Catalysis (A2)

- catalysts (positive catalyst) increase the rate of chemical reaction.
- they do this by providing an alternative pathway for the reaction with lower activation energy.
- there are two main classes:
  i) Homogeneous catalysis
  ii) Heterogeneous catalysis.

Homogeneous catalysis

- Catalyst and reactants are in the same phase.
- reaction proceeds through an intermediate species with lower energy.
- often involves changes in oxidation number of the ions involved in catalysis.
- Example: hydrogen ions catalyse the hydrolysis of ester.

$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \xrightarrow{H^+_{(aq)}} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$

- reactants and catalyst are all in the same phase (aqueous phase).
- Example: small amounts of iodide ions catalyse the decomposition of hydrogen peroxide.
- In the catalysed reaction, iodide ions, I^-, are first oxidised to iodate(I) ions, IO^-. The IO^- ions then react with further molecules of hydrogen peroxide and are reduced back to iodide ions.

$H_2O_{2(aq)} + I^-_{(aq)} \longrightarrow H_2O_{(l)} + IO^-_{(aq)}$

$H_2O_{2(aq)} + IO^-_{(aq)} \longrightarrow H_2O_{(l)} + I^-_{(aq)} + O_{2(g)}$

- The overall equation is:

  $2H_2O_{2(aq)} \xrightarrow{I^-} 2H_2O_{(l)} + O_{2(g)}$

- Ions of transition elements are often good catalysts because of their ability to change oxidation number.

Example: The iodine-peroxodisulfate reaction.

- Peroxodisulfate ions, $S_2O_8^{2-}$ oxidise iodide ions to iodine. This reaction is very slow.

  $S_2O_8^{2-}{}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + I_{2(aq)}$

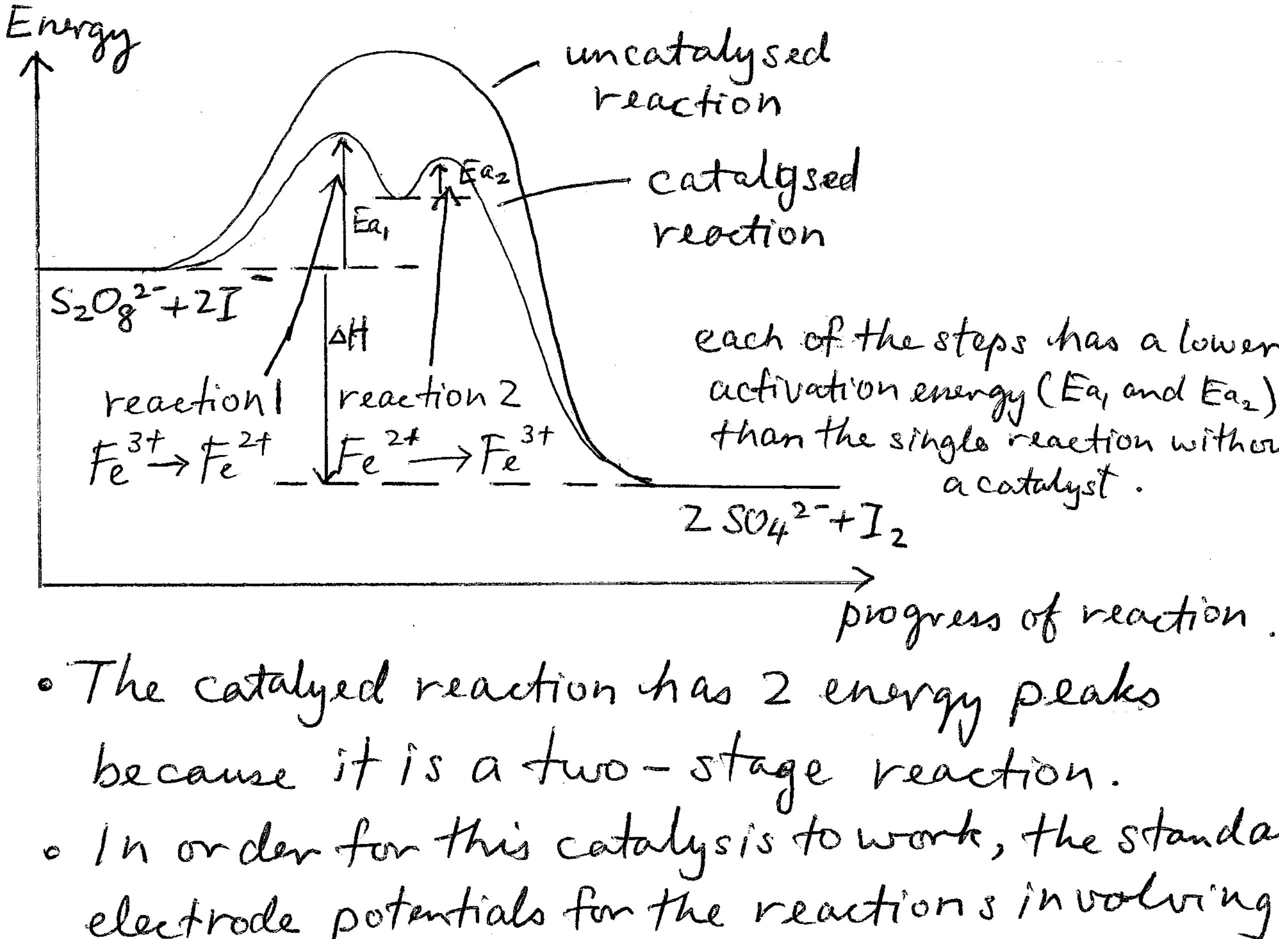
- Both peroxodisulfate and iodide ions have a negative charge.
- In order to collide and react, these ions need considerable energy to overcome the repulsion forces when like charges approach each other.
- $Fe^{3+}_{(aq)}$ ions catalyse this reaction. The catalysis involves 2 redox reactions.
- Reaction 1: reduction of Fe^{3+} ions to Fe^{2+} ions by I^- ions:

  $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(aq)}$

- Reaction 2: oxidation of Fe^{2+} ions back to Fe^{3+} by $S_2O_8^{2-}$:

  $2Fe^{2+}_{(aq)} + S_2O_{8(aq)}^{2-} \longrightarrow 2Fe^{3+}_{(aq)} + 2SO_4^{2-}{}_{(aq)}$

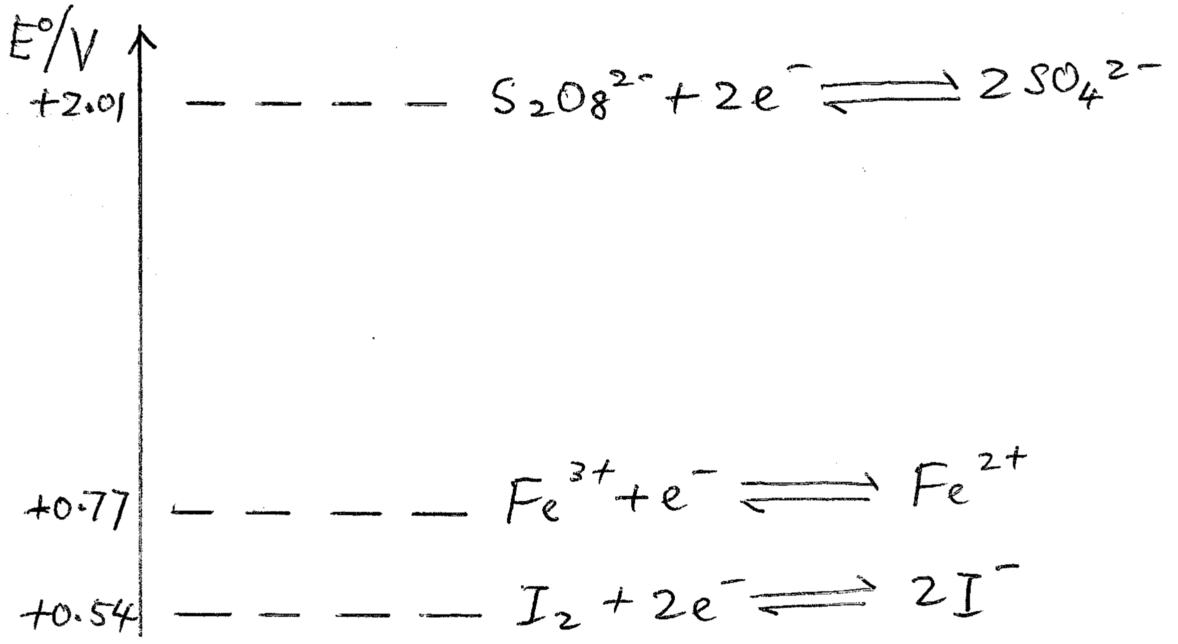
- In both reactions 1 and 2, positively charged iron ions react with negatively charged ions.
- Since ions with opposite charges are attracted to each other, these reactions are more likely to occur than direct reaction between $S_2O_8^{2-}$ and I^- ions.
- The reaction is catalysed by $Fe^{3+}(aq)$ and it is also catalysed by $Fe^{2+}(aq)$.
- It is alright for the reaction 2 to occur first followed by reaction 1.
- Energy profile diagram for catalysed and uncatalyed reactions:



each of the steps has a lower activation energy (Ea_1 and Ea_2) than the single reaction without a catalyst.

- The catalyed reaction has 2 energy peaks because it is a two-stage reaction.
- In order for this catalysis to work, the standard electrode potentials for the reactions involving the catalyst must lie between the electrode potentials involving the two reactants.

- The electrode potential diagram for the catalysis of the reaction $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$



- The use of electrode potentials in this way only predicts that the catalysis is possible. It does not give any information about the rate of reaction.

Example : Nitrogen oxides and oxidation of SO_2

- SO_2 is produced when fossil fuels containing sulfur are burnt.
- When SO_2 escapes into the atmosphere it contributes to acid rain.
- One of the steps in the formation of acid rain is the oxidation of SO_2 to SO_3

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

- Nitrogen (IV) oxide present in the atmosphere can catalyse the oxidation of SO_2.

$$SO_{2(g)} + NO_{2(g)} \longrightarrow SO_{3(g)} + NO_{(g)}$$
$$NO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)}$$

- The nitrogen(IV) oxide is reformed by reaction with atmospheric oxygen.

Exercise

a) Which of the pairs of substances (i) to (iv) below might catalyst the reaction:

$$S_2O_8{}^{2-}{}_{(aq)} + 2I^-{}_{(aq)} \longrightarrow 2SO_4{}^{2-}{}_{(aq)} + I_{2(aq)}$$

Explain your answer.

(i) $Ni^{2+}{}_{(aq)} / Ni_{(s)}$ $E^\ominus = -0.25V$

(ii) $Mn^{3+}{}_{(aq)} / Mn^{2+}{}_{(aq)}$ $E^\ominus = +1.49V$

(iii) $Ce^{4+}{}_{(aq)} / Ce^{3+}{}_{(aq)}$ $E^\ominus = +1.70V$

(iv) $Cu^{2+}{}_{(aq)} / Cu^{+}{}_{(aq)}$ $E^\ominus = +0.15V$

b) Describe in terms of oxidation number change, which species are being oxidised and which are being reduced in these equations:

(i) $SO_{2(g)} + NO_{2(g)} \longrightarrow SO_{3(g)} + NO_{(g)}$

(ii) $NO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)}$

Answers

a) standard electrode potential (from data booklet) $S_2O_8{}^{2-}/SO_4{}^{2-}$ $E^\ominus = +2.01V$
I_2 / I^- $E^\ominus = +0.54V$

Both (ii) Mn^{3+}/Mn^{2+} and (iii) Ce^{4+}/Ce^{3+} might catalyse the rxn. These are the pairs which have $E^\ominus$ values between those of the $S_2O_8{}^{2-}/SO_4{}^{2-}$ and I^-/I_2 pairs.

b) (i)

oxidation no change = −2
reduction

$$\underset{+4}{SO_{2(g)}} + \underset{+4}{NO_{2(g)}} \longrightarrow \underset{+6}{SO_{3(g)}} + \underset{+2}{NO_{(g)}}$$

oxidation
oxidation no change = +2

(ii)

oxidation no change = −2
reduction

$$\underset{+2}{NO_{(g)}} + \underset{0}{\tfrac{1}{2}O_{2(g)}} \longrightarrow \underset{+2\ -2}{NO_{2(g)}}$$

oxidation
oxidation no change = +2

Heterogeneous catalysis

- catalyst is in a different phase to the reactants
- often involves gaseous molecules reacting at the surface of a solid catalyst.
- 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 works in three stages:
- 1. 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.
- 2. 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.
- 3. Desorption – the products are then released from the active sites.

H	eterogeneous
A	dsorption
R	eaction
D	esorption.

Adsorb – to bond to the surface of a substance

Absorb – to move right into the substance. (like a sponge absorbs water)

Example: Iron catalyses the Haber process

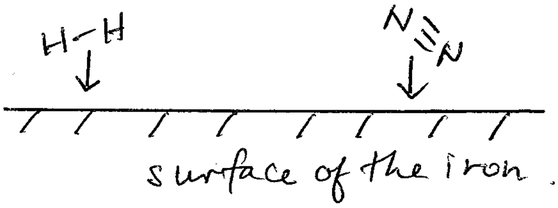
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

conditions: Temperature-500 °C
Pressure-100 atm
Catalyse-Iron

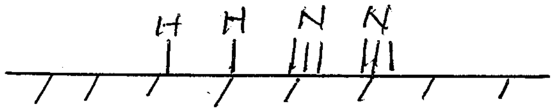
- The catalyst works by allowing hydrogen and nitrogen molecules to come close together on the surface of the iron. They are more likely to react.
- The five steps in this heterogeneous catalysis:
- 1. Diffusion - nitrogen gas and hydrogen gas diffuse to the surface of the iron.
- 2. Adsorption - the reactant molecules are chemically adsorbed onto the surface of the iron. The bonds formed between the reactant molecules and the iron are:
  - strong enough to weaken the covalent bonds within the nitrogen and hydrogen molecules so the atoms can react with each other.
  - weak enough to break and allow the products to leave the surface.
- 3. Reaction - the adsorbed nitrogen and hydrogen atoms react on the surface of the iron to form ammonia.
- 4. Desorption - the bonds between the ammonia and the surface of the iron weaken and are eventually broken.
- 5. Diffusion - ammonia diffuses away from the surface of the iron.

- A possible mechanism for catalysis in the Haber process.

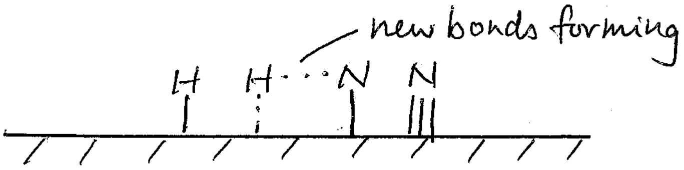
1) diffusion to the surface



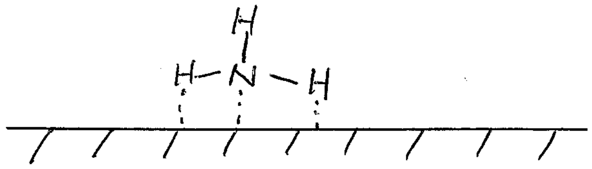
2) adsorption



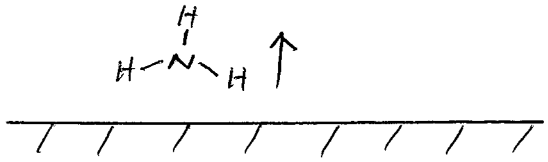
3) reaction (in several steps)



4) desorption



5) diffusion away from surface



Example: Catalytic removal of nitrogen oxides in the exhaust gases from car engines.

- catalytic converters help to convert harmful nitrogen oxides and carbon monoxide present in the exhaust gases from car engines to harmless gases.
- The 'honeycomb' structure inside the catalytic converter contains small beads coated with platinum, palladium or rhodium. These act as heterogeneous catalysts.
- Possible steps in the catalytic process are:
  - adsorption of nitrogen oxides and carbon monoxide onto the catalyst surface.
  - weakening of the covalent bonds within the nitrogen oxides and carbon monoxide.
  - formation of new bonds between:
    - ✓ adjacent nitrogen atoms to form nitrogen molecules
    - ✓ carbon monoxide and oxygen atoms to form carbon dioxide.
  - desorption of nitrogen molecules and carbon dioxide molecules from the surface of the catalyst

Exercise

a) Describe in general terms what is meant by desorption.

b) Nickel acts as a catalyst for the hydrogenation of alkenes. For example:

$$CH_2=CH_2 + H_2 \xrightarrow{Ni} CH_3-CH_3$$

Suggest how nickel catalyses this reaction by referring to the processes of adsorption, reaction on the metal surface and desorption.

c) In catalytic converters, rhodium catalyses the reduction of nitrogen(II) oxide, NO to nitrogen. Draw diagram to suggest:

(i) how NO is adsorbed onto the surface of the rhodium metal.

(ii) how nitrogen is formed.

Answers.

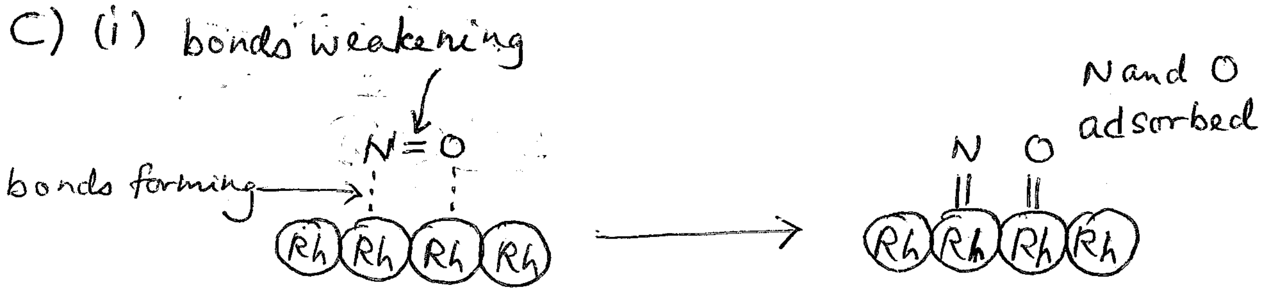
a) Desorption is the releasing of product molecules from the surface of a catalyst.

b) Adsorption – The ethene and hydrogen molecules are adsorbed onto the surface of the nickel. In this process, weak bonds are formed between the ethene and the surface of the nickel and between the hydrogen and the surface of the nickel.

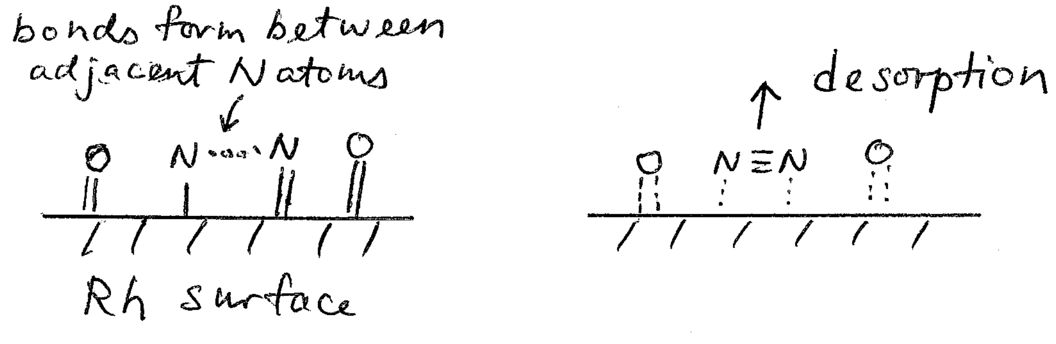
Reaction – The bonds between the hydrogen atoms are weakened and the π bond of the ethene is also weakened. Adsorbed hydrogen atoms close to the adsorbed ethene then react to form ethane.

Desorption – The bonds between the ethane and the surface of the nickel weaken and the ethane moves away from the surface of the catalyst.

c) (i)

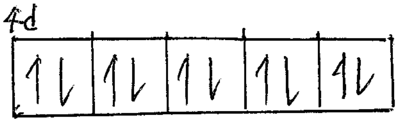


(ii)



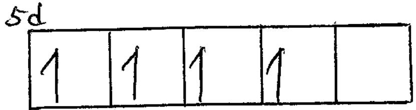
The strength of adsorption is critical . . .

- too weak (Ag)



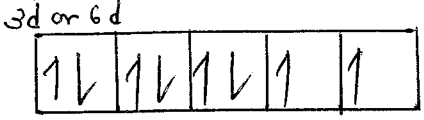
little adsorption – few available d orbitals

- too strong (W)



molecules will remain on the surface and prevent further reaction.

- just right (Ni/Pt)



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 a 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 of using catalyst – to maximise its capacity.

- 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.