15. Transition Metals

**General properties of transition metals**

Transition metal characteristics of elements Sc → Cu arise from an **incomplete d sub-level** in ions.

- **Complex formation**
- **Formation of coloured ions**
- **Variable oxidation state**
- **Catalytic activity**

**Why is Zn not a transition metal?**

Zn can only form a +2 ion. In this ion the Zn$^{2+}$ has a **complete d orbital** and so does not meet the criteria of having an incomplete d orbital in one of its compounds.

**Why is Sc not a transition metal?**

Sc can only form a +3 ion. In this ion the Sc$^{3+}$ has an empty d orbital and so does not meet the criteria of having an incomplete d orbital in one of its compounds.

The successive ionization energies for the elements Sc to Zn show a gradual increase in ionisation energy until all the 4s and 3d electrons have been removed. There is then a big jump as electrons start to be removed from the inner core electrons.

**Complex formation**

- **Complex**: A central metal ion surrounded by ligands.
- **Ligand**: An atom, ion or molecule which can donate a lone electron pair.

Co-ordinate bonding is involved in complex formation.

Co-ordinate bonding is when **the shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**.

**Coordination number**: The number of co-ordinate bonds formed to a central metal ion.

Ligands can be **monodentate** (e.g. H$_2$O, NH$_3$ and Cl$^-$) which can form one coordinate bond per ligand or **bidentate** (e.g. NH$_2$CH$_2$CH$_2$NH$_2$ and ethanedioate ion C$_2$O$_4^{2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. EDTA$^{4-}$ which can form six coordinate bonds per ligand).

The EDTA$^{4-}$ anion has the formula

```
-\(\text{O}---\text{C}---\text{CH}_2\)
\(\text{N}---\text{CH}_2---\text{CH}_2---\text{N}---\text{CH}_2---\text{C}---\text{O}\)
\(---\text{O}---\text{C}---\text{CH}_2\)
```

with six donor sites (4O and 2N) and forms a 1:1 complex with metal(II) ions.

**Electrolytes**

- Sc$^{3+}$ [Ar] 4s$^2$3d$^1$
- Ti$^{3+}$ [Ar] 4s$^2$3d$^2$
- V$^{3+}$ [Ar] 4s$^2$3d$^3$
- Cr$^{3+}$ [Ar] 4s$^2$3d$^5$
- Mn$^{3+}$ [Ar] 4s$^2$3d$^5$
- Fe$^{3+}$ [Ar] 4s$^2$3d$^6$
- Co$^{3+}$ [Ar] 4s$^2$3d$^7$
- Ni$^{3+}$ [Ar] 4s$^2$3d$^8$
- Cu$^{2+}$ [Ar] 4s$^2$3d$^{10}$
- Zn$^{2+}$ [Ar] 4s$^2$3d$^{10}$

When forming ions lose 4s before 3d.

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Formation of coloured ions

**Colour** changes arise from changes in  
1. oxidation state,  
2. co-ordination number  
3. ligand.

### 

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Change</th>
<th>Colour</th>
<th>Change</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{Cu(H}_2\text{O)}_6^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O} ]</td>
<td>oxidation state</td>
<td>blue</td>
<td>co-ordination number</td>
<td>green</td>
</tr>
<tr>
<td>[ \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} ]</td>
<td>ligand</td>
<td>pink</td>
<td>oxidation state</td>
<td>yellow brown</td>
</tr>
<tr>
<td>[ \text{O}_2 ]</td>
<td>oxidation state</td>
<td>yellow</td>
<td>oxidation state</td>
<td>brown</td>
</tr>
</tbody>
</table>

### How colour arises

- Colour arises from **electronic transitions** from the ground state to excited states: between different d orbitals.
- A portion of visible light is absorbed to promote d electrons to higher energy levels. The light that is not absorbed is transmitted to give the substance colour.

A solution will appear blue if it absorbs orange light.

### Changing colour

Changing a ligand or changing the coordination number will alter the energy split between the d-orbitals, changing \( \Delta E \) and hence change the frequency of light absorbed.

### Compounds without colour

- Scandium is a member of the d block, its ion (\( \text{Sc}^{3+} \)) hasn’t got any d electrons left to move around. So there is not an energy transfer equal to that of visible light.
- In the case of \( \text{Zn}^{2+} \) ions and \( \text{Cu}^+ \) ions the d shell is full e.g.3d\(^{10} \) so here there is no space for electrons to transfer. So there is not an energy transfer equal to that of visible light.

### Spectrophotometry

- Absorption of visible light is used in spectrometry to determine the concentration of coloured ions.

**Method**
- Add an appropriate ligand to intensify colour
- Make up solutions of known concentration
- Measure absorption or transmission
- Plot graph of results or calibration curve
- Measure absorption of unknown and compare
transition metal ions commonly form **octahedral** complexes with small ligands (e.g. \( \text{H}_2\text{O} \) and \( \text{NH}_3 \)).

transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g. \( \text{Cl}^- \)).

**square planar** complexes are also formed, e.g. cisplatin

Ag\(^+\) commonly forms **linear** complexes e.g. \( [\text{Ag(NH}_3]^+ \), \( [\text{Ag(S}_2\text{O}_3)_2]^3^- \) and \( [\text{Ag(CN)}_2]^- \) (all colourless).

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**Cisplatin**

The Pt(II) complex cisplatin is used as an anticancer drug.

The cisplatin version only works as two chloride ions are displaced and the molecule joins on to the DNA. In doing this it stops the replication of cancerous cells.

In the body one Cl ligand is substituted by a water molecule

\[
\text{Pt(NH}_3)_2\text{Cl}_2 + \text{H}_2\text{O} \rightarrow [\text{Pt(NH}_3)_2\text{Cl(H}_2\text{O})]^+ + \text{Cl}^-
\]

Be able to apply your knowledge of bonding to given information in the question to explain how it bonds to DNA molecule—generally a combination of dative covalent bonding and hydrogen bonding

Platin binds to DNA of cancer cells and stops cancer cells dividing

![Cisplatin and Transplatin Diagram]

It can also prevent the replication of healthy cells by bonding on to healthy DNA which may lead to unwanted side effects like hair loss

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Fe(II) in haemoglobin enables oxygen to be transported in the blood. Haem is an iron(II) complex with a multidentate ligand.

CO is toxic to humans as CO can from a strong coordinate bond with haemoglobin and replaces oxygen in a ligand exchange reaction. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.
Variable oxidation states

Transition elements show variable oxidation states

Transition metals form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons. The energy differences between the oxidation states are small.

General trends

- Relative stability of +2 state with respect to +3 state increases across the period
- Compounds with high oxidation states tend to be oxidising agents e.g MnO$_4^-$
- Compounds with low oxidation states are often reducing agents e.g V$^{2+}$ & Fe$^{2+}$

Vanadium

Vanadium has four main oxidation states

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2^+$</td>
<td>Yellow</td>
</tr>
<tr>
<td>VO$^{2+}$</td>
<td>Blue</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>Green</td>
</tr>
<tr>
<td>V$^{2+}$</td>
<td>Violet</td>
</tr>
</tbody>
</table>

The ion with the V at oxidation state +5 exists as a solid compound in the form of a VO$_3^-$ ion, usually as NH$_4$VO$_3$ (ammonium vanadate (V)). It is a reasonably strong oxidising agent. Addition of acid to the solid will turn into the yellow solution containing the VO$_2^+$ ion.

Addition of zinc to the vanadium (V) in acidic solution will reduce the vanadium down through each successive oxidation state, and the colour would successively change from yellow to blue to green to violet.

<table>
<thead>
<tr>
<th>Redox Equation</th>
<th>$E^0$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2^+$ + 2H$^+$ + e$^-$ $\rightarrow$ VO$^{2+}$ + H$_2$O</td>
<td>+1.00 V</td>
</tr>
<tr>
<td>VO$^{2+}$ + 2H$^+$ + e$^-$ $\rightarrow$ V$^{3+}$ + H$_2$O</td>
<td>+0.34 V</td>
</tr>
<tr>
<td>V$^{3+}$ + e$^-$ $\rightarrow$ V$^{2+}$</td>
<td>-0.26 V</td>
</tr>
</tbody>
</table>

As zinc has a more negative electrode potential than all the vanadium half equations, zinc will reduce down to V$^{2+}$

Sn$^{2+}$ + 2e$^-$ $\rightarrow$ Sn $E$=-0.136V

Tin metal will only reduce the vanadium to the +3 state
Chromium Reactions

Reducing Chromium

Cr³⁺ (green) and then Cr²⁺ (blue) are formed by reduction of Cr₂O₇²⁻ (orange) by the strong reducing agent zinc in (HCl) acid solution. Fe³⁺ is a less strong reducing agent and will only reduce the dichromate to Cr³⁺.

The Cr²⁺ state can be stabilised by forming a stable complex ion with a ligand such as the ethanoate ion. If the blue Cr²⁺ ions are bubbled through sodium ethanoate, a stable red precipitate of chromium(II) ethanoate is formed.

Redox Potentials

Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O E = +1.33V
Fe³⁺(aq) + e⁻ → Fe²⁺(aq) E = +0.75V
Cr³⁺(aq) + e⁻ → Cr²⁺(aq) E = -0.41V
Zn²⁺ + 2e⁻ → Zn E = -0.76V

The electrode potential of Iron(II) is in between the two chromium half equations, so Fe²⁺ will reduce chromium down to Cr³⁺.

As zinc has a more negative electrode potential than all the chromium half equations, zinc will reduce chromium down to Cr²⁺.

Oxidising Chromium

When transition metals in low oxidation states are in alkaline solution they are more easily oxidised than when in acidic solution. It is easier to remove an electron from a negatively charged ion.

The metal ions can be oxidised by using oxidising agents such as hydrogen peroxide.

For change Cr(OH)₆³⁻ → CrO₄²⁻
Add H₂O to balance O: [Cr(OH)₆]³⁻ →CrO₄²⁻ + 2H₂O + 3e⁻
Add H⁺ to balance H: [Cr(OH)₆]³⁻ →CrO₄²⁻ + 2H₂O + 2H⁺ + 3e⁻
Add OH⁻ to both sides to cancel out H⁺: [Cr(OH)₆]³⁻ +2OH⁻ → CrO₄²⁻ + 2H₂O + 2H⁺ +2OH⁻ + 3e⁻
Chromate/ dichromate equilibrium
The chromate $\text{CrO}_4^{2-}$ and dichromate $\text{Cr}_2\text{O}_7^{2-}$ ions can be converted from one to the other by the following equilibrium reaction.

$$2 \text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$

Yellow solution $\rightarrow$ orange solution

Addition of acid will by application of le chatelier push the equilibrium to the dichromate.
Addition of alkali will remove the $\text{H}^+$ ions and, by application of le chatelier, push the equilibrium to the chromate.

Chromium Summary

+6

$\text{Cr}_2\text{O}_7^{2-}$ (aq) $\rightarrow$ Orange solution

acid $\rightarrow$ $\text{CrO}_4^{2-}$ (aq) $\rightarrow$ Yellow solution

alkali

Zinc and HCl
Or Fe$^{2+}$ acidified with HCl

H$_2$O$_2$

+3

$[\text{Cr(NH}_3)_6]^{3+}$ purple solution

Excess NH$_3$ $\rightarrow$ $[\text{Cr(H}_2\text{O})_6]^{3+}$ (aq) green solution

Limited NaOH or NH$_3$ $\rightarrow$ $\text{Cr(H}_2\text{O})_3(\text{OH})_3$ s) $\rightarrow$ $[\text{Cr(OH)}_6]^{3+}$ Green precipitate

Excess NaOH $\rightarrow$ $\text{Cr(OH)}_6^{3-}$ Green solution

$\text{O}_2$

Hydrogen atmosphere

+2

$[\text{Cr(H}_2\text{O})_6]^{2+}$ (aq) blue solution

Zinc and HCl

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Reactions of Inorganic Compounds in Aqueous Solution

Lewis acids and bases

Definitions: **Lewis acid**: electron pair acceptor  
**Lewis base**: electron pair donor

In the formation of complex ions the ligand is the Lewis base because it is donating a pair of electrons in the dative covalent bond and the metal ion is the Lewis acid.

Metal-aqua ions

Metal aqua ions are formed in aqueous solution.

\[
[M(H_2O)_6]^{2+}, \text{ limited to } M = \text{ Fe (green) }, \text{ Co(pink) and Cu (blue)};
\]

\[
[M(H_2O)_6]^{3+}, \text{ limited to } M = \text{ Cr (ruby) and Fe (violet)};
\]

In solution Cr(III) often appears green and Fe(III) appears yellow/brown due to hydrolysis reactions. The ruby and violet colour is only really seen in solid hydrated salts that contain these complexes.

Acidity or hydrolysis reactions

The following equilibria happen in aqueous solutions of metal ions.

\[
[M(H_2O)_6]^{2+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{+} + H_3O^+ \\
[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H_3O^+
\]

The equilibria lead to generation of acidic solutions with M$^{2+}$ ions, and very weakly acidic solutions with M$^{3+}$ ions. The 3$^+$ ions are noticeably more acidic.

The acidity of $[M(H_2O)_6]^{3+}$ is greater than that of $[M(H_2O)_6]^{2+}$ in terms of the greater polarising power (charge/size ratio) of the 3$^+$ metal ion. The greater the polarising power, the more strongly it attracts the water molecule. This weakens the O-H bond so it breaks more easily.

Reaction with limited OH$^-$ and limited NH$_3$

The bases OH$^-$ and ammonia when in limited amounts form the same hydroxide precipitates. They form in **deprotonation**

\[
[M(H_2O)_6]^{2+} + 2\text{OH}^- (aq) \rightarrow [M(H_2O)_4\text{OH}]^{+} (s) + 2\text{H}_2\text{O} (l) \\
[M(H_2O)_6]^{3+} + 3\text{OH}^- (aq) \rightarrow [M(H_2O)_3\text{OH}]^{2+} (s) + 3\text{H}_2\text{O} (l)
\]

Here the NH$_3$ and OH$^-$ ions are acting as **Bronsted-Lowry bases** accepting a proton

**acid base reactions**

\[
[M(H_2O)_6]^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow [M(H_2O)_4\text{OH}]^{+} (aq) + 2\text{H}_2\text{O} (l) \\
[M(H_2O)_6]^{3+} (aq) + 3\text{OH}^- (aq) \rightarrow [M(H_2O)_3\text{OH}]^{2+} (aq) + 3\text{H}_2\text{O} (l)
\]

**Reaction with excess OH$^-$**

With excess NaOH, the Cr hydroxide dissolves. Cr becomes $[Cr(OH)_3]^{3-}$ (aq) green solution.

These hydroxides are classed as **amphoteric** because they react and dissolve in both acids and bases.

\[
\text{Cr(H}_2\text{O)}_3\text{(OH)}_3 (s) + 3\text{OH}^- (aq) \rightarrow [\text{Cr(OH)}_3]^{3-} (aq) + 3\text{H}_2\text{O} (l) \\
\text{Cr(H}_2\text{O)}_3\text{(OH)}_3 (s) + 3\text{H}^+ (aq) \rightarrow [\text{Cr(H}_2\text{O)}_3]^{3+} (aq)
\]

**Reaction with excess NH$_3$**

With excess NH$_3$, ligand substitution reactions occur with Cu, Co and Cr and their precipitates dissolve.

The ligands NH$_3$ and H$_2$O are similar in size and are uncharged. Ligand exchange occurs without a change of co-ordination number for Co and Cr.

This substitution may, however, be incomplete as in the case with Cu.

\[
\text{Cr(OH)}_3\text{(H}_2\text{O)}_3 (s) + 6\text{NH}_3 (aq) \rightarrow \text{[Cr(NH}_3)_6\text{]}^{3+} (aq) + 3\text{H}_2\text{O} (l) + 3\text{OH}^- (aq) \\
\text{Cu(OH)}_2\text{(H}_2\text{O)}_4 (s) + 4\text{NH}_3 (aq) \rightarrow \text{[Cu(NH}_3)_4\text{(H}_2\text{O)}_2\text{]}^{2+} (aq) + 2\text{H}_2\text{O} (l) + 2\text{OH}^- (aq) \\
\text{Co(OH)}_2\text{(H}_2\text{O)}_4 (s) + 6\text{NH}_3 (aq) \rightarrow \text{[Co(NH}_3)_6\text{]}^{2+} (aq) + 4\text{H}_2\text{O} (l) + 2\text{OH}^- (aq)
\]

In these reactions NH$_3$ is acting as a **Lewis base** donating an electron pair.

Remember this Co complex is oxidised to +3 on standing in air.

Cu becomes $[\text{Cu(NH}_3)_4\text{(H}_2\text{O)}_2\text{]}^{2+}$ deep blue solution

In these reactions NH$_3$ is acting as a **Lewis base** donating an electron pair.
Ligand exchange reactions with chloride ions

Addition of a high concentration of chloride ions (from conc HCl or saturated NaCl) to an aqueous ion leads to a ligand substitution reaction.

The Cl\(^-\) ligand is larger than the uncharged H\(_2\)O and NH\(_3\) ligands so therefore ligand exchange can involve a change of co-ordination number.

Be careful: If solid copper chloride (or any other metal) is dissolved in water it forms the aqueous [Cu(H\(_2\)O)\(_6\)]\(^{2+}\) complex and not the chloride [CuCl\(_4\)]\(^{2-}\) complex.

Stability of complexes

The substitution of monodentate ligand with a bidentate or a multidentate ligand leads to a more stable complex.

This chelate effect can be explained in terms of a positive entropy change in these reactions as more molecules of products than reactants

\[
[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Cu\text{(EDTA)}^{2-} + 6H_2O(l)]
\]

The copper complex ion has changed from having monodentate ligands to a multidentate ligand. In this reaction there is an increase in the entropy of the system because there are more moles of products than reactants (from 2 to 7), creating more disorder.

The stability of the EDTA complexes has many applications. It can be added to rivers to remove poisonous heavy metal ions as the EDTA complexes are not toxic. It is in many shampoos to remove calcium ions present in hard water, so helping lathering.

Ethane-1,2-diamine

Ethane-1,2-diamine is a common bidentate ligand.

\[
[Cu(H_2O)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Cu(NH_2CH_2CH_2NH_2)_3]^{2+} + 6H_2O
\]

There are 3 bidentate ligands in this complex each bonding in twice to the metal ion.

It has a coordination number of 6

Octahedral shape

Bond angle around Cr 90\(^\circ\)

Ethane-1,2-diamine, as a base, can also carry out the deprotonation reactions (similar to those of ammonia) forming hydroxide precipitates.

\[
2[Al(H_2O)_6]^{3+} + 3 H_3NCH_2CH_2NH_3^+ \rightarrow 2Al[OH(H_2O)_2]_2(OH)_2(s) + 3 [H_3NCH_2CH_2NH_3]^{2+} (aq)
\]

Note small molecules such as NH\(_3\) cannot act as bidentate ligands because even though they have two lone pairs they are too close together and would not be able to fit around the metal ion.

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More on some common ligands

**Ethanediolate** \( \text{C}_2\text{O}_4^{2-} \)

\[ \text{Cu(H}_2\text{O)}_6^{2+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow [\text{Cu(C}_2\text{O}_4)_3]^{4-} + 6\text{H}_2\text{O} \]

\[ \text{Cr(H}_2\text{O)}_6^{3+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow [\text{Cr(C}_2\text{O}_4)_3]^{3-} + 6\text{H}_2\text{O} \]

A 6 coordination number complex with bidentate ethanediolate ligands e.g. \([\text{Cr(C}_2\text{O}_4)_3]^{3-}\)

Octahedral shape with 90° bond angles

Partial substitution of ethanediolate ions may occur when a dilute aqueous solution containing ethanediolate ions is added to a solution containing aqueous copper(II) ions. In this reaction four water molecules are replaced and a new complex is formed.

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

Using Silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl⁻ ions acting as ligands inside the complex and Cl⁻ ions outside the complex attracted ionically to it. If silver nitrate is added to such a compound it will only form the silver chloride precipitate with the free chloride ions outside of the complex.

\begin{align*}
\text{e.g. Co(NH}_3)_6\text{Cl}_3 & \text{ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl⁻ ions. So all 3 Cl}^- & \\
& & \text{are outside the complex} \\
\text{e.g. Cr(NH}_3)_5\text{Cl}_3 & \text{ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl}^- & \\
& & \text{ions. So 1 Cl}^- \text{ is a ligand and 2 are outside} & \\
& & \text{the complex} \\
\text{e.g. Cr(NH}_3)_4\text{Cl}_3 & \text{ reacts on a 1:1 mole ratio with silver nitrate as there is one free} & \\
& & \text{Cl}^- \text{ ion. So 2 Cl}^- \text{s are ligands} & \\
& & \text{and 1 is outside the complex} \\
\end{align*}
2+ Ion Summary

- [MCl₂]²⁻
- [CuCl₂]²⁻ → green sol
- [CoCl₂]²⁻ → blue sol
- Water
- Conc Cl⁻
- Few drops OH⁻ or NH₃
- [M(H₂O)₆]³⁺ → M(OH)₂(H₂O)₄
- Excess OH⁻
- [Cu(NH₃)₄(H₂O)₂]²⁺ → deep blue sol
- Excess NH₃
- [Co(NH₃)₆]³⁺ → yellow/light brown sol
- Air or H₂O₂
- [Co(NH₃)₆]³⁺ → brown sol

3+ Ion Summary

- [Cr(OH)₆]³⁻ → green sol
- H₂O₂
- Cr₂O₇²⁻ → orange sol
- H⁺
- OH⁻
- [CrO₄]²⁻ → yellow sol
- Excess OH⁻
- [M(H₂O)₆]³⁺ → [M(OH)₃(H₂O)₃]
- Few drops OH⁻ or NH₃
- [Cr(H₂O)₆]³⁺ → violet sol
- [Fe(H₂O)₆]³⁺ → yellow sol
- H⁺
- [Cr(OH)₃(H₂O)₃] green ppt
- Fe(OH)₃(H₂O)₃ brown ppt
- [Cr(NH₃)₆]³⁺ → violet sol
- Excess NH₃
- [Cr(OH)₆]³⁻ → green ppt
- Fe(OH)₃(H₂O)₃ brown ppt
- [Cr(OH)₃(H₂O)₃] green ppt
- Fe(OH)₃(H₂O)₃ brown ppt
Catalysts increase reaction rates without getting used up. They do this by providing an alternative route with a lower activation energy.

Transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

A heterogeneous catalyst is in a different phase from the reactants
A homogeneous catalyst is in the same phase as the reactants

Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

Strength of adsorption
The strength of adsorption helps to determine the effectiveness of the catalytic activity
Some metals e.g. W have too strong adsorption and so the products cannot be released
Some metals e.g. Ag have too weak adsorption, and the reactants do not adsorb in high enough concentration
Ni and Pt have about the right strength and are most useful as catalysts

Surface area:
Increasing the surface area of a solid catalyst will improve its effectiveness. A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).

Example of heterogeneous catalysts

V₂O₅ is used as a catalyst in the Contact Process.
Overall equation: \(2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3\)
step 1 \(\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4\)
step 2 \(2\text{V}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5\)

Catalytic converters

These remove CO, NOx and unburned hydrocarbons (e.g. octane, \(\text{C}_8\text{H}_{18}\)) from the exhaust gases, turning them into ‘harmless’ \(\text{CO}_2\), \(\text{N}_2\) and \(\text{H}_2\text{O}\).

\(2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2\)
\(\text{C}_8\text{H}_{18} + 25\text{NO} \rightarrow 8\text{CO}_2 + 12\frac{1}{2}\text{N}_2 + 9\text{H}_2\text{O}\)

Converters have a ceramic honeycomb coated with a thin layer of catalyst metals Platinum, Palladium, Rhodium – to give a large surface area.

Adsorption of reactants at active sites on the surface may lead to catalytic action. The active site is the place where the reactants adsorb on to the surface of the catalyst. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency.

Transition Metals can use the 3d and 4s e⁻ of atoms on the metal surface to form weak bonds to the reactants.

Advantages of Heterogeneous catalysts
Heterogeneous catalysts can be filtered off and are easy to separate from any liquid or gaseous products. They are also suited to continuous processes rather than batch processes.

Note the oxidation number of the vanadium changes and then changes back. It is still classed as a catalyst as it returns to its original form.

Steps in Heterogeneous Catalysis in catalytic converter

1. CO and NO molecules form bonds with atoms at active sites on the surface of the catalyst - adsorbed onto the surface
2. As a result bonds in the reactants are weakened and break
3. New bonds form between the reactants held close together on catalyst surface
4. Desorption of \(\text{CO}_2\) and \(\text{N}_2\) product molecules from the surface of the catalyst
Developing New Catalysts

Making ethanoic acid from methanol and carbon monoxide is a preferable industrial production method because it has a high atom economy.

\[ \text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH} \]

A iridium/iodine based catalyst is currently used.

Over the years the catalyst used for this reaction has been developed using different transition metal catalysts. This has lead to greater selectivity of the catalysts, cheaper catalysts, milder conditions being used and improved separation processes.

The scientific community reports and validates new discoveries by publishing new discoveries in scientific journals that are peer reviewed.

Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species

Transition metals can act as homogeneous catalysts because they can form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons.

Example of homogeneous catalysts

**Reaction between iodide and persulphate ions**

The reaction between I\(^-\) and \(\text{S}_2\text{O}_8\text{^2-}\) catalysed by Fe\(^{2+}\) is very slow because the reaction needs a collision between two negative ions. Repulsion between the ions is going to hinder this — meaning high activation energy.

\[
\text{S}_2\text{O}_8\text{^2-} + 2\text{I}\text{-} \rightarrow 2\text{SO}_4\text{^2-} + \text{I}_2
\]

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants, so it can first reduce the reactant with the more positive electrode potential and then in the second step oxidize the reactant with the more negative electrode potential.

Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased.

Fe\(^{3+}\) ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order.

Catalysed alternative route

**stage 1** \(\text{S}_2\text{O}_8\text{^2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4\text{^2-} + 2\text{Fe}^{3+}\)

**stage 2** \(2\text{I}\text{-} + 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+} + \text{I}_2\)

Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

Constructing a catalysed mechanism for a reaction

**Example**

The following reaction is catalysed by Co\(^{2+}\) ions in an acidic solution.

\[ \text{SO}_3\text{^2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4\text{^2-} \]

Write a mechanism for the catalysed reaction by writing two equations involving Co\(^{2+}\) and Co\(^{3+}\) ions

Split full equation into its two half equations

\[ \text{SO}_3\text{^2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4\text{^2-} \]

Add in cobalt to make two new redox equations.

Making sure the oxidised cobalt equation is combined with the original reduced half equation and vice versa

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

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

Check your two mechanism equations add up to the original full non catalysed equation.