



CATALYSIS

- A catalyst is a substance that changes the speed of a chemical reaction, but is not used up in the reaction.
- Catalysts that speed up reactions work by providing an alternative route with a lower activation energy (catalysts do not alter ΔG , ΔH or ΔS for a reaction, only the activation energy).
- Catalysts speed the rate at which an equilibrium is reached by speeding up the forward and reverse reaction - they do not alter the position of the equilibrium.
- Catalysts that slow down reactions are called inhibitors (or negative catalysts).

Heterogeneous catalysis

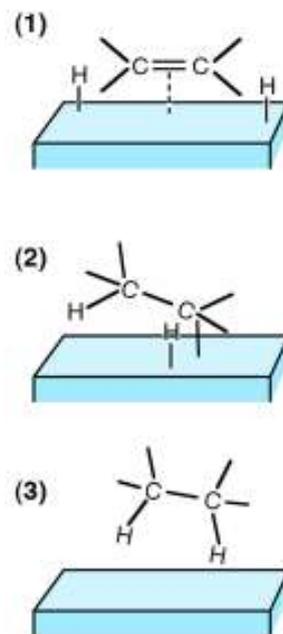
a) What is a heterogeneous catalyst?

- A catalyst that is in a different phase to the reactants is a heterogeneous catalyst.
- The catalyst is usually a solid and the reaction takes place on the surface.
- The bulk of industrial processes involve heterogeneous catalysis.

e.g.	Haber process	$3 \text{H}_2 + \text{N}_2 \rightleftharpoons 2 \text{NH}_3$	Fe catalyst
e.g.	Contact process	$2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$	V_2O_5 catalyst
e.g.	making methanol	$\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	Cr_2O_3 catalyst

b) How does a heterogeneous catalyst work?

- At least one of the reactants is **adsorbed** onto the surface (i.e. forms bonds to the atoms in the solid surface).
- The places on the surface where molecules are adsorbed are called **active sites**.
- In an effective catalyst, the molecules can move about the surface, bonding to different active sites.
- The adsorption of reactants onto the surface can result in increased reaction in a number of ways:
 - a) adsorption onto the surface effectively concentrates the reactants, i.e. brings them closer together than in the gas phase, so increasing the likelihood of collision;
 - b) it may weaken some of the bonds in the molecule, making reaction easier;
 - c) it may position the molecule in a favourable orientation for reaction.



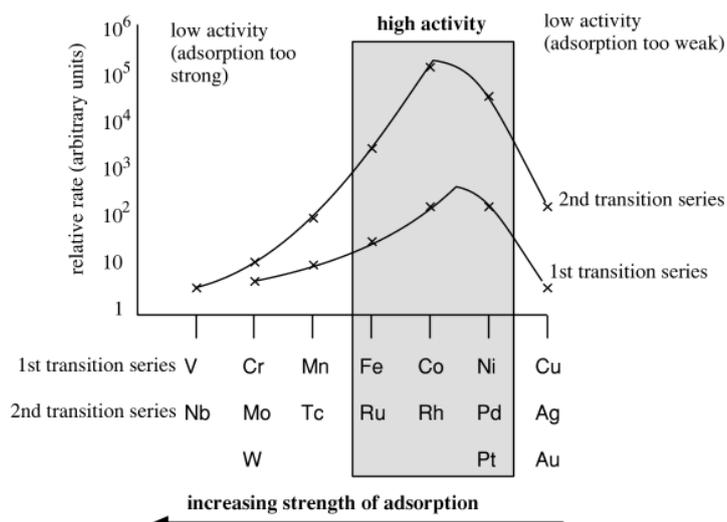
- For the catalyst to work, molecules must be adsorbed onto the surface. However if:
 - adsorption is too weak: not many molecules will be adsorbed so the catalyst will have very little effect
 - adsorption is too strong: molecules will not be able to move around the active sites, and so be less likely to meet another reactant and so be less likely to react (also any product will tend to remain adsorbed on the surface)

- There is a fine balance between adsorption being too weak and too strong. For a catalyst to be effective it must have adsorption of the right strength. Examples are:

Ag adsorption usually too weak - poor catalyst

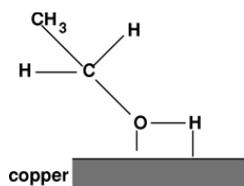
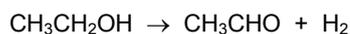
W adsorption usually too strong - poor catalyst

Ni & Pt ideal adsorption strength - so make excellent catalysts

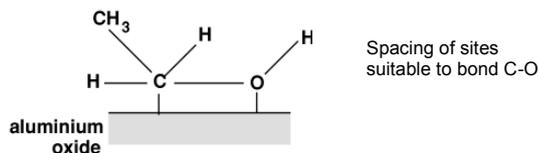


- It should be noted that surface catalysts are highly specific, i.e. the reaction that a particular surface catalyses is very specific, and it may not catalyse other similar reactions, or other similar catalysts may not catalyse the same reaction. e.g. reactions of ethanol:

Cu catalyst - dehydrogenation



Al_2O_3 catalyst - dehydration



c) The nature of the catalyst

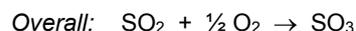
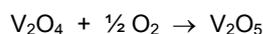
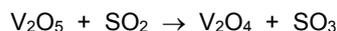
- It is obvious that the larger the surface area of these catalysts, the less quantity of catalyst that is needed to produce the same effect.
- Many surface catalysts are very expensive, and so maximising surface area has important cost savings.
- The surface area is maximised by using a very thin coating of the catalyst on some type of support medium (a support is required as the layer is too thin to support itself - often a ceramic "honeycomb" structure is used as support - note that the catalyst must be able to bind to the support).

d) Catalyst poisoning

- Some surface catalysts are prone to poisoning, where other substances adsorb strongly to the surface, blocking the active sites.
 - This lowers the efficiency of the catalyst, or makes it totally ineffective depending on the extent of the poisoning.
 - These poisons are extremely difficult to remove and the catalyst is ruined, which can be very costly (particularly with expensive catalysts).
- e.g. lead poisoning of catalytic converters in cars - both the Rh and Pt catalysts are poisoned by lead (from leaded petrol) - and are very expensive to replace.
- e.g. sulphur poisoning in the Haber process - the hydrogen is obtained from natural gas which is contaminated by S, which if not removed will poison the Fe catalyst (S is added to natural gas to give it an odour, so leaks can be smelt).

e) Contact process

- More conc H_2SO_4 is manufactured than any other chemical. The key step in this process (the Contact process) is the conversion of SO_2 to SO_3 which is a slow, reversible reaction.
- It is catalysed by vanadium (V) oxide, V_2O_5 .



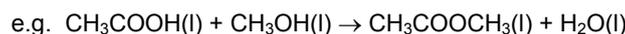
Homogeneous catalysis

a) What is a homogeneous catalyst?

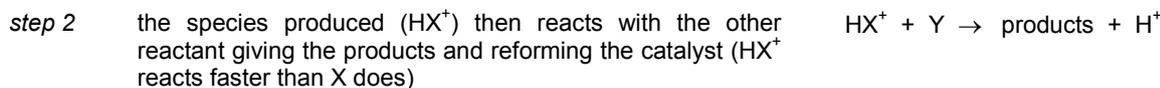
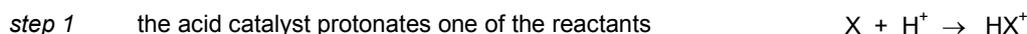
- A homogeneous catalyst is one that is in the same phase as the reactants.
- Most reactions involving homogeneous catalysts take place in solution (where all species are either liquids or are dissolved, so they are all in the same phase).
- Reactions involving homogeneous catalysis proceed via an intermediate species formed from a reactant and the catalyst, which then reacts further and regenerates the catalyst.

b) How does an acid homogeneous catalyst work?

- An example of an acid catalysed reaction is esterification:



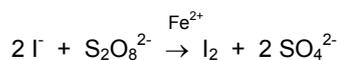
- Imagine a reaction catalysed by an acid: $\text{X} + \text{Y} \xrightarrow{\text{cat H}^+} \text{products}$



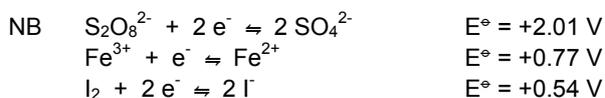
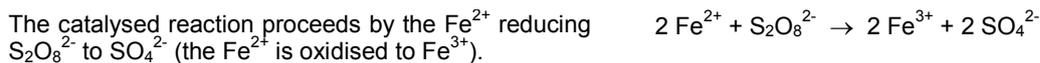
c) How does a transition metal homogeneous catalyst work?

- Transition metal compounds have the ability to vary their oxidation states which allows them to act as catalysts.

Example 1 – reaction between iodide ions and peroxodisulphate ions

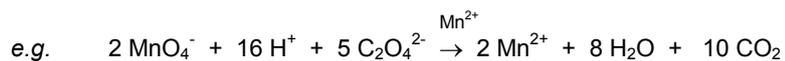


- This reaction is very slow in the absence of a catalyst because it involves the reaction of two negative ions (they repel each other so collision is difficult).
- However it is catalysed by $\text{Fe}^{2+}(\text{aq})$, which can act as a catalyst because it easily changes between the oxidation states Fe(+2) and Fe(+3).



- $\text{Fe}^{3+}(\text{aq})$ also catalyses this reaction. In the first step Fe^{3+} oxidises I^- to I_2 , and then the Fe^{2+} formed reduces $\text{S}_2\text{O}_8^{2-}$ to SO_4^{2-} .

Example 2 – autocatalysis in the reaction between manganate (VII) ions and ethandioate ions



- This reaction is very slow in the absence of a catalyst because it involves the reaction of two negative ions (they repel each other so collision is difficult).
- However it is catalysed by $\text{Mn}^{2+}(\text{aq})$, which can act as a catalyst because it easily changes between the oxidation states Mn(+2) and Mn(+3).
- The catalyst is a product of the reaction – this reaction is slow until some Mn^{2+} is formed, but then it speeds up as catalyst is formed.
- Reactions which produce their own catalyst are known as autocatalysis reactions

The catalysed reaction proceeds by the Mn^{2+} reducing MnO_4^- to Mn^{3+} . $4 \text{Mn}^{2+} + \text{MnO}_4^- + 8 \text{H}^+ \rightarrow 5 \text{Mn}^{3+} + 4 \text{H}_2\text{O}$

The Mn^{3+} then oxidises the $\text{C}_2\text{O}_4^{2-}$ to CO_2 , reforming Mn^{2+} . $2 \text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{CO}_2 + 2 \text{Mn}^{2+}$