Cambridge (CIE) A Level Chemistry

Your notes

Homogeneous & Heterogeneous Catalysts

Contents

Homogeneous & Heterogeneous Catalysis

- **Catalysts** increase the rate of reaction by providing an alternative pathway which has a lower **activation energy**
- Catalysts can be either **homogeneous** or **heterogeneous**

Homogeneous catalysts

- Homogeneous catalysts are those that are in the same phase as the reaction mixture
- For example, in the esterification of ethanoic acid (CH_3COOH) with ethanol (CH_3CH_2OH) to form ethyl ethanoate ($CH_3COOCH_2CH_3$) under acidic conditions:

$$CH_3COOH\,(aq) + CH_3OH\,(aq) \xrightarrow{H^+\,(aq)} CH_3COOC_2H_5\,(aq) + H_2O\,(l)$$

- The H^+ is a homogeneous catalyst and like the reactants and product it is in the **aqueous** phase

Heterogeneous catalysts

- Heterogeneous catalysts are those that are in a different phase to the rest of the reaction mixture
- For example, in the Born-Haber process to form ammonia (NH_3) from nitrogen (N_2) and hydrogen (H_2) an iron (Fe) catalyst is used:

$$N_2\,(g) + 3H_2\,(g) \xrightarrow{Fe\,(s)} 2NH_3\,(g)$$

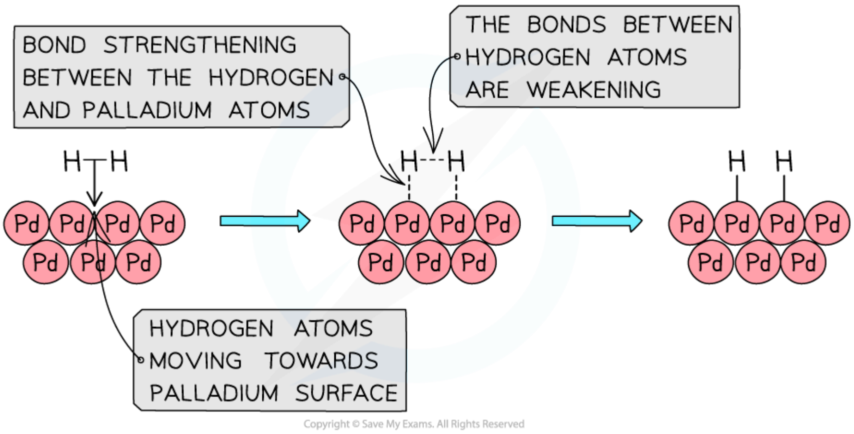
- The Fe catalyst is a heterogeneous catalyst as it is in **the** solid phase, whereas the reactants and products are all in the **gas** phase

Heterogeneous Catalysis

- In **heterogeneous catalysis,** the molecules react at the surface of a solid catalyst
- The mode of action of a heterogeneous catalyst consists of the following steps:
- **Adsorption** (or **chemisorption**) of the reactants on the catalyst surface
  - The reactants diffuse to the surface of the catalyst
  - The reactant is **physically adsorbed** onto the surface by **weak forces**
  - The reactant is **chemically adsorbed** onto the surface by **stronger bonds**
  - Chemisorption causes **bond weakening** between the atoms of the reactants
- **Desorption** of the products

- The bonds between the products and catalyst weaken so much that the products break away from the surface
- For example, the adsorption of hydrogen molecules onto a palladium (Pd) surface

How heterogeneous catalysts generally work



The reactants are adsorbed on the catalyst surface causing bond weakening and eventually desorption of the products

Iron in the Haber process

- In the **Haber process** ammonia (NH_3) is produced from nitrogen (N_2) and hydrogen (H_2)
- An **iron catalyst** is used which speeds up the reaction by bringing the reactants close together on the metal surface
- This increases their likelihood to react with each other
- The mode of action of the iron catalyst is as follows:
  - **Diffusion** of the nitrogen and hydrogen gas to the iron surface
  - **Adsorption** of the reactant molecules onto the iron surface by forming bonds between the iron and reactant atoms
    - These bonds are so strong that they weaken the covalent bonds between the nitrogen atoms in N_2 and hydrogen atoms in H_2
    - But they are weak enough to break when the catalysis has been completed
  - **The reaction** takes place between the adsorbed nitrogen and hydrogen atoms which react with each other on the iron surface to form NH_3
  - **Desorption** occurs when the bonds between the NH_3 and iron surface are weakened and eventually broken
  - The formed NH_3 **diffuses** away from the iron surface

Iron as a heterogeneous catalyst in the Haber Process

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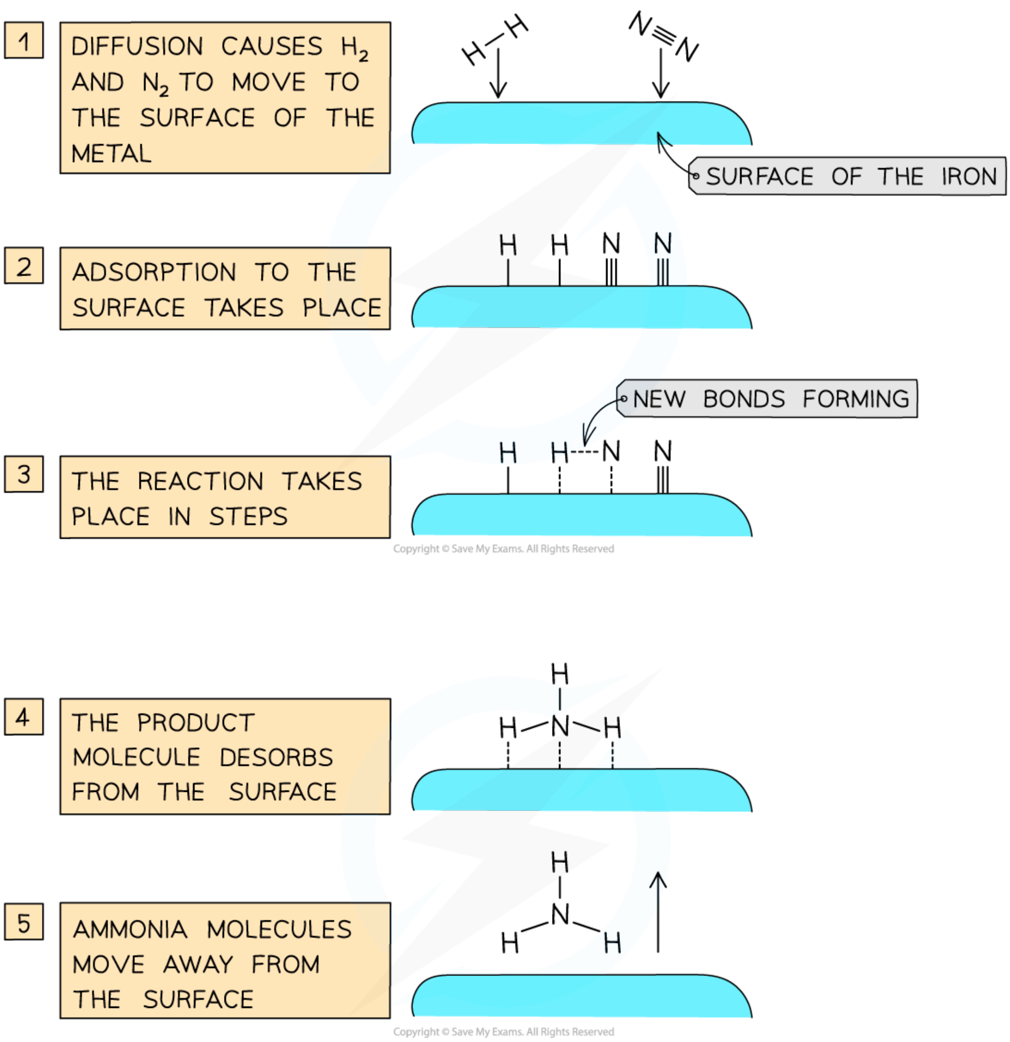

Iron brings the nitrogen and hydrogen closer together so that they can react and hence increases the rate of reaction

Heterogeneous catalysts in catalytic converters

- Heterogeneous catalysts are also used in the **catalytic removal** of oxides of nitrogen from the exhaust gases of car engines
- The catalysts speed up the conversion of:
  - Nitrogen oxides (NO_y) into **harmless nitrogen gas** (N_2)
  - Carbon monoxide (CO) into carbon dioxide (CO_2)
- The catalytic converter has a **honeycomb** structure containing small beads coated with **platinum, palladium,** or **rhodium metals** which act as **heterogeneous catalysts**
- The mode of action of the catalysts is as follows:
  - **Adsorption** of the nitrogen oxides and CO onto the catalyst surface
  - **The weakening** of the covalent bonds within nitrogen oxides and CO

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- Formation of new bonds between:
    - Adjacent nitrogen atoms to form N_2 molecules
    - CO and oxygen atoms to form CO_2 molecules
  - **Desorption** of N_2 and CO_2 molecules which eventually **diffuse** away from the metal surface

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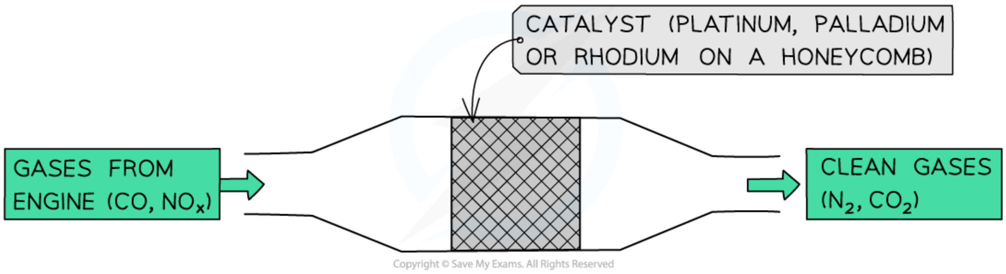
Heterogeneous catalysts in car exhausts



The metals in catalytic converters speed up the conversion of nitrogen oxides and carbon monoxide into nitrogen and carbon dioxide respectively

Homogeneous Catalysis

- **Homogeneous catalysis** often involves **redox reactions** in which the ions involved in catalysis undergo changes in their **oxidation number**
  - As ions of transition metals can change oxidation number they are often good catalysts
- Homogeneous catalysts are used in one step and are reformed in a later step

The iodine-peroxydisulfate reaction

- This is a very **slow** reaction in which the peroxydisulfate ($S_2O_8^{2-}$) ions **oxidise** the **iodide** to **iodine**

$$S_2O_8^{2-}\,(aq) + 2I^-\,(aq) \rightarrow 2SO_4^{2-}\,(aq) + I_2\,(aq)$$

- Since both the $S_2O_8^{2-}$ and I^- ions have a negative charge, it will require a lot of energy for the ions to overcome the **repulsive forces** and collide with each other
- Therefore, Fe^{3+} (aq) ions are used as a **homogeneous catalyst**
- The catalysis involves two **redox reactions**:
  - First, Fe^{3+} ions are **reduced** to Fe^{2+} by I^-

$$2Fe^{3+}\,(aq) + 2I^-\,(aq) \rightarrow 2Fe^{2+}\,(aq) + I_2\,(aq)$$

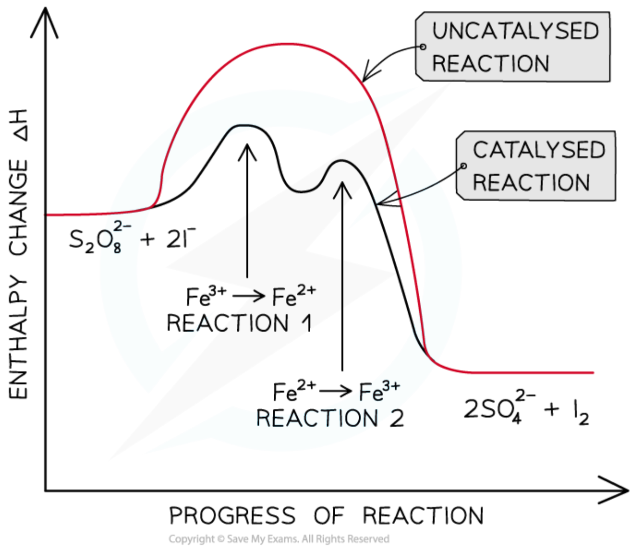
- Then, Fe^{2+} is **oxidised** back to Fe^{3+} by $S_2O_8^{2-}$

$$2Fe^{2+}\,(aq) + S_2O_8^{2-}\,(aq) \rightarrow 2Fe^{3+}\,(aq) + 2SO_4^{2-}\,(aq)$$

- By reacting the reactants with a positively charged Fe ion, there are no repulsive forces, and the activation energy is significantly lowered

- The order of the two reactions does not matter
  - So, Fe^{2+} can be first oxidised to Fe^{3+} followed by the reduction of Fe^{3+} to Fe^{2+}

The reaction pathway diagram for a two-stage catalysed reaction



The catalysed reaction has two energy 'humps' because it is a two-stage reaction

Nitrogen oxides & acid rain

- As fossil fuels contain sulfur, burning the fuels will release sulfur dioxide which oxidises in air to sulfur trioxide, and then **dilute sulfuric acid** (H_2SO_4) is formed by reaction with water. The result is acidification of rain:

$$\mathbf{SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)}$$

- Nitrogen oxides can act as **catalysts** in the formation of acid rain by catalysing the oxidation of SO_2 to SO_3

$$\mathbf{NO_2\,(g) + SO_2\,(g) \rightarrow SO_3\,(g) + NO\,(g)}$$

- The formed NO gets oxidised to regenerate NO_2

$$\mathbf{NO\,(g) + ½\,O_2\,(g) \rightarrow NO_2\,(g)}$$

- The regenerated NO_2 molecule can again oxidise another SO_2 molecule to SO_3 which will react with rainwater to form H_2SO_4 and so on

