Catalysts

**Definition:** Catalysts increase reaction rates without getting used up.

Explanation: They do this by providing an alternative route or mechanism with a lower activation energy.

Comparison of the activation energies for an un catalysed reaction and for the same reaction with a catalyst present.

If the activation energy is lower, more particles will have energy \( > E_A \) so there will be a higher frequency of effective collisions. The reaction will be faster.

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.

**Steps in Heterogeneous Catalysis**
1. Reactants 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. This in turn weakens bonds between product and catalyst and product leaves (desorbs).
How do Heterogeneous Catalysts Work?

Reactants adsorb on to atoms on the **surface of the catalyst**.

This can result in the bonds within the reactant molecules becoming weaker and may break.

New bonds form between the reactants held close together on catalyst surface.

This in turn weakens bonds between product and catalyst and product leaves.
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.

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).

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.

Examples of heterogeneous catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_2O_5</td>
<td>2SO_2 + O_2 \rightarrow 2SO_3</td>
</tr>
<tr>
<td>Overall equation</td>
<td></td>
</tr>
<tr>
<td>step 1</td>
<td>SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4</td>
</tr>
<tr>
<td>step 2</td>
<td>2V_2O_4 + O_2 \rightarrow 2V_2O_5</td>
</tr>
</tbody>
</table>

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.

Cr_2O_3 catalyst is used in the manufacture of methanol from carbon monoxide and hydrogen.
CO + 2H_2 \rightarrow CH_3OH

Fe is used as a catalyst in the Haber Process
N_2 + 3H_2 \rightarrow 2NH_3

Catalytic converters
These remove CO, NO_x and unburned hydrocarbons (e.g. octane, C_8H_18) from the exhaust gases, turning them into ‘harmless’ CO_2, N_2 and H_2O.

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

Lead petrol cannot be used in cars fitted with a catalytic converter since lead strongly adsorbs onto the surface of the catalyst.

Poisoning Catalysts
Catalysts can become poisoned by impurities and consequently have reduced efficiency.

It is important to ensure the purity of the reactants if poisoning can occur.

Poisoning has a cost implication e.g. poisoning by sulphur in the Haber Process and by lead in catalytic converters in cars means that catalysts lose their efficiency and may need to be replaced.
Homogeneous catalysis

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

The intermediate will often have a different oxidation state to the original transition metal. At the end of the reaction the original oxidation state will reoccur. This illustrates importance of variable oxidation states of transition metals in catalysis.

Explaining homogeneous catalysis using E values

The reaction between I\(^{-}\) and S\(_2\)O\(_8\)\(^{2-}\) catalysed by Fe\(^{2+}\) overall

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

The uncatalysed reaction 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

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

\[
\begin{align*}
\text{S}_2\text{O}_8^{2-} + 2\text{e}^- & \rightarrow 2\text{SO}_4^{2-} & E^0 &= +2.01 \text{V} \\
\text{Fe}^{3+} + \text{e}^- & \rightarrow \text{Fe}^{2+} & E^0 &= +0.77 \text{V} \\
\text{I}_2 + 2\text{e}^- & \rightarrow 2\text{I}^- & E^0 &= +0.54 \text{V}
\end{align*}
\]

Catalysed alternative route

stage 1 \[ \text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+} \]

stage 2 \[ 2\text{I}^- + 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+} + \text{I}_2 \]

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

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.

\[ \text{Fe}^{3+} \] ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

Catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

Nitrogen dioxide catalyses the conversion of sulphur dioxide to sulphur trioxide.

The first step of the reaction is

\[ \text{NO}_2 (g) + \text{SO}_2 (g) \rightarrow \text{SO}_3 (g) + \text{NO} (g) \]

The second step of the reaction is

\[ \text{NO} (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{NO}_2 (g) \]

The nitrogen dioxide is regenerated at the end of the reaction so it is classed as a catalyst.
Autocatalytic Reaction between Ethanedioate and Manganate ions

The autocatalysis by $\text{Mn}^{2+}$ in titrations of $\text{C}_2\text{O}_4^{2-}$ with $\text{MnO}_4^{-}$

overall $ 2 \text{MnO}_4^{-} + 5 \text{C}_2\text{O}_4^{2-} + 16 \text{H}^{+} \rightarrow 2\text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$

Catalysed alternative route

Step 1 $ 4\text{Mn}^{2+} + \text{MnO}_4^{-} + 8 \text{H}^{+} \rightarrow 5\text{Mn}^{3+} + 4 \text{H}_2\text{O}$

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

The initial uncatalysed reaction is slow because the reaction is a collision between two negative ions which repel each other leading to a high activation energy.

The $\text{Mn}^{2+}$ ions produced act as an autocatalyst and therefore the reaction starts to speed up because they bring about the alternative reaction route with lower activation energy.

The reaction eventually slows as the $\text{MnO}_4^{-}$ concentration drops.

This is an example of **autocatalysis** where one of the products of the reaction can catalyse the reaction.

Following the reaction rate

This can be done by removing samples at set times and titrating to work out the concentration of $\text{MnO}_4^{-}$. It could also be done by use of a spectrometer measuring the intensity of the purple colour. This method has the advantage that it does not disrupt the reaction mixture, using up the reactants and it leads to a much quicker determination of concentration.

### Constructing a catalysed mechanism for a reaction

**Example**

The following reaction is catalysed by $\text{Co}^{2+}$ ions in an acidic solution. $\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-}$.

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

Split the full equation into its two half equations

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

$\frac{1}{2} \text{O}_2 + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2\text{O}$

$\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^{+} + 2\text{e}^{-}$

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

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

$\frac{1}{2} \text{O}_2 + 2\text{H}^{+} + 2\text{Co}^{2+} \rightarrow \text{H}_2\text{O} + 2\text{Co}^{3+}$

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

$2\text{Co}^{3+} + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^{+} + 2\text{Co}^{2+}$

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