

CATALYSIS

2.8 CATALYSIS

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CATALYSIS

2.8 INTRODUCTION

The word “**catalyst**” was introduced into science by the great **Swedish chemist Jons Jakob Berzelius (1779-1848)**.

Catalysts are of immense importance in chemistry and biology. All enzymes are catalysts that carry out the biochemical reactions necessary for life. (eg) Enzymes in saliva accelerate the conversion of starch to glucose.

Terminologies

Catalyst / Catalysis

A catalyst is a substance which alters the rate of a chemical reaction, and remains chemically unchanged at the end of the reaction. This phenomenon is termed as catalysis.

CHARACTERISTICS OF CATALYSTS OR CRITERIA FOR CATALYSIS

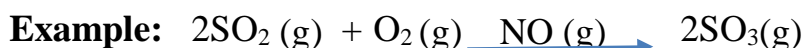
1. The catalyst remains unchanged (in mass and chemical composition) in the reaction.
2. A small quantity of the catalyst is required. {e.g. One mole of colloid Pt catalyzes 10^8 liters of H_2O_2 }.
3. The catalyst does not change the equilibrium constant. But the equilibrium approaches earlier.
4. The catalyst is specific in nature.
5. The catalyst cannot make impossible reaction to occur and does not initiate a reaction.
6. The **activity of the catalyst** can be **increased** by the presence of **promoters** and decreased by the presence of **poisons**.
e.g. Mo acts as a promoter in the manufacture of ammonia by Haber’s process and arsenic destroys the catalytic activity of the platinum catalyst in the manufacture of sulphuric acid.
7. Catalyst will never change the nature of products of the reaction.

8. The catalyst exhibits maximum activity at a particular temperature which is known as **optimum temperature**.

TYPES OF CATALYSIS

1. Homogeneous catalysis

When the reactants and the catalyst are in the same phase (i.e. solid, liquid or gas) it is said to be **homogeneous catalysis**.



2. Heterogeneous catalysis

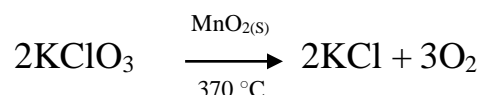
When the reactants and the catalyst are in the different phase it is known as **heterogeneous catalysis**.



3. Positive catalysis

When the rate of the reaction is accelerated by a catalyst, it is said to be a **positive catalyst** and phenomenon as **positive catalysis**.

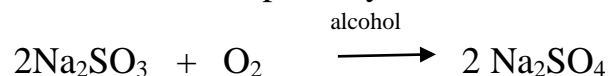
Example: Decomposition of KClO_3 by MnO_2



4. Negative catalysis

The substances that retard the reaction rate instead of increasing it are called **negative catalyst** or **inhibitors** and the phenomenon is known as **negative catalysis**.

Example: Oxidation of sodium sulphite by alcohol



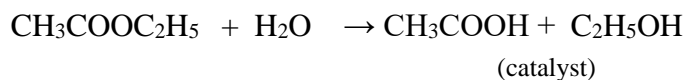
5. Autocatalysis

When one of the products of reaction itself acts as a catalyst for that reaction the

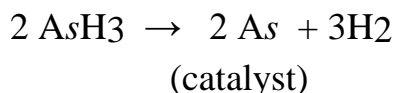
phenomenon is called autocatalysis.

Examples

(1) Hydrolysis of an Ester: The hydrolysis of ethyl acetate forms acetic acid (CH_3COOH) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.



(2) Decomposition of Arsine: The free arsenic produced by the decomposition of arsine (AsH_3) autocatalyses the reaction.



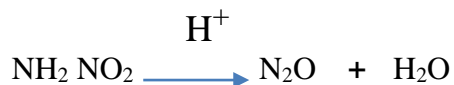
6. Acid - Base catalysis

The reactions that are catalysed by acids or bases, or both acids and bases are referred to as acid-base catalysis.

- Acid catalysis is brought about by H^+ ions supplied by strong acids, while base catalysis is caused by OH^- ions supplied by strong bases.
- Many reactions are catalyzed by both acids and bases.

Examples of acid-base Catalysis

1) Decomposition of nitramide



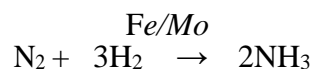
Catalytic promoters

A substance which promotes the activity of a catalyst is called a catalytic promoter. These substances when added in small concentration can increase the activity of a catalyst.

Example of promoters

Molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron

catalyst in the Haber's synthesis for the manufacture of ammonia.



Function of promoters

- Change of crystal lattice spacing of the catalyst.
- Increase of peaks and cracks in the catalyst.
- Changes the pathway of the reaction.

Catalytic poisoning

A substance which decrease or destroy the activity of the catalyst is called a catalytic poison and the process is called catalytic poisoning.

E.g. arsenic destroys the catalytic activity of the platinum catalyst in the manufacture of sulphuric acid.

Explanation of catalytic poisoning

The poison is adsorbed on the catalyst surface in preference to the reactants. Even a Mono molecular layer renders the surface unavailable for further adsorption of thereactants.

Application of catalysis

Catalytic converter

- A **catalytic converter** is an emission control device that converts toxic gases and pollutants from an exhaust engine to less toxic pollutants by catalyzing aredox reaction.
- Catalytic converters are used in internal combustion engines, heaters and stoves.

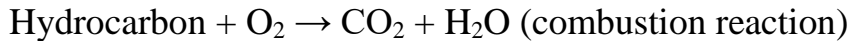
Types of catalytic converter

1. **Two- way catalytic converter**
2. **Three- way catalytic converter**

1. Two- way catalytic converter

A two-way catalytic converter has two simultaneous tasks:

- a) Oxidation of carbon monoxide to carbon dioxide: $2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$
- b) Oxidation of hydrocarbons (unburned and partially burned fuel) to carbon dioxide and water.

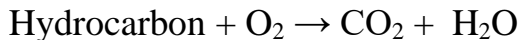


- This type of catalytic converter is widely used on diesel engines to reduce hydrocarbon and carbon monoxide emissions.
- Here Pt, Rh and Pd are used as catalysts.
- This cannot reduce emissions of NO_x.

2. Three- way catalytic converter

Three-way catalytic converters have the additional advantage of controlling the emission of nitric oxide and nitrogen dioxide (NO_x). A three-way catalytic converter has three simultaneous tasks,

- a) Reduction of nitrogen oxides to nitrogen and oxygen: $2 \text{NO}_x \rightarrow \text{O}_2 + \text{N}_2$
- b) Oxidation of carbon monoxide to carbon dioxide: $2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$
- c) Oxidation of unburnt hydrocarbons (HC) to carbon dioxide and water



A basic catalytic converter is shown in the figure,

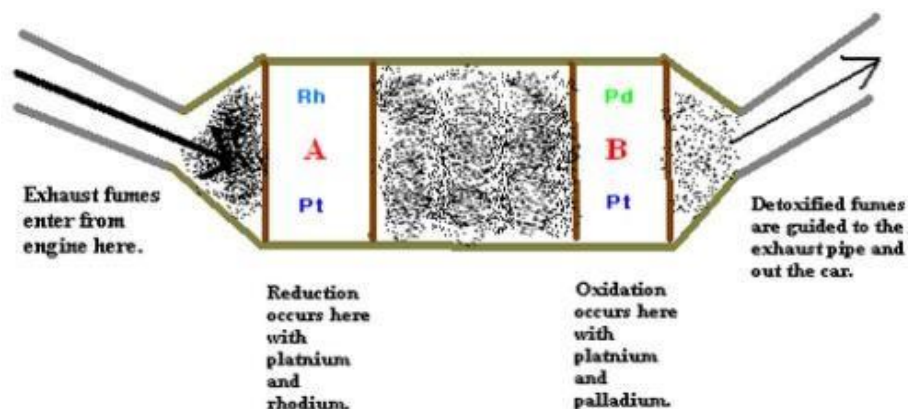


Figure 2.8.1 Basic catalytic converter

[Source:[https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Kinetics/07%3A_Case_Studies-_Kinetics/7.01%3A_Catalytic_Converters](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/07%3A_Case_Studies-_Kinetics/7.01%3A_Catalytic_Converters)]

2.9 Enzyme Catalysis

Terminologies

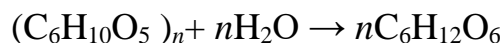
Enzymes

Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells.

Enzyme catalysis

The catalysis brought about by enzymes is known as enzyme catalysis.

Eg.(i) Amylase is an enzyme which breaks down starch into glucose.



Starch

glucose

Characteristics of enzyme catalysis

1. Enzymes speed up reactions by lowering the activation energy.
2. Enzymes do not
 - change the equilibrium constant for a reaction.
 - change G(free energy) for a reaction.

- convert a non-spontaneous reaction into a spontaneous reaction.
- 3. Enzymes are highly efficient. (A single molecule of this catalyst can transform a million molecules of the reactants per second).
- 4. Enzymes are specific in nature. (The same catalyst cannot be used in more than one reaction).
- 5. The effectiveness of a catalyst is the maximum at its optimum temperature.
- 6. Enzyme catalysis is dependent upon the pH of the solution. A catalyst works best at an optimum pH from 5 to 7.
- 7. The activity of the enzymes usually increases in the presence of a co-enzyme or activators such as Na^+ , Co^{2+} , etc.

KINETICS OF ENZYME CATALYSIS

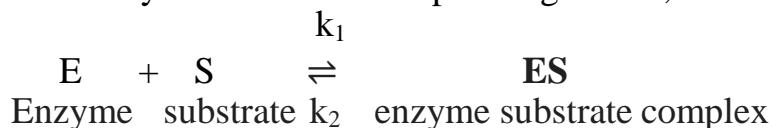
Michaelis Menten Equation (Rate Equation for enzyme catalysis)

This mechanism was proposed by L. Michaelis & M. Menten in 1913.

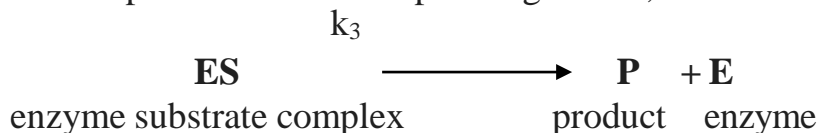
The Michealis Menten equation can be derived as follows,

An enzyme catalyzed reaction can be written as,

- I. Formation of enzyme- substrate complex is given as,



- II. Decomposition of the complex is given as,



where, k_1 , k_2 and k_3 are the rate constants.

The rate of formation of the product,

$$= k_3 [\text{ES}] \dots\dots\dots (1)$$

Calculation of concentration of ES - [ES]

rate of formation of ES = $k_1 [E] [S]$

rate of disappearance of ES = $k_2 [ES] + k_3 [ES]$

Applying steady state principle,

rate of formation of ES = rate of disappearance of ES

$$k_1 [E] [S] = k_2 [ES] + k_3 [ES]$$

$$k_1 [E] [S] = (k_2 + k_3) [ES]$$

$$[ES] = \frac{[E][S]}{K_m + [S]} \quad (2)$$

The total concentration of the enzyme is E_0 , is given as,

$$[E_0] = [E] + [ES]$$

$$\therefore [E] = [E_0] - [ES] \quad (3)$$

Substitute the value of $[E]$ in equation (2).

$$[ES] = k_1 \frac{[E_0][S] - [ES][S]}{k_2 + k_3 + [S]}$$

Solving for $[ES]$, and substituting the value of $[ES]$ in equation (1), we get,

$$\text{Rate} = k_3 \frac{[E_0][S]}{K_m + [S]} \quad (4)$$

where K_m is the Michealis Menten constant, whose value is $K_m = k_2 + k_3 / k_1$.

Equation (4) is Michealis Menten equation.

Case (i) At lower substrate concentration, $[S] \ll K_m$,

$$\therefore r = \frac{k_3 [E_0][S]}{K_m}$$

At lower substrate concentration, the **rate is first order** with respect to substrate.

Case (ii) At higher substrate concentration, $[S] \gg K_m$,

$$\therefore r = \frac{[E]_0 [S]}{K_m + [S]}$$

At higher substrate concentration, the **rate is zero** order with respect to substrate.

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