Kinetics of Catalysis

A **catalyst** is a substance that takes part in a chemical reaction and speeds it up, but itself undergoes no permanent chemical change.

Catalysts therefore do not appear in the overall chemical equation, but their presence very much the rate law, modifying and speeding existing pathways or, more commonly, providing completely new pathways, alternative route, (mechanism .: a different, lower activation energy, E_A) by which a reaction can occur.

Catalysts exert significant effects on reaction rates even when they are present in very small amounts. Catalysts are usually specific, i.e., one catalyst will only catalyse a certain reaction. Although a catalyst can be recovered chemically, unchanged, however physical state may change during the reaction. A catalyst is not consumed but regenerated.

Note that a catalyst does not initiate a reaction, it merely alters the rate of an existing reaction.

The process of increasing the rate of a reaction through the use of a catalyst is referred to as catalysis.

In industrial chemistry, great effort is devoted to finding catalysts that will accelerate particular desired reactions without increasing the generation of undesired products.

Catalysts work in two main ways:

(1) Rate constant, **k = A . e (to the power of -E_A/RT)**
Therefore, if T is constant (i.e., dT = 0), and if E_A is lowered, then k would increase, meaning the rate would increase.
Generally, a catalyst forms an intermediate compound during the reaction.

(2) If A is altered (what is A? Check previous notes...), then k increases. Hence, the rate of the reaction increases.

There is no single theory to explain catalysis and many catalysts were discovered simply by trial and error. They are usually divided into two types: (1) homogeneous, and, (2) heterogeneous

In **homogeneous** catalysis, the catalyst is present in the same physical state as the reactants. A homogeneous catalyst takes an active chemical part in the reaction and is subsequently regenerated, through the formation of a reaction intermediate. The catalyst provides a new reaction path with a lower activation energy than the reaction without the catalyst. An example of a homogeneous catalyst is $NO_{2(g)}$, as seen in the following reaction:

$$SO_{2(g)} + \frac{1}{2} O_{2(g)} + H_2O_{(g)} \xrightarrow{NO_{2(g)}} H_2SO_{4(g)}$$

Intermediate Compound Theory

$$SO_2 + NO_2 \longrightarrow SO_3.NO$$
$$SO_3.NO + H_2O \longrightarrow H_2SO_4 + NO$$
$$NO + \tfrac{1}{2} O_2 \longrightarrow NO_2$$

This is explained by the theory that the NO_2 catalyst first combines with one of the reactants eg. SO_2 to from an intermediate compound $SO_3.NO$ This is a very quick reaction (involving v. low E_A)
The intermediate compound $SO_3.NO$, then reacts with the 2nd reagent i.e. $H_2O_{(g)}$, releasing the catalyst NO_2, (or as in this case the NO reacts + $O_2 \longrightarrow NO_2$). All these reactions are faster than the reaction: $SO_2 + \tfrac{1}{2} O_2 + H_2O \longrightarrow H_2SO_4$

In **heterogeneous** catalysis, the catalyst is present in a distinct phase (meaning a phase other than those of the reactants, different phases are separated by a distinct boundary).

Many examples of heterogeneous catalysis involve transition metals. Their empty d orbitals allow them to bond with many substances to form reactive intermediates.

The most case is the catalytic action on the surface of the solid catalyst (btw, **adsorption** refers to the collection of one substance on the surface of another substance; adsorption is a surface phenomenon). The gases are adsorbed on the surface of the metal, i.e. they form weak bonds with the metal atoms. The catalyst provides an energy store — it provides energy to split bonds of reactants on its surface. The catalyst provides the correct configuration for reaction.

Therefore, an increase in the surface area of the catalyst should increase the rate of the reaction; since the catalyst will be more effective when spread over a large surface area.
An example of a heterogeneous catalyst is MnO_2, (or $Pb_3O_{4(s0,}$ or $KI_{(s)}$), which when added to H_2O_2, speeds up its decomposition into water, and $O_{2(g)}$. **Demo**: pink and the yellow snake.

Transition metals and their compounds frequently catalyse redox reactions because transition metals have variable oxidation numbers and can act as a temporary 'warehouse' for electrons.

Enzymes are catalysts (an enzyme is a large protein molecule with a typical molar mass of ~20 000 g/mol (or more! — but you should have known that by now, seeing as you are a brilliant student) and has a structure capable of carrying out a **specific** reaction, or a series of reactions; i.e an enzyme catalyses the reactions of only one substance or a very limited range of substances.

The substance which an enzyme enables to react is called the **substrate**. Like other proteins, enzymes have a 3-D configuration, the tertiary structure of the protein. This structure is dependent on pH and temperature, thus enzyme activity is sensitive to pH and temperature.

[The reason for the specificity of an enzyme is that the substrate must fit into the **active site** of the enzyme. The fit between an enzyme and its substrate has been compared with that of a lock and a key: the **lock and key theory** ... as a key fits a lock ... the active site of the enzyme binds to the substrate ... and catalyses its reaction; Emil Fischer, 1894.]

Auto-catalysis is a reaction in which one of the products of the reaction acts as a catalyst for the reaction. Once a reaction starts, more catalyst is produced so that the rate of reaction increases with time.
Demo: An example is the auto-catalytic oxidation of the ethanediote ions, (the oxalate ions, $C_2O_4^{2-}$) by the permanganate ion, catalysed by the manganese (II) ions (of course...).

$$2MnO_4{}^{-1}{}_{(aq)} + 16\,H^{+1}{}_{(aq)} + 5\,(COOH)_2{}^{-2}{}_{(aq)} \longrightarrow 2\,Mn^{+2}{}_{(aq)} + 10\,CO_{2(g)} + 8\,H_2O_{(l)}$$

The reaction rate increases as the reaction proceeds and then slows down. The increase in rate happens because the reaction is catalysed by Mn^{+2}, and Mn^{+2} ions are formed by the oxidation. The later decrease in rate is due to the reactants being used up.

And now for the dark side of the world of catalysis.... There exist in the world a new, and dreaded type of substance: those that are called by chemists and evil drug lords alike, the inhibitors. Ahhhh!!!! An **inhibitor** plays an opposite role to that of a catalyst, by frequently increasing the activation energy of a reaction, thus reducing its rate.
In the food industry, inhibitors are called **Preservatives**, since they slow down the decay of food and preserve it for long periods of time (putting these evil chemicals into our bodies – and being an informed scientist we know how good they can be for us !!!).
A list of ingredients on many different types of food indicates the presence of these preservatives.

There are two major types of preservatives:
1) **"Antimicrobials**"(prevent spoilage by bacteria, molds, fungi and yeasts)
2) "**Antioxidants**" (prevent changes in colour or flavour because of oxidation)

Examples of Antimicrobial
a) ascorbic acid (vitamin C)
b) benzoic acid, sorbic acid (potassium sorbate or calcium sorbate)
c) sodium benzoate
d) citric acid
e) lactic acid
f) calcium lactate
g) methyl or propyl or butyl: paraben
h) propionic acid
i) Na or K or Ca: propionate
j) Na erythorbate
m) $NaNO_3$ / $NaNO_2$

Examples of Antioxidants
a) ascorbic acid (vitamin C)
b) BHA (butylated hydroxyanisole)
c) BHT (butylated hydroxytoluene)
d) citric acid
e) EDTA (ethylenediaminetetraacetic acid)
f) propyl gallate
g) TBHQ (tertiary-butylhydroquinone)

Catalytic Converters

A catalytic converter is used to convert pollutants in vehicle exhaust gases into harmless products. The choice of catalyst is a transition metal, with the right ability to absorb the reactants and to release the products.
Poisoning of catalysts: