Edexcel Chemistry A-Level

Topic 15: Transition Metals

Detailed Notes

Topic 15A: Transition Metal Chemistry

The transition metals are elements in the **d-block** of the periodic table with a **partially filled d-orbital**. They lose electrons to form positive ions with the s-orbital electrons being removed first.

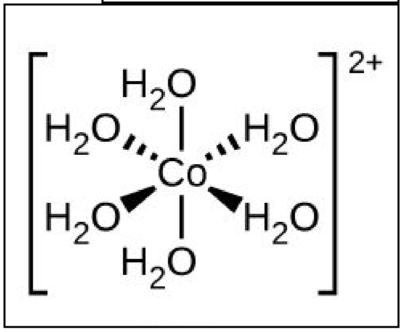
All transition metals have **similar physical properties** including atomic radius, high densities and high melting and boiling points. They all also have **special chemical properties**:

- They form complexes
- They form coloured ions in solution
- Variable oxidation states
- Good catalysts.

Complexes

These form from transition metals, consisting of a **central metal ion** surrounded by **ligands**.
Example:

Image courtesy of BC Open Textbooks



They can also be represented in formulas using square brackets.
Example:

$[Co(H_2O)_6]^{2+}$

Ligands

A ligand is a molecule or ion with a **lone electron pair** that is able to form a **coordinate bond** to the central metal ion by donating this electron pair. Common ligands include:

- Cl^-
- H_2O
- NH_3

Coordination Number

This is equal to the number of **coordinate bonds** formed around the central metal ion. Silver complexes have a coordination number of 2 and platinum complexes commonly have a coordination number of 4.

Coloured Ions

Transition metal ions can be identified by their **colour**, which changes depending on the **coordination number** of the complex, type of **ligand** bonded to the ion and the **oxidation state**.

Observing colour

Colour arises because of how substances **absorb and reflect** light. When white light shines on a substance, some of the wavelengths of light are absorbed but the remaining wavelengths are **reflected and transmitted** to the human eye. These reflected wavelengths wavelengths correspond to a specific colour which is then observed by the human eye.

Example:

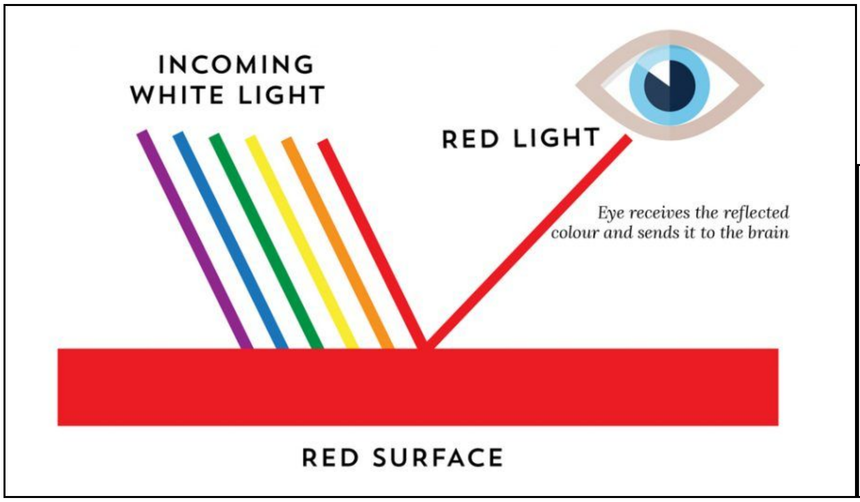
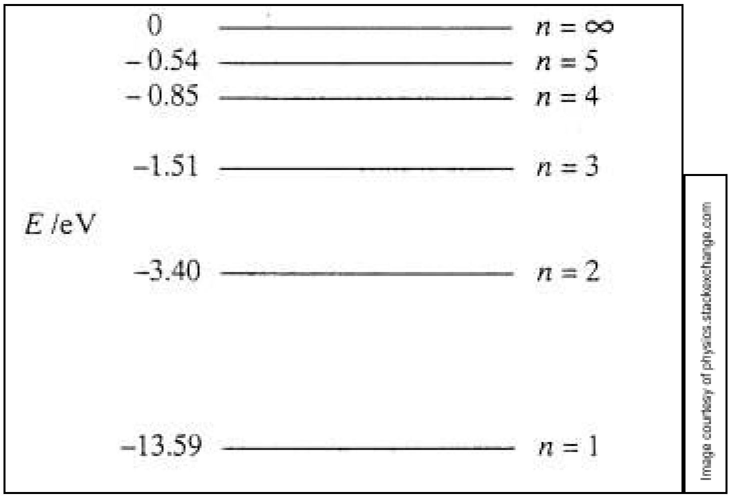


Image courtesy of Emma Brooks Design

In transition metals, ligands cause the d-orbital to split meaning electrons exist in a slightly higher energy level in an **'excited state'**.

The change in energy (ΔE) between these states corresponds to a **wavelength and frequency** of light.

Example:



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Ligand Substitution Reactions

The ligands NH_3 and H_2O are **similar in size** and are both uncharged. They both contain single lone electron pairs that are able to form a single coordinate bond, known as monodentate ligands.

This means they can be exchanged without a change in coordination number via a **ligand substitution reaction**.

Example:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+} + 6H_2O$$

With copper complexes and **NH_3 in excess**, this substitution is **incomplete** and the complex formed has a combination of water and ammonia ligands.

Example:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$$

This complex ion product forms as a **deep blue solution**.

The Cl^- ligand is much **larger** than the NH_3 and H_2O ligands meaning substitution with this ligand results in a **change in coordination number** for that complex.

Example:

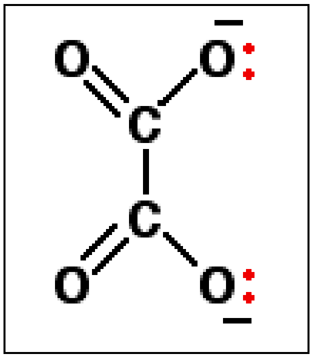
$$[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2+} + 6H_2O$$

Complexes with just Cl- ligands always have a coordination number of **four**, producing a **tetrahedral** shaped complex.

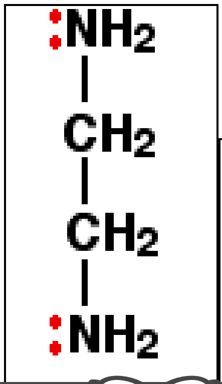
Bidentate Ligands

These ligands are able to form **two coordinate bonds** to the central metal ion as they have **two lone electron pairs**. There are two common bidentate ligands:

- Ethanedioate ions - a lone electron pair on two of the oxygen atoms

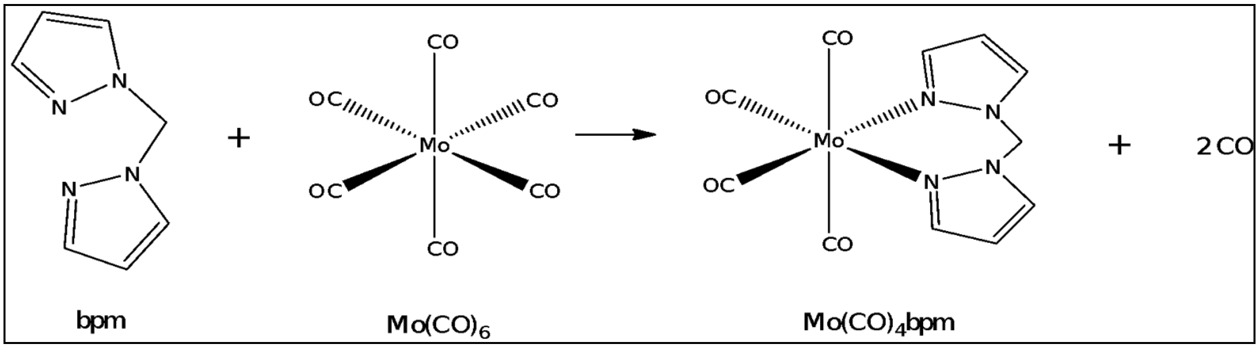


- Ethane-1,2-diamine - a lone electron pair on each of the nitrogen atoms



Images courtesy of ChemGuide

These can replace two unidentate ligands but the **coordination number remains at six** as six coordinate bonds still form.
Example:



Multidentate Ligands

These ligands are able to form **upto six coordinate bonds** to the central metal ion as they have multiple lone electron pairs. The most common multidentate ligand is **EDTA** (ethylenediaminetetraacetic acid). It form six coordinate bonds in a ligand substitution reaction.

Example:

$$[Fe(H_2O)_6]^{3+} + EDTA^{4-} \longrightarrow [FeEDTA]^{-1} + 6H_2O$$

Haem, a component of haemoglobin is another common multidentate ligand. It consists of six coordinate bonds around a central Fe^{2+} ion. Its shape and structure allow it to **transport oxygen** around the body.

Example:

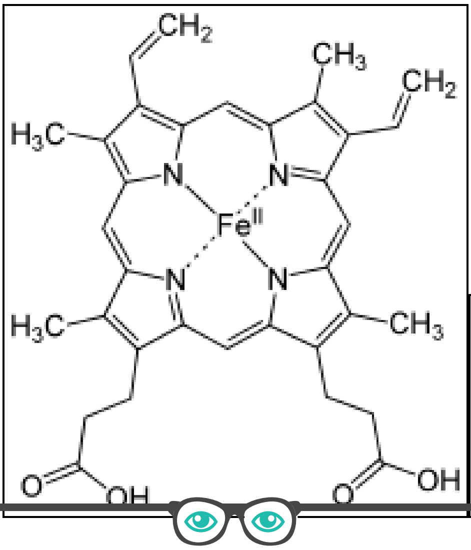


Image courtesy of Wikipedia

Carbon monoxide is **toxic** to humans as it **replaces the oxygen** in the haem complex, preventing it from being transported around the body.

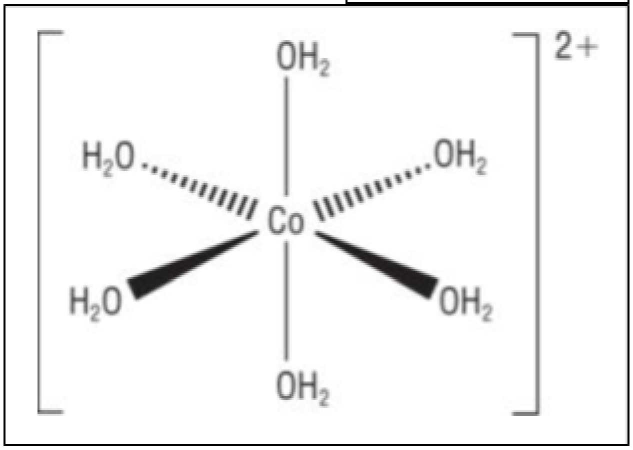
Shapes of Complex Ions

Octahedral Complexes

Transition metal complexes with H_2O and NH_3 ligands commonly form **octahedral** complexes with a **bond angle of 90°**.

Example:

Image courtesy of chemhume.co.uk

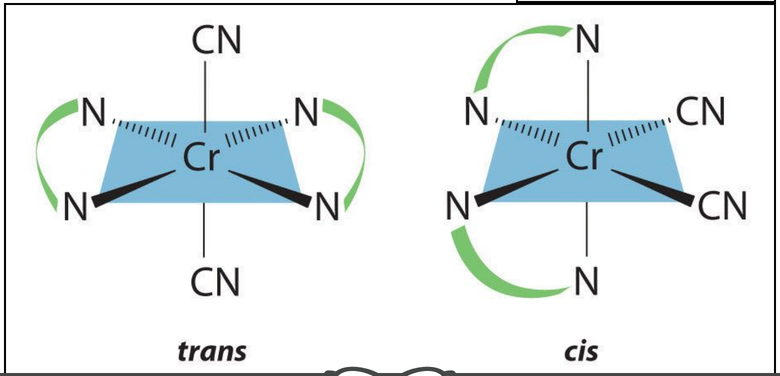


Cis-trans Isomerism

This type of isomerism is shown by octahedral complexes with different types of **unidentate** ligands. Ligands of the same type can either be **next to or opposite each other**. The ***trans*** isomer has two of the same ligands opposite each other and the ***cis*** isomer has them next door to each other.

Example:

Image courtesy of Chemistry LibreTexts



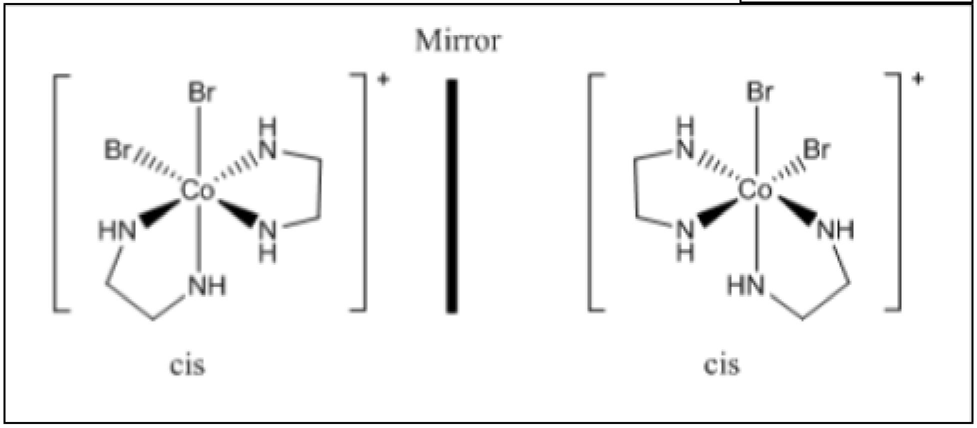
trans ***cis***

Optical Isomerism

This type of isomerism is shown by octahedral complexes with **bidentate** ligands. The two isomers are **mirror images** of each other.

Example:

Image courtesy of chegg.com

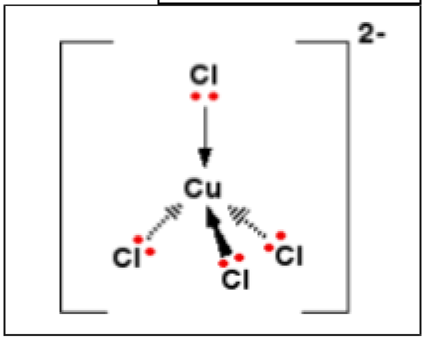


Tetrahedral Complexes

When complexes form with **larger ligands** such as Cl^-, they form **tetrahedral** complexes with a **bond angle of 109.5°**. Tetrahedral complexes can also show optical isomerism.

Example:

Image courtesy of Chemguide

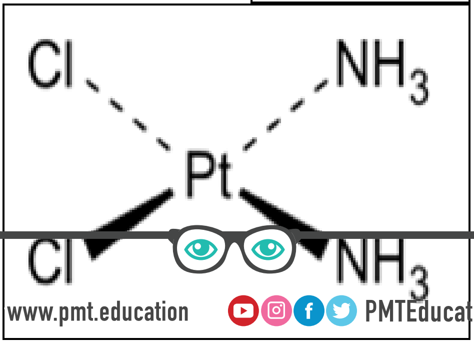


Square Planar Complexes

Platinum and nickel complexes form in a **square planar** shape. This consists of four coordinate bonds with a **bond angle of 90°**.

Example:

Image courtesy of biolegend.com

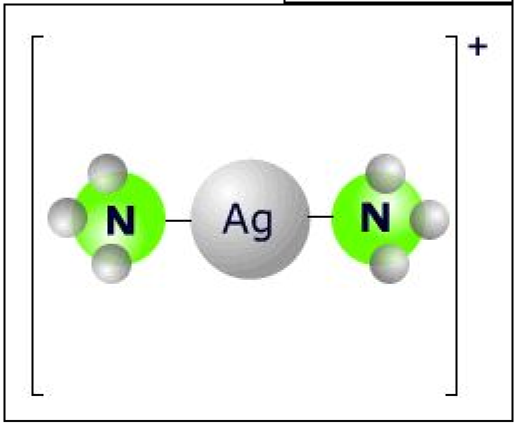


Linear Complexes

Silver complexes always have a **linear shape** with two coordinate bonds around the central metal ion. The **bond angle is 180°**.

Example:

Image courtesy of alevelchem.com



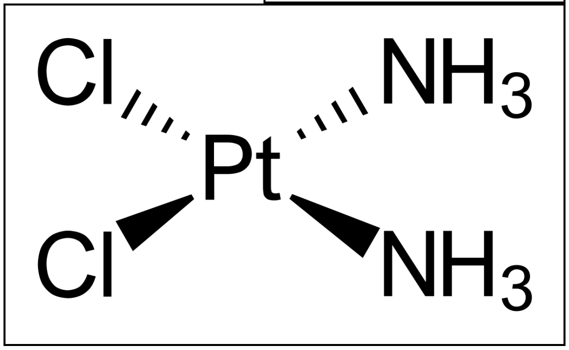
This is the type of complex present in **Tollen's reagent, $[Ag(NH_3)_2]^+$**.

Cisplatin

This is the ***cis* isomer** of a square planar complex of **platinum**. It is commonly used as a **cancer therapy drug**.

Cells in the natural world are **chiral** so only one isomer of the drug will be the correct orientation to 'fit' the cells. Therefore only this **single isomer will work** and cure the disease.

Image courtesy of Wikipedia



Cisplatin can cause serious **side effects** such as hair loss, meaning it has to be administered in **small amounts** to try and reduce these effects.

Topic 15B: Reactions of Transition Metal Elements

Oxidation States of Vanadium

One of the key chemical properties of transition metals is their **variable oxidation states**. Vanadium has four possible oxidation states from +5 to +2 each of which produces a **different coloured compound**. These different species can be produced from the **reduction** of vanadium by zinc in acidic solution.
Example:

Oxidation State	Ion Formula	Ion Colour
+5	VO_2^+	yellow
+4	VO^{2+}	blue
+3	V^{3+}	green
+2	V^{2+}	violet

These colours can be remembered by the phrase: You Better Get Vanadium

The **pH** of the reaction conditions determines whether a transition metal is **oxidised or reduced**. For ions to be reduced (oxidation state = more negative), **acidic** conditions are required.
Example:

$$2VO_2^+ + 2e^- + 4H^+ \longrightarrow 2VO^{2+} + 2H_2O$$

For ions to be oxidised (oxidation state = more positive), they react with water to produce OH^- ions and therefore an **alkaline** solution.
Example:

$$VO^{2+} + H_2O \longrightarrow VO_2^+ + 2H^+ + e^-$$

Tollens Reagent

The silver complex **$[Ag(NH_3)_2]^+$** is reduced by aldehydes to form **silver atoms**, seen as a “silver mirror”. This means it is used as the **test for aldehydes**.

Example:

$$RCHO + 3OH^- + 2[Ag(NH_3)_2]^+ \longrightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O$$

Redox Titrations

These are some of the **longest calculation** questions on the A-Level exam and are often worth many, **high tariff marks**. The redox reactions involved are limited to **three main reactions** and it is useful to learn these reactions and the **reacting molar ratios**:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$MnO_4^- : C_2O_4^{2-}$	$MnO_4^- : Fe^{2+}$	$C_2O_4^{2-} : Fe^{2+}$
2 : 5	1 : 5	1 : 2

The Chelate Effect

In ligand substitution reactions, a **positive entropy change is favourable** as it means a more stable complex is being formed. Therefore it is favourable to have more moles on the right than the left.

This is achieved by substituting unidentate ligands with bidentate or multidentate ligands, known as the **chelate effect**.

The greater the entropy change, the **more negative** the free energy change (ΔG) will be, meaning the reaction is **more favourable**.

Enthalpy Change

The enthalpy change (ΔH) for ligand substitution reactions is **very small** as the bonds being formed are very similar to the bonds that were broken. Therefore overall enthalpy change is **near zero**.

Catalysts

A catalyst is a substance that **speeds up the rate of a reaction without being used up** in the reaction. It provides an alternative reaction pathway with a lower activation energy. Catalysts don't affect the position of equilibrium but allow it to be **reached faster.** Transition metals make good catalysts due to their variable oxidation states.

There are two main types of catalyst; **heterogeneous and homogeneous**.

Heterogeneous Catalysts

These are catalysts that are in a **different phase or state** to the species in the reaction. An example of this is the Haber Process, where a **solid iron catalyst** is used to speed up the reaction between hydrogen and nitrogen gases.

Transition metals make good catalysts due to their variable oxidation states. **Electrons are transferred** to produce a **reactive intermediate** and speed up the reaction rate. An example of this is the **Contact Process** which uses a vanadium oxide catalyst to speed up the conversion of sulfur dioxide to sulfur trioxide.

Example:

Overall:

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

Intermediate Reactions:

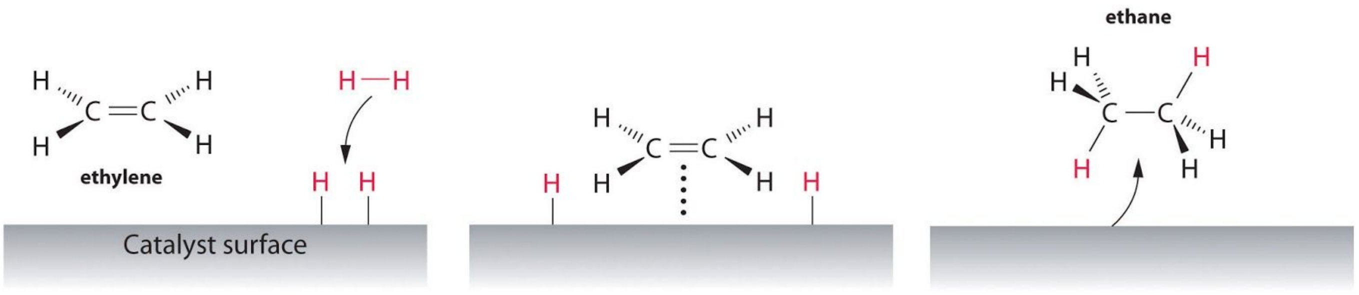
$$V_2O_5 + SO_2 \longrightarrow V_2O_4 + SO_3$$

$$V_2O_4 + 1/2O_2 \longrightarrow V_2O_5$$

Vanadium is reduced from +5 to +4 and is then **reformed** in its original oxidation state, showing it has acted as a catalyst for the reaction.

Adsorption

A solid catalyst works **adsorbed** molecules onto an **active site** on the surface of the catalyst. These active sites **increase the proximity** of molecules and **weaken the covalent bonds** in the molecules so that reactions occur more easily and rate is increased.
Example:



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

The strength of adsorption depends on the **type of catalyst** and can affect how much it affects the rate of the reaction. **Iron, cobalt and nickel** make the best catalysts as they are relatively cheap and increase the rate of reaction the most out of all the period 4 transition metals.

This process occurs inside **catalytic converters** where carbon and nitrogen monoxide adsorb onto the surface of the catalyst weakening their bonds allowing reactions to occur. As a result, CO_2 and N_2 then **desorb** form the catalyst surface.

Catalyst Poisoning

Heterogeneous catalysts can be **poisoned by impurities** which **block the active sites** and **prevent adsorption**. Therefore the bonds of the molecules remain strong and the catalyst has no effect on the rate of the reaction.

Reaction impurities can lead to an **increase in chemical production costs** in industry as the catalyst has to be **replaced or cleaned** regularly.

Sulfur impurities poison the solid iron catalyst used in the Haber Process.

Homogeneous Catalysts

These are catalysts that are in the **same phase** to the species in the reaction. An example of this is the reaction between **$S_2O_8^{2-}$ ions and I^- ions** where Fe^{2+} has to be used as a catalyst. Without a catalyst, these negative ions would naturally repel each other and never react.

Example:

Overall:

$$S_2O_8^{2-} + 2I^- \xrightarrow{Fe^{2+}} I_2 + 2SO_4^{2-}$$

Intermediate Reactions:

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

The catalyst works by combining with the reactants to produce a **reactive intermediate**. This **changes the reaction pathway** as the enthalpy change for the formation of the intermediate is much lower than the original reaction. The **activation energy is lower** so the reaction is more feasible.

Example:

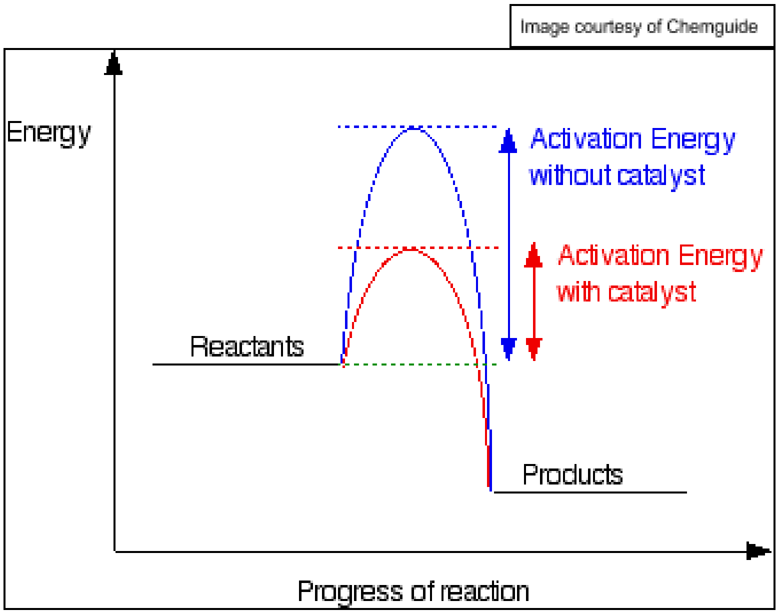


Image courtesy of Chemguide

Autocatalysis

In some reactions, one of the **products can act as a catalyst** for the reaction. This means that over time, as the amount of product increases, the rate of the reaction also increases as it becomes catalysed. An example of this is the redox reaction between **MnO_4^- ions and $C_2O_4^{2-}$ ions** in acidic conditions, where the **Mn^{2+} ions produced act as a catalyst** for the reaction.

Example:

Overall:

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Intermediate Reactions:

$$4Mn^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Mn^{3+} + 4H_2O$$

$$2Mn^{3+} + C_2O_4^{2-} \longrightarrow 2CO_2 + 2Mn^{2+}$$

A small amount of **initial heating** is required in order to produce some **Mn^{2+} ions** so that the reaction can be **autocatalysed**. Following this, the rate of reaction increases on its own without further heating.