

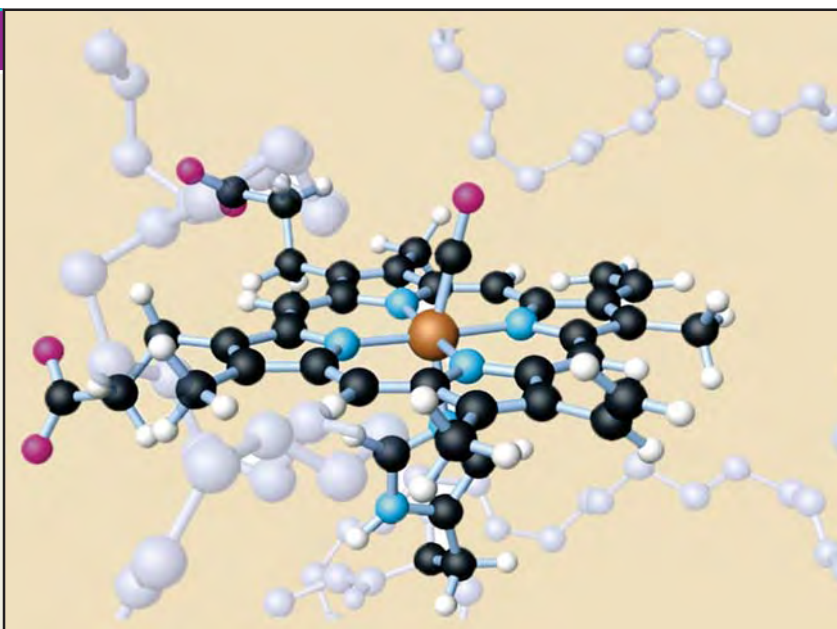
## 21

## Catalysis

## CHAPTER

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Berzelius (1836) realised that there are substances which increase the rate of a reaction without themselves being consumed. He believed that the function of such a substance was to loosen the bonds which hold the atoms in the reacting molecules together. Thus he coined the term **Catalysis** (Greek *kata* = wholly, *lein* = to loosen).

There is no doubt that usually a catalyst accelerates a reaction as was originally thought by Berzelius. But a number of cases are now known where the catalyst definitely retards (slows down) the rate of reaction.

**A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called Catalysis.**

As evident from the above definition, a catalyst may increase or decrease the rate of a reaction.

A catalyst which enhances the rate of a reaction is called a **Positive catalyst** and the process **Positive catalysis** or simply **Catalysis**.

A catalyst which retards the rate of a reaction is called a **Negative catalyst** and the process **Negative catalysis**.

## JÖNS JAKOB BERZELIUS

Jöns Jakob Berzelius (1779-1848), Swedish chemist, considered one of the founders of modern chemistry.

Berzelius was born near Linköping. While studying medicine at the University of Uppsala, he became interested in chemistry. After practicing medicine and lecturing, he became a professor of botany and pharmacy at Stockholm in 1807. From 1815 to 1832 he was professor of chemistry at the Caroline Medico-Chirurgical Institute in Stockholm. He became a member of the Stockholm Academy of Sciences in 1808 and in 1818 became its permanent secretary. For his contributions to science, Berzelius was made a baron in 1835 by Charles XIV John, king of Sweden and Norway.



Berzelius's research extended into every branch of chemistry and was extraordinary for its scope and accuracy. He discovered three chemical elements—cerium, selenium, and thorium—and was the first to isolate silicon, zirconium, and titanium. He introduced the term catalyst into chemistry and was the first to elaborate on the nature and importance of catalysis. He introduced



Statue of Berzelius in the center of Berzelii Park, Stockholm

the present system of chemical notation, in which each element is represented by one or two letters of the alphabet. In addition, Berzelius was primarily responsible for the theory of radicals, which states that a group of atoms, such as the sulphate group, can act as a single unit through a series of chemical reactions. He developed an elaborate electrochemical theory that correctly stated that chemical compounds are made up of negatively and positively charged components. All of his theoretical work was supported by elaborate experimental measurements. His greatest achievement was the measurement of atomic weights.

We will first proceed to discuss 'positive catalysis' or catalysis as it is commonly designated.

## TYPES OF CATALYSIS

There are two main types of catalysis :

- (a) Homogeneous catalysis
- (b) Heterogenous catalysis

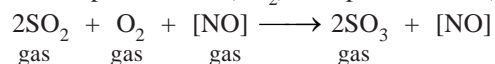
Also, there is a third types of catalysis known as **Enzyme catalysis** which is largely of biological interest. This will be discussed separately at a later stage.

## HOMOGENEOUS CATALYSIS

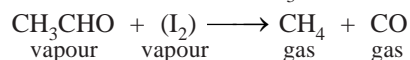
In homogeneous catalysis, **the catalyst is in the same phase as the reactants and is evenly distributed throughout.** This type of catalysis can occur in gas phase or the liquid (solution) phase.

## Examples of Homogeneous Catalysis in Gas Phase

- (a) Oxidation of sulphur dioxide ( $\text{SO}_2$ ) to sulphur trioxide ( $\text{SO}_3$ ) with nitric oxide (NO) as catalyst,



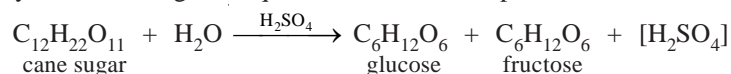
(b) Decomposition of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) with iodine ( $\text{I}_2$ ) as catalyst,



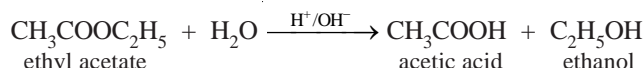
### Examples of Homogeneous Catalysis in Solution Phase

Many reactions in solutions are catalysed by acids ( $\text{H}^+$ ) and bases ( $\text{OH}^-$ ).

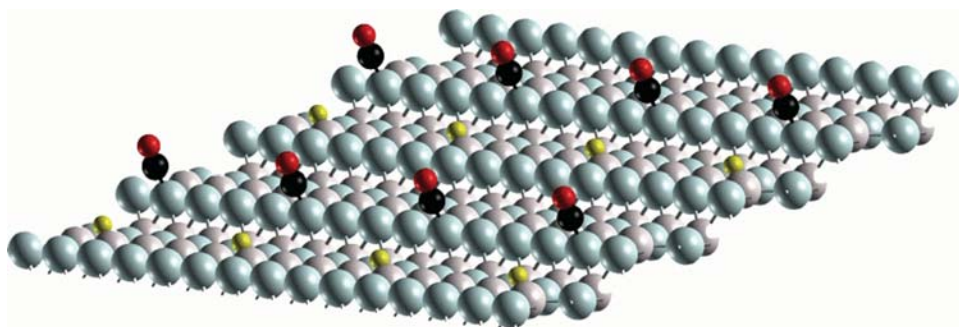
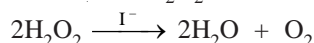
(a) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,



(b) Hydrolysis of an ester in the presence of acid or alkali,



(c) Decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the presence of iodide ion ( $\text{I}^-$ ) as catalyst,



### HETEROGENEOUS CATALYSIS

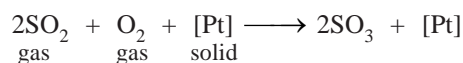
The catalysis in which the catalyst is in a different physical phase from the reactants is termed **Heterogeneous catalysis**. The most important of such reactions are those in which the reactants are in the gas phase while the catalyst is a solid. The process is also called **Contact catalysis** since the reaction occurs by contact of reactants with the catalyst surface. In contact catalysis, usually the catalyst is a finely divided metal or a gauze. This form of catalysis has great industrial importance.

#### Examples of Heterogeneous Catalysis

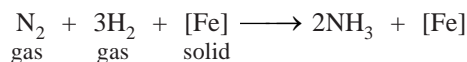
Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are listed below.

(1) **Heterogeneous catalysis with gaseous reactants (Contact catalysis)**

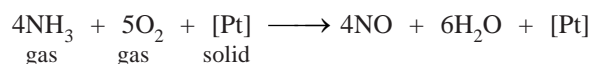
(a) Combination of sulphur dioxide ( $\text{SO}_2$ ) and oxygen in the presence of finely divided platinum or vanadium pentoxide,  $\text{V}_2\text{O}_5$ , (*Contact Process for Sulphuric acid*).



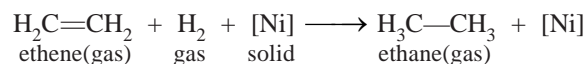
(b) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron, (*Haber Process for Ammonia*).



(c) Oxidation of ammonia to nitric oxide ( $\text{NO}$ ) in the presence of platinum gauze (a stage in manufacture of Nitric acid).



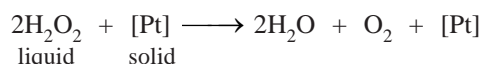
(d) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel.



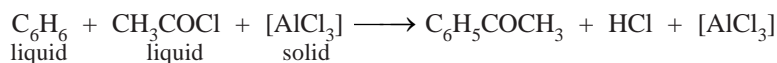
Vegetable oils are triesters of glycerol with higher unsaturated acid (oleic acid). When hydrogen is passed through the *vegetable oils* in the presence of nickel, the carbon-carbon double bonds of the acid portions are hydrogenated to yield *solid fats* (*Vanaspati ghee*).

### (2) Heterogeneous catalysis with liquid reactants

(i) The decomposition of aqueous solutions of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is catalysed by manganese dioxide ( $\text{MnO}_2$ ) or platinum in colloidal form,

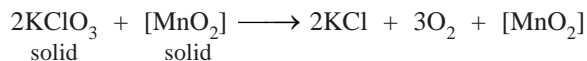


(ii) Benzene and ethanoyl chloride ( $\text{CH}_3\text{COCl}$ ) react in the presence of anhydrous aluminum chloride to form phenyl methyl ketone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ),



### (3) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ( $\text{KClO}_3$ ) is catalysed by manganese dioxide ( $\text{MnO}_2$ ).



## CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them.

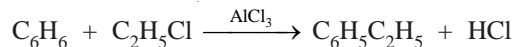
### (1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction

Qualitative and quantitative analysis show that a catalyst undergoes no change in mass of chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide ( $\text{MnO}_2$ ) used as a catalyst in the thermal decomposing of potassium chlorate is left as a fine powder at the end to the reaction.

### (2) A small quantity of catalyst is generally needed to produce almost unlimited reaction

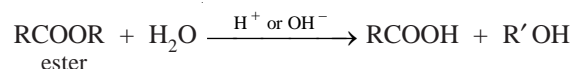
Sometimes a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,



anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene.

For the acid and alkaline hydrolysis of an ester,



the rate of reaction is proportional to the concentration of the catalyst ( $\text{H}^+$  or  $\text{OH}^-$ ).