AQA Chemistry A-Level

3.2.5: Transition Metals

Detailed Notes
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:

![Complex structure with water molecules around cobalt ion]

They can also be represented in formulas using square brackets.

Example:

\[[\text{Co(H}_2\text{O)}_6^{2+}\]

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\(_2\)O
- NH\(_3\)

Image courtesy of BC Open Textbooks
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 NH₃ and H₂O 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:

\[
[\text{Co(H}_2\text{O)}_6^{2+}] + 6\text{NH}_3 \rightarrow [\text{Co(NH}_3)_6^{2+}] + 6\text{H}_2\text{O}
\]

With copper complexes and NH₃ in excess, this substitution is incomplete and the complex formed has a combination of water and ammonia ligands.

Example:

\[
[\text{Cu(H}_2\text{O)}_6^{2+}] + 4\text{NH}_3 \rightarrow [\text{Cu(H}_2\text{O)}_2(\text{NH}_3)_4]^{2+} + 4\text{H}_2\text{O}
\]

This complex ion product forms as a deep blue solution.

The Cl⁻ ligand is much larger than the NH₃ and H₂O ligands meaning substitution with this ligand results in a change in coordination number for that complex.

Example:

\[
[\text{Cu(H}_2\text{O)}_6^{2+}] + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}
\]

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 **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:*

\[
[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{EDTA}^{4-} \rightarrow [\text{FeEDTA}]^{-1} + 6\text{H}_2\text{O}
\]

**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 (\(\Delta G\)) will be, therefore meaning the reaction is **more favourable**.
Enthalpy Change
The enthalpy change ($\Delta H$) 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:

![Image of linear complex](image.png)

This is the type of complex present in Tollens’ reagent, \([\text{Ag(NH}_3]_2]^+\).

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 of cisplatin](image.png)

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 ($\Delta E$) between these states corresponds to a wavelength and frequency of light which can be calculated:

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

($\nu = \text{frequency in hertz}$) ($\lambda = \text{wavelength in meters}$) ($h = \text{Planck’s constant, } 6.63 \times 10^{-34}$)

**Colourimetry**

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 calorimeter 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 reduction of vanadium by zinc in acidic solution.

Example:

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Ion Formula</th>
<th>Ion Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>+5</td>
<td>VO$_2^+$</td>
<td>yellow</td>
</tr>
<tr>
<td>+4</td>
<td>VO$_{2}^{2+}$</td>
<td>blue</td>
</tr>
<tr>
<td>+3</td>
<td>V$^{3+}$</td>
<td>green</td>
</tr>
<tr>
<td>+2</td>
<td>V$^{2+}$</td>
<td>violet</td>
</tr>
</tbody>
</table>

*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 positive) acidic conditions are required.

Example:

\[2\text{VO}_2^+ + 2\text{e}^- + 4\text{H}^+ \rightarrow 2\text{VO}^{2+} + 2\text{H}_2\text{O}\]

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

Example:

\[\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + 2\text{H}^+ + \text{e}^-\]

**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.

Examples:

\[\text{RCHO} + 2[\text{Ag(NH}_3\text{)}_2]^+ \rightarrow \text{RCOO}^- + 2\text{Ag}^+ + 4\text{NH}_3 + 2\text{H}_2\text{O}\]
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:

\[
\text{MnO}_4^- + 8H^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4H_2O
\]

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-
\]

\[
\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^-
\]

\[
\begin{array}{|c|c|}
\hline
\text{MnO}_4^- & \text{C}_2\text{O}_4^{2-} \\
2 & 5 \\
\hline
\text{MnO}_4^- & \text{Fe}^{2+} \\
1 & 5 \\
\hline
\text{C}_2\text{O}_4^{2-} & \text{Fe}^{2+} \\
1 & 2 \\
\hline
\end{array}
\]

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:

| Overall: | $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_5} 2\text{SO}_3$ |
| Intermediate Reactions: | $\text{V}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$ |

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:

\[
\begin{align*}
\text{Overall:} \quad 2S_2O_8^{2-} + 2I^- & \quad \stackrel{Fe^{2+}}{\longrightarrow} \quad I_2 + 2SO_4^{2-} \\
\text{Intermediate} \\
\text{Reactions:} \\
2S_2O_8^{2-} + 2Fe^{2+} & \quad \longrightarrow \quad 2Fe^{3+} + 2SO_4^{2-} \\
2Fe^{3+} + 2I^- & \quad \longrightarrow \quad 2Fe^{3+} + I_2
\end{align*}
\]

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

*Example:*

\[
\text{Overall: } 2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2
\]

**Intermediate Reactions:**

\[
4\text{Mn}^+ + \text{MnO}_4^- + 16\text{H}^+ \rightarrow 5\text{Mn}^{3+} + 4\text{H}_2\text{O}
\]

\[
2\text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{Mn}^{2+}
\]

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.