

Catalysis

What is Catalysis?

Catalysis is the phenomenon in which the rate of any reaction is altered (accelerated or retarded) by the presence of a substance, which itself remains unchanged chemically in the reaction. The substance which alters the rate of the reaction is called catalyst.

On the basis of phases involved catalysis are of two types:

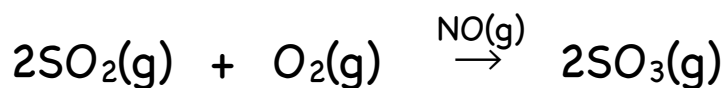
- homogenous catalysis
- heterogeneous catalysis

Homogeneous Catalysis:

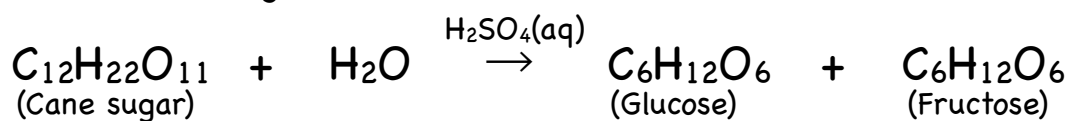
When the reactants and catalysts are in the same physical state i.e. catalyst is in the same phase as the reactant is called homogenous catalysis.

For Example

- Lead Chamber Process:



- Inversion of Cane Sugar:



Heterogeneous Catalysis:

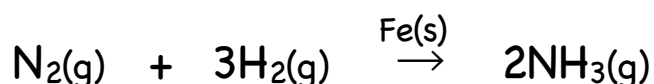
A catalytic process in which the catalyst and the reactants are in different phases is called heterogeneous catalysis. This process is also known as **surface catalysis** or **contact catalysis**.

For Example

- Decomposition of H_2O_2 :



- Haber's Process:



What is a Catalyst?

Catalyst is a substance which alters the rate of chemical reaction (may increase or decrease the rate) without being consumed itself during the course of reaction.

Based on behaviour, catalysts can be classified into four types:

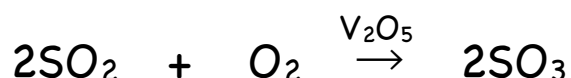
- Positive catalyst
- Negative catalyst
- Induced catalyst
- Auto catalyst

Positive catalyst:

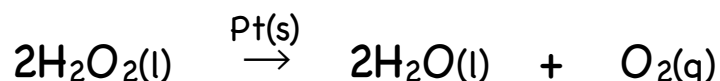
The substance which increases the rate of reaction is known as positive catalyst. It acts by decreasing the activation energy for reaction. The phenomenon is known as positive catalysis.

Examples:

- V_2O_5 used in contact process:



- Decomposition of H_2O_2 in the presence of Platinum.



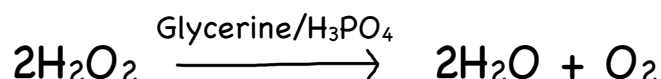
Negative catalyst:

The substance which decreases the rate of reaction is known as negative catalyst. It acts by increasing the activation energy for reaction. These are also known as **inhibitor or retarder**. The phenomenon is known as negative catalysis.

Negative catalysts work by providing an alternate path to the reaction having a higher activation energy than the uncatalysed reaction. So that lesser molecules will have sufficient energy to cross the barrier and the reaction will be slower.

Example:

- Decomposition of hydrogen peroxide(H_2O_2) decreases in the presence glycerine.



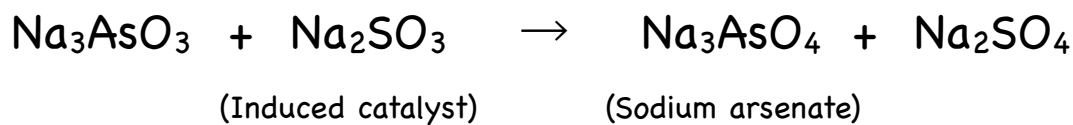
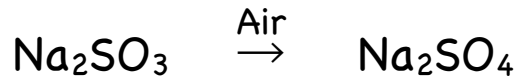
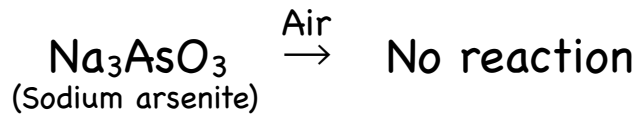
- Similarly phosphoric acid(H_3PO_4) also prevents decomposition of H_2O_2 .
- Alcohol acts as a negative catalyst in the oxidation of Na_2SO_3 .

Induced catalyst:

When one reactant influences the rate of other reaction which doesn't occur under ordinary conditions is known as induced catalyst. Or we can say, when a chemical reaction increases the rate of another chemical reaction, it is called induced catalysis.

Example:

Sodium arsenite solution is not oxidised by air. but when air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, simultaneous oxidation of both takes place. Thus the oxidation of sodium arsenite is induced by oxidation of sodium sulphite.



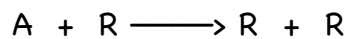
Here sodium sulphite act as an induced catalyst.

Auto catalyst:

In certain reactions, one of the product formed acts as a catalyst for the reaction is known as auto catalyst and the phenomenon is known as auto catalysis.

Example:

In the oxidation of oxalic acid($\text{C}_2\text{H}_2\text{O}_4$) by potassium permanganate(KMnO_4), Mn^{2+} ion formed from MnSO_4 act as catalyst and increases the rate of reaction.



$$(-r_a) = k_A C_A C_R = k_A C_A (C_0 - C_A)$$

$$C_0 = C_A + C_R = C_{A_0} + C_{R_0} = \text{Constant}$$

For $(-r_A)_{max}$,

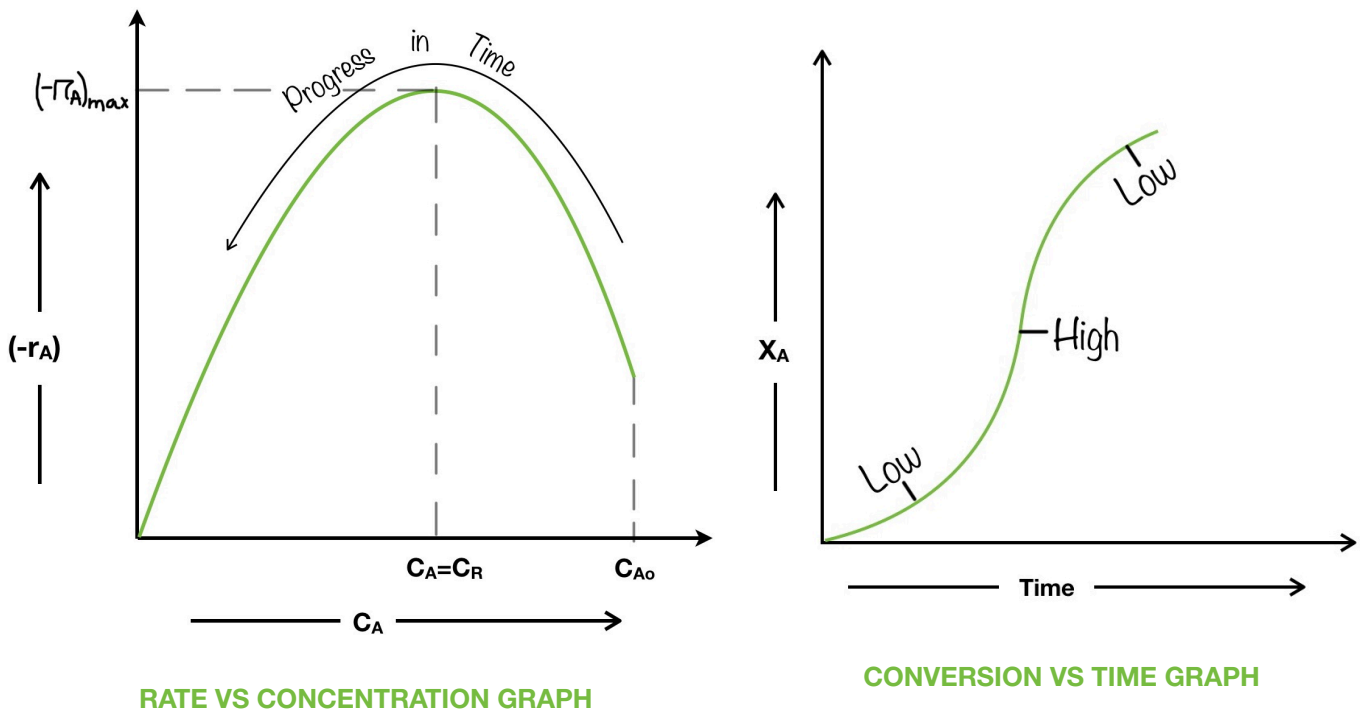
$$\frac{d(-r_A)}{dC_A} = k_A [C_A \cdot (-1) + (C_0 - C_A) \cdot 1] = 0$$

$$\implies k_A [-C_A + C_0 - C_A] = 0$$

$$\implies C_A = C_0 - C_A = C_R$$

$$\implies C_A = C_R$$

That means the rate is maximum when $C_A = C_R$.



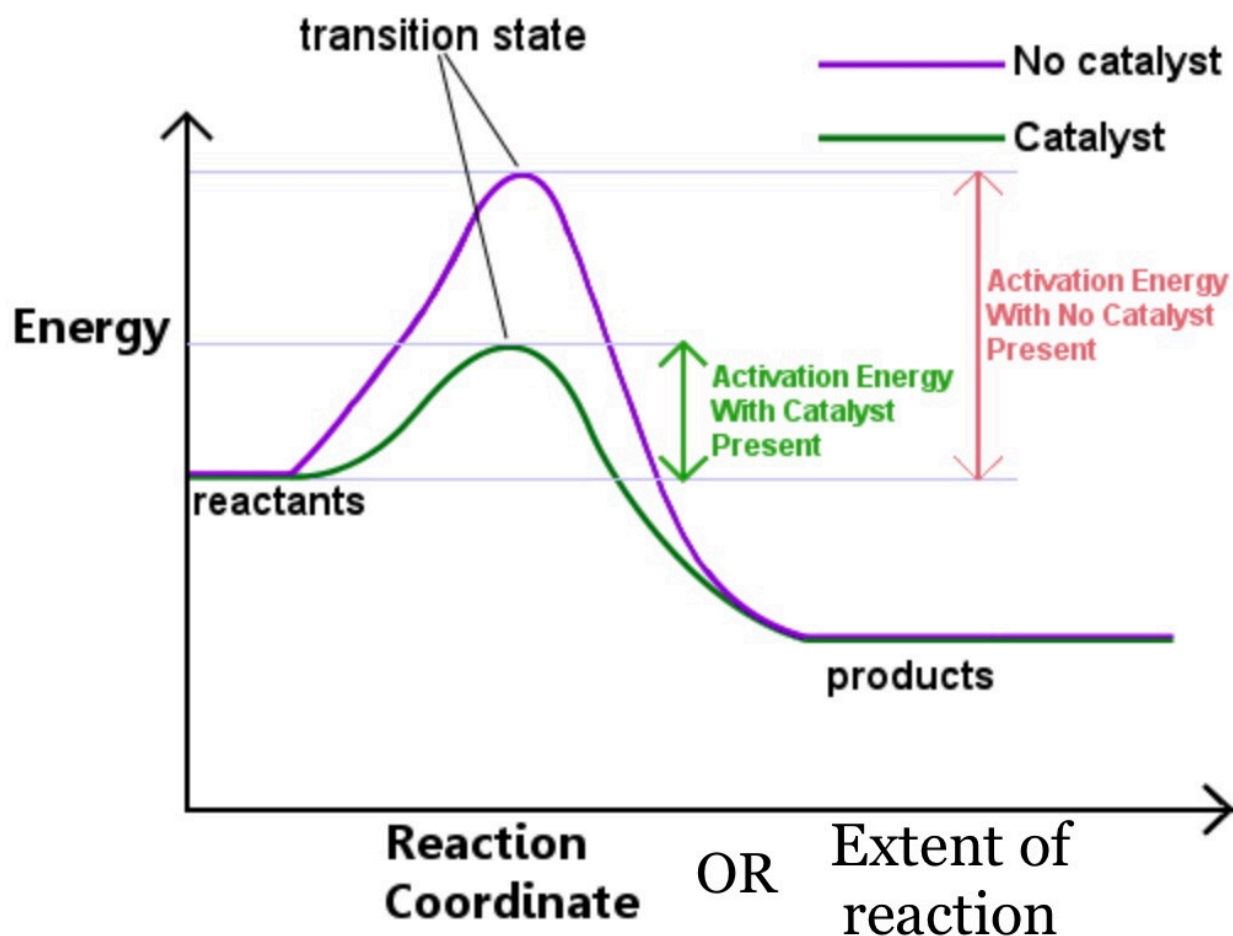
Here the concentration of C_A in the beginning is maximum (C_{A0}), means the $(C_0 - C_A)$ term will be minimum. Then as the reaction proceeds the rate of increase of $(C_0 - C_A)$ is more than the rate of decrease of C_A . So graph increases. Then there will be a time, when rate of increase of $(C_0 - C_A)$ is equal to rate of decrease of C_A . Now rate reaches maximum. After this rate of decrease of C_A is more than the rate of increase of $(C_0 - C_A)$. That's why graph will now decrease.

Initially, when the rate is low, conversion will also be low. Then there comes a time when rate is maximum and that's why conversion will also be high. Then again when rate is low, conversion will also be low.

Characteristics of Catalytic Reactions:

- The catalyst remains unchanged in mass and chemical composition at the end of the reaction; it may, however, undergo considerable change in physical form.
- Catalysts are highly efficient i.e. a small quantity of the catalyst is capable of producing the desired effect.
- The action of a catalyst is specific to a large extent.
- The catalyst does not initiate a reaction. The function of a catalyst is only to alter the speed of the reaction which is already occurring at a particular rate.
- A catalyst does not change the position of equilibrium in a reversible reaction. It catalyse both forward and backward reaction to the same extent and thus have no effect on the equilibrium constant.

- A certain minimum energy must be possessed by the reactants so that they may react and produce the products. This is called the **activation energy (E_a)** for the reaction. A catalyst lowers the activation energy which increase the rate of the reaction. Thus, a catalyst increases the rate of a reaction by providing an alternate pathway whose activation energy is lower than the activation energy of the uncatalysed reaction.



In order for a reaction to occur, reactant molecules must contain sufficient energy to break their bonds and cross a potential energy barrier, i.e. the activation energy. All molecules possess varying amounts of energy. But, generally only a few of them have sufficient energy for reaction (i.e. to break their bonds and cross the potential energy barrier). The lower the potential energy barrier to reaction, the more reactants have sufficient energy and, hence, the faster the reaction will occur. All catalysts, including enzymes, function by forming a transition state, with the reactants, of lower free energy than would be found in the uncatalysed reaction. Even quite modest reductions in this potential energy barrier may produce large increases in the rate of reaction

Theories/mechanism of Catalysis:

There is no any fixed mechanism for the action of all the catalysts. This is because the catalytic reactions are of various types. However, the two theories of catalytic action which are followed are.

- Intermediate compound formation theory of catalysis
- Adsorption theory of catalysis

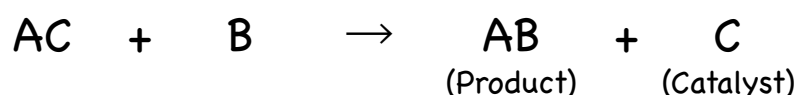
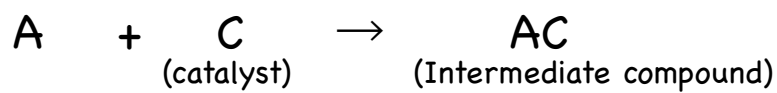
Intermediate Compound Formation Theory:

According to intermediate compound formation theory, the catalyst reacts with one of the reactants to form an unstable intermediate compound. The formation of this intermediate compound requires less energy than needed for the actual reaction. The intermediate compound formed is unstable and thus combines with the other reactant to form the final product and the catalyst is regenerated.

For example, a reaction of the type



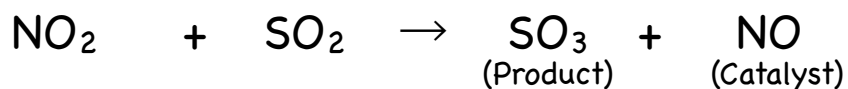
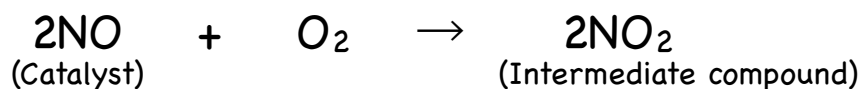
Which occurs in the presence of a catalyst C, may take place as



In simple words we can say that, a catalyst increases the rate of any reaction by providing an alternative pathway for the reaction to proceed with lower activation energy.

A large number of catalytic reactions can be explained on the basis of this theory
For example:

Catalytic oxidation of SO_2 to SO_3 in lead chamber process in the presence of NO as catalyst



This theory provides explanation for the fact that catalyst remains unchanged in mass and chemical composition at the end of reaction and its effectiveness even in small quantities.

Adsorption Theory of Catalysis:

Adsorption theory of catalysis explains the mechanism of heterogeneous catalysis.

The old point of view was that when the catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of catalyst, which is utilised on enhancing the chemical activity of reacting molecules.

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory.

In this theory the following steps are involved:

1. Diffusion of reactant from bulk of the fluid to the surface of catalyst.
2. Diffusion of reactant inside the pores from surface of catalyst.
3. Adsorption of reactant molecules on active site of the catalyst inside the pores.
4. Occurrence of chemical reaction on the active sites.
5. Desorption of reaction product from active site.
6. Diffusion of product from inside the pores to surface of the catalyst.
7. Diffusion of product from surface of catalyst to bulk of the fluid.

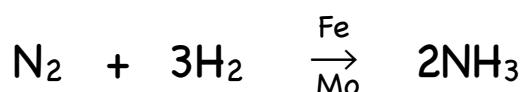
Among all the steps, 3rd, 4th and 5th are the slowest as compared to others. Hence, the overall or global rate of reaction is not affected by 1st, 2nd, 6th and 7th step. Or we can say, the overall rate of reaction is controlled by slowest step among 3rd, 4th and 5th.

Promoters/Catalytic Promoters:

Those substances which do not themselves act as catalyst but their presence increases the activity of a catalyst are called catalytic promoters.

Examples:

- In Haber's Process, Iron(Fe) is used as a catalyst while Molybdenum(Mo) acts as a promoter.



Inhibitors/catalytic poisons:

The substance whose presence decreases or destroys the activity of a catalyst is called inhibitors/catalytic poisons.

If the action of catalyst reduced is reversible then it is called inhibitor.

If the action of catalyst reduced is irreversible then it called catalytic poison.

Examples:

- Platinum(Pt) catalyst used in the oxidation of sulphur dioxide(SO₂) in contact process is poisoned by Arsenious oxide(As₂O₃).
- Iron(Fe) catalyst used in the synthesis of ammonia(NH₃) by Haber's process is poisoned by Hydrogen sulphide(H₂S) or carbon monoxide(CO).

Enzyme catalysis:

The increase in rate of a process using a biological molecule is known as enzyme catalysis. Most of the enzyme catalysts are proteins. Or we can say these are biological catalysts.

Mechanism:

Step 1: binding of substrate to active site of the enzyme.

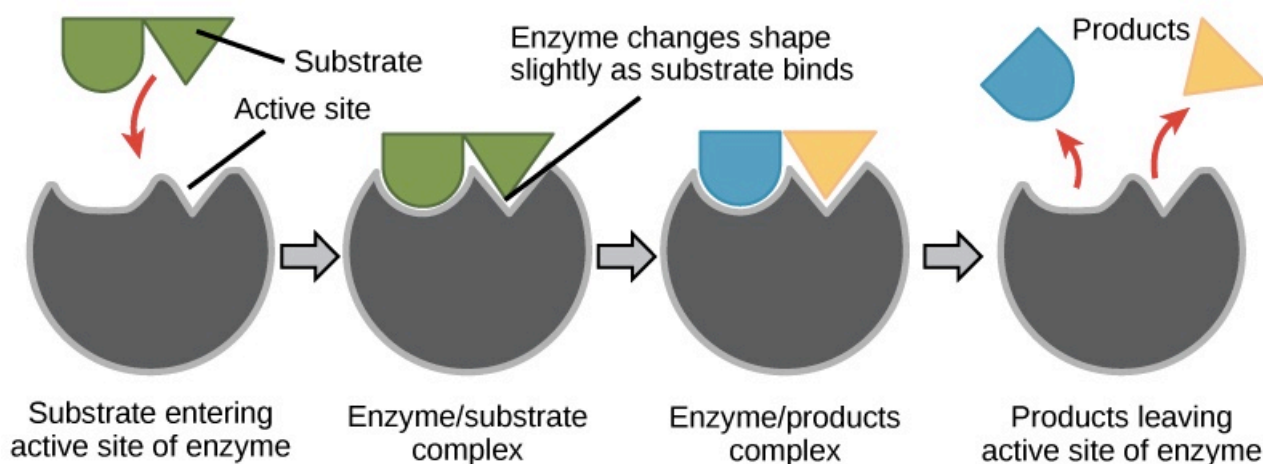
Step 2: formation of enzyme-substrate complex.



Step 3: decomposition of enzyme-substrate complex to form enzyme-product complex.



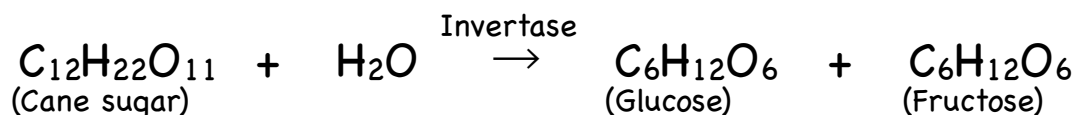
Step 4: products leaving active site of the enzyme.



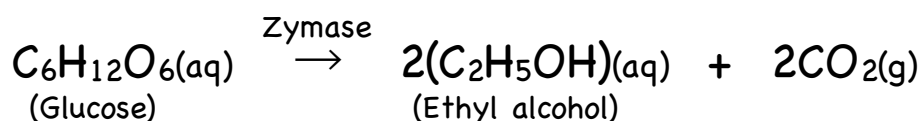
ACTION OF ENZYME AND SUBSTRATE

Examples:

- Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.



- Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into alcohol and carbon dioxide.



Catalysts in Industries:

Industrial process	Catalyst used
Haber's process for manufacturer of ammonia	Finely divided iron with molybdenum as promoter
Ostwald's process for manufacturer of nitric acid	Platinum (platinized asbestos)
Lead chamber process for manufacturer of H_2SO_4	Nitric oxide
Contact process for manufacturer of H_2SO_4	Vanadium pentoxide or platinized asbestos
Synthesis of methanol	Zinc oxide with chromic oxide as promoter
Hydrogenation of vegetable oil	Nickel
Bosch's process for manufacture of hydrogen	Ferric oxide with chromic oxide as promoter
Bergius process for synthesis of petrol	Ferric oxide
Deacon's process for manufacturer of chlorine	Cupric chloride
Manufacture of ethyl alcohol from molasses	Yeast (Invertase and Zymase)

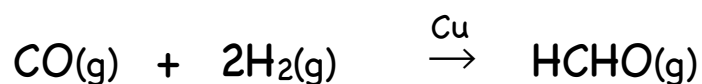
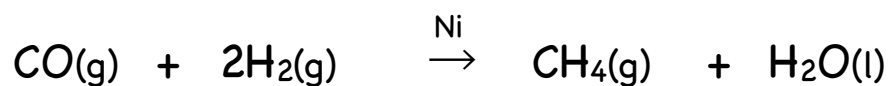
Activity of Catalyst:

Activity of a catalyst is the ability of catalyst to accelerate a chemical reaction. The degree of acceleration can be as high as 10^{10} times in certain reactions. Reaction between H_2 and O_2 to form H_2O in presence of platinum as catalyst takes place with explosive violence. In absence of catalyst, H_2 and O_2 can be stored indefinitely without any reaction.

Selectivity of Catalyst:

Selectivity of a catalyst is its ability to direct a reaction to yield particular product (excluding other)

For example:



Active sites/active centers:

The catalytic surface has unbalance chemical bonds on it. The reactant gaseous molecules are adsorbed on the surface by these free bonds. The distribution of free bonds on the catalytic surface is not uniform. These are crowded at the peaks, cracks and corners of the catalyst. The catalytic activities due to adsorption of reacting molecules takes place at these spots. These are therefore referred as active sites. If a catalyst has more active sites, then its catalytic activities will also be more.

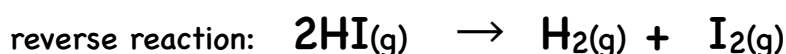
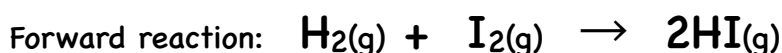
Chemical equilibrium

Reversible reaction:

A reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously is called a reversible reaction.

One example of a reversible reaction is the reaction of hydrogen gas and iodine vapour to form and from hydrogen iodide.

The forward and reverse reaction can be written as follows:



In the forward reaction, hydrogen and iodine combine to form hydrogen iodide.

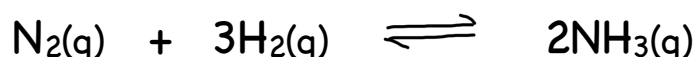
In the reverse reaction, hydrogen iodide decomposes back into hydrogen and iodine. These two reaction can be combined into one equation by the use of double arrow.



The double arrow is the indication that the reaction is reversible.

Some more examples of reversible reaction are:

1. Production of Ammonia by Haber's process.



2. When ammonium chloride heated, it sublime into ammonia and hydrogen chloride gas. On cooling the two gases recombine to form ammonium chloride again.



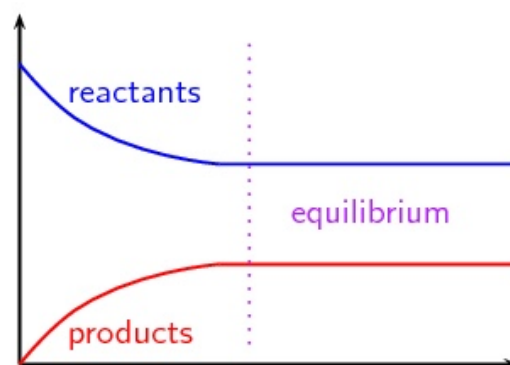
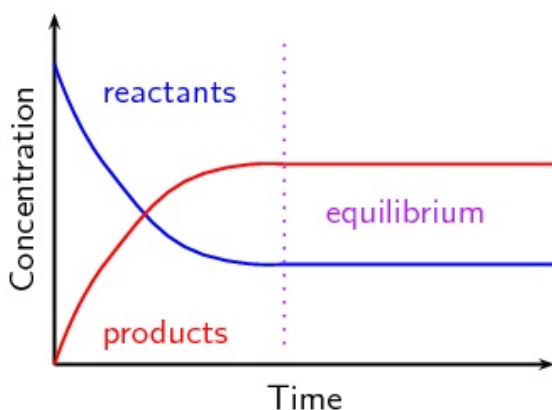
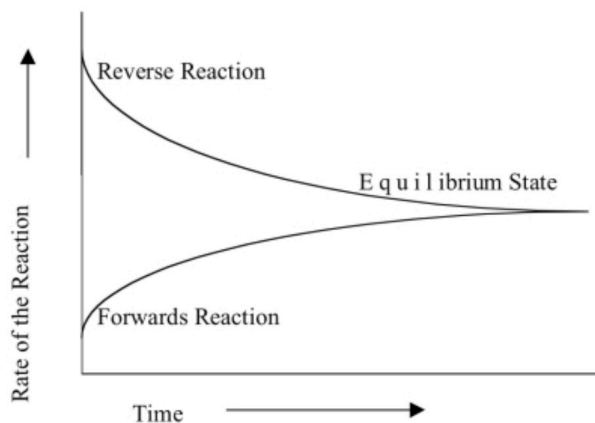
Equilibrium State:

It is the state, in which measurable properties of a system such as pressure, concatenation of species, temperature , etc, do not change with time and are uniform within the system under a given set of conditions.

Chemical Equilibrium:

Chemical equilibrium is a state in which the rate of forward reaction equals the rate of backward reaction. In other words, there is no net change in concentration of reactants and products.

- This kind of equilibrium is also called dynamic equilibrium.

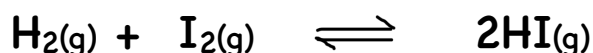


Characteristics of chemical equilibrium:

1. The equilibrium state can only be reached if the chemical reaction takes place in a closed system. Otherwise, some of the products may escape, leading to the absence of a reverse reaction.
2. The rate of the forward reaction is equal to the rate of the reverse reaction.
3. The state of chemical equilibrium is characterised by consistency of certain properties such as concentration, density, pressure or colour. However, the state of equilibrium is observed only as long as the reaction conditions such as temperature and pressure are kept constant.
4. Chemical equilibrium is always dynamic in nature. At equilibrium also there is change in concentrations of reactants and products. But there is no net change in concentrations of reactants and products as rate of both the forward and backward reaction is same.
5. Catalysts alter the rate of a chemical reaction. That means the state of equilibrium can be attained at a faster or slower rate in the presence of a catalyst. But it has no effect on the state of equilibrium or we can say it does not affect the equilibrium constant.
6. Chemical equilibrium can be attained from either direction. Because chemical equilibrium is seen in only reversible reactions in which the product can also act as reactants. Hence is it possible to attain the state of equilibrium even in reverse direction i.e. taking the actual products as the reactants. The equilibrium state is same in both the forward and backward reaction.

Law of mass action:

At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to the corresponding stoichiometric coefficient that appears in the balanced chemical equation.



Rate of forward reaction (r_f) is proportional to $[\text{H}_2]^1[\text{I}_2]^1$. i.e. $r_f = k_f[\text{H}_2]^1[\text{I}_2]^1$

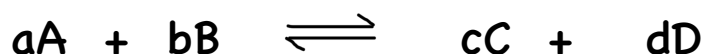
Rate of backward reaction (r_b) is proportional to $[\text{HI}]^2$. i.e. $r_b = k_b[\text{HI}]^2$

Equilibrium constant:

When a chemical reaction reaches equilibrium, the concentrations of the chemical species involved bear a constant relation to each other, which is described by an equilibrium constant.

- Equilibrium constant does not depend upon concentration and pressure of reactants and products. It only depends upon the temperature.

If we have a reversible reaction of the form



Rate of forward reaction (r_f) is proportional to $[\text{C}_A]^a[\text{C}_B]^b$. i.e. $r_f = k_f[\text{C}_A]^a[\text{C}_B]^b$

Rate of backward reaction (r_b) is proportional to $[\text{C}_C]^c[\text{C}_D]^d$. i.e. $r_b = k_b[\text{C}_C]^c[\text{C}_D]^d$

At equilibrium,

Rate of forward reaction is equal to rate of backward reaction.

$$\text{i.e. } r_f = r_b \quad \Rightarrow \quad k_f[\text{C}_A]^a[\text{C}_B]^b = k_b[\text{C}_C]^c[\text{C}_D]^d$$

Then equilibrium constant, $K_C = \frac{k_f}{k_b} = \frac{[\text{C}_C]^c[\text{C}_D]^d}{[\text{C}_A]^a[\text{C}_B]^b}$, at a constant temperature.

In other words we can also say that the equilibrium constant is the ratio of rate constant of forward reaction to the rate constant of backward reaction at a constant temperature.

If the reaction involves gases, then we can do all the above mentioned things on the basis of pressure also. Here we just need to replace the concentration of each species with their respective partial pressures.

$$\text{Then equilibrium constant, } K_p = \frac{k_f}{k_b} = \frac{[p_C]^c [p_D]^d}{[p_A]^a [p_B]^b}$$

Le chatelier's principle:

Le chatelier's principle states that when an external stress (change in pressure, temperature or concentration) is applied to a system in chemical equilibrium, the equilibrium will change in such a way as to reduce the effect of the stress.

Le Chatelier's principle is an observation about chemical equilibria of reactions. It states that changes in the temperature, pressure, volume, or concentration of a system will result in predictable and opposing changes in the system in order to achieve a new equilibrium state. Le Chatelier's principle can be used in practice to understand reaction conditions that will favour increased product formation

Effect of changes in concentration:

- According to Le Chatelier's principle, adding additional reactant to a system will shift the equilibrium to the right, towards the side of the products. By the same logic, reducing the concentration of any product will also shift equilibrium to the right.
- The converse is also true. If we add additional product to a system, the equilibrium will shift to the left, in order to produce more reactants. Or, if we remove reactants from the system, equilibrium will also be shifted to the left.
- Thus, according to Le Chatelier's principle, reversible reactions are self-correcting; when they are thrown out of balance by a change in concentration, temperature, or pressure, the system will naturally shift in such a way as to "re-balance" itself after the change.

Effect of changes in pressure and volume:

- A change in pressure or volume will result in an attempt to restore equilibrium by creating more or less moles of gas.
- For example, if the pressure in a system increases, or the volume decreases, the equilibrium will shift to favour the side of the reaction that involves fewer moles of gas.
- Similarly, if the volume of a system increases, or the pressure decreases, the production of additional moles of gas will be favoured.

Effect of changes in temperature:

- The effect of temperature on equilibrium is related with the heat of reaction.
- For an endothermic reaction, heat is absorbed in the reaction, and the value is positive. Thus, for an endothermic reaction, we can consider heat as being a reactant.
- For an exothermic reaction, the situation is just the opposite. Heat is released in the reaction. So heat is a product, and the value of heat of reaction is negative.
- If we raise the temperature on an endothermic reaction, it is essentially like adding more reactant to the system, and therefore, by Le Chatelier's principle, the equilibrium will shift the right to consume all the added temperature.
- Conversely, lowering the temperature on an endothermic reaction will shift the equilibrium to the left, since lowering the temperature in this case is equivalent to removing a reactant.
- Similarly, For an exothermic reaction, increasing the temperature will shift the equilibrium to the left, while decreasing the temperature will shift the equilibrium to the right.

Effect of adding inert:

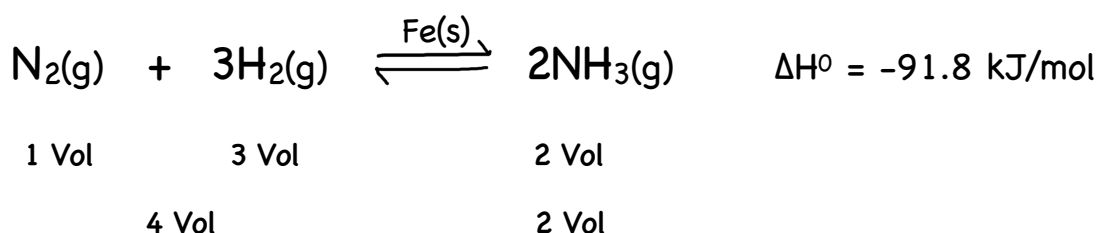
As inert gases doesn't react with other elements or compounds, adding an inert gas into a gas-phase equilibrium at constant volume does not result in a shift in equilibrium. This is because the addition of inert gases appears on both sides of a chemical reaction equation.

Conditions for maximum yield in industrial processes:

Application of Le-Chatelier's Principle to Haber's process (Synthesis of Ammonia):

Ammonia is manufactured by using Haber's process. In this reaction Nitrogen and Hydrogen in ratio 1:3 by volume are made to react at 773 K and 200 atm. Pressure

The chemical reaction is



From this reaction it is clear that the reaction is exothermic and accompanied by the decrease in volume

Effect of Concentration:

From Le Chatelier's principle; the increase in concentration of one of the reactant will shift equilibrium towards right. And here increase in concentration of hydrogen (as more moles of it are used) in preference to Nitrogen has more effect.

Effect of Pressure:

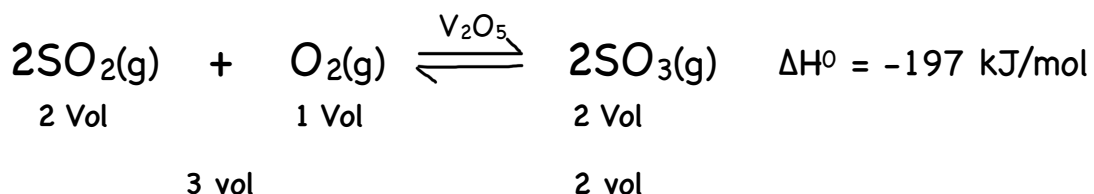
Above reaction indicate that formation of ammonia takes place with decrease in volume. As pressure and volume are two opposing effects, hence increase in pressure will favour forward reaction. Optimum pressure for maximum yield of ammonia is about 200 atm.

Effect of Temperature:

The reaction is exothermic, so lowering the temperature will favour forward reaction. But decrease in temperature results in the decrease in the rate of reaction. Hence temperature of 773K is maintained and iron is used as catalyst.

Application of Le-Chatelier's Principle to contact process (Synthesis of Sulphur Trioxide):

H₂SO₄ is manufactured by contact process. In this reaction sulphur dioxide(SO₂) is oxidised to sulphur trioxide(SO₃). Sulphur trioxide is further used for manufacturing of sulphuric acid.



From this reaction it is clear that, the reaction is exothermic and accompanied by the decrease in volume.

Effect of Concentration:

From Le Chatelier's principle; increase in concentration of one of the reactant will shift equilibrium towards right. And here increase in concentration of sulphur dioxide(as more moles of it are used) in preference to oxygen has more effect.

Effect of Pressure:

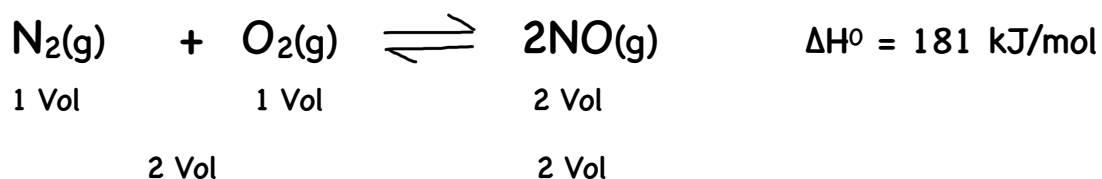
Above reaction indicate that formation of sulphur trioxide takes place with decrease in volume. Hence increase in pressure will favour forward reaction. Optimum pressure for maximum yield of sulphur trioxide is about 1.5 atm to 1.7 atm

Effect of Temperature:

The reaction is exothermic, so lowering the temperature will favour forward reaction. But decrease in temperature results in the decrease in the rate of reaction. Hence temperature of 723 K is maintained and vanadium pentoxide is used as catalyst.

Application of Le-Chatelier's Principle to manufacturer of Nitric Oxide:

The reaction is



From this reaction it is clear that, the reaction is endothermic and accompanied by no change in volume.

Effect of Concentration:

From Le Chatelier's principle; increase in concentration of one of the reactant will shift equilibrium towards right. And here increase in concentration of nitrogen or oxygen increases the rate of forward reaction.

Effect of Pressure:

Formation of nitric oxide takes place with no change in volume, which indicate that pressure has no effect on the equilibrium.

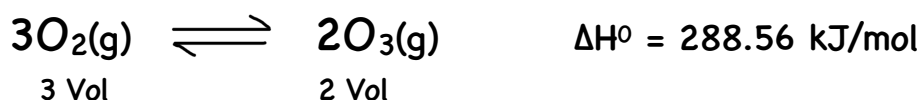
Effect of Temperature:

The reaction is endothermic, so increasing the temperature will favour forward reaction. Due to increase in temperature heat will be absorbed by the reaction.

Application of Le-Chatelier's Principle to manufacturer of Ozone:

Ozone is manufactured by passing electric current through pure oxygen.

The reaction is



From this reaction it is clear that, the reaction is endothermic and accompanied by the decrease in volume.

Effect of Concentration:

From Le Chatelier's principle; increase in concentration of one of the reactant will shift equilibrium towards right. And here increase in concentration of oxygen increases the rate of forward reaction

Effect of Pressure:

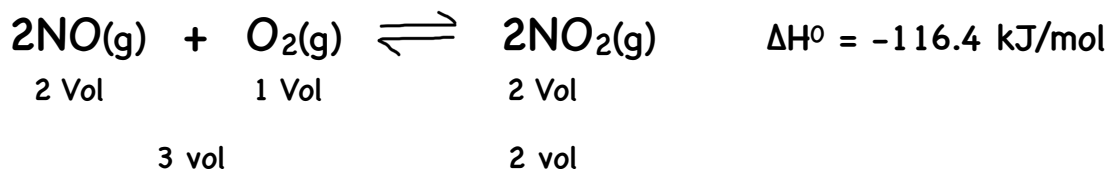
Above reaction indicate that formation of ozone takes place with decrease in volume. Hence increase in pressure will favour forward reaction.

Effect of Temperature:

The reaction is endothermic, so increasing the temperature will favour forward reaction. Due to increase in temperature heat will be absorbed by the reaction.

Application of Le-Chatelier's Principle to manufacturer of Nitrogen Dioxide:

The reaction is



From this reaction it is clear that, the reaction is exothermic and accompanied by decrease in volume.

Effect of Concentration:

From Le Chatelier's principle; increase in concentration of one of the reactant will shift equilibrium towards right. And here increase in concentration of nitrogen or oxygen increases the rate of forward reaction. Due to use of more number of moles, the increase in concentration of nitrogen oxide has a prominent effect.

Effect of Pressure:

Above reaction indicate that formation of nitrogen dioxide takes place with decrease in volume. Hence increase in pressure favour forward reaction.

Effect of Temperature:

The reaction is exothermic, so decreasing the temperature will favour forward reaction. Due to the decrease in temperature heat will be removed from the reaction.

