Catalysts

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CATALYSIS

•Catalyst: a substance that increases the rate of a reaction without being consumed in the reaction

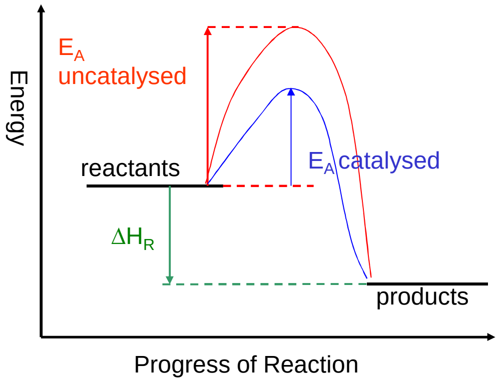
• Catalysts work by providing alternative pathways that have lower activation energies

Transition metals and their compounds are effective and important catalysts *Industrially and biologically.*

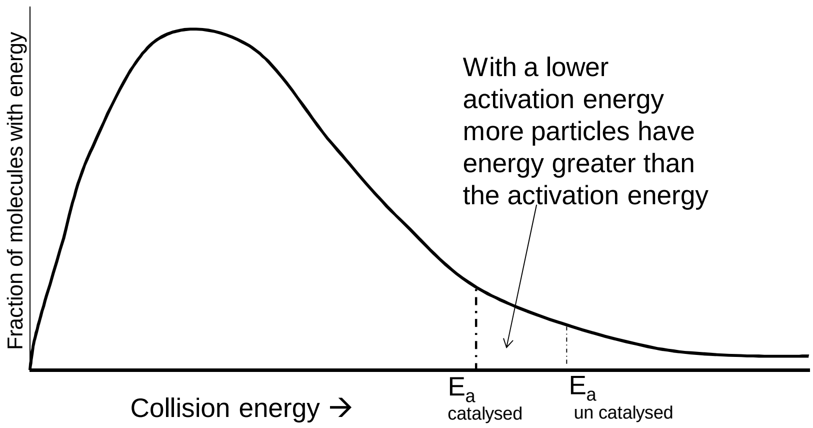
Factors which make Transition metals good catalysts:
availability of 3d and 4s shells
ability to change oxidation number

Catalysts increase reaction rates by providing an alternative route with a lower activation energy

Comparison of the activation energies for an uncatalysed 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 and a faster rate



2 TYPES OF CATALYSTS

HOMOGENEOUS	HETEROGENEOUS
Reactants and catalyst in same physical state. e.g Enzyme catalysed reactions in cells all take place in aqueous solutions	When a catalyst is of a different state to the reactants e.g iron used in the Haber process

Homogeneous Catalysts

Homogeneous catalysts are in the same phase as the reactants. Usually means reaction takes place in aqueous phase, e.g. aqueous acid with aqueous reactants

In this case the catalyst may lead to another mechanism or it may stabilise an intermediate compound. The new mechanism will have a lower activation energy.

A transition metal catalyst may change oxidation state during the reaction and a colour change due to this may result but the original colour should reform.

Explaining homogeneous catalysis

Persulphate ions , $S_2O_8^{2-}$, are powerful oxidising agents. Iodide ions are very easily oxidised to iodine. The reaction between them, however, is very slow without a catalyst

If you look at the equation, it is easy to see why that is:

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

The reaction needs a collision between two negative ions. Repulsion between the ions is going stop this.

The catalysed reaction avoids this problem
The catalyst can be iron(II) ions.

The persulphate ions oxidise the iron(II) ions to iron(III) ions. In the process the persulphate ions are reduced to sulphate ions.

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

The iron(III) ions are strong enough oxidising agents to oxidise iodide ions to iodine. In the process, they are reduced back to iron(II) ions again.

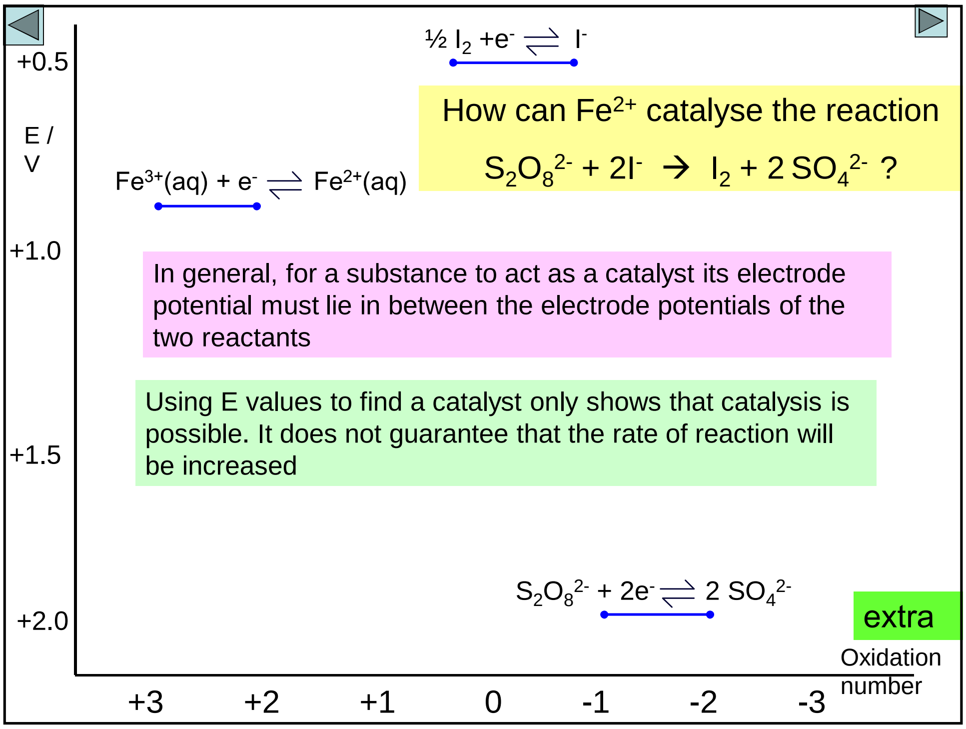
$$2I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$$

Both of these individual stages in the overall reaction involve collision between positive and negative ions and will have lower activation energies

This is a good example of the use of transition metal compounds as catalysts because of their ability to change oxidation state.

Ignoring colour changes due to iodine formation there will be a change from green iron II to brown iron III and then a reforming of the green colour as the catalyst reforms

Both Fe^{2+} and Fe^{3+} can act as the catalyst in this reaction because the two steps in the catalysed mechanism can occur in any order



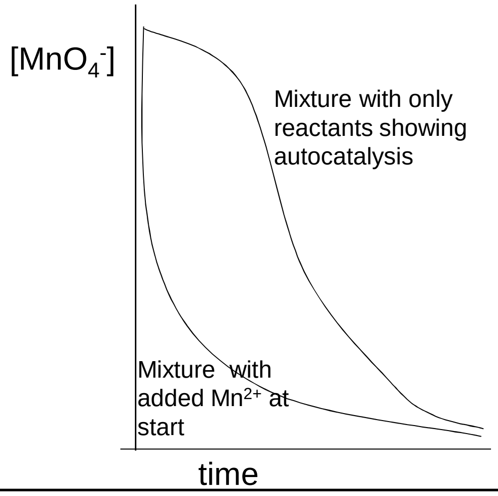
Autocatalysis experiment

The equation for the oxidation of ethanedioate by permanganate in acidic solution is

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

Click here for video stills of reaction between MnO_4^- & $H_2C_2O_4$

Explain the shape of the two curves



Mechanism for catalysed reaction

In mixture 1 the reaction is slow to begin with as both reactants are **negatively charged** and so do not collide easily as **they repel**.

It speeds up as Mn^{2+} forms which can act as a catalyst for the reaction using the following mechanism.

Catalysed mechanism

Step 1

$4Mn^{2+} + MnO_4^- + 8\ H^+ \rightarrow 5Mn^{3+} + 4\ H_2O$

Step 2

$2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2\ CO_2$

Constructing a catalysed mechanism for a reaction

Example

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

$SO_3^{2-} + ½ O_2 \rightarrow SO_4^{2-}$

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

$SO_3^{2-} + ½ O_2 \rightarrow SO_4^{2-}$

$½ O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

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

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

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

$½ O_2 + 2H^+ + 2Co^{2+} \rightarrow H_2O + 2Co^{3+}$

$2Co^{3+} + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2Co^{2+}$

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

Heterogeneous Catalysis

Heterogeneous catalyst which is in a different phase to the reactants. Usually means solid transition metal catalyst with reactants in liquid or gas phases

In this case the reactants tend to adsorb (chemically bond) on to the surface of the catalyst this

- **weakens bonds**
- **brings molecules closer**
- **more favourable orientation**.

Transition Metals can

use the 3d and 4s e^- of atoms on the metal surface to form weak bonds to the reactants.

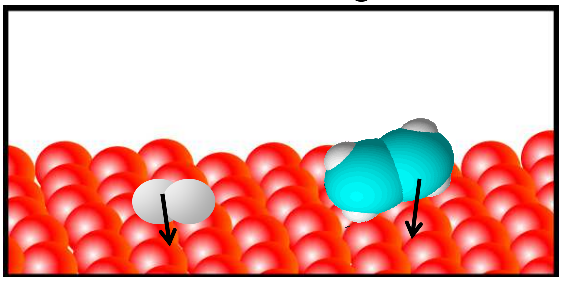
Once the reaction has occurred on the metal surface, these bonds can break to release products

Active sites

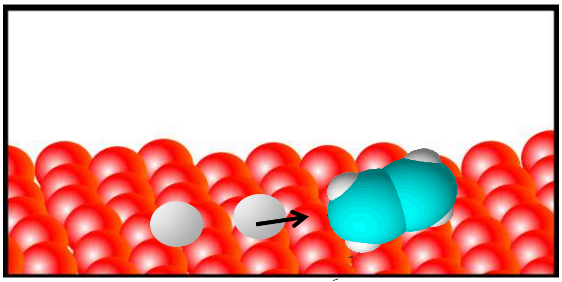
Adsorption of reactants at active sites on the surface may lead to catalytic action. The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**.

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.

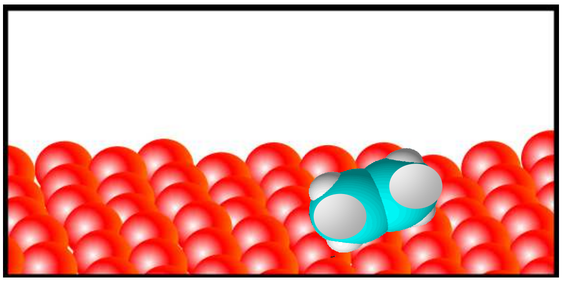
How do Heterogeneous Catalysts Work?



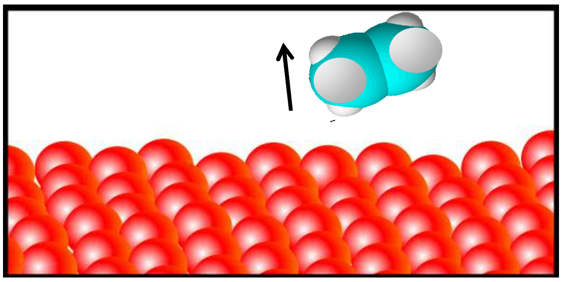
Reactants adsorb on to atoms on the **surface of the catalyst**.



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

Which transition metal to use as a catalyst

Adsorption of reactants at active sites on the surface may lead to catalytic action.

- The strength of adsorption helps to determine the activity

e.g. W adsorbs too strongly and so the products cannot be released

Ag adsorbs too weakly however

Ni and Pt have about the right strength and are most useful as catalysts

•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).

Examples of uses of catalysts

- V_2O_5 is used as a catalyst in the Contact Process
- Car exhaust systems
- Zeolites are used in industry as catalysts e.g in the cracking of petroleum fuels
- Iron in the Haber process

Contact process

This is an example of a heterogeneous reaction where the catalyst changes oxidation state during the reaction

Sulphur dioxide oxidised to sulphur by vanadium (v) oxide

$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

The vanadium has been reduced to vanadium(IV). It is oxidised back to the starting vanadium (V) oxide by oxygen

$2V_2O_4 + O_2 \rightarrow 2V_2O_5$

the vanadium(v)oxide is unchanged at the end of the reaction.

CATALYTIC CONVERTERS

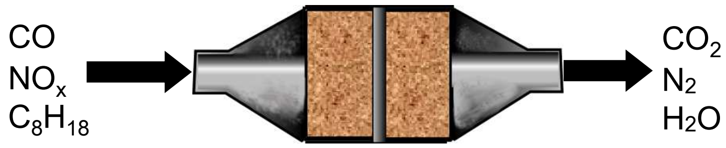
•Catalytic converters remove harmful gases from car exhausts.

•It consists of a honeycomb of ceramic with metals such as platinum,palladium and rhodium coated on the honeycomb

•It removes up to 90% of the harmful gases

•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).

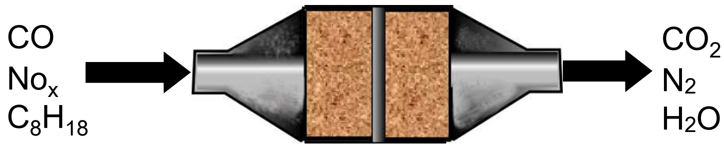
Catalytic converter



EQUATIONS FOR REACTIONS IN THE CATALYTIC CONVERTER

$2\,CO + 2\,NO \longrightarrow 2\,CO_2 + N_2$

$C_8H_{18} + 25\,NO \longrightarrow 8\,CO_2 + 12\tfrac{1}{2}\,N_2 + 9H_2O$



Catalyst poisoning

Catalysts can be poisoned.

In heterogeneous catalysis the 'poison' molecules are adsorbed more strongly to the catalyst surface than the reactant molecules, the catalyst becomes inactive

The Iron catalyst can be poisoned by sulphur in the Haber Process

EXAMPLES OF POISONING OF CATALYSTS

Leaded petrol cannot be used in cars fitted with a catalytic converter since lead strongly absorbs onto the surface of the catalyst

Cannot use copper or nickel in a catalytic converter on a car instead of the expensive platinum or Rhodium. REASON :- Any SO_2 present in the exhaust fumes (trace amounts) would poison the catalyst

Once the catalytic converter has become inactive it cannot be regenerated

REGENERATION OF CATALYST

This is possible sometimes.

- Catalytic cracking of long-chain hydrocarbons produces carbon
- This can coat the zeolite catalyst, making it become inactive .
- The catalyst is recycled through a container where hot air is blown over it.
- Oxygen in the air converts the carbon to carbon dioxide and the catalyst is regenerated.