PRINCIPLES OF CATALYTIC ACTION

Introduction The two basic types of catalytic action ... **heterogeneous** and **homogeneous**

Heterogeneous Catalysis

Are in a **different phase to the reactants**; *e.g. a solid catalyst in a gaseous reaction*

**Action**
- takes place at **active sites** on the **surface** of a solid (*e.g. a metal*)
- gases are **adsorbed onto the surface** and form weak bonds with metal atoms

*Catalysis is thought to work in **three stages** as follows ...*

**Adsorption**
- formation of bonds with the metal may use some of the electrons from bonds within the gas molecules thus weakening these bonds and making a subsequent reaction easier.

**Reaction**
- adsorbed gases may be held on the surface of the metal in just the right orientation for a reaction to occur. This increases the chances of favourable collisions taking place.

**Desorption**
- the products are then released from the active sites

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HARD **Hetero** = **Adsorption** + **Reaction** + **Desorption**
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The **strength of adsorption is critical** ...  
- too weak (Ag) [ ] [ ] [ ] [ ] [ ] little adsorption - few available d orbitals
- too strong (W) [ ] [ ] [ ] [ ] [ ] molecules will remain on the surface and prevent further reaction
- just right (Ni/Pt) [ ] [ ] [ ] [ ] [ ]

*read about VOLCANO CURVES*

**Rate** Catalysis of gaseous reactions can lead to an increase in rate in several ways ...
- one species is adsorbed onto the surface and is more likely to undergo a collision
- one species is held in a favourable position for reaction to occur
- adsorption onto the surface allows bonds to break and fragments react quicker
- two reactants are adsorbed alongside each other give a greater concentration

**Format**
- used in a **finely divided** form increases the surface area provides more collision sites.
- mounted in a **support** medium maximises surface area and reduces costs.

**Examples of catalysts**
- Metals Ni, Pt hydrogenation reactions
  Fe Haber Process
- Oxides Al₂O₃ dehydration reactions
  V₂O₅ Contact Process
**Specificity** In some cases the choice of catalyst can influence the products... ethanol undergoes two different reactions depending on the metal used as the catalyst.

The **distance between active sites** and their similarity with the length of bonds determines the method of adsorption and affects which bonds are weakened.

**Copper** Dehydrogenation (oxidation)

\[ C_2H_5OH \rightarrow CH_3CHO + H_2 \]

**Alumina** Dehydration

\[ C_2H_5OH \rightarrow C_2H_4 + H_2O \]

**Poisoning** Impurities in a reaction mixture can also **adsorb onto the surface** of a catalyst thus **removing potential sites** for gas molecules and decreasing efficiency.

**expensive** because the catalyst has to **replaced**
the process has to be **shut down**

**examples** Sulphur Haber process
Lead catalytic converters in cars

**Homogeneous Catalysis**

**Action** Catalyst and reactants are in the **same phase**.
- reaction proceeds through an **intermediate** species with **lower energy**
- there is usually more than one reaction step
- transition metal ions are often involved - **oxidation state changes** during the reaction

**Energy profile for non-catalysed reaction**

*Each of the steps has a lower activation energy than the single reaction without a catalyst*
Examples

**Acids**
e.g. hydrolysis of esters

**Gases**

OZONE in the atmosphere breaks down naturally as follows ...

\[
O_3 \rightarrow O + O_2
\]

However it breaks down more easily in the presence of chlorofluorcarbons (CFC's).

There is a series of complex reactions but the basic process is :-

- CFC's break down in the presence of UV light to form chlorine radicals
  \[
  CCl_2F_2 \rightarrow Cl^- + \cdotCClF_2
  \]

- chlorine radicals then react with ozone
  \[
  O_3 + Cl^- \rightarrow ClO^- + O_2
  \]

- chlorine radicals are regenerated
  \[
  ClO^- + O \rightarrow O_2 + Cl^-
  \]

Overall, chlorine radicals are not used up so a small amount of CFC's can destroy thousands of ozone molecules before they take part in a termination stage.

**Transition metal compounds**

These work because of their ability to change oxidation state.

**Example 1**

Reaction between iron(III) and vanadium(III) is catalysed by Cu\(^{2+}\)

\[
\begin{align*}
\text{step 1} & \quad Cu^{2+} + V^{3+} \rightarrow Cu^+ + V^{4+} \\
\text{step 2} & \quad Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} \\
\text{overall} & \quad Fe^{3+} + V^{3+} \rightarrow Fe^{2+} + V^{4+}
\end{align*}
\]

**Example 2**

Reaction between I\(^{-}\) and S\(_2\)O\(_8\)\(^{2-}\):

The reaction is slow because REACTANTS ARE NEGATIVE IONS \(\because\) REPULSION

Addition of iron(II) catalyses the reaction

\[
\begin{align*}
\text{step 1} & \quad S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+} \\
\text{step 2} & \quad 2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \\
\text{overall} & \quad S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2
\end{align*}
\]
**Autocatalysis**  Occurs when a **product of the reaction catalyses the reaction** itself
It is found in the reactions of manganate(VII) with ethandioate
\[
2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2
\]
- the titration needs to be carried out at 70°C because the reaction is slow
- as Mn\(^{2+}\) is formed the reaction speeds up; the Mn\(^{2+}\) formed acts as the catalyst

**ENZYMES**

**Action**
- enzymes are extremely effective **biologically active** catalysts
- they are **homogeneous** catalysts, reacting in solution with body fluids
- active sites are such that only one type of molecule will fit; “lock and key mechanism”
- makes enzymes **very specific** as to what they catalyse.

![Substrate, Active site, Enzyme, Products](image)

A  Only species with the correct shape can enter the active site in the enzyme
B  Once in position, the substrate can react with a lower activation energy
C  The new products do not have the correct shape to fit so the complex breaks up

**Other points**  Activity is **affected by** ...
- **temperature** - it increases until the protein is denatured
- **substrate concentration** - reaches a maximum when all sites are blocked
- **pH** - many catalysts are made up of amino acids which can be protonated
- **being poisoned** - when the active sites become “clogged” with unwanted molecules

**Q.1**  What is the importance of the following enzymes ?

- amylase
- catalase
- invertase
- protease