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

HARD **H***etero* = **A***dsorption* + **R***eaction* + **D***esorption*

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

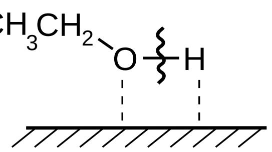
• Metals	Ni, Pt	hydrogenation reactions
	Fe	Haber Process
• Oxides	Al_2O_3	dehydration reactions
	V_2O_5	Contact Process

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.

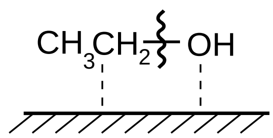
Copper Dehydrogenation (oxidation)

C_2H_5OH ——> CH_3CHO + H_2



Alumina Dehydration

C_2H_5OH ——> C_2H_4 + H_2O



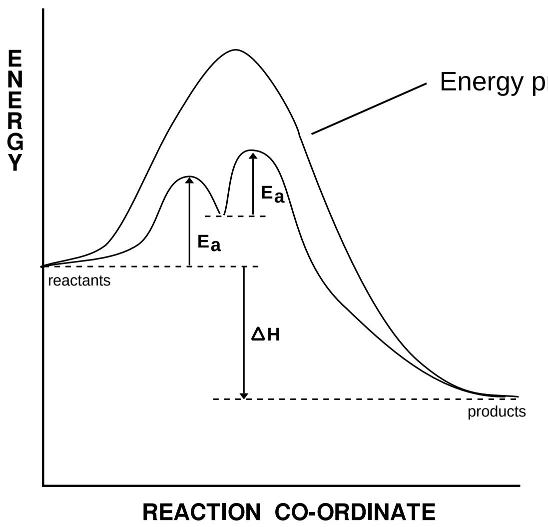
Poisoning **Impurities** in a reaction mixture can also **adsorb onto the surface** of a catalyst thus **removing potential sites** for gas molecules and decreasing efficiency.

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



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 ...

$$\mathbf{O_3 \longrightarrow O + O_2}$$

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* $\mathbf{CCl_2F_2 \longrightarrow Cl\bullet + \bullet CClF_2}$
- *chlorine radicals then react with ozone* $\mathbf{O_3 + Cl\bullet \longrightarrow ClO\bullet + O_2}$
- *chlorine radicals are regenerated* $\mathbf{ClO\bullet + O \longrightarrow O_2 + Cl\bullet}$

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+}

step 1 $Cu^{2+} + V^{3+} \longrightarrow Cu^{+} + V^{4+}$

step 2 $Fe^{3+} + Cu^{+} \longrightarrow Fe^{2+} + Cu^{2+}$

overall $\mathbf{Fe^{3+} + V^{3+} \longrightarrow Fe^{2+} + V^{4+}}$

Example 2 Reaction between I^{-} and $S_2O_8^{2-}$

The reaction is slow because REACTANTS ARE NEGATIVE IONS ∴ REPULSION
Addition of iron(II) catalyses the reaction

step 1 $S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$

step 2 $2Fe^{3+} + 2I^{-} \longrightarrow 2Fe^{2+} + I_2$

overall $\mathbf{S_2O_8^{2-} + 2I^{-} \longrightarrow 2SO_4^{2-} + I_2}$

Autocatalysis Occurs when a **product of the reaction catalyses the reaction** itself
It is found in the reactions of manganate(VII) with ethandioate

$$2MnO_4^{-} + 16H^{+} + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

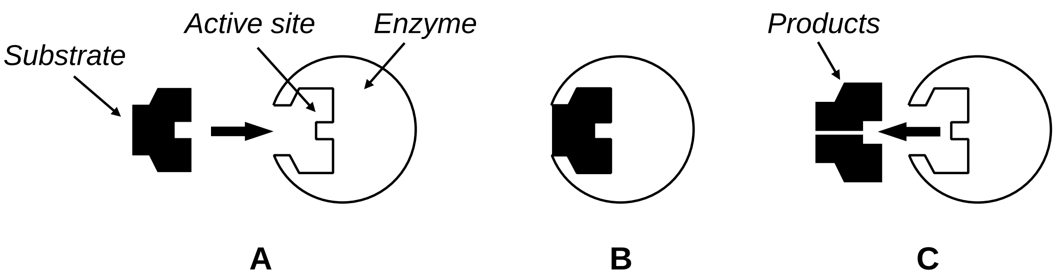
- the titration needs to be carried out at 70°C because the reaction is slow
- as Mn^{2+} is formed the reaction speeds up; the Mn^{2+} formed acts as the catalyst

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.



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*