Edexcel Chemistry A-level

Topic 15: Transition Metals

Detailed Notes

Topic 15A: Transition Metal Chemistry

Introduction

The transition metals are elements in the **d-block** of the periodic table that form one or more **stable ions** with a **partially filled d-orbital**. Transition metals 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. In addition, they all have **special chemical properties**:

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

Transition metals have **variable oxidation states** because the 4s and 3d orbitals are very **close** in energy levels. This not only makes it possible for electrons to be lost from both orbitals relatively easily, but also means the remaining electrons can form **stable configurations.**

Examples:

Scandium - atomic number 21 - [Ar] $4s^2$ $3d^1$

Nickel - atomic number 28 - [Ar] $4s^2$ $3d^7$

Iron - atomic number 26 - [Ar] $4s^2$ $3d^6$
Fe^{2+} - atomic number 26 (=24 electrons) - [Ar] $4s^0$ $3d^6$ or [Ar] $3d^6$

Vanadium - atomic number 23 - [Ar] $4s^2$ $3d^3$
V^{2+} - atomic number 23 (=21 electrons) - [Ar] $4s^0$ $3d^3$ or [Ar] $3d^3$

Exceptions

Copper and **chromium** are exceptions to the rule that the 4s sub-shell is filled before the 3d sub-shell.

Chromium has 24 electrons. According to the above rule, its electron configuration should be [Ar] $4s^2$ $3d^4$. However, it is more stable if one of the electrons from the 4s orbital is instead in the 3d orbital, **so that each 3d orbital contains one unpaired electron**. Therefore, the actual electron configuration of chromium is [Ar] $4s^1$ $3d^5$.

Similarly with copper, instead of the electron configuration [Ar] $4s^2$ $3d^9$, it is more stable if the 3d sub-shell is **completely filled**. Therefore, one of the 4s electrons is moved to a 3d orbital to give the electron configuration [Ar] $4s^1$ $3d^{10}$.

Complexes

Transition metals form **complexes**, consisting of a **central metal ion** surrounded by **ligands**.

Example:

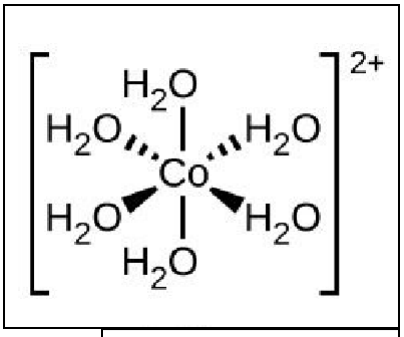


Image courtesy of BC Open Textbooks

They can also be represented by formulas using square brackets.

Example:

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

Ligands

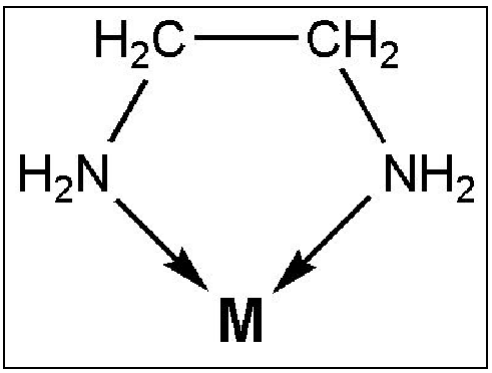
A ligand is a molecule or ion with a **lone electron pair** that is able to form a **dative (coordinate) bond** to the central metal ion by donating this electron pair. Common ligands include:

- Cl^-
- H_2O
- NH_3

Monodentate ligands each form **one** coordinate bond. Examples: H_2O, Cl^-, NH_3.

Bidentate ligands each form **two** coordinate bonds. Example: $NH_2CH_2CH_2NH_2$.

Example: Bidentate ligand $NH_2CH_2CH_2NH_2$



Hexadentate ligands each form six coordinate bonds. Example: $EDTA^{4-}$. **'Polydentate'** and **'multidentate' ligands** are general terms for any ligands that form **more than one** coordinate bond.

Coordination Number

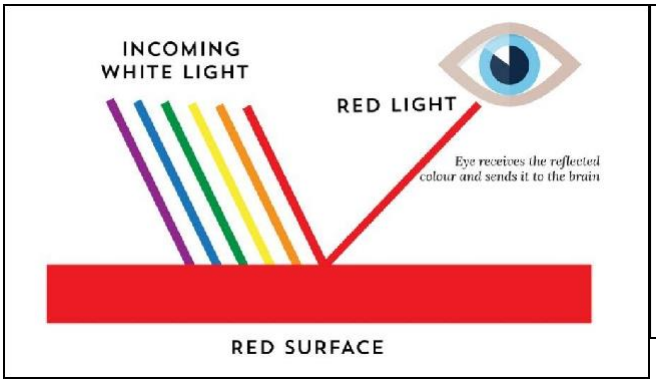
The coordination number of a transition metal complex is the total number of **coordinate bonds** formed with the central metal ion. Silver complexes have a coordination number of 2 and platinum complexes commonly have a coordination number of 4.

Coloured Ions

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

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:



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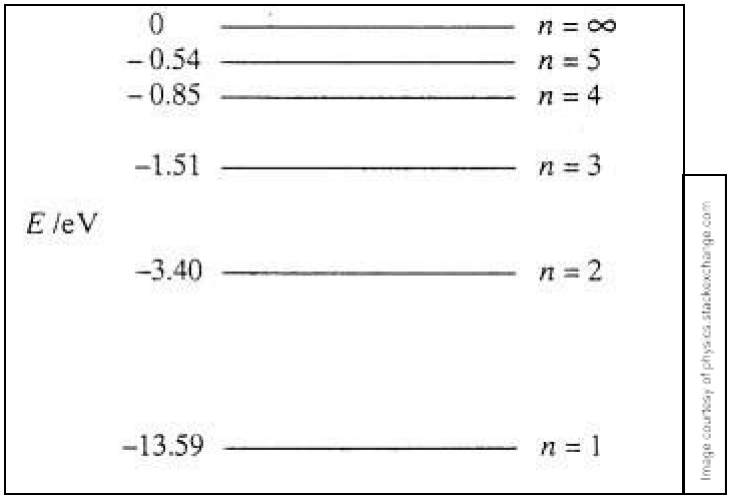
In transition metal complexes, ligands cause the d-orbital to split, meaning some electrons exist in a slightly higher energy level (in an **'excited state'**).

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

Example:



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Colourless Ions

Some metal ions and complexes are colourless. Colour arises when some wavelengths of light are absorbed while others are reflected, which involves the **excitation of electrons.** Ions and complexes where there are **no available electrons to excite** and move around cannot absorb light and are therefore **colourless**.

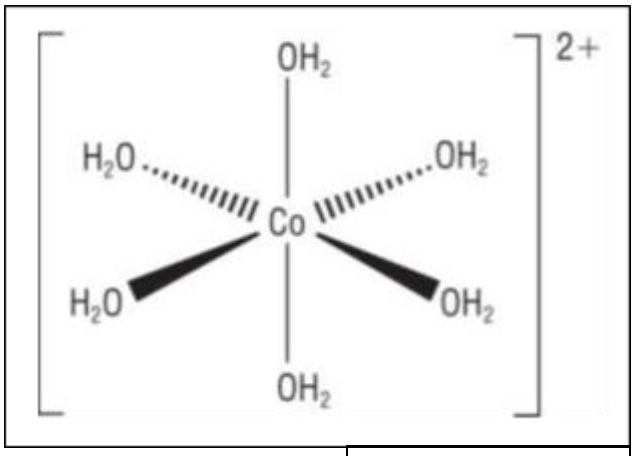
For example, zinc is in the d-block of the periodic table and has completely filled d-orbitals. Therefore, there are **no unfilled or partially filled d orbitals** into which an electron can be promoted. Therefore, zinc is colourless.

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 90º**. Octahedral complexes are formed when there is six-fold coordination with monodentate ligands.

Example:



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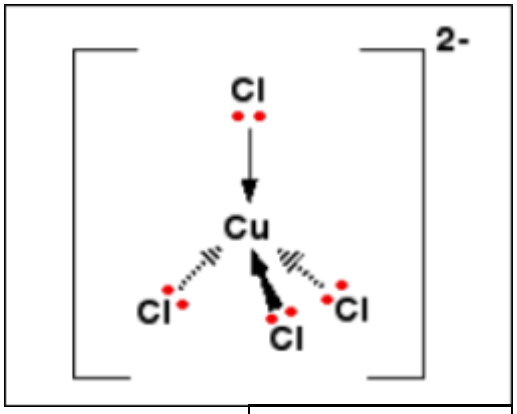
Tetrahedral Complexes

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

Example:



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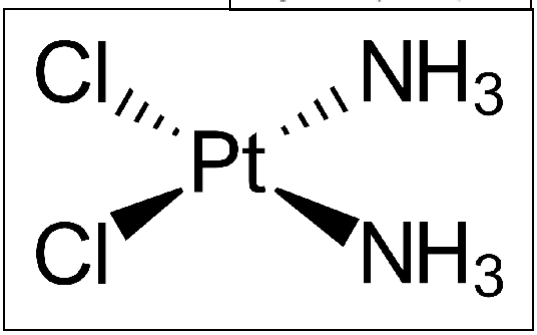
Square Planar Complexes

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

Cisplatin

This is the ***cis* isomer** of a square planar complex of **platinum**. It is commonly used as a **cancer therapy drug**. Drugs like cisplatin target components of cells that 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.

Ligand Substitution

Ligands in a transition metal complex can be exchanged for other ligands.

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:

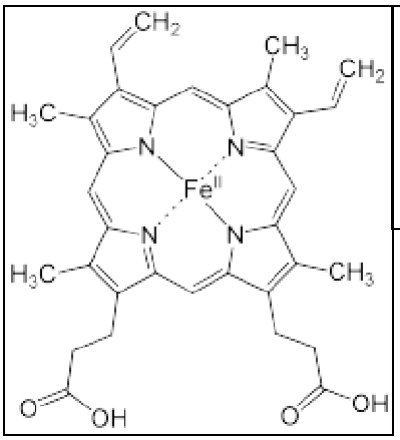


Image courtesy of Wikipedia

A **ligand substitution reaction** occurs when the oxygen usually bound to haem is replaced with carbon monoxide. Therefore, carbon monoxide is **toxic** to humans as it prevents oxygen from being transported around the body.

Topic 15B: Reactions of Transition Metal Elements

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

Vanadium can be reduced from an oxidation state of +5 all the way to +2 via reduction with **zinc** in **acidic conditions**. The E_{cell} values are given below for the reduction steps:

Reduction step	Chemical equation	E_{cell} value (V)
Vanadium(V) → Vanadium(IV)	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	+1.00
Vanadium(IV) → Vanadium(III)	$VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$	+0.34
Vanadium(III) → Vanadium (II)	$V^{3+} + e^- \rightarrow V^{2+}$	-0.26

These E_{cell} values show that **reduction** becomes **less favourable** as the oxidation state of vanadium decreases, to the point where the oxidation of V^{2+} to V^{3+} is more favourable than the reduction of V^{3+} to V^{2+}.

The Role of pH

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

Example:

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

For ions to be oxidised (the oxidation state becomes more positive), they react with water to produce OH^- ions and therefore **alkaline** conditions are required.

Example:

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

Chromium

The most stable oxidation states of chromium are +6, +3 and +2, found in the species **$Cr_2O_7^{2-}$, Cr^{3+} and Cr^{2+}** respectively. These can be interconverted by oxidation and reduction reactions.

$Cr_2O_7^{2-}$ can be reduced to Cr^{3+} and Cr^{2+} ions by **reduction** with **zinc** in **acidic conditions**.

Cr^{3+} can be **oxidised** to $Cr_2O_7^{2-}$ by **hydrogen peroxide** in **alkaline conditions**. The reaction first forms CrO_4^{2-} which is then converted to $Cr_2O_7^{2-}$ by **acidification**.
This occurs because there is an **equilibrium** between the two chromium(VI)-containing species:

$$\mathbf{2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O}$$

Acidification of a solution containing CrO_4^{2-} will, therefore, cause the equilibrium to **shift** to the right (to use up the additional H^+ ions), so the concentration of $Cr_2O_7^{2-}$ will **increase**.

Reactions of Transition Metal Ions with Sodium Hydroxide and Ammonia

Metal ions become **hydrated** in water where **H_2O ligands** form around the central metal ion. The reactions of five major metal aqua ions must be known for this specification: **chromium(III), iron(II), iron(III), cobalt(II) and copper(II)**. These metal aqua ions react with sodium hydroxide and ammonia to form **coloured precipitates.** These can be used to identify the transition metal present.

Solutions of metal aqua ions react as **acids** with aqueous sodium hydroxide. Some react further with **excess sodium hydroxide:**

Transition Metal Ion	Metal-aqua ion	With OH^-	With excess OH^-
Cr^{3+}	Violet solution $[Cr(H_2O)_6]^{3+}$	Green precipitate $Cr(OH)_3(H_2O)_3$	Green solution $[Cr(OH)_6]^{3-}$
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{2+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change
Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(H_2O)_3(OH)_3$	No change
Co^{2+}	Pink solution $[Co(H_2O)_6]^{2+}$	Blue precipitate $Co(OH)_2(H_2O)_4$	No change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	No change

The number of OH- substituted is the same as the value of the charge on the initial ion.

Example equations:

$$[Fe(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

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

$$[Fe(H_2O)_6]^{3+} + 3OH^- \longrightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$$

Solutions of metal aqua ions react as **acids** with aqueous ammonia. Some react further with

excess ammonia:

Transition Metal Ion	Metal-aqua ion	With NH_3	With excess NH_3
Cr^{3+}	Violet solution $[Cr(H_2O)_6]^{3+}$	Green precipitate $Cr(OH)_3(H_2O)_3$	Purple solution $[Cr(NH_3)_6]^{3+}$
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{2+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change
Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(H_2O)_3(OH)_3$	No change
Co^{2+}	Pink solution $[Co(H_2O)_6]^{2+}$	Blue precipitate $Co(OH)_2(H_2O)_4$	Yellow solution $[Co(NH_3)_6]^{2+}$
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	Dark blue solution $[Cu(NH_3)_4(H_2O)_2]^{2+}$

The number of OH- substituted is the same as the value of the charge on the initial ion.

Example equations:

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$

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

Amphoteric Metal Hydroxides

The metal hydroxides formed from the reactions of metal aqua ions with sodium hydroxide and ammonia will all dissolve in acid and **accept protons**. Some metal hydroxides will also react with bases and **donate protons**. These metal hydroxides are called **amphoteric** since they can react with both acids and bases.

Example:

Chromium hydroxide precipitate, like all hydroxides, can react with **acid**:

$$Cr(OH)_3(H_2O)_3 + 3H^+ \rightarrow [Cr(H_2O)_6]^{3+}$$

Chromium hydroxide precipitate can also react with **base**:

$$Cr(OH)_3(H_2O)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-} + 3H_2O$$

Ligand Substitution Reactions

Ligands in a transition metal complex can be exchanged for other ligands.

Copper and cobalt aqua ions can undergo substitution with chloride ions.
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:

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

Blue solution → Yellow solution

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

Pink solution → Blue solution

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

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 of the reaction than on the left. This is achieved by substituting monodentate ligands with bidentate or polydentate 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 to 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

Heterogeneous catalysts 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.

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:

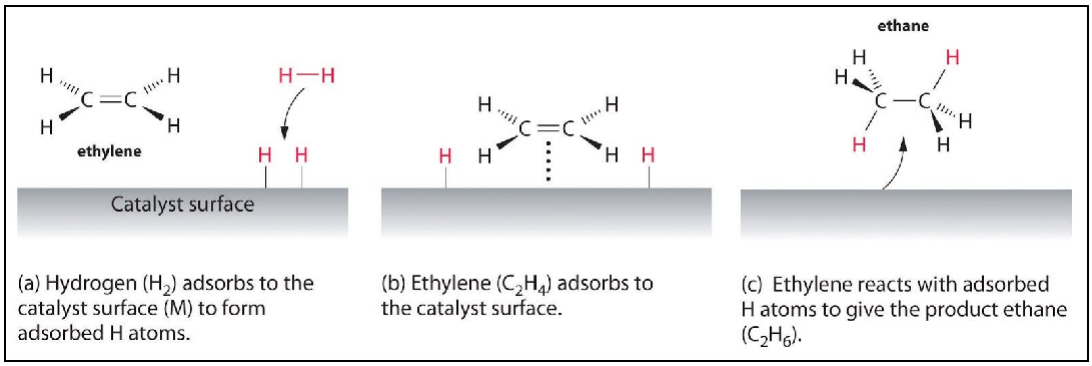
$V_2O_5 + SO_2 \longrightarrow V_2O_4 + SO_3$

$V_2O_4 + 1/2O_2 \longrightarrow V_2O_5$

The **oxidation state of vanadium** is first reduced from +5 to +4. It is then **reformed** to its original oxidation state, showing it has acted as a catalyst for the reaction.

Adsorption

A solid catalyst works by **adsorbing** 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. This increases the rate of reaction.



(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).

Adsorption occurs inside **catalytic converters** where carbon and nitrogen monoxide adsorb onto the surface of the catalyst. This weakens their bonds and allows reactions to occur. As a result, CO_2 and N_2 are **desorbed** from the catalyst surface.

Catalyst Poisoning

Heterogeneous catalysts can be **poisoned by impurities** which **block the active sites** and **prevent adsorption**. When this happens, 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

Homogeneous catalysts 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+} is used as a catalyst. Without a catalyst, these negative ions would naturally repel each other and would never react.

Example:

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

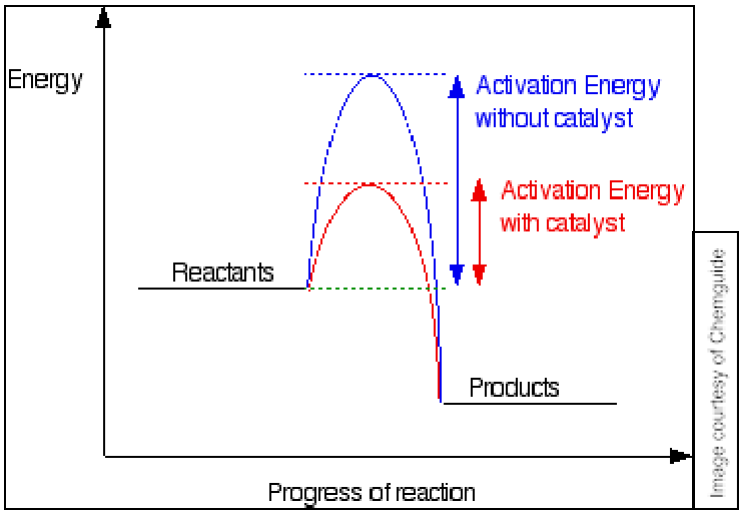
Intermediate Reactions:

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

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

The catalyst works by combining with the reactants to produce a **reactive intermediate**. This **changes the reaction pathway** since the enthalpy change of the formation of the intermediate is much lower than the enthalpy change of the original reaction. Thus, 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. 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** for **autocatalysis**. Following this, the rate of reaction increases on its own without further heating.