Chem Factsheet

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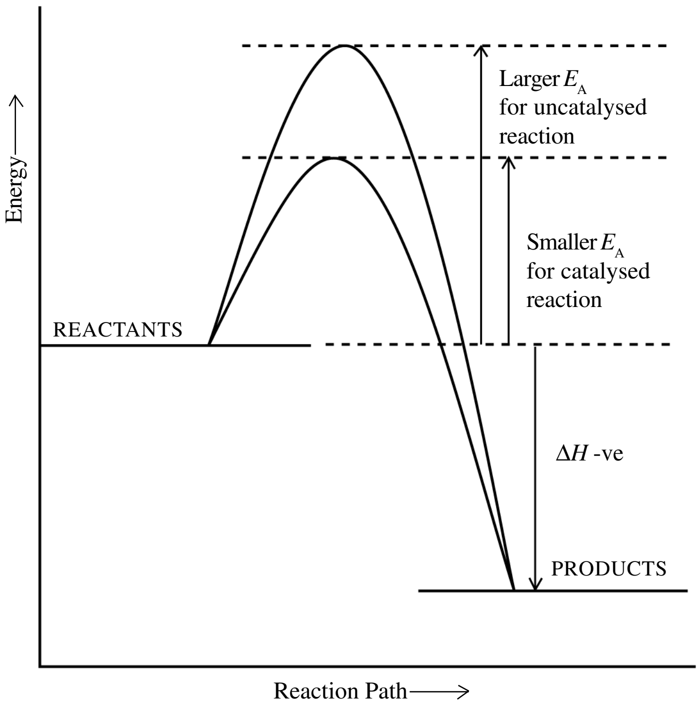
The Chemistry and Benefits of Catalysts

Introduction

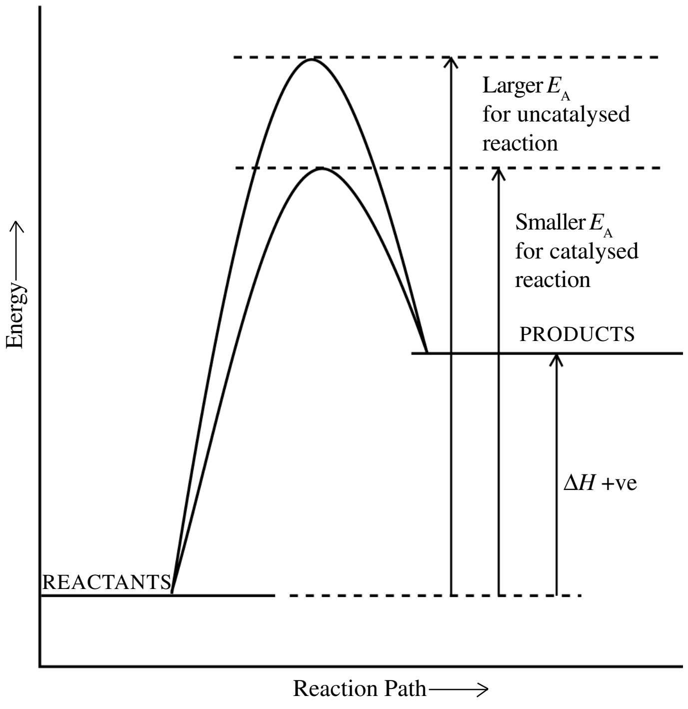
A catalyst may be defined as: a "substance" that speeds up a chemical reaction without being consumed by the overall reaction.

The catalyst does take part in the reaction in that it provides an alternative reaction route with a lower activation energy (E_A) than the route without the catalyst. There are more particles with energies equal to or greater than this lower E_A resulting in more successful collisions per second and hence a greater reaction rate. Since E_A is reduced the catalyst alters the energy profile, there being an E_A for each step of the alternative route.

Energy profile for an exothermic reaction



Energy profile for an endothermic reaction



Since a catalyst is not used up it can, in theory, be used continuously. However a catalyst can combine with impurities and hence cease to work – it is said to be "poisoned". This reduces the catalyst's efficiency and adds to the cost of the chemical process. For example, in the Haber Process used to synthesise ammonia from nitrogen and hydrogen, the hydrogen is obtained from methane which contains sulphur compounds as impurities. Sulphur poisons the iron catalyst that is used in the Haber Process. This means that, if the sulphur is not removed, the company will have the expense of stopping production and replacing the poisoned catalyst.

(Note There is also the added cost of safe disposal of a spent catalyst since it cannot be simply dumped because of its toxicity. Many catalysts will be recycled especially expensive metals, e.g. Pt.)

The most common types of substance that are catalysts are transition metals and their compounds. They are able to act as catalysts since they have variable oxidation states. (s-block metals do not usually act as catalysts as they have only one oxidation state (apart from zero).)

However, not all are related to transition metals, as illustrated by the following summary of some of the catalysts you may encounter (and need to remember!) in your course.

1	Pt(s) / Pd(s) / Rh(s) alloy in a catalytic convertor for $2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$
2	Zeolites for petroleum cracking, isomersiation and reforming
3	Chlorofluorocarbons (CFC's) for ozone depletion $2O_3(g) \rightarrow 3O_2(g)$ a troublesome catalyst!
4	Pt for petroleum reforming
5	Iron for the Haber Process when making ammonia
6	Ni for $>C=C<(g) + H_2(g) \rightarrow >CH\text{-}CH<(g)$; making margarine
7	H^+ for esterification and hydrolysis reactions
8	V_2O_5 for $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; the Contact Process
9	Enzymes in many biological and chemical processes
10	Cr_2O_3 in the manufacture of methanol from CO and H_2
11	The autocatalyst Mn^{2+} which catalyses: $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 16H_2O + 2Mn^{2+}$
12	Fe^{2+} or Fe^{3+} which catalyse $2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$

Catalysts may be divided into two groups:

(a) ***Homogeneous* catalysts** are in the same phase as the reactants – examples include numbers 3, 7, 11 and 12

(b) ***Heterogeneous* catalysts** are in a different phase from the reactants – examples include numbers 1, 2, 4, 5, 6, 8 and 10.

Solid catalysts have irregular surfaces with "active sites" at which the catalysis occurs. It is important to make the surface area available as large as possible to increase the catalyst's efficiency. For example a catalyst may be powdered to increase its available surface area and then spread out on a ceramic honey-combed support to maximise the exposed surface area. The support being ceramic provides strength at high temperatures. Only a thin layer is needed as the catalysis occurs on the surface atoms. In catalytic converters the layer of platinum / rhodium is only a few atoms thick which keeps expense to a minimum.

A heterogeneous catalyst, since it is in a different phase to both the reactants and the products, can easily be separated from them. They have this advantage over homogeneous catalysts.

A2 only: A catalyst does not alter $\Delta H_{\text{reaction,}}$ K_c or K_p, ΔS_{system} or $\Delta G_{\text{reaction}}$ since these are thermodynamic parameters which are not related to kinetics.

Autocatalysis

A *reaction product* speeds up the reaction that produced that product.

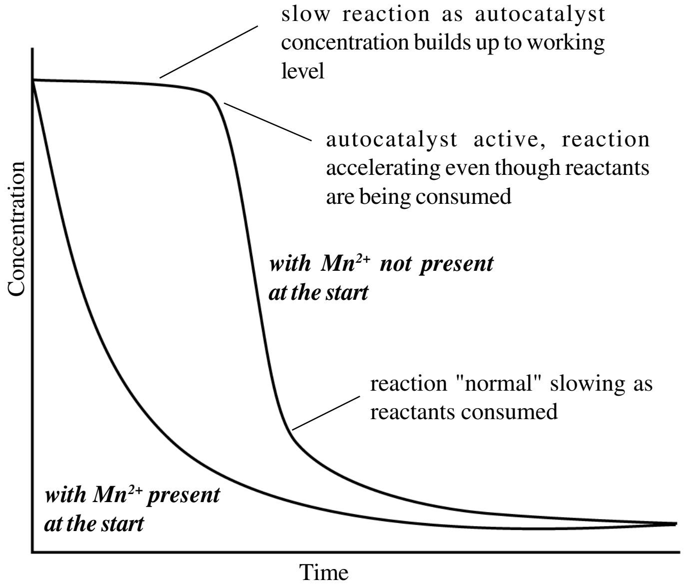
e.g. The oxidation of ethanedioate ions by manganate(VII) ions in the presence of excess acid produces manganese(II) ions which speed up the reaction.

$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 16H_2O(l) + 2Mn^{2+}(aq)$

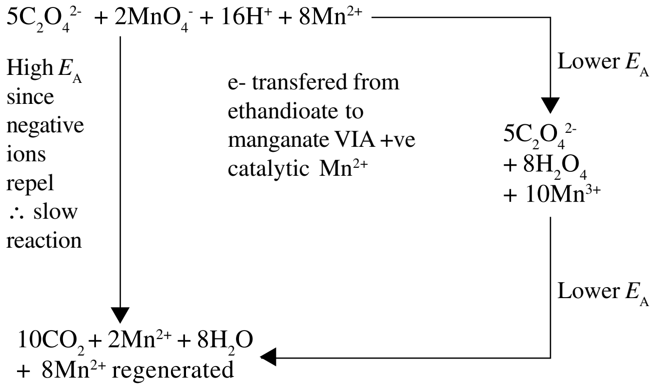
As seen in the diagrams below , this reaction begins slowly because the activation energy has a relatively high value as a result of the repulsions between the negatively charged ions.

Soon the rate increases because the product, Mn^{2+}, provides and alternative route of lower activation energy – see diagrams below. Finally the rate decreases to zero as reactants are used up and their concentrations decrease.

Kinetics of an autocatalytic reaction



Autocatalytic oxidation of ethandioate by manganate(VII)



Benefits of catalysts

1. Catalysts increase the rates of the chemical reactions and hence lower production costs

This initially benefits the manufacturers as the products are made quicker, and more cheaply which benefits the customers.

2. Certain catalytic reactions are of great economic importance to a country

The Haber Process: $\frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$, uses iron, a heterogeneous catalyst.

Contact Process: $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, uses vanadium(V) oxide, a heterogeneous catalyst.

Poly(ethene): $nCH_2{=}CH_2 \rightarrow (\ CH_2{-}CH_2\ )_n$, uses a Ziegler–Natta heterogeneous catalyst.

The sale of ammonia, sulphuric acid and poly(ethene) brings to a country many millions of pounds of tax revenue per year. Also, following the production of ammonia and sulphuric acid, fertilisers can be made and these allow greater crop yields and reduce third world malnutrition.

3. Reduce the energy required to attain the same rate as at higher temperature

Both the Haber Process and the Contact Process operate at 450°C using catalysts. To achieve the same reaction rates higher temperatures would be required which would result in higher energy costs. The use of catalysts saves energy and hence, money. The saving of energy has an added benefit when the energy is produced by burning fossil fuels since less carbon dioxide is released into the air, so limiting global warming. Less toxic carbon monoxide and less acidic oxides (SO_2 and NO_x) which cause acid rain would also be emitted, so also benefiting the environment.

The Haber Process also operates at high pressure (e.g. 200 kPa) but not as high as would be necessary without a catalyst. The catalyst allows an economic rate of reaction at lower pressure, even though the overall yield would be lowered. The use of lower pressure saves energy, reduces plant costs and is safer.

4. Benefits to the environment and health

Catalytic converters are used to minimise the emission of harmful pollutants such as carbon monoxide, CO, oxides of nitrogen, NO_x, and un-burnt hydrocarbons into the atmosphere from road vehicles. Various very expensive metals including Pt, Pd and Rh are used as heterogeneous catalysts resulting in the rapid conversion of CO and NO_x to less problematic CO_2 along with harmless N_2.

e.g. $2CO + 2NO \rightarrow 2CO_2 + N_2$

Oxides of nitrogen (NO_x) are formed inside an engine because, at the very high temperatures some molecules of N_2 and O_2 have energies $\geq E_A$ and hence may react on collision.

$$N_2 + O_2 \rightarrow 2NO \text{ and } N_2 + 2O_2 \rightarrow 2NO_2$$

NO_x are partly responsible for acid rain. Acid rain corrodes stone buildings, iron constructions (e.g. bridges), harms trees and decreases the pH of rivers and lakes thus harming fish etc. The removal of NO_x protects the environment.

Carbon monoxide and un-burnt hydrocarbons are formed in the engine when incomplete combustion of the hydrocarbon fuel occurs. The emission of CO, NO_x and un-burnt hydrocarbons in the presence of sunlight leads to photochemical smog which contains ozone. Low level ozone causes eye irritation, headaches, fatigue and respiratory problems. Thus using catalytic convertors to remove the harmful pollutants is a benefit to peoples' health and to the financial cost to the health service.

CO alone is harmful because the CO molecules form strong coordinate (dative) bonds to the iron(II) ions of haemoglobin. Thus the haemoglobin transports less oxygen to the cells and hence a person will suffer breathing problems through lack of oxygen and death can result.

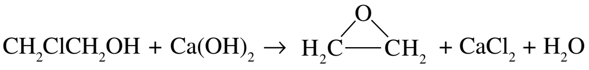
The removal of CO, NO_x and un-burnt hydrocarbons by using catalytic converters not only protects the environment from their harmful effects but saves a lot of money that would have to be used in correcting the harmful effects.

5. Benefits of a higher atom economy

Otherwise slow and uneconomical reactions, which happen to have a high atom economy, can become economically viable if a suitable catalyst becomes available.

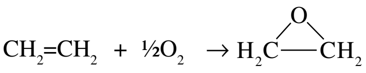
e.g. Epoxyethane used to be prepared by a two step route from ethene: atom economy of 23%.

$$CH_2{=}CH_2 + Cl_2 + H_2O \rightarrow CH_2ClCH_2OH + HCl$$



$$CH_2ClCH_2OH + Ca(OH)_2 \rightarrow H_2C{-}CH_2(O) + CaCl_2 + H_2O$$

A single step route was developed using a silver catalyst with an atom economy of 100%.

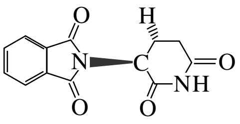


$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \rightarrow H_2C{-}CH_2(O)$$

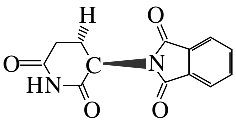
It is preferable to produce products by reactions with high atom economies since there are fewer waste products that need safe disposal, especially if they are harmful to the environment.

6. Benefits of stereospecificity (A2)

A stereospecific catalyst enables a single stereoisomer to be formed. The atom economy is double that which applies when both stereoisomers (a racemic mixture) are formed. There are less waste products and lower product separation costs. Separation is especially difficult and expensive for optical isomers since they have the same physical properties, apart from their optical activities. In the case of chiral drug molecules, it may be essential that only one optical isomer (enantiomer) is formed (unless an expensive separation process is to be carried out) because the other optical isomer may have harmful effects. The thalidomide tragedy of the late 1950s was a result of a racemic mixture being taken in the early stages of pregnancy instead of a single optical isomer.



"good" thalidomide



"bad" thalidomide

C. The chemistry of how two heterogeneous catalysts work

1. Removal of carbon monoxide and nitrogen monoxide by catalytic converters

These gaseous molecules are initially adsorbed into the active sites on the surface of the catalyst (Pt / Rh). Adjacent molecules now react on the surface, ($CO + NO \rightarrow CO_2 + ½N_2$). The carbon dioxide and nitrogen are then desorbed, leaving the metal surface free to adsorb more reactant molecules.

The strength of the bonds holding the CO and NO to the surface are most important. If they are too weak the molecules will not remain long enough on the surface for them to react. If they are too strong the products desorb too slowly. In both cases the metal will be an inefficient catalyst.

It is essential that unleaded petrol is used since fuels containing lead additives poison the catalyst by being adsorbed into the "active sites" on the surface of the metal. The harmful pollutants would then enter the air.

2. Solid vanadium(V) oxide, a heterogeneous catalyst in the Contact Process

Vanadium(V) oxide is the catalyst for : $SO_2(g) + ½O_2(g) \rightleftharpoons SO_3(g)$.

In V_2O_5 the vanadium is in its maximum oxidation state of +5 and therefore acts as an oxidant, converting the SO_2 to SO_3.

$V_2O_5(s) + SO_2(g) \rightarrow V_2O_4(s) + SO_3(g)$

The catalyst is then reformed when the V_2O_4 is oxidised by the oxygen.

$V_2O_4(s) + ½O_2(g) \rightarrow V_2O_5(s)$

The activation energies for these two reactions are less than that of the uncatalysed reaction.

Practice Questions

1. Carbon monoxide and nitrogen dioxide are produced inside a car engine when the fuel burns.
   (a) State how these oxides are removed from the exhaust gases of a modern car and write an equation for the reaction that occurs.
   (b) What are two benefits to the environment in removing these gases?
   (c) When these gases are removed, two other gases are produced. Explain which of these gases is harmless.
   (d) What harmful gas is not removed by a catalytic converter?
2. How does vanadium(V) oxide increase the rate of the reaction between sulfur dioxide and oxygen in the Contact Process? In your answers include appropriate equations.
3. Industrial research chemists are always searching of new and better catalysts. Choose one reaction that would benefit the environment if a better catalyst was found. Write the equation for the reaction and state the present catalyst and the conditions used. Explain why the better catalyst would benefit the environment.
4. Ethanoic acid can be made by reacting methanol with carbon monoxide. In the late 1990s and iridium based catalyst (cis-$[Ir(CO)_2I_2]^-$) replaced a rhodium based catalyst (*cis*-$[Rh(CO)_2I_2]^-$). Benefits of the iridium catalyst include: i) it lasts longer; ii) it produces less organic by-products and less CO_2.
   (a) Write an equation for the formation of ethanoic acid and state the theoretical atom economy.
   (b) Why don't catalysts last forever?
   (c) Give one reason why the formation of less organic by-products is a benefit.
   (d) Why is the production of less CO_2 a benefit?

Answers

1. (a) See C1. $2CO + NO_2 \rightarrow 2CO_2 + ½N_2$.
   (b) See B4.
   (c) e.g. N_2 it is unreactive / ≈ 80% of the air.
   (d) CO_2.
2. The V_2O_5 provides an alternative route of lower E_A so the reaction rate is increased. Alt. route see C2.
3. See B3 or B5
4. (a) $CH_3OH + CO \rightleftharpoons CH_3COOH$. 100%.
   (b) Catalysts become poisoned.
   (c) The cost of separating the ethanoic acid is less.
   (d) Less global warming.

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