

# CIE A Level Chemistry



# 26.2 Homogeneous & Heterogeneous Catalysts

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# Homogeneous & Heterogeneous Catalysts

# Your notes

# 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<sub>3</sub>COOH) with ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) to form ethyl ethanoate (CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub>) under acidic conditions:

$$CH_{3}COOH(aq) + CH_{3}OH(aq) \xrightarrow{H^{+} (aq)} CH_{3}COOC_{2}H_{5}(aq) + H_{2}O(I)$$

■ The H<sup>+</sup> 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<sub>3</sub>) from nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) an iron (Fe) catalyst is used:

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

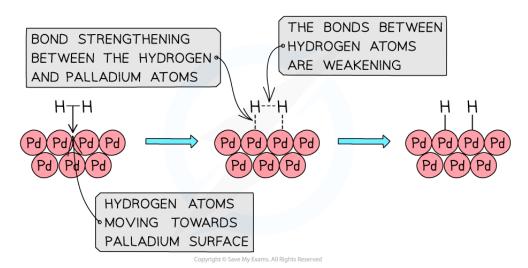
 The Fe catalyst is a heterogeneous catalyst as it is in the solid phase, whereas the reactants and products are all in the gas phase



### **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

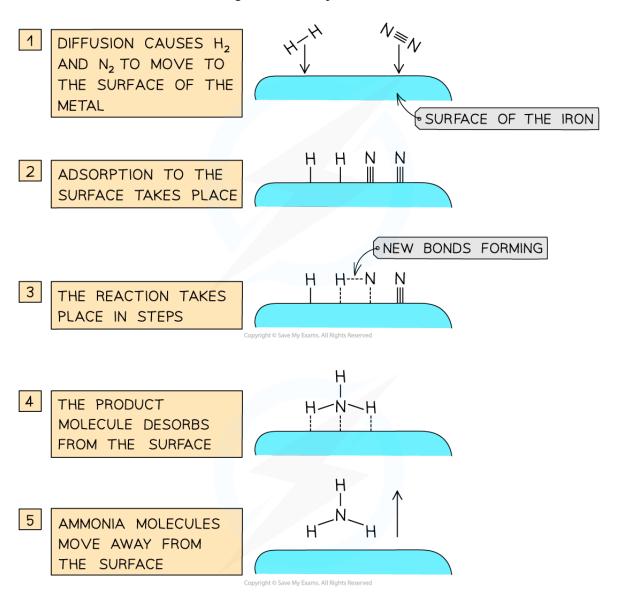
- In the **Haber process** ammonia ( $NH_3$ ) is produced from nitrogen ( $N_2$ ) and hydrogen ( $H_2$ )
- An **iron catalyst** is used which speeds up the reaction by bringing the reactants close together on the metal surface
- This increases their likelihood to react with each other
- The mode of action 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<sub>2</sub> and hydrogen atoms in H<sub>2</sub>
- 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<sub>3</sub>
- **Desorption** occurs when the bonds between the NH<sub>3</sub> and iron surface are weakened and eventually broken
- The formed NH<sub>3</sub> **diffuses** away from the iron surface

#### Iron as a heterogeneous catalyst in the Haber Process







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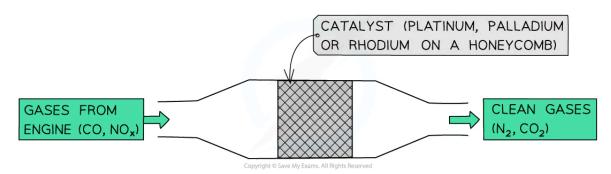
Iron brings the nitrogen and hydrogen closer together so that they can react and hence increases the rate of reaction

# Your notes

#### 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<sub>v</sub>) into harmless nitrogen gas (N<sub>2</sub>)
  - Carbon monoxide (CO) into carbon dioxide (CO<sub>2</sub>)
- 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
    - Formation of new bonds between:
    - Adjacent nitrogen atoms to form N<sub>2</sub> molecules
    - CO and oxygen atoms to form CO<sub>2</sub> molecules
  - **Desorption** of N<sub>2</sub> and CO<sub>2</sub> molecules which eventually **diffuse** away from the metal surface

#### Heterogeneous catalysts in car exhausts



The metals in catalytic converters speed up the conversion of nitrogen oxides and CO into  $N_2$  and  $CO_2$  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  $(S_2, O_8^{2-})$  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<sub>2</sub>O<sub>8</sub><sup>2-</sup> and I<sup>-</sup> 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<sup>3+</sup> (aq) ions are used as a homogeneous catalyst
- The catalysis involves two **redox reactions**:
  - First, Fe<sup>3+</sup> ions are **reduced** to Fe<sup>2+</sup> by I<sup>-</sup>

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

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

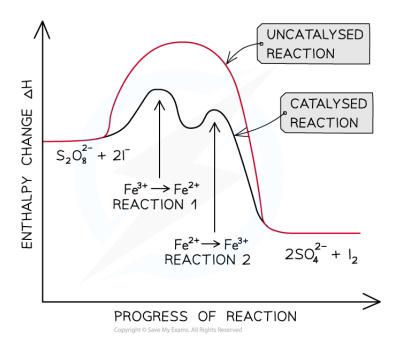
$$2Fe^{2+}$$
 (aq) +  $S_2O_8^{2-}$  (aq)  $\rightarrow 2Fe^{3+}$  (aq) +  $2SO_4^{2-}$  (aq)

- 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<sup>2+</sup> can be first oxidised to Fe<sup>3+</sup> followed by the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>

The reaction pathway diagram for a two-stage catalysed reaction







Your notes

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<sub>2</sub>SO<sub>4</sub>) is formed by reaction with water. The result is acidification of rain:

$$SO_3(g) + H_2O(I) \rightarrow H_2SO_4(aq)$$

 Nitrogen oxides can act as catalysts in the formation of acid rain by catalysing the oxidation of SO<sub>2</sub> to SO<sub>3</sub>

$$NO_2(g) + SO_2(g) \rightarrow SO_3(g) + NO(g)$$

■ The formed NO gets oxidised to regenerate NO<sub>2</sub>

$$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$$

■ 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