

AQA Chemistry A-level

3.2.5: Transition Metals

Detailed Notes

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3.2.5.1 - Transition Metal Properties

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.

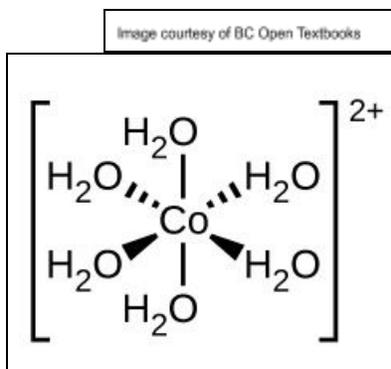
All transition metals have **similar physical properties** including atomic radius, high densities and high melting and boiling points. They all also have **special chemical properties**:

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

Complexes

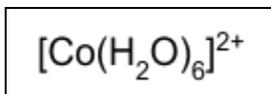
These form from transition metals, consisting of a **central metal ion** or atom surrounded by **ligands**.

Example:



They can also be represented in formulas using square brackets.

Example:



Ligands

These are molecules or ions with a **lone electron pair** that is able to form a **coordinate bond** to the central metal ions 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.

3.2.5.2 - Ligand Substitution Reactions

The ligands NH_3 and H_2O are **similar in size** and are both uncharged. This means they can be exchanged without a change in coordination number via a **ligand substitution reaction**.

Example:



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:



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:



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

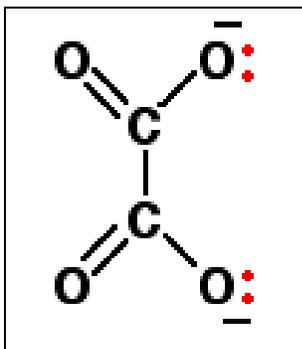




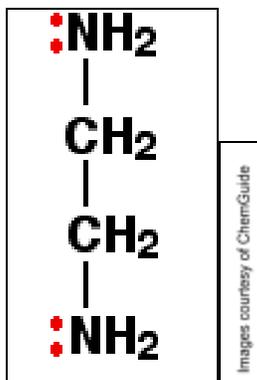
Bidentate Ligands

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

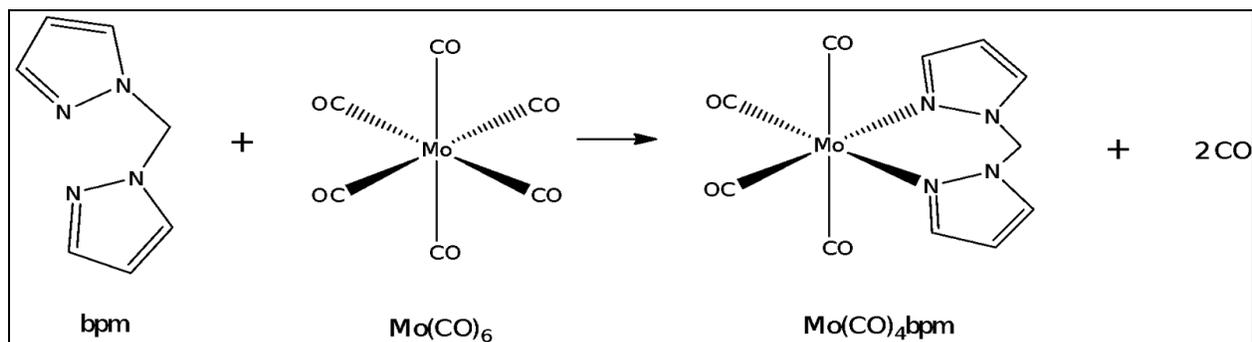


- Ethane-1,2-diamine - a lone electron pair on each of the nitrogen atoms



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

Example:





Multidentate Ligands

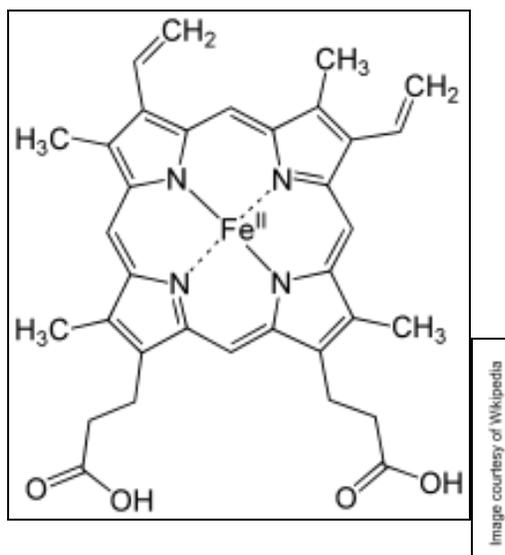
These ligands are able to form **up to six coordinate bonds** to the central metal ion as they have multiple lone electron pairs. The most common multidentate ligand is **EDTA** (ethylenediaminetetraacetic acid). It forms six coordinate bonds in a ligand substitution reaction.

Example:



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:



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

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, therefore meaning the reaction is **more favourable**.





Enthalpy Change

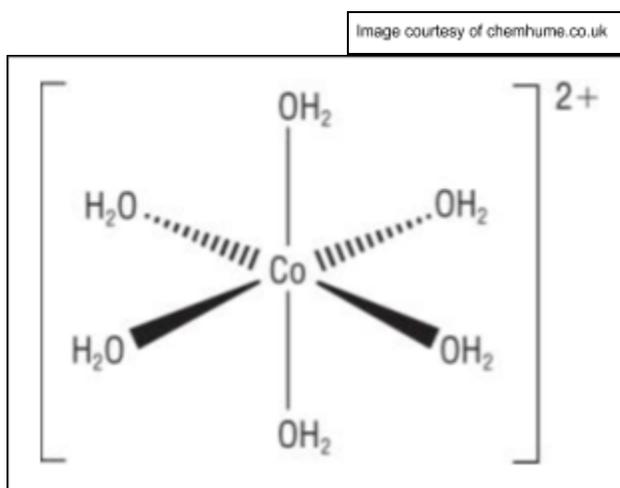
The enthalpy change (ΔH) for ligand substitution reactions is **very small** as the bonds being formed are very similar to the bonds that were broken. Therefore overall enthalpy change is **near zero**.

3.2.5.3 - 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°** .

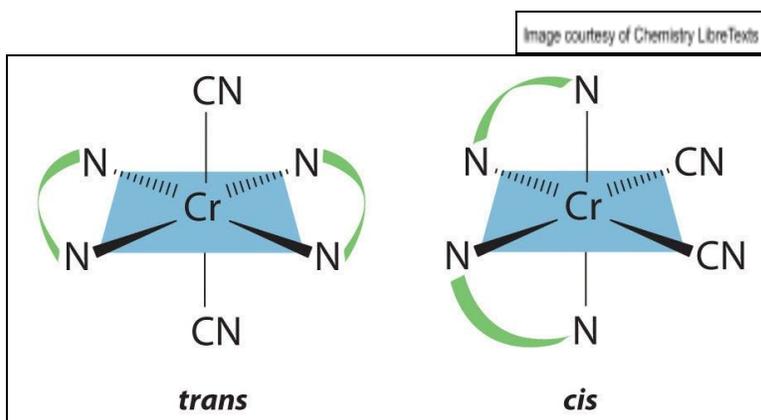
Example:



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:

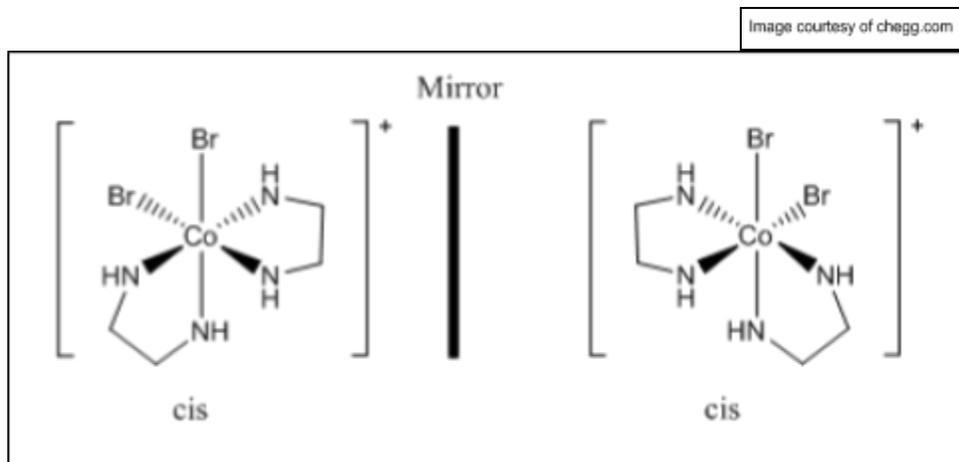




Optical Isomerism

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

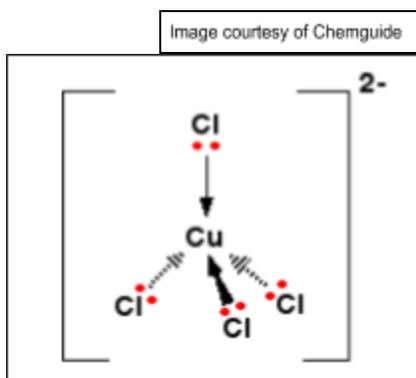
Example:



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.

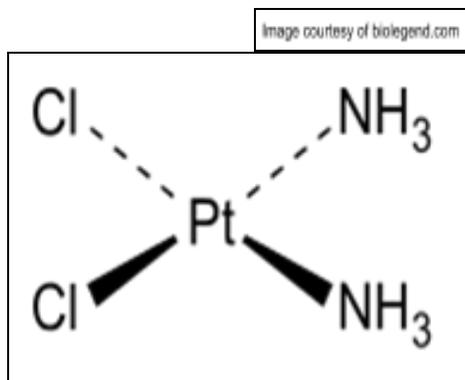
Example:



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:

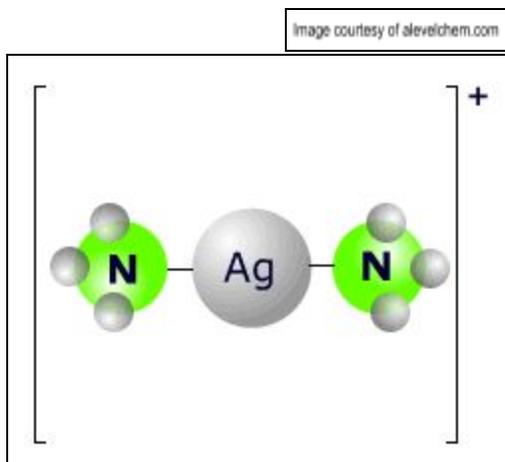




Linear Complexes

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

Example:

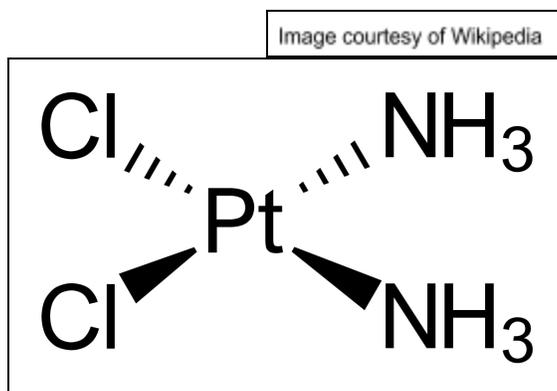


This is the type of complex present in **Tollen's reagent**, $[\text{Ag}(\text{NH}_3)_2]^+$.

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.



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.





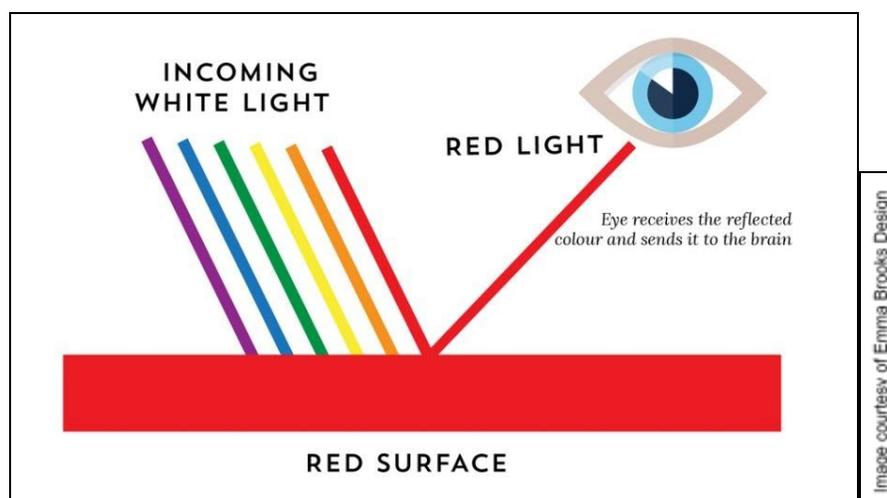
3.2.5.4 - Coloured Ions

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

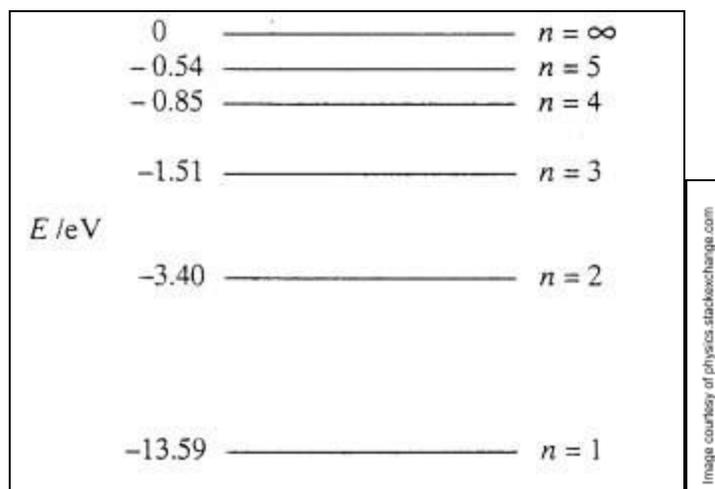
Observing colour

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 correspond to a **specific colour** which is then observed by the human eye.

Example:



Electrons in the d-orbital exist in a series of **energy states**. When they are given energy, they move from **ground state** ($n=1$) to a higher energy state called an '**excited state**'.



The change in energy (ΔE) between these states corresponds to a **wavelength and frequency** of light which can be calculated:

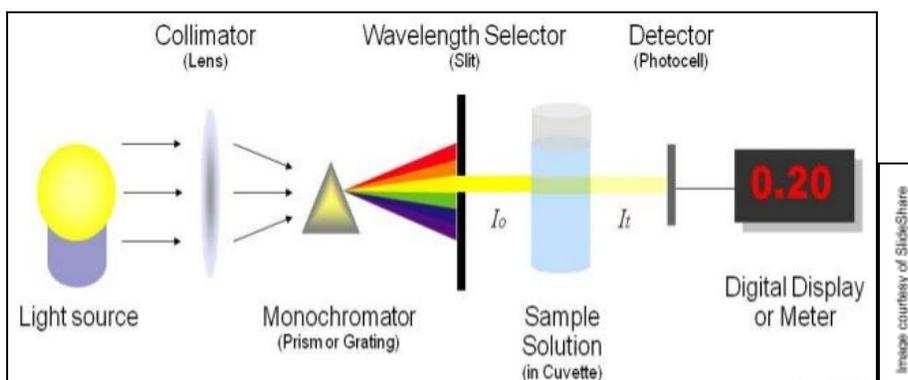


(ν = frequency in hertz) (λ = wavelength in meters) (h = Planck's constant, 6.63×10^{-34})

Colorimetry

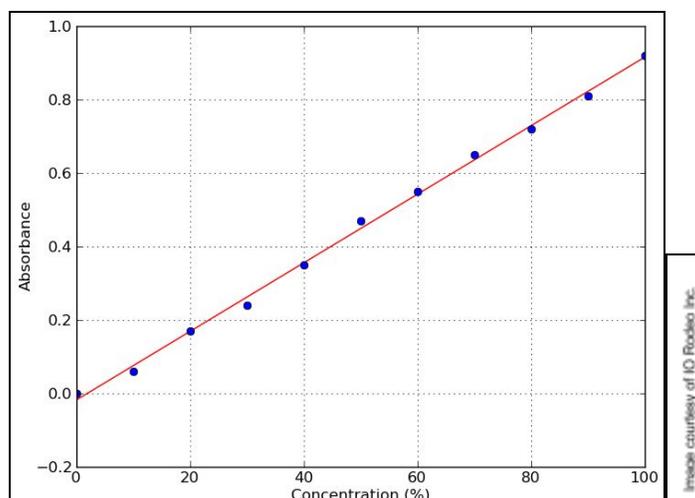
This is an **analytical technique** that uses the **absorption** of visible light to determine the **concentration** of coloured ions by measuring absorbance.

Example:



A **calibration graph** is produced by measuring solutions of known concentrations which can then be used to calibrate the colorimeter on a graph of **relative absorbance** against **concentration**. This graph can then be used to determine the concentration of an **unknown substance**.

Example:





3.2.5.5 - Variable Oxidation States

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 **oxidation** 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:



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

Example:



Tollens Reagent

The silver complex $[\text{Ag}(\text{NH}_3)_2]^+$ is reduced by aldehydes to form **silver atoms**, seen as a silver mirror. This means it is used as the **test for aldehydes**.

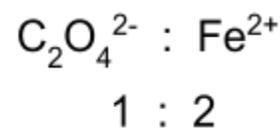
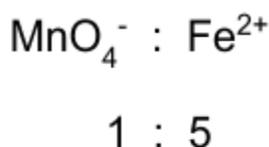
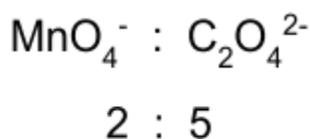
Examples:





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 reaction and the **reacting molar ratios**:



3.2.5.6 - 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 path with a lower activation energy. Catalysts don't affect the position of equilibrium but allow it to be **reached faster**. There are two main types of catalyst; **heterogeneous and homogeneous**.

Heterogeneous Catalysts

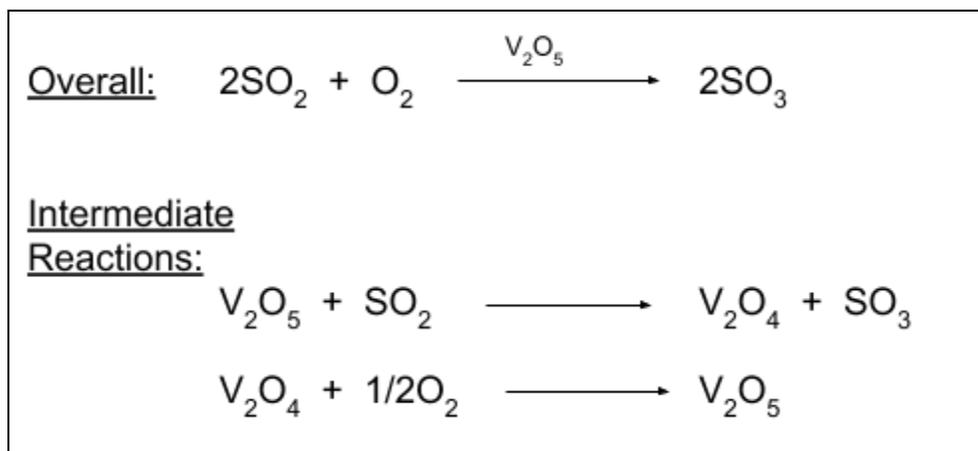
These are catalysts that are in a **different phase or state** to the species in the reaction. An example of this is the Haber Process, where a **solid iron catalyst** is used to speed up the reaction between hydrogen and nitrogen gases.

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:

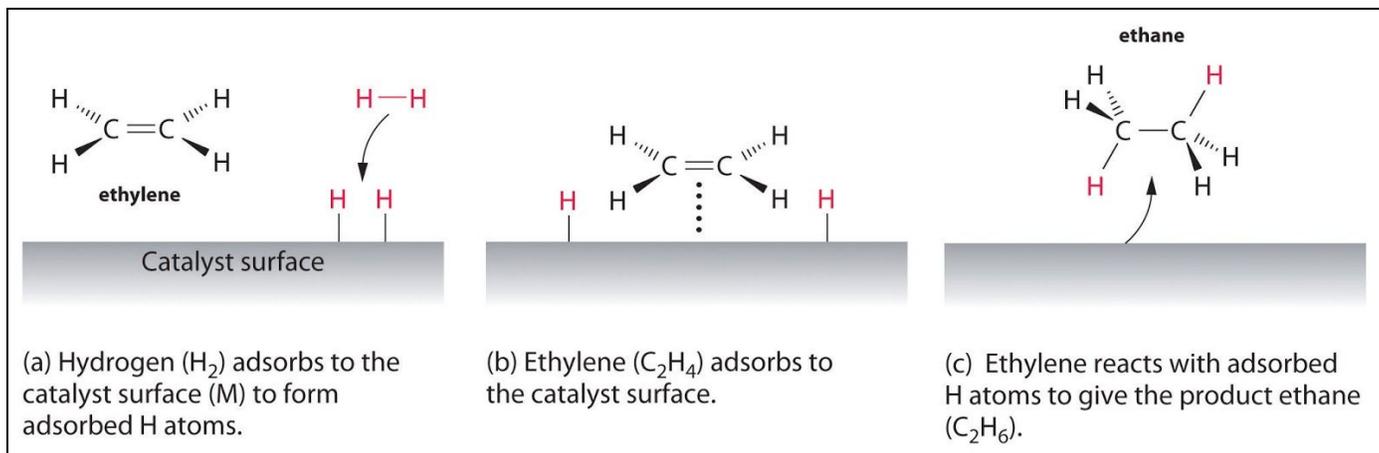


Vanadium is reduced from +5 to +4 and is then **reformed** in its original oxidation state, showing it has acted as a catalyst for the reaction.

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:



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.





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.

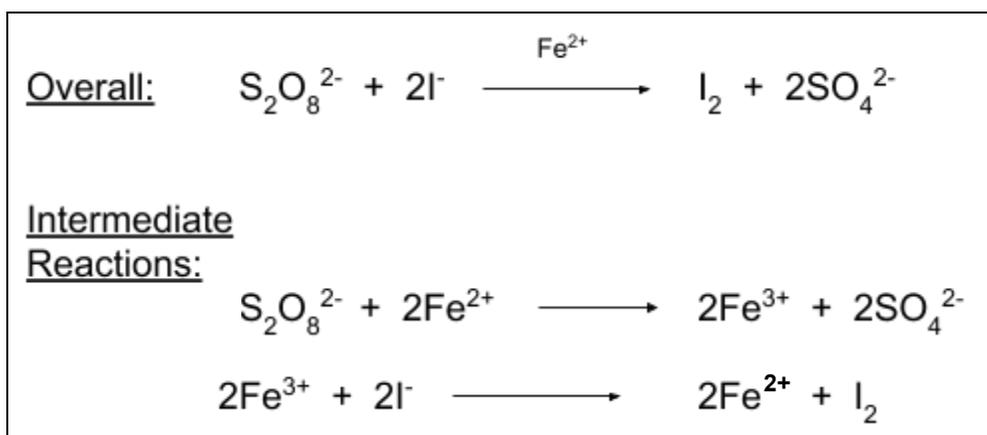
Reaction impurities can lead to an **increase in chemical production costs** in industry as the catalyst has to be **replaced or cleaned** regularly.

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

Homogeneous Catalysts

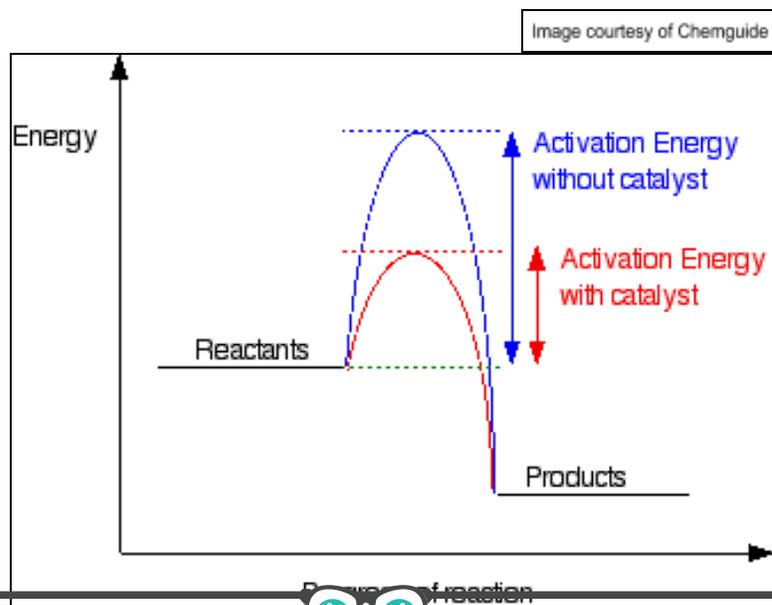
These are catalysts that are in the **same phase** to the species in the reaction. An example of this is the reaction between **$S_2O_8^{2-}$ ions and I^- ions** where Fe^{2+} has to be used as a catalyst. Without a catalyst, these negative ions would naturally **repel** each other and never react.

Example:



The catalyst works by combining with the reactants to produce a **reactive intermediate**. This **changes the reaction path** 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:

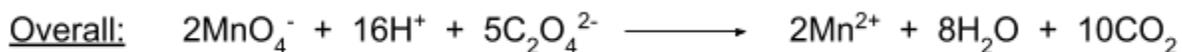




Autocatalysis

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 $\text{C}_2\text{O}_4^{2-}$ ions** in acidic conditions, where the **Mn^{2+} ions produced act as a catalyst** for the reaction.

Example:



Intermediate

Reactions:



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.

