane** to propene is used as an example:



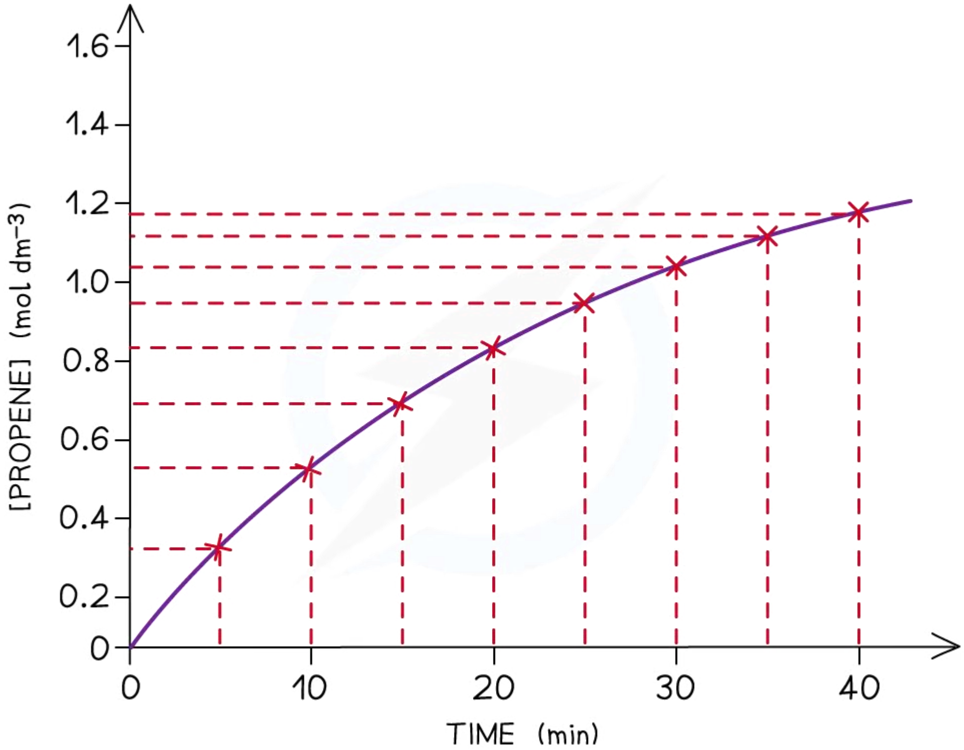
Isomerisation of cyclopropane

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

Concentrations of Cyclopropane & Propene Table

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

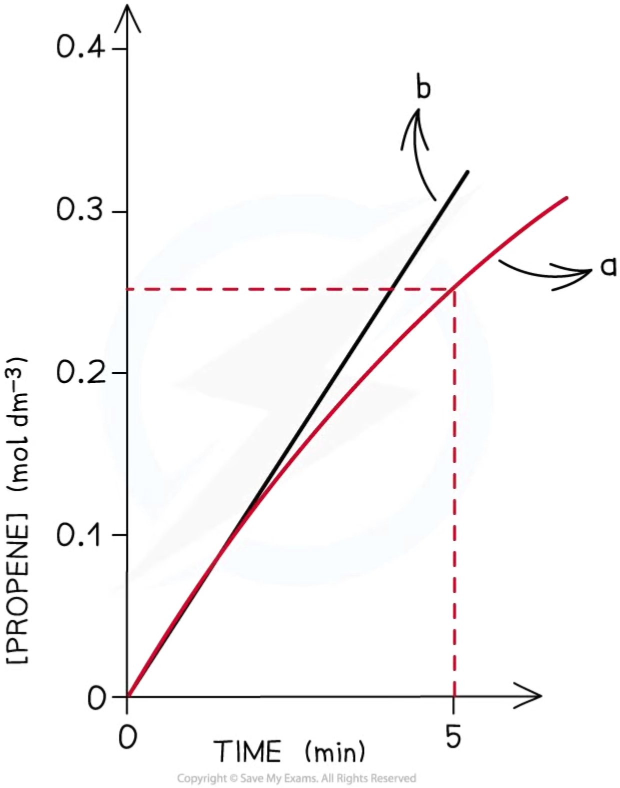
- When taking the measurements, the **temperature** should be kept constant as a **change** in temperature will change the **rate of reaction**
- A **concentration–time graph** for the concentration of propene as well as cyclopropane can be obtained from the above results
  - As an example, the concentration-time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



The graph shows that the concentration of propene increases with time

Calculating the rate at the start of a reaction

- At the start of the reaction, the concentration-time curve looks almost linear:



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

- The rate at this point can therefore be found by treating the curve as a linear line and by using:

$$\text{Rate of reaction} = \frac{\text{change in amount of reactants or products (mol dm}^{-3}\text{)}}{\text{time (s)}}$$

- The average rate of the reaction over the first 5 minutes for propene is:

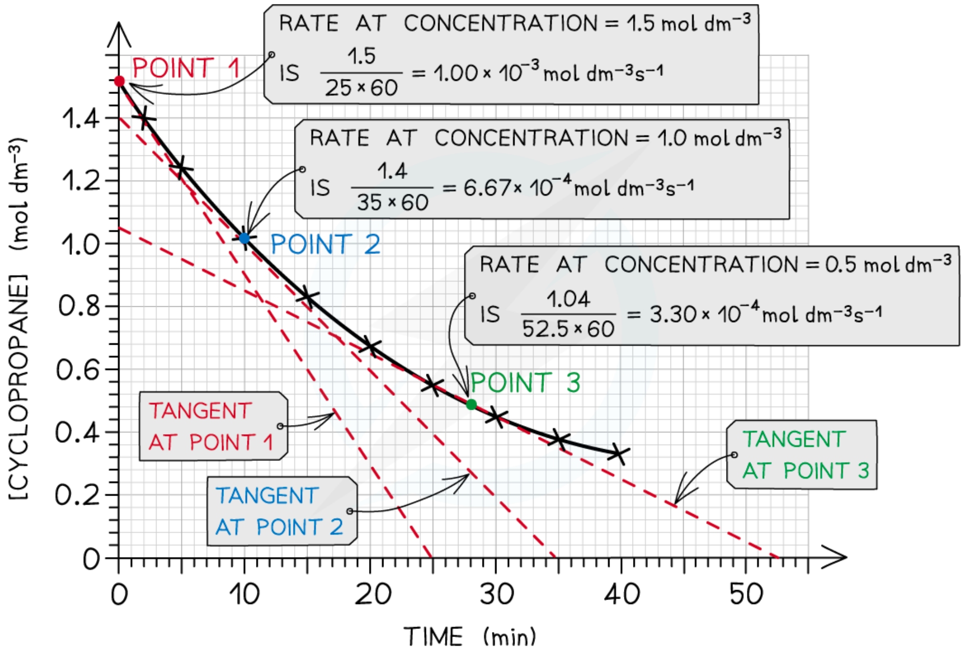
$$\text{Rate of reaction} = \frac{0.27}{300} = 0.0009 \text{ mol dm}^{-3} \text{ s}^{-1}$$

Calculating the rate as the reaction proceeds

- The curve becomes shallower with time which means that the rate decreases with time
- The rate of reaction can be calculated by taking short time intervals
  - For example. you can calculate the rate of reaction from 15 to 20 minutes during which the concentration of propene increases from 0.68 to 0.83 mol dm^{-3}

$$\text{Rate of reaction} = \frac{(0.83) - (0.68)}{(1200) - (900)} = \frac{0.15}{300} = 0.0005 \text{ mol dm}^{-3} \text{ s}^{-1}$$

- The smaller the time intervals, the more accurate the reaction rate value is
- It is even more accurate to find the rate of reaction at **different concentrations** of reactant or product at **particular time points**
- This can be done by drawing **tangents** at several points on the graph
  - As an example, the rates of reaction at different concentrations of cyclopropane are calculated by drawing the appropriate tangents:



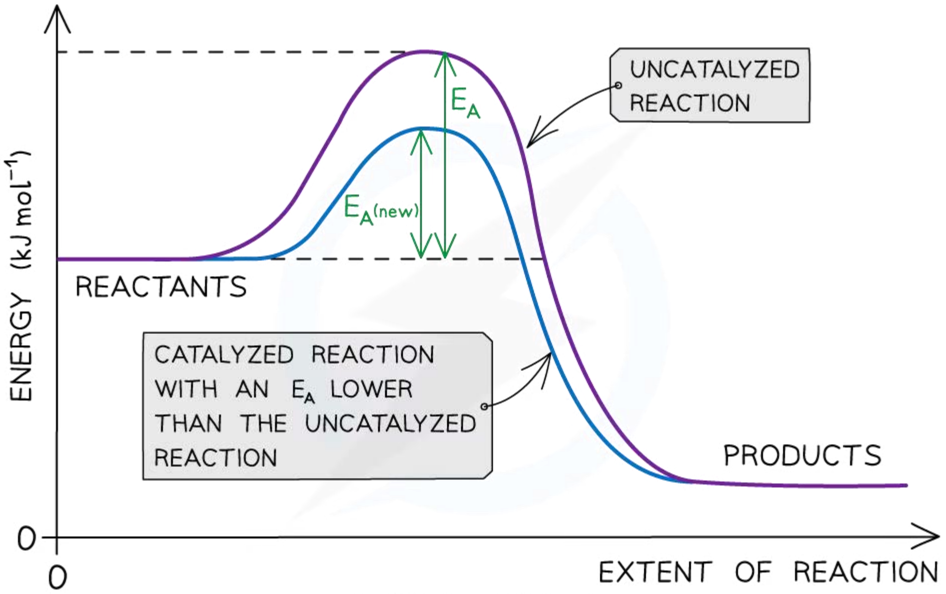
The rate of reaction at three different concentrations of cyclopropane is calculated by drawing tangents at those points in the graph

Exam Tip

Other suitable physical quantities you could monitor to measure reaction rate include gas volume and mass

The Role of a Catalyst

- A **catalyst** is a substance that **increases** the **rate of reaction** by providing the particles with an alternative mechanism with a lower activation energy
  - Catalysts do not have to be directly involved in the chemical reaction
  - They can provide a surface for the reaction to occur on, e.g. iron in the Haber process
  - Alternatively, they can provide a particle (often an ion) to start the reaction but this particle is regenerated at the end so the catalyst appears unaltered, e.g. chlorine radicals in ozone depletion



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

Importance of Catalysts

- 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

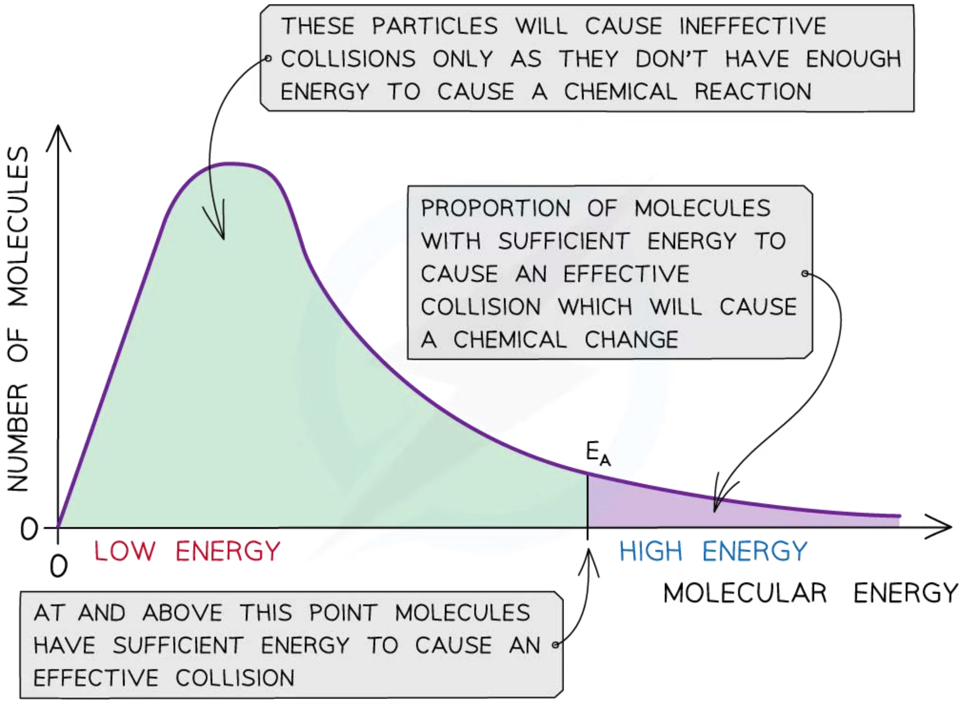
Benefits of catalysts

- 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 CO_2 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

The Boltzmann Distribution & Activation Energy

Maxwell-Boltzmann distribution curve

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



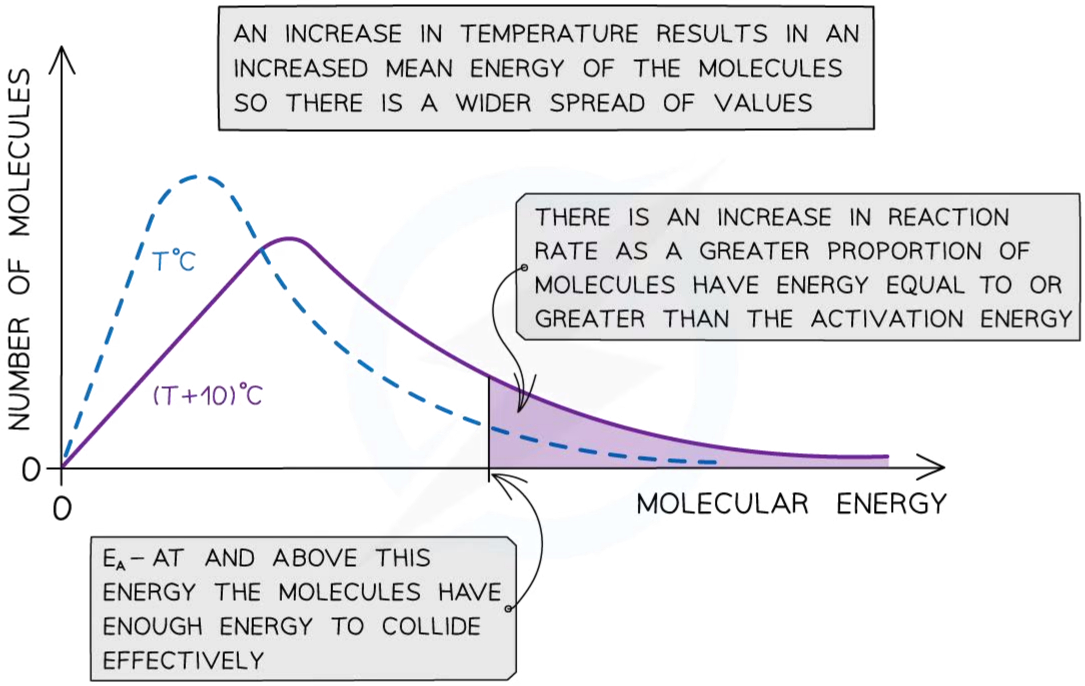
The Maxwell–Boltzmann distribution curve shows the distribution of the energies and the activation energy

- The graph shows that only a small proportion of molecules in the sample have enough energy for an **effective collision** and for a **chemical reaction** to take place
- The energy distribution should go through the origin because there are no molecules with no energy
- The energy distribution should never meet the x axis, as there is no maximum energy for molecules
- The area underneath the curve represents the total number of particles present

Changes in temperature

- When the temperature of a reaction mixture is increased, the particles gain more kinetic energy
- This causes the particles to move around faster resulting in more **frequent collisions**

- Furthermore, the proportion of **successful collisions** increases, meaning a higher **proportion** of the particles possess the minimum amount of energy (activation energy) to cause a chemical reaction
- With higher temperatures, the Boltzmann distribution curve **flattens** and the peak **shifts** to the right



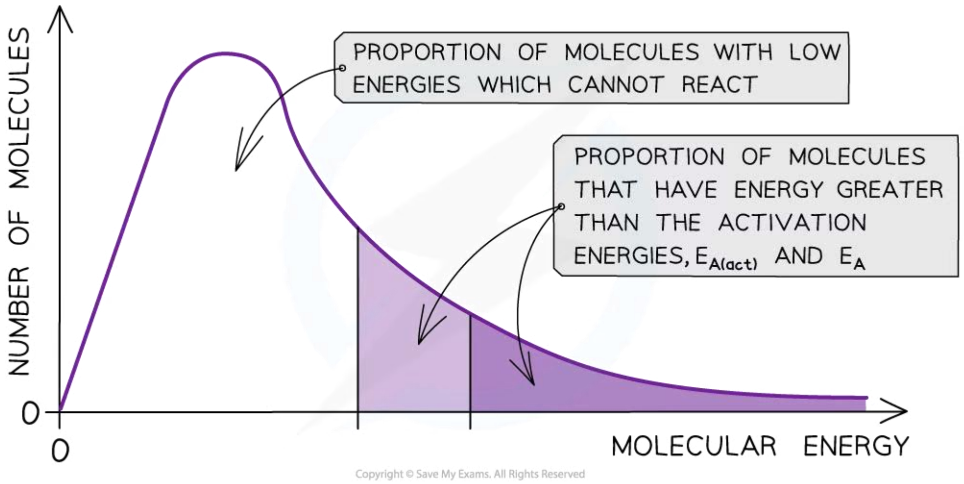
The Maxwell–Boltzmann distribution curve at T °C and when the temperature is increased by 10 °C

Therefore, an increase in temperature causes an increased rate of reaction due to:

- There being **more effective collisions** as the particles have **more kinetic energy**, making them move around faster
- A **greater proportion** of the molecules having **kinetic energy** greater than the **activation energy**

Effect of catalysts

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



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

Exam Tip

Remember that despite the curve shifting with changes in temperature the total area under the curve should remain constant because the total number of particles is constant

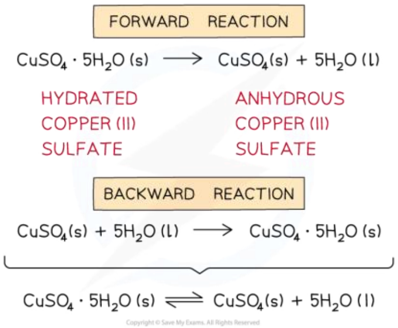
3.6 Chemical Equilibrium

3.6.1 Dynamic Equilibrium

Dynamic Equilibrium

Reversible reaction

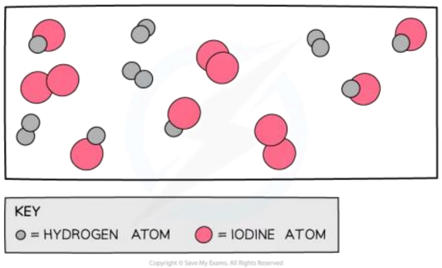
- Some reactions go to completion where the reactants are used up to form the products
  - The reaction stops when all of the reactants are used up
- In **reversible reactions**, the products can react to reform the original reactants
  - To show a reversible reaction, two opposing half arrows are used: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



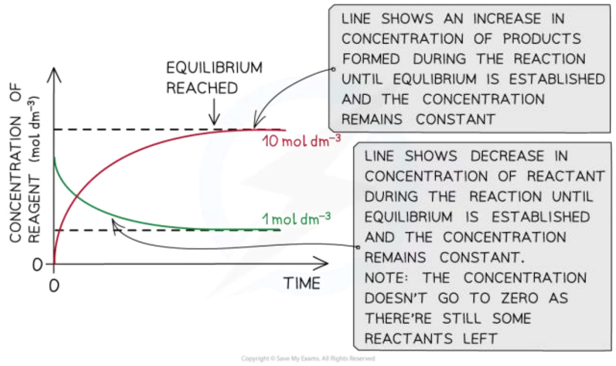
The diagram shows an example of a forward and backward reaction that can be written as one equation using two half arrows

Dynamic equilibrium

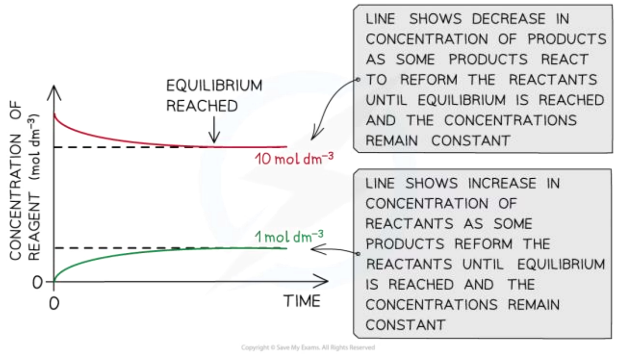
- In a **dynamic equilibrium**, the reactants and products are **dynamic** (they are constantly moving)
- In a dynamic equilibrium, the **rate** of the **forward** reaction is the same as the rate of the **backward** reaction in a **closed system**, and the **concentrations** of the **reactants** and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



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

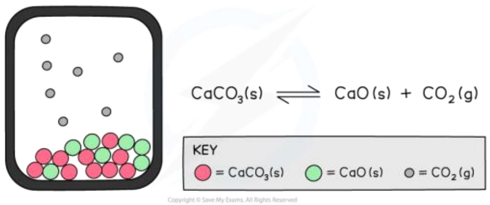


The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)

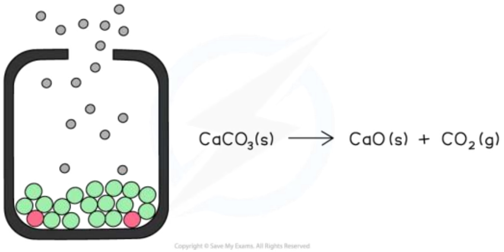


The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using products)

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



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



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

Exam Tip

A common misconception is to think that the concentrations of the reactants and products are equal.

They are not equal but they **remain constant** at dynamic equilibrium (i.e. the concentrations are not changing).

The concentrations will change as the reaction progresses, only until the equilibrium is reached.

Equilibrium & Reaction Conditions

Position of the equilibrium

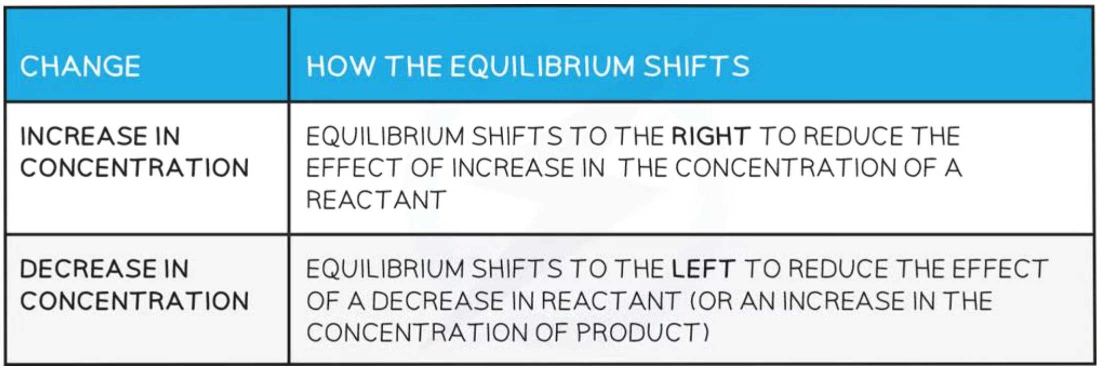
- The **position of the equilibrium** refers to the relative amounts of products and reactants in an equilibrium mixture
- When the position of equilibrium shifts to the **left**, it means the concentration of **reactants** increases
- When the position of equilibrium shifts to the **right**, it means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

Le Chatelier's principle

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

Effects of concentration

How the equilibrium shifts with concentration changes



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

Worked Example

Changes in equilibrium position

Using the reaction below:

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

Explain what happens to the position of equilibrium when:

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

Using the reaction below:

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

Explain what happens to the position of equilibrium when

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

Answer 1:

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

Answer 2:

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

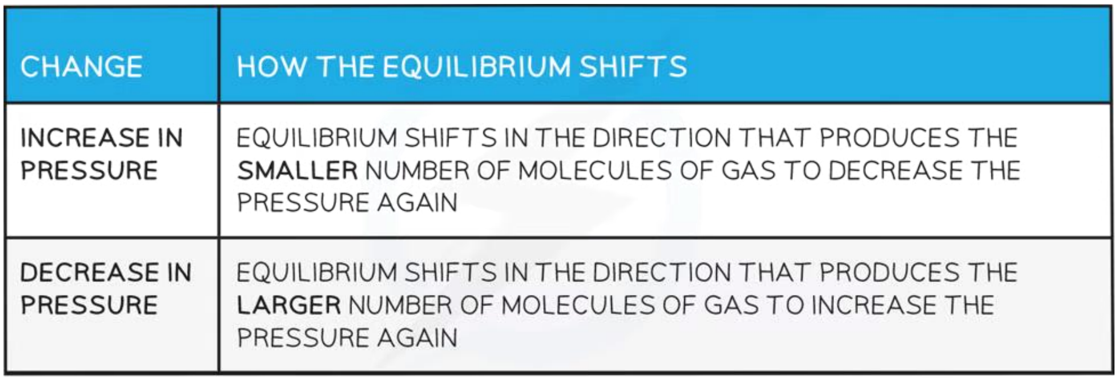
Answer 3:

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

Effects of pressure

- Changes in pressure only affect reactions where the reactants or products are gases

How the equilibrium shifts with pressure changes



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

Worked Example

Changes in pressure

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

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

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

3. $2NO_2$ (g) ⇌ 2NO (g) + O_2 (g)

Answer 1:

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

Answer 2:

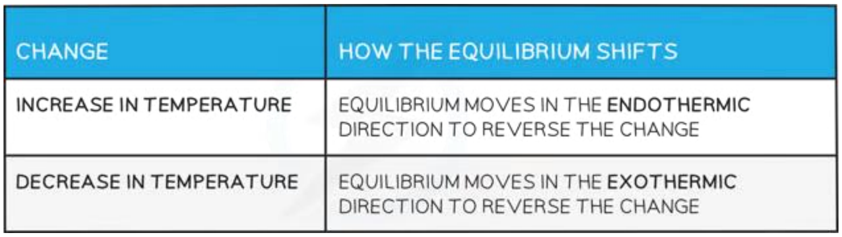
- The equilibrium shifts to the left as there are no gas molecules on the left but there is CO_2 on the right
- This causes a decrease in pressure

Answer 3:

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

Effects of temperature

How the 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:

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

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

Using the reaction below:

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

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

Explain your answer

Answer 1:

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

Answer 2:

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

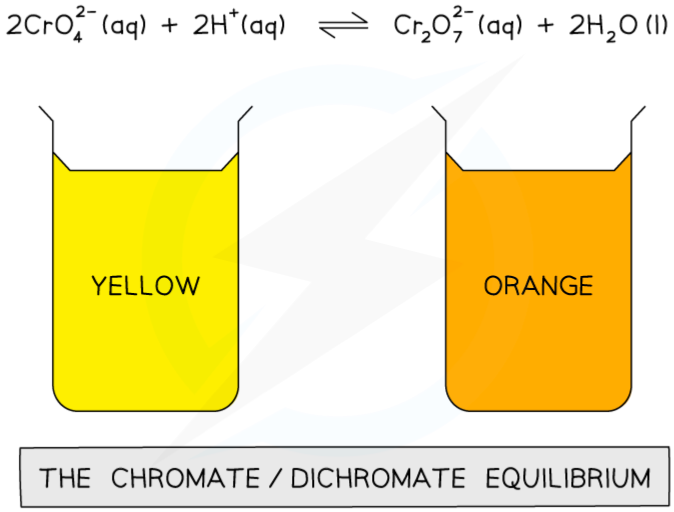
Equilibrium & Catalysts

Effects of catalysts

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

Investigating changes to the equilibrium position with concentration

- The equilibrium between aqueous chromate ions, CrO_4^{2-}, and dichromate ions, $Cr_2O_7^{2-}$ is sensitive to changes in acid concentration
- Solutions of chromate and dichromate ions have different colours so it is easy to see any shift in the equilibrium position



THE CHROMATE / DICHROMATE EQUILIBRIUM

- By adding dilute sulfuric acid, we can increase the concentration of H^+ (aq) in the solution
- This increases the rate of the forward reaction causing the equilibrium position to shift to minimise the change in H^+ (aq) concentration
  - This decreases the concentration of the added reactant, H^+ (aq)
  - Equilibrium shifts to the right, making more products
  - Solution turns orange due to the formation of more $Cr_2O_7^{2-}$ (aq)
- By adding aqueous sodium hydroxide, we can decrease the concentration of H^+ (aq) in the solution
- The added OH^-(aq) ions react with H^+(aq) ions forming waterH^+
- (aq) + OH^- (aq) → H_2O (l)
- This decreases the rate of the forward reaction causing the equilibrium position to shift to minimise the change in H^+(aq) concentration
  - This decreases the concentration of reactant that has been removed, H^+ (aq)
  - Equilibrium shifts to the left, making more H^+ (aq) reactant
  - Solution turns yellow due to the formation of more CrO_4^{2-} (aq)

Investigating changes in equilibrium position with temperature

- Cobalt chloride, $CoCl_2$, dissolves in water to form a pink solution
- The dissolving process produces an equilibrium between two different coloured cobalt complexes

$$[Co(H_2O)_6]^{2+}\ (aq) + 4Cl^-\ (aq) \rightleftharpoons [CoCl_4]^{2-}\ (aq) + 6H_2O\ (l)$$

  - The forward reaction in this process is endothermic and the backward reaction is exothermic
- By heating up the solution we can increase the amount of heat energy in the system
  - This causes the equilibrium to shift to minimise the change
    - Equilibrium shifts to the right favouring the endothermic reaction (ΔH is positive)
    - This allows the system to take heat energy in and minimise the increase in temperature
    - The solution turns blue as more $CoCl_4^{2-}$ (aq) is formed
- Cooling down the solution removes the heat energy from the system
  - This again causes the equilibrium to shift to minimise the change
    - Equilibrium shifts to the left favouring the exothermic reaction (ΔH is negative)
    - This allows the system to release heat energy and minimise the decrease in temperature
    - The solution turns pink as more $Co(H_2O)_6^{2+}$ (aq) is formed

Operational Conditions

YOUR NOTES
⬇

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

Haber process

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

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

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

Maximising the ammonia yield

Pressure

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

Temperature

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

Catalysts

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

Contact process

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

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

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

Maximising the sulfuric acid yield

Pressure

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

Temperature

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

Catalysts

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

3.6.3 The Equilibrium Constant, Kc

Equilibrium Constant Expressions

Equilibrium expression & constant

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

$$\mathbf{aA + bB \rightleftharpoons cC + dD}$$

the K_c is defined as follows:

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

[A] AND [B] = EQUILIBRIUM REACTANT CONCENTRATIONS (mol dm^{-3})
[C] AND [D] = EQUILIBRIUM PRODUCT CONCENTRATIONS (mol dm^{-3})
a, b, c AND d = NUMBER OF MOLES OF REACTANTS AND PRODUCTS

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

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

Worked Example

Deducing equilibrium expressions

Deduce the equilibrium expression for the following reactions:

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

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

Equilibrium Constant Calculations

Calculations involving K_c

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

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

Equation to calculate concentration from number of moles and volume

Worked Example

Calculating K_c of ethanoic acid

In the reaction:

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

ethanoic acid ethanol ethyl ethanoate water

500 cm^3 of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.035 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of K_c for this reaction.

Answer

Step 1: Calculate the concentrations of the reactants and products

- $[CH_3COOH\ (l)] = \dfrac{0.235}{0.500} = 0.470 \text{ mol dm}^{-3}$
- $[C_2H_5OH\ (l)] = \dfrac{0.035}{0.500} = 0.070 \text{ mol dm}^{-3}$
- $[CH_3COOC_2H_5\ (l)] = \dfrac{0.182}{0.500} = 0.364 \text{ mol dm}^{-3}$
- $[H_2O\ (l)] = \dfrac{0.182}{0.500} = 0.364 \text{ mol dm}^{-3}$

Step 2: Write the equilibrium constant for this reaction in terms of concentration

- $K_c = \dfrac{[H_2O]\ [CH_3COOC_2H_5]}{[C_2H_5OH]\ [CH_3COOH]}$

Step 3: Substitute the equilibrium concentrations into the expression

- $K_c = \dfrac{[0.364] \times [0.364]}{[0.070] \times [0.470]} = 4.03$

Step 4: Deduce the correct units for K_c

- $K_c = \dfrac{[mol\ dm^{-3}] \times [mol\ dm^{-3}]}{[mol\ dm^{-3}] \times [mol\ dm^{-3}]}$
- All units cancel out

Therefore, K_c = **4.03**

Exam Tip

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

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

Worked Example

Calculating K_c of ethyl ethanoate

Ethyl ethanoate is hydrolysed by water:

$CH_3COOC_2H_5$ (l) + H_2O (l) ⇌ CH_3COOH (l) + C_2H_5OH (l)

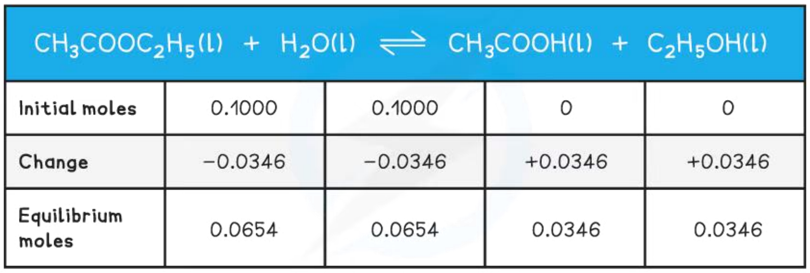
ethyl ethanoate water ethanoic acid ethanol

0.1000 mol of ethyl ethanoate are added to 0.1000 mol of water. A little acid catalyst is added and the mixture made up to 1.00 dm^3. At equilibrium, 0.0654 mol of water are present.

Use this data to calculate a value of K_c for this reaction.

Answer

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



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

Step 2: Calculate the concentrations of the reactants and products

- $[CH_3COOC_2H_5\ (l)] = \frac{0.0654}{1.00} = 0.0654\ \text{mol dm}^{-3}$
- $[H_2O\ (l)] = \frac{0.0654}{1.00} = 0.0654\ \text{mol dm}^{-3}$
- $[CH_3COOH\ (l)] = \frac{0.0346}{1.00} = 0.0346\ \text{mol dm}^{-3}$
- $[C_2H_5OH\ (l)] = \frac{0.0346}{1.00} = 0.0346\ \text{mol dm}^{-3}$

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

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

Step 4: Substitute the equilibrium concentrations into the expression

- $K_c = \frac{[0.0346] \times [0.0346]}{[0.0654] \times [0.0654]} = 0.28$

Therefore, K_c = **0.28**

Estimating the position of equilibrium

- The magnitude of K_c indicates the relative concentrations of reactants and products in the mixture
    - If K_c is very large (Kc >>1) the equilibrium lies to the RHS so the reaction mixture contains mostly products
    - If K_c is very small (Kc << 1) the equilibrium lies to the LHS so the reaction mixture contains mostly reactants
    - If K_c is close to 1 the mixture contains a similar concentration of both reactant and products