

B.Sc. Semester – I

Subject: - CHE - 101: Catalysis and Adsorption

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✓ **Adsorption**

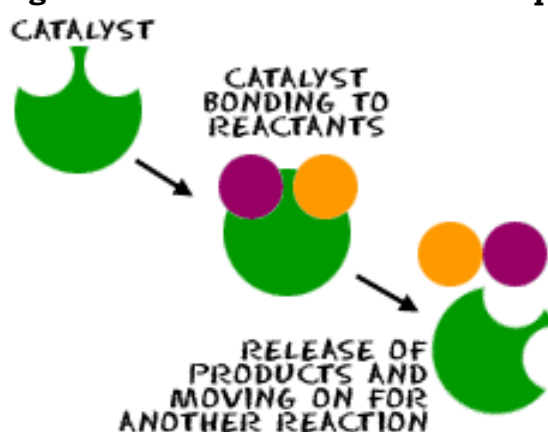
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Introduction (Catalysis)

Jöns Jakob Berzelius (1836) realized that, there are substances which, **increases rate** of a reaction **without** themselves being **consumed**. He believed that 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 n reaction.

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.

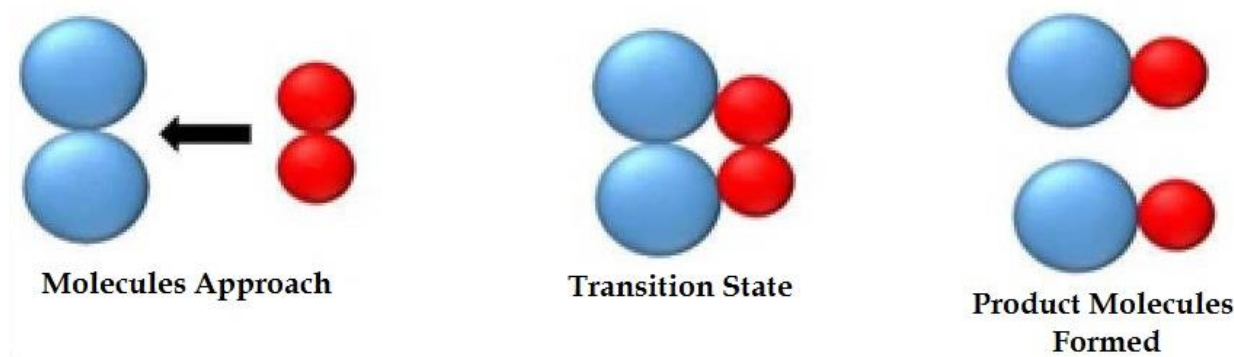
A catalyst which **retards** the rate of a reaction is called a **Negative Catalyst** or **inhibitors** and the process Negative Catalysis.

Mechanism of Catalysis

Catalysts work by changing the activation energy for a reaction, i.e., the minimum energy needed for the reaction to occur. This is accomplished by providing a new mechanism or reaction path through which the reaction can proceed. When the new reaction path has a lower activation energy, the reaction rate is increased and the reaction is said to be catalyzed.

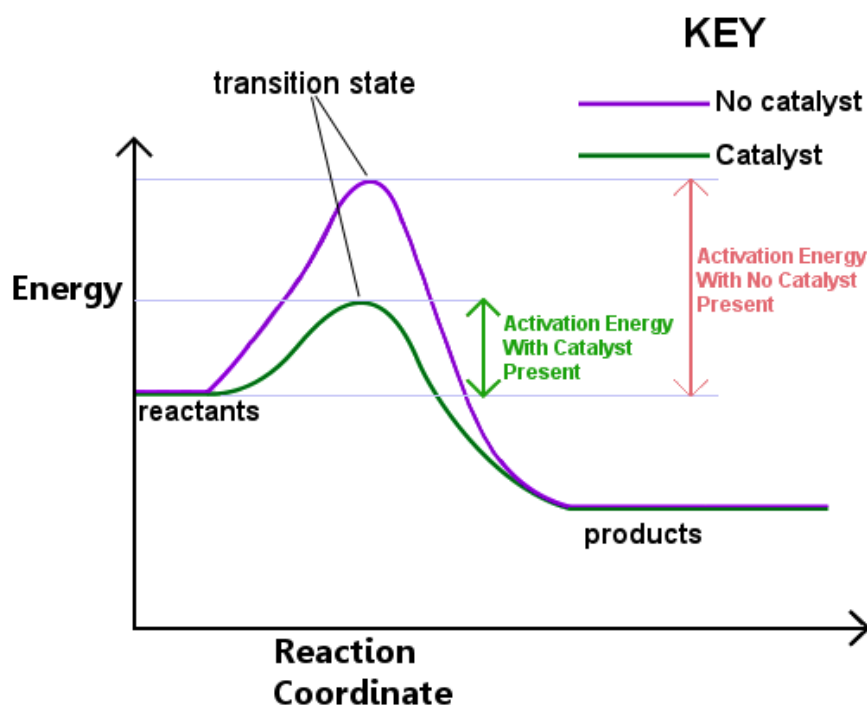
Activation Energy and Catalysis

According to the collision theory, a reaction occurs by the collisions between the reactant molecules (or ions).



At ordinary temperature, the molecules do not possess enough energy and hence the collisions are not effective. However, when the temperature of the system is raised, the kinetic energy of the molecules increases. But the molecules do not react unless they attain a minimum amount of energy. **The minimum amount of energy required to cause a chemical reaction is known as the Activation energy.** The Activation Energy (E_a) determines how fast a reaction occurs, the higher Activation barrier, the slower the reaction rate, the lower the Activation barrier, the faster the reaction. The activated molecules on collision first form an Activated Complex. As a result of breaking and forming of new bonds, the activated complex dissociates to yield product molecules.

When a catalyst is present, it lowers the activation energy of the reaction by providing a new pathway (mechanism). Thus larger numbers of effective collisions occur in the presence of the catalyst than would occur at the same temperature without the presence of the catalyst. In this way, the presence of the catalyst makes the reaction go faster, other conditions remaining the same.



Energy diagram of reaction with and without catalyst, showing clearly lowering of activation energy by catalyst

Types of Catalyst

There are two main types of Catalyst

- ✓ Homogeneous Catalyst
- ✓ Heterogeneous Catalyst

Some other Types of Catalyst

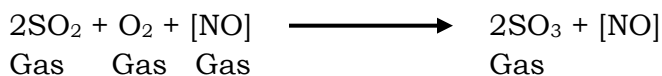
- ✓ Positive Catalyst
- ✓ Negative Catalyst
- ✓ Auto Catalyst
- ✓ Acid-Base Catalyst
- ✓ Enzyme Catalyst

Homogeneous catalysis

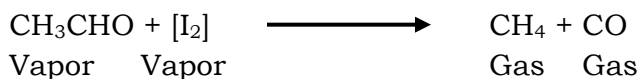
In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) phase.

1. Examples of homogeneous catalysis in gas phase

- a. Oxidation of sulfur dioxide (SO₂) to sulfur trioxide (SO₃) with nitric oxide (NO) as catalyst



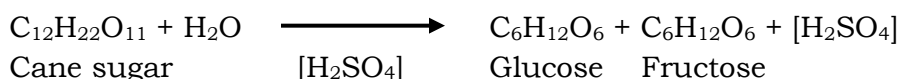
- b. Decomposition of Acetaldehyde (CH₃CHO) with iodine (I₂) as catalyst



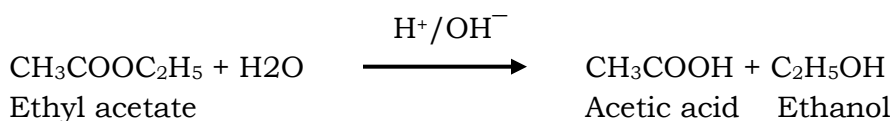
2. Examples of homogeneous catalysis in solution phase

Many reactions in solutions are catalyzed by acids (H⁺) and bases (OH⁻)

- a. Hydrolysis of cane-sugar in aqueous solution in presence of mineral acid as catalyst



- b. Hydrolysis of an ester in the presence of acid or alkali,



Heterogeneous catalysis

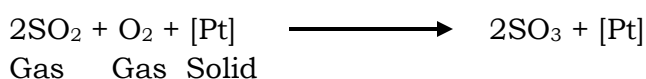
The Catalysis, in which the catalyst is in a different physical phase from the reactant, is termed Heterogeneous catalysis. The most important of such reactions are those in which the reactants are in the gas phase, while the catalyst is a solid. The process is called Contact catalysis since the reaction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

Examples of Heterogeneous Catalysis

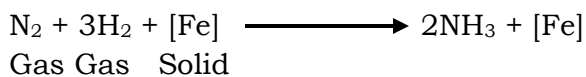
Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are listed below.

1. Heterogeneous catalysis with gaseous reactants (Contact catalysis)

- a. Combination of sulfur dioxide (SO₂) and oxygen in the presence of finely divided platinum or vanadium pentoxide V₂O₅ (contact process for sulfuric acid)

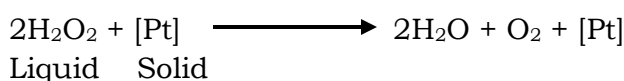


- b. Combination of Nitrogen and Hydrogen to form ammonia in the presence of finely divided iron, [Haber process for ammonia]

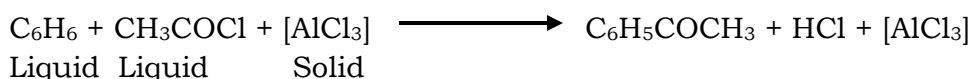


2. Heterogeneous catalysis with liquid reactants

- a. The decomposition of aqueous solutions of hydrogen peroxide (H₂O₂) is catalyzed by manganese dioxide (MnO₂) or platinum in colloidal form.

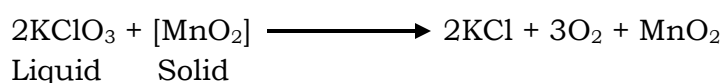


- b. Benzene and ethenoyl chloride (CH₃COCl) react in the presence of anhydrous aluminum chloride to form phenyl methyl ketone (C₆H₅COCH₃)



3. Heterogeneous catalysis with Solid reactant

The decomposition of potassium chlorate (KClO₃) is catalyzed by manganese dioxide (MnO₂)



Positive catalysis

Catalysts that speed the reaction are called positive catalysts. A positive catalyst lower the activation energy, increase the reaction rate.

Example:

1. In Haber's process for the synthesis of ammonia, iron which acts as a catalyst.



2. The decomposition of aqueous solutions of hydrogen peroxide (H_2O_2) is catalyzed by platinum

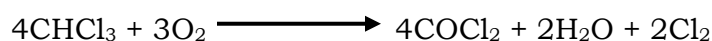


Negative catalysis (Inhibitor)

When a catalyst reduces the rate of a reaction, it is called a Negative catalyst or Inhibitor. This phenomenon is called Negative catalysis or Inhibition. Negative catalysis is useful to slow down or stop altogether an unwanted reaction.

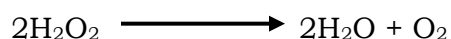
Example:

1. Oxidation of trichloromethane (CHCl_3). Trichloromethane (or chloroform) is used an anesthetic upon oxidation by air, it forms carbonyl chloride (COCl_2) which is a poisonous substance.



2% of ethanol ($\text{C}_2\text{H}_5\text{OH}$) when added to chloroform act as a negative catalyst and suppresses the formation of carbonyl chloride.

2. Decomposition of Hydrogen peroxide. The decomposition of hydrogen peroxide is retarded by the presence of dilute acids or glycerol.



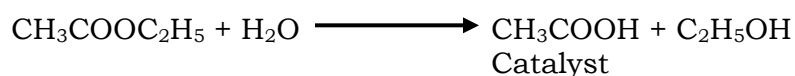
Auto catalysis

When one of the products of a reaction itself acts as a catalyst for that reaction the phenomenon is called auto-catalysis. In auto-catalysis, the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily.

Examples:

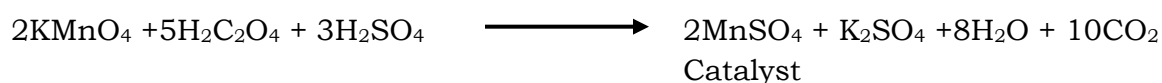
1. Hydrolysis of an ester

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. Oxidation of oxalic acid

When oxalic acid is oxidized by acidified potassium permanganate, manganese sulfate produced during the reaction acts as catalyst for the reaction.



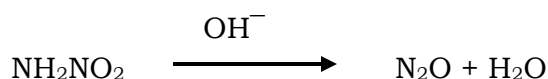
Acid Base catalysis

A number of homogeneous catalytic reactions are known which are catalyzed by acids or bases or both acids and bases. These are often referred to as Acid-Base Catalysts.

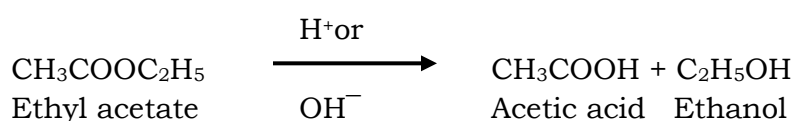
Arrhenius pointed out that acid catalysis was, in fact, brought about by H^+ ions supplied by strong acids, while base catalysis was caused by OH^- ions supplied by strong bases.

Examples:

1. Decomposition of nitramide



2. Hydrolysis of an Ester



Enzyme catalysis

This will be discussed separately at a later stage.

Characteristic of Catalyst

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them. These features are often referred to as the criteria of catalysis

1. A catalyst remains unchanged in mass and chemical composition at the end of reaction

Qualitative and Quantitative analysis shows that catalyst undergoes no change in mass or chemical nature however; it may undergo a physical change. Thus, granular manganese dioxide (MnO_2) used as catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.

2. A small quantity of catalyst is generally needed to produce almost unlimited reaction

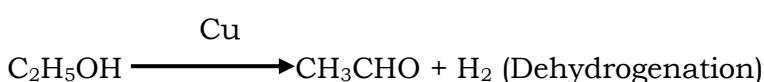
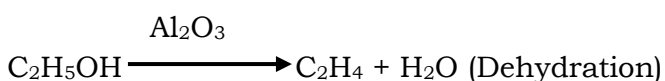
Sometimes a trace of a metal catalyst is required to affect very large amount of reactant, For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyze the decomposition of hydrogen peroxide.

3. A catalyst is more effective when finely divided

In heterogeneous catalysis the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinized asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

4. A catalyst is specific in its action

While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol ($\text{C}_2\text{H}_5\text{OH}$) gives ethane (C_2H_6) when passed over hot aluminum oxide, but with hot copper it gives ethanal (CH_3CHO)



5. A catalyst in general, cannot initiate a reaction

In most cases, a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction.

6. A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium

It implies that in a reversible reaction the catalyst accelerates the forward and reverse reaction equally. Thus the ratio of the rates of two opposing reactions i.e. equilibrium constant, remains unchanged

7. Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst

We have already studied the effect of temperature change on reversible reactions under Le Chatelier's Principle. Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise in the temperature may cause their coagulation. In such a case, the rate of reaction increases up to a certain point and then gradually decreases. The rate of reaction is maximum at a particular temperature; the optimum temperature.

Homogeneous catalytic reaction and Heterogeneous catalytic reaction

1. Phase

a. Homogeneous: Liquid.

When a reactant is in the gas form such as in hydrogenation, what reacts is actually the gas dissolved in the liquid phase, and not the one in the gas phase.

b. Heterogeneous: Liquid, Gas, Solid

2. Operative Temperature

a. Homogeneous: Generally low temperatures.

The presence of a solvent, which needs to dissolve the catalyst, might limit the temperature of the reaction.

b. Heterogeneous: The only limitation is the stability of the catalyst under harsh conditions.

3. Diffusivity

- a. Homogeneous: High diffusivity. Having all reactants and catalyst in one phase enhances dramatically the diffusivity under proper stirring.
- b. Heterogeneous: Diffusivity might be an issue for catalysts with low surface area.

4. Heat Transfer

- a. Homogeneous: High Heat Transfer. Having all reactants and catalyst in one phase enhances dramatically the heat transfer under proper stirring.
- b. Heterogeneous: Heat Transfer might be an issue due to the different heat capacities of reactants and catalyst.

5. Catalyst Separation

- a. Homogeneous: The separation of the products from the catalyst is generally expensive, the only exception being in biphasic catalysis.
- b. Heterogeneous: The separation of the products from the catalyst is usually straightforward.

6. Recycling

- a. Homogeneous: Recycling is expensive due to difficult treatment of the spent catalyst.
- b. Heterogeneous: Recycling is usually straightforward, although the catalyst might need reactivating treatment.

7. Active site

- a. Homogeneous: Usually well-defined. Catalysts are generally single atom transition metal stabilized by ligands.
- b. Heterogeneous: Mainly not well-defined. When dealing with metal particles on a support, the active site might be only a few percent of the metal (usually small particles), and different zones of the same particle might have different catalytic properties.

8. Catalyst modification

- a. Homogeneous: Relatively easy. Tuning of the electronic and steric properties on the metal can be done by varying donor atoms in the ligands or by tuning the donating abilities of the ligands.
- b. Heterogeneous: Relatively difficult. Control of the particle size and of the active site in general at the molecular level is extremely difficult. Few synthetic methods are available.

9. Reaction Mechanism

- a. Homogeneous: Easier to find out due to more techniques available. Direct methods are available.
- b. Heterogeneous: Difficult to find out. Mainly by indirect methods.

10. Selectivity

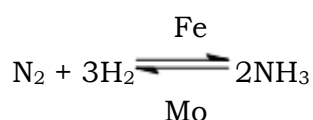
- a. Homogeneous: High. It is a consequence of the easier fine-tuning of the steric and electronic properties of the catalyst and of the easier way of finding out the reaction mechanism.
- b. Heterogeneous: Low. It is a consequence of more difficult fine-tuning of the steric and electronic properties of the catalyst and of the more difficult way of finding out the reaction mechanism.

Promoters of Catalysis (Activators)

The activity of a catalyst can often be increased by addition of in small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble-catalyst. **A substance, which though itself not a catalyst, promotes the activity of a catalyst, is called a promoter.**

Example:

Molybdenum (Mo) or aluminum oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.



Characteristics of enzyme catalysis

In general, **enzymes** behave like **inorganic heterogeneous catalysts**. However, they are unique in their efficiency and high degree of specificity. Some more **important features of enzyme catalysis** are listed below.

1. Enzymes are the most efficient catalysts known

The enzyme catalyzed reactions proceed at fantastic high rates in comparison to those catalyzed by inorganic substances. Thus one molecule of an enzyme may transform one million molecules of the substrate (reactant) per minute. Like inorganic catalysis, enzymes function by lowering the activation energy of a reaction. For example, the activation energy of the decomposition of hydrogen peroxide without a catalyst is 18kcal/mole. With colloidal platinum (inorganic catalyst), the activation energy is lowered by 11.7 kcal/mole. The enzyme catalyze lowers the activation energy of the same reaction to less than 2 kcal/mole.

2. Enzyme catalysis is marked by absolute specificity

An enzyme as a rule catalysis just one reaction with a particular substance. For example, urease (an enzyme derived from soya bean) catalysis the hydrolysis of urea and no other amide, not even methyl urea.

3. The rate of enzyme-catalyzed reaction is maximum at the optimum temperature

The rate of enzyme catalyzed reaction is increased with the use of temperature but up to a certain point. There after the denatured as its protein attendance is gradually destroyed. Thus the rate of reaction eventually drops drop and eventually becomes zero when the enzyme is completely destroyed the rate of an enzyme reaction with raising of temperature gives a bell-shaped curve. The temperature at which the reaction rate is maximum is called as optimum temperature.

4. Rate of enzyme catalyzed reaction is maximum at the optimum pH

The rate of an enzyme-catalyzed reaction varies with pH of the system. The rate passes through a maximum at a particular pH, known as the optimum pH. The enzyme activity is lower at other values of pH. Thus many enzymes of the body function best at pH of about 7.4, the pH of the blood and body fluids.

5. Enzymes are markedly inhibited or poisoned

The catalytic **activity** of an enzyme is often reduced (inhibited) or complete **destroyed** (poisoned) by **addition of other substances**. These inhibitors or poisons interact with the active functional groups on the enzyme surface. For example, heavy metal ions (Ag^+ , Hg^+) react with the $-\text{SH}$ groups of the enzyme and poison it.

6. Catalytic activity of enzymes in greatly enhanced by the presence of Activators or Coenzymes

Activators are **metal ions** Na^+ , Mn^{2+} , Co^{2+} , Cu^{2+} etc., which got weakly bonded to enzyme molecules and **promote** their catalytic action. Thus it has been found that the addition of sodium chloride (Na^+) makes amylose catalytically very active. Often, a small non-protein (vitamin) termed a coenzyme when present along with an enzymes, promotes the catalytic activity of the latter.

Introduction (Adsorption)

Many physical and chemical processes occur at different interfaces. Adsorption (not to be confused with absorption) is one of the main and basic surface phenomena. Adsorption is found to occur in many natural physical, biological, and chemical systems. It is widely used in laboratory research and industrial applications.

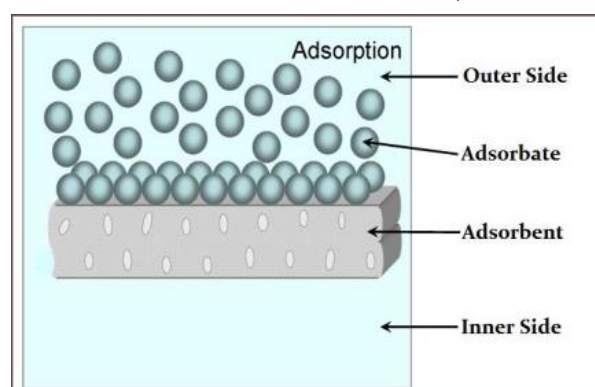
Solid surfaces show strong affinity for gas molecules that come in contact with them, and some of them are trapped on the surface.

Adsorption: In adsorption process spontaneous accumulation of a gas or vapor (adsorbate) takes place at the solid surface (adsorbent or substrate) as compared to the bulk phase.

The reverse process of adsorption is called **desorption**.

Adsorbent: A solid on which adsorption occurs (usually it is a porous material of a large specific surface (m/g)).

Adsorbate: A substance (gas or vapor) which is adsorbed on a solid surface (adsorbent).



Absorption: A process in which a gas diffuses into the solid absorbing medium.

Sorption: It is often difficult to find the difference between adsorption and absorption, and that is why the term sorption is used.

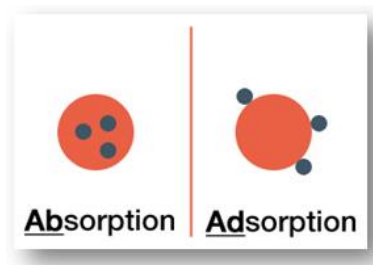
Positive adsorption: If the concentration of adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption. Example: When a concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption.

Negative adsorption: If the concentration of the adsorbate is less than its concentration in the bulk then it is called negative adsorption. Example: When a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption.

What is the difference Between Adsorption and Absorption?

The distinction between absorption and adsorption should be clearly understood. Some of the differences are:

- ✓ Adsorption is surface phenomenon, while absorption concerns with the whole mass of the absorbent.
- ✓ In adsorption, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid. Absorption implies that substance is uniformly distributed throughout the body of the solid or liquid.
- ✓ In adsorption, the concentration of the adsorbed molecules is always greater in the immediate vicinity of the surface than in the free phase. Absorption involves bulk penetration of the molecules into the structure of the solid or liquid by some process of diffusion.
- ✓ Adsorption is a rapid process and equilibrium is attained in a short time. In absorption the equilibrium takes place slowly.



Examples of Adsorption and Absorption

- ✓ Water vapors is absorbed by anhydrous calcium chloride, while it is adsorbed by silica gel.
- ✓ Ammonia is absorbed in water forming NH_4OH , while adsorbed by charcoal.
- ✓ Acetic acid and iodine are adsorbed.
- ✓ Nitrogen gas is adsorbed on mica.
- ✓ Oxygen is adsorbed by tungsten surface.
- ✓ Decolorisation of sugar solution by activated charcoal is adsorption of coloring matter on charcoal.
- ✓ If a blotting paper is kept in contact with ink, the latter is absorbed, because it penetrates uniformly into the absorbent, the blotting paper.

Examples of Adsorbent and Adsorbate

The common adsorbents are charcoals (both vegetable and animal charcoal), silica gel (it can be prepared by heating a mixture of sodium silicate with 10% HCl at 50°C). Metals, such as Ni, Cu, At, Pt and Pd (these are prepared by reducing their oxide or their salts under suitable experimental conditions), and colloids, as they possess high surface area per unit mass.

Various gases, such as He, Ne, H_2 , N_2 , O_2 , SO_2 , NH_3 etc. and substances, such as NaCl, KCl etc. in solution can be adsorbed by suitable adsorbents.

Reversible and Irreversible Adsorption

The adsorption is **reversible**, if the adsorbent can be easily removed from the surface of the adsorbent by physical methods. It is called **irreversible adsorption**, if the adsorbate cannot be removed from the surface of the adsorbent. A gas adsorbed on a solid surface can be completely removed in vacuum. It is, therefore, reversible adsorption. Examples of irreversible adsorption are adsorption of oxygen on tungsten adsorbate and adsorption of CO on tungsten surface.

Characteristics of Adsorption

- ◆ The phenomenon of adsorption strictly refers to the existence of a higher concentration of any particular component at the surface of a liquid or a solid phase than is present in the bulk or interior. For example, five types of interfaces can exist (i) gas solid (ii) liquid solid (iii) liquid – liquid, (iv) solid – solid and gas solid.
- ◆ Adsorption is a specific and selective phenomenon. In other words, to what extent a certain substance will be adsorbed by an adsorbent depends on the physical and chemical nature of both adsorbent as well as the adsorbate. It is not possible to predict the extent of

adsorption in any combination. However, it has actually been found that easily liquefiable gases are more easily adsorbed.

- ◆ Adsorption is accompanied by a decrease in the free energy of the system (dG is negative). Adsorption will continue to such an extent that dG continues to be negative. When dG becomes zero, i.e., $dG = 0$, adsorption equilibrium is said to be established. Since decrease in dH (Heat content) appears as heat, adsorption process is always **exothermic**.

Factors Affecting Adsorption

- **Temperature:** Adsorption is an exothermic process. Therefore in accordance with Le Chatelier's principle, the magnitude of adsorption should increase with decrease in temperature. It is in the case of physical adsorption. Chemical adsorption first increases with rise in the temperature and then starts decreasing.
- **Pressure:** With increase of pressure, adsorption increases up to certain extent till saturation level is achieved no more adsorption takes place no matter how high the pressure applied.
- **Surface area:** It's a surface phenomenon therefore adsorption capacity of adsorbent increases with increase in its surface area. Smaller the size of particles of solid adsorbents more is the extent of adsorption at its surface interface
- **Activation of Solid Adsorbent:** Activation of adsorbent surface done so as to provide more vacant sites on surface. This can be done by breaking solid crystal in small pieces, breaking lump of solid into powders or sub-dividing the adsorbent
- **Nature of Adsorbate and Adsorbent:** The amount of the gas adsorbed depends upon the nature of adsorbent and the gas (adsorbate), which is to be adsorbed. It has been found that easily liquefiable gases such as NH_3 , HCl , Cl_2 , SO_2 , CO_2 etc. are more readily adsorbed than so the called permanent gases such as O_2 , N_2 , H_2 etc. This is because that molecules of the former type of gases have greater Vander waal's or molecular force of attraction.

Physical and chemical adsorption

The adsorption process is generally classified as either

- ◆ Physisorption (physical adsorption) or
 - ◆ Chemisorption (chemical adsorption).
- Physisorption is the most common form of adsorption.

Physisorption (physical adsorption)

Adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapors, and which do not involve a significant change in the electronic orbital patterns of the species involved.

Chemisorption (chemical adsorption)

Chemisorption (or chemical adsorption) is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds.

Difference between Physisorption and Chemisorption

Physisorption (Physical adsorption)	Chemical adsorption
In this type of adsorption, the adsorbate is attached to the surface of the adsorbent with weak van der Waal's forces of attraction.	In this type of adsorption, strong chemical bonds are formed between the adsorbate and the surface of the adsorbent.
No new compound is formed in the process.	New compounds are formed at the surface of the adsorbent.
Depends on nature of gas. Easily liquefiable gases are adsorbed readily.	Much more specific and depends upon the nature of the both the adsorbate and adsorbent.
Enthalpy of adsorption is low as weak van der Waal's forces of attraction are involved. The values lie in the range of 20-40 $kJ\ mol^{-1}$.	Enthalpy of adsorption is high as chemical bonds are formed. The values lie in the range of 40-400 $kJ\ mol^{-1}$.
It is generally found to be reversible in nature.	It is usually irreversible in nature.
Occurs at low temperature; decreases with increase in temperature.	Takes place at high temperature. first increases and then starts decreasing with rise in temperature

It is an example of multi-layer adsorption.	It is an example of mono-layer adsorption.
Increase of pressure increases adsorption	High pressure is favorable. Decrease of pressure does not cause desorption.
Equilibrium is attained readily and it is reversible.	Equilibrium is attained slowly and mostly not reversible.

Freundlich Adsorption Isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.

$$\frac{x}{m} = kp^n$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. (x/m) = amount of adsorption.

Explanation of Freundlich Adsorption equation

At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$\frac{x}{m} \propto p^1$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero).

$$\frac{x}{m} \propto p^0$$

Therefore at intermediate value of pressure, adsorption is directly proportional to pressure raised to power 1/n. Here n is a variable whose value is greater than one.

$$\frac{x}{m} \propto p^{\frac{1}{n}}$$

Using constant of proportionality, k, also known as adsorption constant we get

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

The above equation is known as Freundlich adsorption equation.

As per Freundlich adsorption equation

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

Taking log both sides of equation, we get,

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log p$$

The equation above equation is comparable with comparable with equation of straight line, $y = m x + c$ where, m represents slope of the line and c represents intercept on y axis.

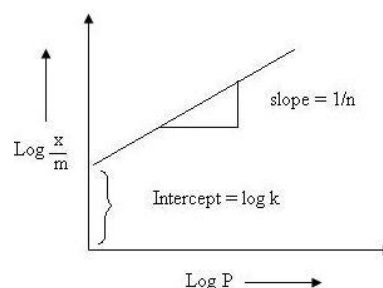
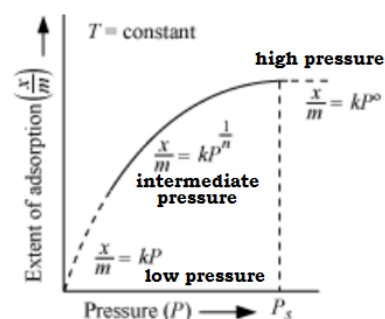
Plotting a graph between $\log(x/m)$ and $\log p$, we will get a straight line with value of slope equal to $1/n$ and $\log k$ as y-axis intercept.

The value of 'n' is generally greater than one and thus the reciprocal, $1/n$, can have values between 0-1. Based on this, Freundlich isotherm is able to explain the monolayer adsorption isotherm as follows:

- ✓ When $\frac{1}{n} = 0$, $\frac{x}{m} = \text{constant}$. This means that extent of adsorption is independent of pressure.
- ✓ When $\frac{1}{n} = 1$, $\frac{x}{m} = kp$. This means that extent of adsorption varies linearly with pressure.
- ✓ In the intermediate range, $\frac{1}{n}$ varies between 0-1. This accounts for the fact that the increase in adsorption is not as fast as the increase in pressure.

Although, Freundlich isotherm gave satisfactory results, it was associated with the following limitations:

- It was an empirical relation; there was no theoretical foundation.
- It failed at high pressures as the experimental isotherm approached saturation at high pressures, which Freundlich isotherm could not explain.
- K and n are not true constants for a particular adsorbate-adsorbent system. They show temperature dependence.

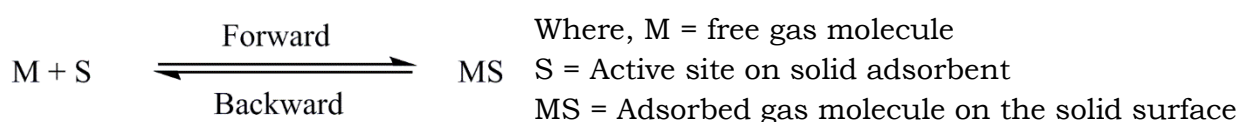


Langmuir Adsorption isotherm

Freundlich adsorption isotherm is empirical. There is no theoretical basis. Langmuir derived a new isotherm on basis of kinetic theory of gases which is called Langmuir adsorption isotherm.

The various assumption of Langmuir adsorption isotherm are as follows:

1. Adsorption of adsorbate molecules takes place only on fixed number of adsorption sites that are available on the surface of (solid) adsorbent.
2. Adsorption is a process of 'sticky collision'.
3. All active sites on the adsorbent surface are energetically equivalent, i.e., they involve constant heat of adsorption.
4. The surface of the solid adsorbent is assumed to be completely flat and uniform on microscopic dimensions.
5. Under conditions of low pressure and moderately high temperature, a monomolecular layer of adsorbate molecules is formed on the adsorbent surface.
6. There are no interactions between the gas molecules that are getting adsorbent on the adsorbent surface; adsorption of gas molecules takes place independent of the occupation of the neighboring sites. These gaseous molecules are thus assumed to behave ideally.
7. A state of dynamic equilibrium exists as follows:



This means that adsorption takes place on vacant sites and desorption takes place from occupied sites, till a state of equilibrium is attained.

As per the law of mass action,

Rate of forward reaction (adsorption) = $K_f[M][S]$

Rate of back ward reaction (desorption) = $K_b[MS]$

At equilibrium, Rate of adsorption = rate of desorption

$$K_f [M][S] = K_b[MS]$$

$$K_1 = \frac{K_f}{K_b} = \frac{[MS]}{[M][S]}$$

Where, K_1 = equilibrium constant for distribution of adsorbate molecules between adsorbent surface and gas phase

Derivation of Langmuir adsorption isotherm

On the basis of above postulates, Langmuir derived the equation as follows.

Under conditions of constant temperature and pressure, let the number of adsorbate molecules hitting unit area of the adsorbent in unit time t , = N

Let the fraction of surface area of the adsorbent that is covered = θ

Therefore, the uncovered surface area of the adsorbent = $1 - \theta$

Now,

Rate of desorption $\propto \theta$

or Rate of desorption = $K_d\theta$

Where K_d is a constant for desorption

The rate of adsorption will be proportional to uncovered surface area of the adsorbent, and the number of adsorbate molecules hitting unit area of adsorbent in unit time. The latter, in turn, will be proportional to the pressure of the gas.

Thus, we have

Rate of adsorption $\propto P(1-\theta)$

or Rate of adsorption = $K_aP(1-\theta)$

Where K_a is a constant for adsorption

At equilibrium,

Rate of adsorption = Rate of desorption

$$K_aP(1-\theta) = K_d\theta$$

$$K_aP - K_aP\theta = K_d\theta$$

$$K_d\theta + K_aP\theta = K_aP$$

$$\theta = \frac{K_a P}{K_d + K_a P} \quad \theta = \frac{K_a/K_d P}{1 + K_a/K_d P}$$

$$\theta = \frac{K_1 P}{1 + K_1 P}$$

Where, $K_1 = K_a/K_d$

This is known as the Langmuir adsorption equation.

Explanation of Langmuir adsorption isotherm

One of the main approximations for Langmuir adsorption isotherm is the formation of monolayer of adsorbate molecules on the surface of the adsorbent.

Therefore, mass of gas molecules, x , adsorbed on a unit mass, m , of the adsorbent, will be directly proportional to the fractional coverage, θ ,

$$\frac{x}{m} \propto \theta$$

$$\frac{x}{m} = K_2 \theta$$

Substituting the value of θ from above

We get,

$$\frac{x}{m} = \frac{K_2 K_1 P}{1 + K_1 P} \text{----- (A)}$$

Using this equation, monolayer adsorption isotherm can be explained as follows:

[i] At low pressure, $K_1 P \ll \ll 1$,

Therefore,

$$\frac{x}{m} \cong K_2 K_1 P$$

Or,

$$\frac{x}{m} \propto P$$

Thus, at low pressures, the extent of adsorption is directly proportional to the pressure of the gas. This explain the monolayer adsorption isotherm at low pressures.

[ii] At high pressure, $K_1 P \gg \gg 1$,

Therefore,

$$\frac{x}{m} \cong \frac{K_2 K_1 P}{K_1 P}$$

Or,

$$\frac{x}{m} = K_2$$

Thus, at high pressure, the extent of adsorption becomes independent of the pressure of the gas. This explain the monolayer adsorption isotherm at high pressures.

[iii] For intermediate values of pressure, the variation in the extent of adsorption is not proportional to the latter.

This is because of the presence of a pressure dependent term in the denominator of equation (A), because of which the denominator increases faster with pressure, as compared to the numerator.

Thus,

$$\frac{x}{m} \propto P^n$$

where, $n = 0-1$

Thus, under conditions of intermediate pressure, Langmuir adsorption can be reduced to Freundlich isotherm equation.

The validity of Langmuir adsorption isotherm can be verified by the graphical method.

Using equation (A),

$$\frac{x}{m} = \frac{K_2 K_1 P}{1 + K_1 P}$$

$$\frac{m}{x} = \frac{1 + K_1 P}{K_2 K_1 P} = \frac{1}{K_2 K_1 P} + \frac{1}{K_2}$$

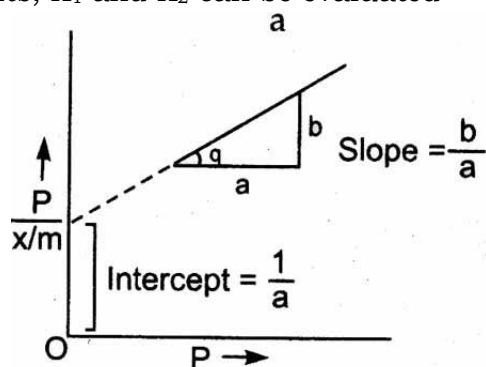
or,

$$\frac{P}{x/m} = \frac{1}{K_2 K_1} + \frac{P}{K_2}$$

Compare this equation $Y = MX + C$

A straight line plot between $\frac{P}{x/m}$ and P will validate Langmuir adsorption isotherm. This will give slope, $\frac{1}{K_2}$ and intercept, $\frac{1}{K_2 K_1}$.

From these values, the constants, K_1 and K_2 can be evaluated



Sometimes, deviations are observed from linearity. This means that for a particular adsorbate-adsorbent system, plot between $\frac{P}{x/m}$ and P does not give a straight line.

This may be due to the following reasons:

- Partial adsorption or multilayer formation of adsorbent molecules on the surface of the adsorbent occurs.
- There occurs some chemical reaction between adsorbate molecules and adsorbent surface.
- The active sites on the surface of adsorbent are not energetically equivalent.

Application or uses of adsorption:

There are many application of adsorption phenomenon some of them are as follows:

- ◆ Charcoal adsorbent is used to produce high vacuum in adsorption of small proportion of gases.
- ◆ While working in the atmosphere of poisonous gas like chlorine, the gas mask that are used contains active charcoal as adsorbent which adsorbs poisonous gas and provides protection.
- ◆ Silica gel is used as adsorbent for keeping electronic instruments etc. free from moisture.
- ◆ Activated charcoal is used for removal of impurity of color from sugar and other substances.
- ◆ Vanadium pentoxide used as heterogeneous catalyst in production of sulfuric acid and iron powder used as heterogeneous catalyst in production of ammonia are useful as solid adsorbents.
- ◆ In separation of inert gases by Dewar's method activated charcoal is used as adsorbent.
- ◆ Substances used for treatment of certain diseases act as adsorbent and adsorb the microorganism.
- ◆ In froth floatation method, in concentration of sulphide minerals, turpentine oil or pine oil are used as adsorbents.
- ◆ In certain titration eosin or fluorescein is used as indicator e.g. in the titration of halide with silver nitrate adsorbate like fluorescein is adsorbed on the precipitates of silver halide such indicators are called adsorption indicators.
- ◆ In chromatographic separation, solid substance can be used as adsorbent and separation of inorganic anions, mixtures of amino acid, analysis of dyes in the ink can be carried out by adsorption chromatography.

Strong Concepts + Smart Practice = Success

Best of Luck