Chem Factsheet

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Catalysts

Before working through this Factsheet you should
- Know the effect of change in conditions on rate of reaction;
- Know the significance of a reaction's activation energy;
- Know that a catalyst changes the rate of a chemical reaction but remains chemically unchanged at the end;
- Familiariseyourself with reaction profiles and Maxwell-Boltzman distribution curves, (covered in Factsheet 10 - Kinetics 1 – Rates of Reaction);
- Understand the atomic structure of transition elements and their general properties (Factsheet 38).

After working through this Factsheet you will
- Know that there are two types of catalyst, homogeneous and heterogeneous;
- Be able to recall examples of both types of catalysis;
- Understand how catalysts affect reaction rate;
- Understand why transition elements make good catalysts;
- Know that enzymes are biological catalysts.

- *For reactant particles to react and change into products they must **collide**.*
- *Not all collisions result in chemical change.*
- *There is a minimum energy on collision that must be achieved or exceeded for products to form.*
- *This minimum energy is known as the **activation energy (E_a)** for that reaction.*
- *A catalyst **lowers the activation energy** of the reaction, therefore **more** collisions result in **product** formation.*

Exam Hint: *If a question asks for an explanation of **how** a catalyst works remember that it does **not** increase the energy, or rate of collision, of **reactant particles**. It **lowers** the **activation** energy of the **reaction** itself.*

Catalysts are widely used in the chemical industry, as they
- speed up chemical reactions, and **time costs money!**
- are not used up in the reaction. **Reactants cost money also!**

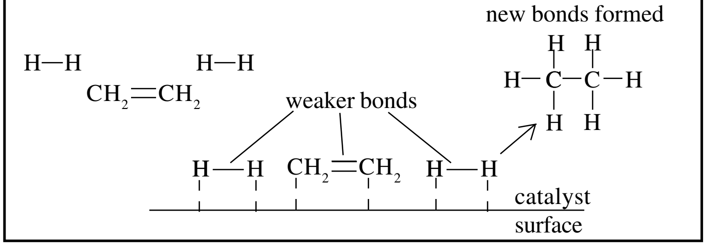
Note however that some reactions may be too fast, even explosive. **Negative catalysts (inhibitors)** are added to slow down such reactions. For example, an organic compound, acetanilide is added to stored hydrogen peroxide to slow down its decomposition into oxygen and water.

Heterogeneous catalysis

*A **heterogeneous** catalyst is in a **different phase (physical state)** to the reactants. The most common examples involve **gaseous** reactants and a **solid** catalyst.*

The speeding up of the reaction takes place on the **catalyst surface**. **Adsorption** *(which is absorption on a surface)* of reactant molecules onto **active sites** on the catalyst surface causes a **weakening** of the bonds **within** the molecules. Bonds break, new bonds form and the product molecule(s) are **desorbed** and leave the catalyst surface. e.g. Catalytic hydrogenation of ethene.

$$\underset{\text{ethene}}{CH_2{=}CH_2(g)} + H_2(g) \xrightarrow[\text{heat}]{\text{Ni Catalyst}} \underset{\text{ethane}}{C_2H_6(g)}$$



The catalyst has caused an increase in reaction rate because
- there is an increase in concentration of reactants at the catalyst surface enabling a greater chance of particle collision.
- there will be more collisions between molecules with favourable orientation and less energy is needed to break the weakened bonds, encouraging chemical reaction. The **activation energy** of the reaction has been **lowered**.

Factors which affect the effectiveness of a heterogeneous catalyst

- The **smaller** the particle size of the catalyst, the **more surface area** available for adsorption of reactant particles and the more effective the catalyst. (***Finely divided Raney Nickel is used in the manufacture of margarine***).
- Adsorption onto the catalyst surface must be *good* but neither too weak nor too strong.

  Too strong and the product particles cannot easily leave, blocking active sites for adsorption of other reactant molecules.
  Too weak and reactant bonds are hardly weakened. The activation energy, and hence the reaction rate, is **little changed**.

Ideal adsorption	Adsorption too strong	Adsorption too weak
Nickel, platinum, palladium	Tungsten	Silver

- **Catalyst poisons** adversely affect the effectiveness of a catalyst. The offending molecules adsorb more strongly onto the catalyst surface than reactant molecules. The catalyst becomes inactive.

Process	Catalyst	Poison
Haber Process	Iron	Carbon monoxide
Contact Process	Platinum	Arsenic containing substances
Catalytic converter	Platinum, rhodium and palladium	Lead
Catalytic cracking	Zeolite catalyst (an aluminosilicate)	Carbon (soot)
Production of $H_2(g)$ for Haber Process ($CH_4(g) + H_2O(g)$)	Nickel	Sulphur containing compounds

- Addition of a **catalyst promoter** improves the effectiveness of the catalyst. Sodium hydroxide can be added to iron in the Haber Process. The optimum temperature for the process can now be reduced by as much as 100K.

Catalytic converters

In a catalytic converter in the exhaust system of a motor vehicle**,** harmful **carbon monoxide** and **oxides of nitrogen** are converted into **nitrogen and carbon dioxide.** $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$

The catalyst consists of platinum, palladium and rhodium. These are very expensive. To save on costs, they are thinly spread on a cheap ceramic material. (*A technique often used in industry for economic reasons*). The support medium is like a **honeycomb** in structure thus giving maximum surface area available for catalysis to take place. ***Catalytic converters are approximately 90% efficient***.

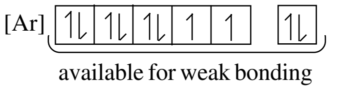
Process	**Reaction**	**Product**	**Catalyst**
Manufacture of margarine	Vegetable oils(l), $H_2(g)$	Margarine	Nickel
Haber process	$N_2(g)$, $H_2(g)$	$NH_3(g)$	Iron
Contact process	$SO_2(g)$, $O_2(g)$	$SO_3(g)$	Vanadium(V)oxide
Manufacture of nitric acid	$NH_3(g)$, $O_2(g)$	NO(g)	Platinum
Catalytic cracking	High b.p alkanes (big molcules)	Low b.p alkanes and alkenes	Zeolite catalyst
Catalytic reforming and isomerisation	Straight chain alkanes	Branched chain alkanes	Platinum

[Three of the above examples are **reversible** reactions. The presence of a catalyst does **<u>not</u>** affect the **position** of equilibrium (**K_c is not affected**) but if does speed up the **attainment** of that equilibrium].

Transition elements

All the catalysts indicated in the above table are *transition elements* or their compounds. They are used widely as heterogeneous catalysts. Transition elements in the first transition series, for example, have both 3d and 4s electrons and orbitals available at the catalyst surface, which can form weak bonds with reactant molecules. e.g. Nickel

$_{28}Ni$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$



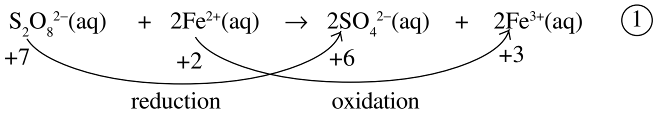
Homogeneous catalysis

A **homogeneous** catalyst and the reactants are in the **same** physical state.

Most examples are in aqueous solution and involve hydrated **ions**. Here, the catalyst **does** take part in the reaction. An **intermediate** is formed which is then converted back to the catalyst.

For example, the reaction between peroxodisulphate ions [$S_2O_8^{2-}(aq)$] and iodide ions [$I^-(aq)$] is very slow. Both ions are negatively charged and **repel** each other.

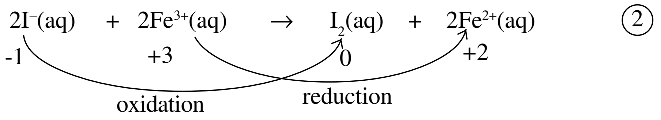
The reaction is catalysed by the addition of $Fe^{2+}(aq)$.
The $Fe^{2+}(aq)$ reacts with $S_2O_8^{2-}(aq)$ to give $SO_4^{2-}(aq)$, a **reaction product**, and $Fe^{3+}(aq)$, the **intermediate** ion.



$$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq) \quad ①$$

The reacting ions are **oppositely** charged and reaction rate is consequently **faster**.

The $Fe^{3+}(aq)$ now reacts with the other reactant ion, $I^-(aq)$ to give the second product, $I_2(aq)$ and the $Fe^{2+}(aq)$ catalyst back again.

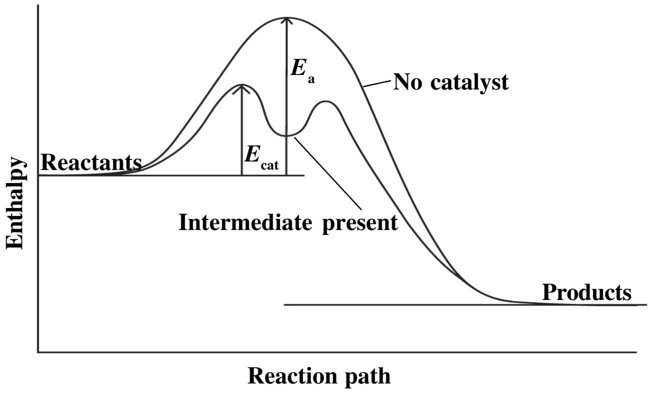


$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq) \quad ②$$

Note that

- $Fe^{3+}(aq)$ is also a catalyst for the reaction.
- Adding equations 1 and 2 gives the **overall** equation for the reaction.
  $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-} + I_2(aq)$
- The catalyst does **not** appear in the overall equation.
- All the reactions are **redox reactions**.
- The catalyst has provided an **alternative route** with *a* **lower activation energy**.

The **reaction profile** for a typical reaction involving **two** stages is



Transition metal ions, because of their ability to change oxidation state, are used in redox reactions involving homogeneous catalysis.

The redox reaction between acidified manganate(VII) ions and ethanedioate ions is an example of **autocatalysis**.

$$2MnO_4^-(aq) + 6H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Both $MnO_4^-(aq)$ and $C_2O_4^{2-}(aq)$ are negatively charged and repel.
A **product** of the reaction, **$Mn^{2+}(aq)$** now speeds it up.

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

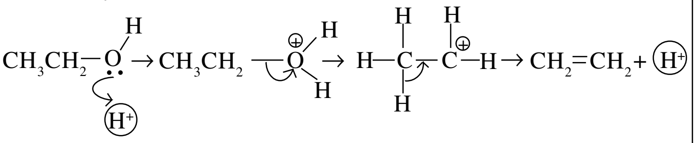
$$2Mn^{3+}(aq) + C_2O_4^{2-}(aq) \rightarrow 2CO_2 + 2Mn^{2+}(aq)$$

$Mn^{2+}(aq)$ is the **autocatalyst**. $Mn^{3+}(aq)$ is the **intermediate ion**.
When a little $C_2O_4^{2-}(aq)$ is added to purple $MnO_4^-(aq)$ decolourisation is **slow** at first but as the product $Mn^{2+}(aq)$ concentration increases, decolourisation is **fast**.

Quite a number of reactions are **acid-catalysed**.

Reaction	**Product**	**Catalyst**
Alcohol + halide ion	Halogenalkane	Conc H_2SO_4
Alcohol + Carboxylic acid (esterification)	Ester	Conc. H_2SO_4
Dehydration of alcohols	Alkene	Conc. phosphoric acid

In the dehydration of alcohols



1. H^+ ions from the acid *protonate* the oxygen of the hydroxyl group, -OH.
2. A water molecule leaves, *enhancing* the reactive site C^+.
3. A *double* carbon-carbon bond forms to give the alkene. H^+, the catalyst, is regenerated.

The acid catalyst has enhanced the reactive site.

The reaction between iodine and propanone (CH_3COCH_3) has the overall reaction

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

The reaction is **acid-catalysed**.
Experiments show that the rate of reaction = $k[CH_3COCH_3][H^+]$
The reaction is first order with respect to **propanone**.

It is also **first order** with respect to **H^+(aq)** even though H^+(aq) does not appear in the overall equation.

It is **zero order** with respect to **iodine** even though iodine **does** appear in the overall equation. (Factsheet 43 – Orders of Reaction).

This information about the kinetics of the reaction is extremely useful in the determination of its mechanism - the rate equation indicates that the rate determining step involves the reaction between **1 mole of propanone and 1 mole of H^+(aq)**.

Even though H^+(aq) is not apparent from the overall equation, it is involved in the reaction mechanism.

An example of homogeneous catalysis where reactants and catalyst are in the **gaseous** phase is illustrated in the destruction of the ozone layer by CFC emission.

In the presence of uv-light, chlorofluorocarbon molecules are decomposed to give **chlorine free radicals**.

$$CCl_3F \xrightarrow[\text{light}]{\text{u-v}} CCl_2F\bullet + Cl\bullet$$

The chlorine radical is the **catalyst**. The ClO· is the **intermediate** radical.

$$Cl\bullet + O_3 \rightarrow O_2 + ClO\bullet$$
$$ClO\bullet + O\bullet \rightarrow O_2 + Cl\bullet$$

The following reaction sequence now takes place

Enzymes are **biological catalysts**. They speed up chemical reactions in the body. They are complex **protein** molecules which have **highly specific molecular shapes**. Their **active sites** match **exactly** the structure of the reactant molecule. The two structures have **an exact fit**.

Biological washing powders contain enzymes to assist in the cleaning process. The enzymes break down blood, food and fats. They enable washing to take place **more quickly** and at **low temperature**. High temperatures cause the enzymes to **denature** and lose their specific shape. They become non-effective. They have also been known to cause **allergies** and **asthma**.

Like other catalysts, enzymes lower the activation energy of a reaction

Reaction	Activation energy ($kJmol^{-1}$)		
	No catalyst	Pt catalyst	Enzyme catalyst
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$	+79	+49	+23

Practice Questions

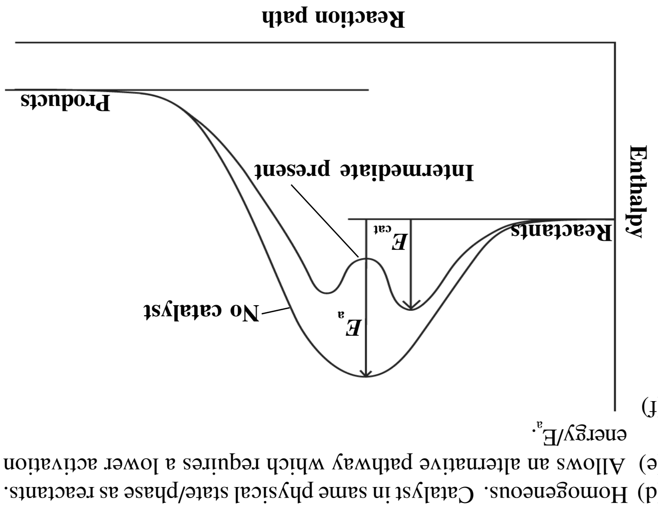
1. (a) What features of the catalysts in a catalytic converter present in the exhaust system of a motor vehicle make it more efficient and less expensive?
   (b) The converter changes NO(g) and CO(g) into N_2(g) and CO_2(g).
      (i) Write an equation for this conversion.
      (ii) **Explain** how this conversion occurs at the catalyst surface.

2. In the following reaction mechanism
   $Cu^{2+}(aq) + V^{3+}(aq) \rightarrow Cu^+(aq) + V^{4+}(aq)$
   $Cu^+(aq) + Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$
   (a) Construct the overall equation.
   (b) Name the catalyst.
   (c) Which is the intermediate ion?
   (d) What **type** of catalysis is represented here? How do you know?
   (e) How does the catalyst increase the reaction rate?
   (f) Sketch a reaction profile which illustrates a typical **two stage** mechanism involving a catalyst.

Answers

1. (a) They are thinly coated onto a cheap, inert ceramic material in a honeycomb structure (*to increase surface area available*).
   (b) (i) $2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$
      (ii) NO and CO molecules are adsorbed onto the catalyst surface. Bonds in the reactant molecules are weakened. Product bonds are formed and the product molecules are desorbed/leave the catalyst surface.

2. (a) $V^{3+}(aq) + Fe^{3+}(aq) \rightarrow V^{4+}(aq) + Fe^{2+}(aq)$
   (b) Cu^{2+}(aq).
   (c) Cu^+(aq).
   (d) Homogeneous. Catalyst in same physical state/phase as reactants.
   (e) Allows an alternative pathway which requires a lower activation energy/E_a.
   (f)



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