

WJEC Chemistry A-level

3.4: Chemistry of the *d*-block Transition Metals

Detailed Notes

Welsh Specification

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Transition Metal Properties

The transition metals are elements in the **d-block** of the periodic table with a **partially filled d-orbital** of electrons. 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

Variable Oxidation States

A key chemical property of the d-block transition metals is that they can exist in **variable oxidation states**. Elements such as **vanadium**, **manganese**, **chromium** and **iron** all show variable oxidation states because the **energy levels** of the **4s** and **3d** sublevels are very close to one another. This means that different numbers of electrons can be gained or lost using **similar amounts of energy**.

Generally, the **oxidation state** of the metal ion formed depends on the **energetics** of the reaction.

Iron is a transition metal with variable oxidation states. Fe^{2+} and Fe^{3+} are the main ions it commonly forms but Fe^{6+} can also be produced as part of ferrate(VI) ions, FeO_4^{2-} .

Most Stable Oxidation States

Transition Metal	Oxidation States
Chromium (Cr)	+2, +3, +6
Manganese (Mn)	+2, +4, +7
Iron (Fe)	+2, +3
Cobalt (Co)	+2, +3
Copper (Cu)	+1, +2





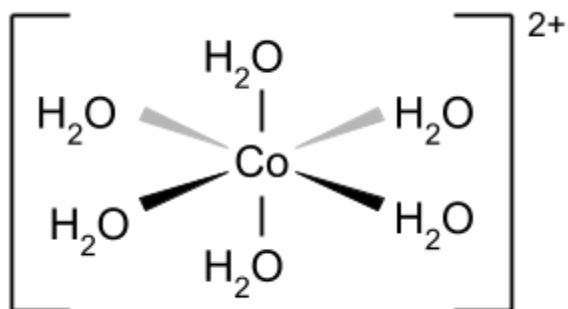
These different oxidation states can also produce different coloured aqueous solutions:

Metal Species	Solution Colour
Cr^{3+}	Green
CrO_4^{2-}	Yellow
$\text{Cr}_2\text{O}_7^{2-}$	Orange
MnO_4^-	Purple
Co^{2+}	Pink
Fe^{2+}	Pale green
Fe^{3+}	Brown to yellow

Complexes

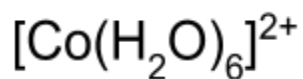
Complexes form from transition metals, consisting of a central metal ion or atom surrounded by coordinately bonded ligands.

Example:



They can also be represented in formulas using square brackets.

Example:





Ligands

Ligands are **molecules**, **atoms** or **ions** which donates a **pair of electrons** to a central transition metal ion to form a **coordinate bond**.

Common ligands include:

- Cl^-
- H_2O
- NH_3

Coordination Number

The coordination number is equal to the **number of coordinate bonds** formed around the central metal ion.

Common coordination numbers are **6** and **4**. For **small ligands**, like NH_3 or H_2O , the coordination number is 6. However, for **larger ligands** like Cl^- , only 4 can fit around the central metal ion so the coordination number is 4.

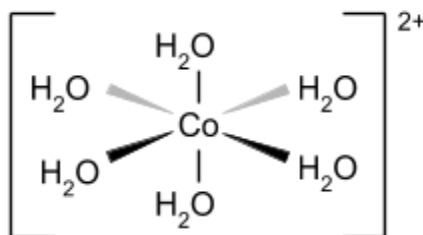
Some **silver complexes** have a coordination number of 2 as they only form **2 coordinate bonds**. This gives the complex a **linear** shape:



Octahedral Complexes

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

Example:



The ligands don't all have to be the same, but they must be of a **similar size** to maintain the octahedral shape.

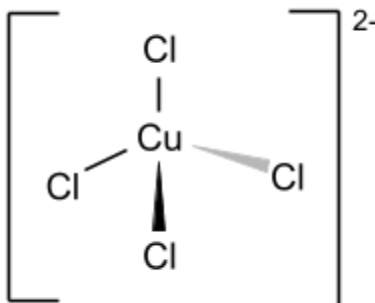




Tetrahedral Complexes

When complexes form with **larger ligands** such as **Cl⁻**, they form **tetrahedral complexes** with a bond angle of **109.5°**.

Example:

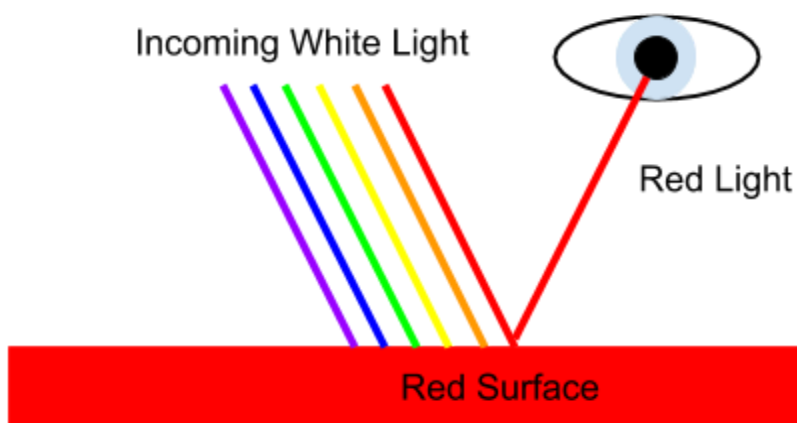


Coloured Compounds

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**.

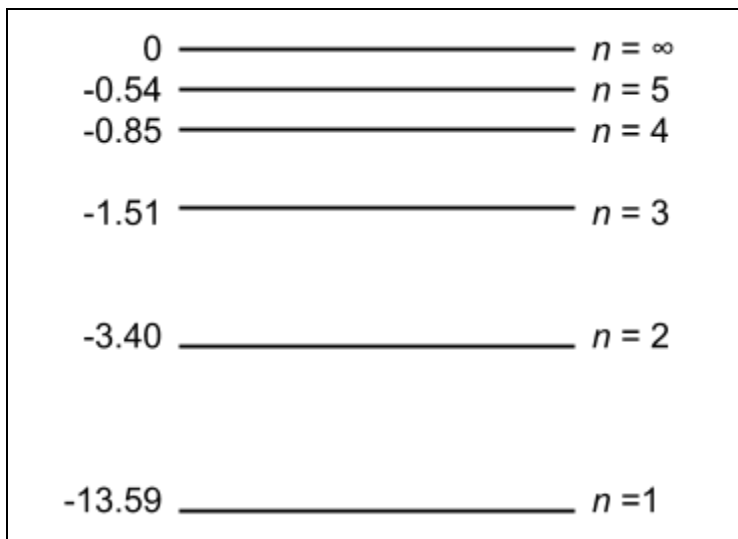
Observing colour

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.

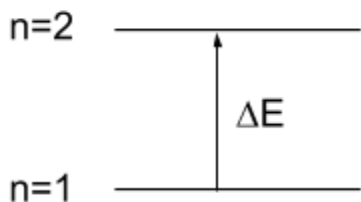




Electrons in the **d-orbital** exist in a series of **energy states**. When they are given energy, they move from **ground state** ($n=1$) to a higher energy state called an '**excited state**'.



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



$$\Delta E = \frac{hc}{\lambda} = h\nu$$

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

When the **ligands** form a **coordinate bond** with the transition metal ion, there is **repulsion** from the **ligands' electrons** and the electrons in the **d orbitals** of the metal ion. This **increases** the **energy** of the d orbitals, but due to the **spatial arrangement** of the d orbitals, the energies are not all raised by the same amount. This **splits** the orbitals into groups.

Different ligands on the metal complex lead to **different splittings** of the d orbitals, which is why the different complexes display **different colours**.





Colours of Octahedral Compounds

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ - When present, these complex ions produce a **pale blue solution**.

$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ - When present, these complex ions produce a **deep blue solution**.

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ - When present, these complex ions produce a **pink solution**.

These compounds can all undergo substitution reactions with **chloride ions** to produce **tetrahedral complexes**. A change of colour also will occur.

$[\text{CuCl}_4]^{2-}$ - When present, these complex ions produce an **olive green solution**.

$[\text{CoCl}_4]^{2-}$ - When present, these complex ions produce a **deep blue solution**.

Ligand Substitution Reactions

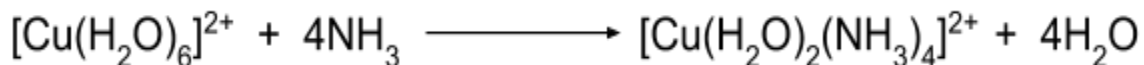
One ligand can be swapped for another ligand in a **ligand exchange** or **substitution** reaction. The ligands NH_3 and H_2O are **similar in size** and are both **uncharged**. This means they can be exchanged **without a change in coordination number** via a ligand substitution reaction.

Example: In this reaction the solution **changes colour** from **pink** to a **yellow straw colour**.



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: In this reaction the solution **changes colour** from **pale blue** to **deep blue**.



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. These substitution reactions take place when **concentrated HCl** is reacted with the metal complex.





Example: The solution **changes colour** from **pale blue** to **yellow**.



Example: The solution **changes colour** from **pink** to **blue**.



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

Transition Metals as Catalysts

Many transition metals and their compounds have good **catalytic properties**. 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. There are two main types of catalyst: **heterogeneous** and **homogeneous**.

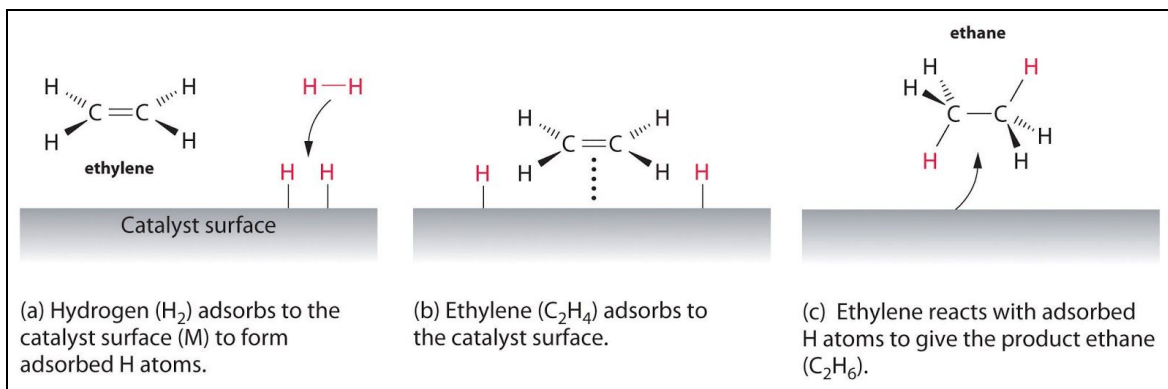
Heterogeneous Catalysts

Heterogeneous catalysts 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. Similarly, a **nickel catalyst** is used in the **hydrogenation of alkenes**. Heterogeneous catalysts use the process of **adsorption**:

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 and **rate of reaction is increased**.





<https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s18-08-catalysis.html>

Bruce A. Averill / CC BY-SA 3.0

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 affordable** 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 **minimal 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**. The sulfur impurities occur from the **natural gas** which is used to obtain methane - this methane is then used to produce hydrogen.

Homogeneous Catalysts

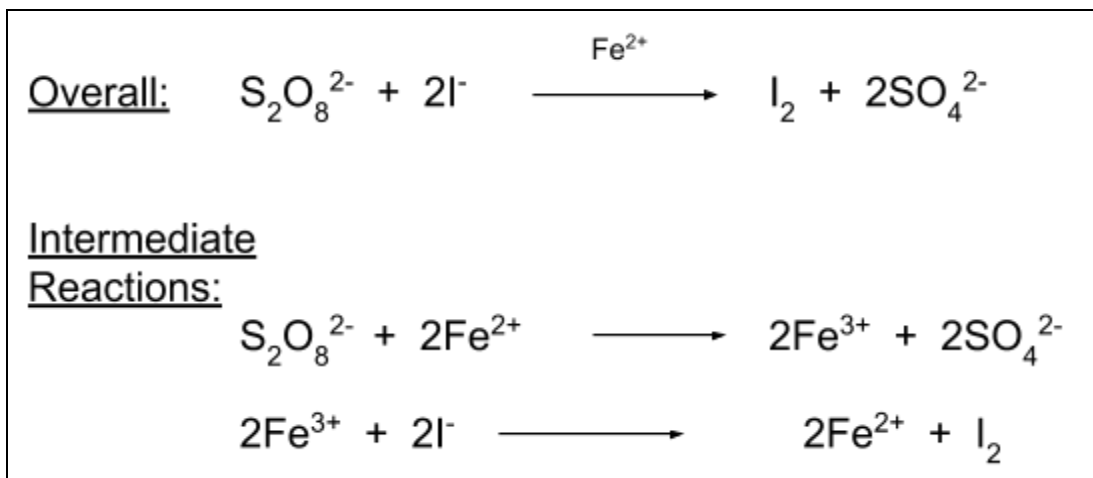
Homogeneous catalysts are catalysts that are in the **same phase** to the species in the reaction. They work by reacting with the reactants to form **an intermediate species**, which will then react to form the products, and **reform** the catalyst.

An example of a homogeneous catalyst being used 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 never react.





Example:

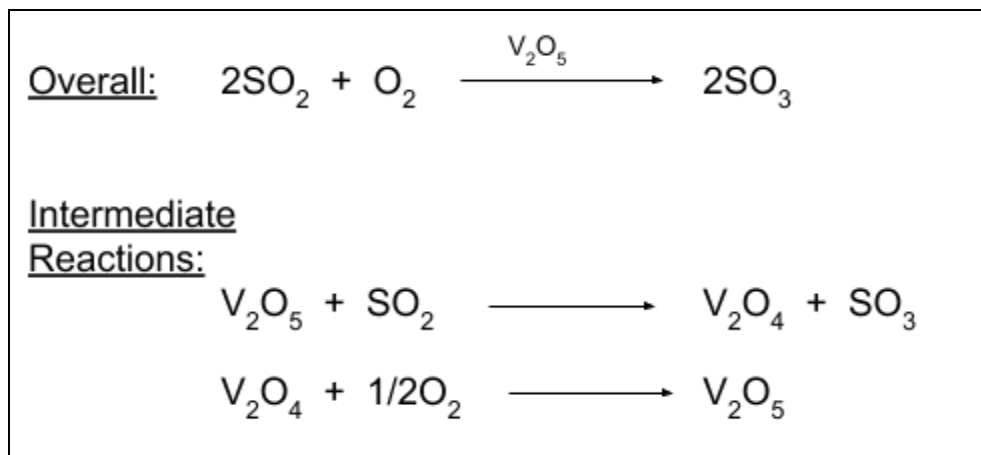


By forming a **reactive intermediate**, the reaction **pathway is changed** as the **enthalpy change** for the formation of the intermediate is much **lower** than the original reaction. The **activation energy is lower** so the reaction is more feasible.

Transition metals make good **homogeneous catalysts** due to their **variable oxidation states**. **Electrons are transferred** to produce a reactive intermediate and speed up the reaction rate.

The **Contact Process** 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.

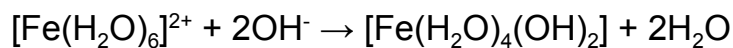
Manganese(IV) oxide is another transition metal used as a **homogeneous catalyst**. It is used as a catalyst for the **decomposition of hydrogen peroxide**.



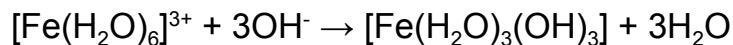


Reactions of Aqueous Ions

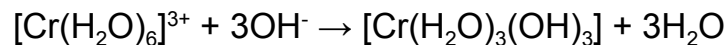
Solutions of transition metal ions **react as acids** with aqueous OH^- ions via a **neutralisation** reaction to form a **salt and water**. These reactions **hydrolyse** the metal ions to form **coloured precipitates**. The **salt precipitates** formed all have a **colour** allowing them to be **identified**.



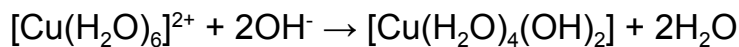
The green solution forms a green precipitate.



The yellow solution forms a brown precipitate.



The violet-blue solution forms a violet-blue precipitate.



The blue solution forms a blue precipitate.

It is easiest to remember the formulas of the precipitates by remembering that the number of OH^- substituted is the same as the value of the charge on the initial ion.

