

SURFACE CHEMISTRY

TOPIC-1

Concepts of adsorption and absorption, Langmuir and Freundlich adsorption isotherms and effects of temperature on surface phenomena, Catalysis and types of catalysis

VERY SHORT ANSWER QUESTIONS

1. What is adsorption?

Adsorption: The phenomenon in which the molecules of a substance are attracted and adhered to the surface of a solid or liquid. Adsorption is a surface phenomenon. Adsorption is an exothermic reaction. Released heat is called Heat of adsorption.

2. What is absorption?

When a substance is uniformly distributed throughout the bulk of another substance, this shows that absorption has taken place. It occurs at the uniform rate throughout the body of the material

3. What is physisorption?

Physical adsorption : In physisorption Weak – Vanderwall's forces exist between adsorbent and adsorbate.

Eg: Charcoal adsorbs gases. Charcoal adsorbs acetic acid ; Silica jel adsorbs moisture

4. What is Chemisorption?

Chemical adsorption: In chemisorption strong chemical forces will exist between adsorbate and adsorbent and these forces may be ionic or covalent.

Eg: Adsorption of H₂, N₂, O₂ gases by Ni, Pd, Pt etc..

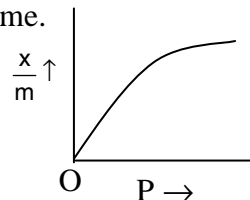
5. Give the mathematical equation relating the pressure (P) and the extent of adsorption (x/m) of gas on metal.

These adsorption isotherms will explain the variation magnitude of adsorption with pressure at given temperature. These are obtained by plotting magnitude of adsorption Vs pressure.

As shown below rate of adsorption increases with pressure after reaching a limiting value rate of adsorption remains constant and that pressure is called equilibrium pressure. At that stage, rate of adsorption and rate of desorption are same.

Freundlich adsorption isotherm,

$$\frac{x}{m} \propto p^{1/n}; \quad \frac{x}{m} = kp^{1/n}$$

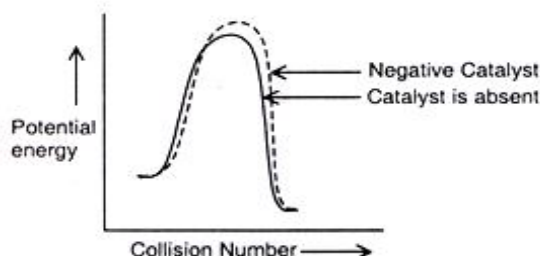


6. What is a catalyst?

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

7. What is negative catalyst?

(ii) **Negative catalysis (Inhibitor or retarder):** Chemical reactions are sometimes retarded by the presence of a foreign substance the substance is known as a negative catalyst.



Examples

Alcohol, Acetanilide: Prevents oxidation of Na_2SO_3 by air

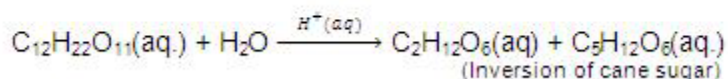
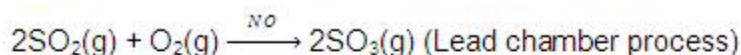
H_3PO_4 : Prevents decomposition of H_2O_2 .

8. What is auto catalysis?

Auto catalysis: In this type of catalysis, one of the products of the reaction catalyses the reaction. In the oxidation of oxalic acid by KMnO_4 , Mn^{2+} ion formed is known to accelerate the reaction. So, when KMnO_4 solution is run into warm solution of oxalic acid (+ dil. H_2SO_4), initially there is a time lag before decolourisation occurs; as more KMnO_4 is added, the decolourisation becomes almost instantaneous.

9. What is Homogeneous catalysis?

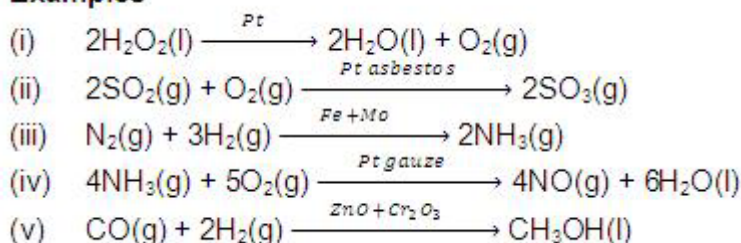
Homogeneous catalysis: A catalytic process in which the catalyst is in the same phase as the reactant is called homogenous catalysis.



10. What is Heterogeneous catalysis?

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

Examples



11. What is induced catalysis?

Induced catalyst: When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

SHORT ANSWER QUESTIONS

1. Explain the types of adsorptions.

Adsorption: The phenomenon in which the molecules of a substance are attracted and adhered to the surface of a solid or liquid. There are two types of adsorption. They are;

- **Physical adsorption**
- **Chemical adsorption**

Physical adsorption: In physical adsorption Weak – Vander wall’s forces exist between adsorbent and adsorbate.

Eg: Charcoal adsorbs gases. Charcoal adsorbs acetic acid; Silica gel adsorbs moisture

Chemical adsorption: In chemisorption strong chemical forces will exists between adsorbate and adsorbent and these forces may be ionic or covalent.

Eg: Charcoal adsorbs gases. Charcoal adsorbs acetic acid; Silica gel adsorbs moisture..

2. Write the differences between Physical adsorption and chemical adsorption.

Adsorption	Absorption
1. Charcoal adsorbs acetic acid from solutions.	Sponge absorbs water.
2. Animal charcoal adsorbs colours and impurities from cane sugar solutions.	Anhydrous CaCl_2 absorbs moisture
3. Activated charcoal adsorbs noble gases.	NaOH absorbs moisture and $\text{CO}_2 \rightarrow$ hygroscopic
4. Silica gel adsorbs moisture	Ammonical cuprous chloride absorbs

	CO and acetylene.
5. Transition metals adsorb gases like H ₂ , N ₂ , O ₂ etc.,	Terpentine oil absorbs ozone.
6. Fuller's earth (impure clay) adsorbs impurities from vegetable oils.	Pyrogallol absorbs oxygen.
7. Ni adsorbs H ₂ gas in the manufacture of Dalda.	Chalk dipped in ink.

3. Explain the factors that effect the adsorption of gases on metals.

Ans:

Adsorption of a gas by solids:

1. Activation: Removal of impurities and cleaning the surface of adsorbent is called activation. Activation is done by heating in vacuum or in presence of inert gas. Activated adsorbent has more adsorption capacity.

2. Nature of the gas: The gas with higher critical temperature is easily liquefiable. The easily liquefiable gases are more readily adsorbed.

Eg: HCl, SO₂, NH₃, CO₂

Pressure: With increase in pressure physical adsorption increases, effect of pressure on chemical adsorption is negligible

Temperature: Low temperature favours physical adsorption and high temperature favours chemical adsorption. In some cases increases in temperature will convert physical adsorption into chemical adsorption.

Eg: At 463 K N₂ is physically adsorbed by iron.

At 773 K N₂ is chemically adsorbed by iron

4. Explain Freundlich adsorption isotherm

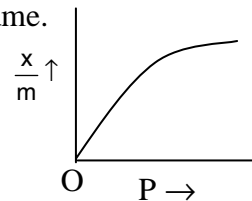
Adsorption isotherm : These adsorption isotherms will explain the variation magnitude of adsorption with pressure at given temperature. These are obtained by plotting magnitude of adsorption Vs pressure.

As shown below rate of adsorption increases with pressure after reaching a limiting value rate of adsorption remains constant and that pressure is called equilibrium pressure. At that stage, rate of adsorption and rate of desorption are same.

Freundlich adsorption isotherm,

$$\frac{x}{m} \propto p^{1/n} ; \frac{x}{m} = kp^{1/n}$$

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



$$\frac{x}{m} = \text{magnitude of adsorption. } P = \text{pressure}$$

x = amount of gas adsorbed m = mass of adsorbent

value of n is equal to 0 to 1

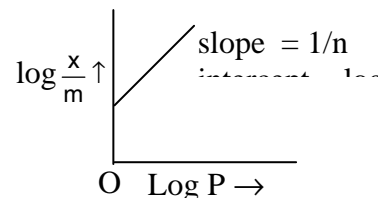
at low pressure n = 1

at high pressure n = 0

at optimum pressure n = > 0 / < 1

by applying logarithm on both sides of Freundlich equation.

$\text{Log } \frac{x}{m} = \text{logk} + \frac{1}{n} \text{logp}$ by plotting $\text{log}(x/m)$ verses 'logp' a straight line is obtained, slope gives n and intercept gives 'logk'.



5. Explain Langmuir adsorption isotherm

Langmuir adsorption isotherm: Langmuir has theoretically derived the following expression which explains the variation of adsorption with pressure at given temperature

$$\frac{x}{m} = \frac{bp}{1+ap} \quad \text{p = pressure, a, b = constant}$$

Freundlich isotherm is a special case of Langmuir adsorption isotherms.

Langmuir adsorption isotherms are applicable for uni molecular layer adsorption.

Both Freundlich and langmuir adsorption isotherms hold good at low pressure and fail at high pressure.

LONG ANSWER QUESTIONS

1. Explain the terms adsorption and absorption with at least two examples. Give the differences between physical adsorption and chemical adsorption.

Adsorption

The phenomenon of existence of a substance in different concentrations at the surface of another substance than in the bulk phases is called **adsorption**.

The substance whose surface **adsorbs** molecular species of another substance is called adsorbent and the substance, which gets adsorbed, is called **adsorbate**.

Ex: 1. Charcoal adsorbs gases. Charcoal adsorbs acetic acid; Silica gel adsorbs moisture.

2. Charcoal adsorbs gases. Charcoal adsorbs acetic acid; Silica gel adsorbs moisture

Absorption

When a substance is uniformly distributed throughout the bulk of another

substance, this shows that absorption has taken place. It occurs at the uniform rate throughout the body of the material.

Ex: Absorption of water by Sponge.

In certain cases, both the adsorption and the absorption take place simultaneously and it is not easy to distinguish them. Such substance is said to be absorbed and the phenomenon is known as absorption.

The differences between physisorption and chemisorption are;

Adsorption	Absorption
1. Charcoal adsorbs acetic acid from solutions.	Sponge absorbs water.
2. Animal charcoal adsorbs colours and impurities from cane sugar solutions.	Anhydrous CaCl_2 absorbs moisture
3. Activated charcoal adsorbs noble gases.	NaOH absorbs moisture and $\text{CO}_2 \rightarrow$ hygroscopic
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7. Ni adsorbs H_2 gas in the manufacture of Daldal.	Chalk dipped in ink.

2. Give an account of adsorption of gases by metals with examples.

Adsorption of Gases on Solids

The extent of adsorption of a gas on the surface of a solid depends on the following factors:

- Nature of gas
- Nature of solid
- Specific area of solid
- Pressure of gas
- Temperature
- Activation of solid

(i) Nature of gas:

Since physical adsorption is non-specific in nature, any gas will be adsorbed on the surface of a solid to some extent or other. However, under any given conditions of temperature and pressure, easily liquefiable gases such as NH_3 , CH_4 , HCl , Cl_2 , SO_2 , CO etc. are adsorbed more than permanent gases like H_2 , O_2 , N_2 etc. Chemisorption is specific in nature. Therefore, only those gases will be adsorbed which form chemical bonds with it.

(ii) Nature of solid:

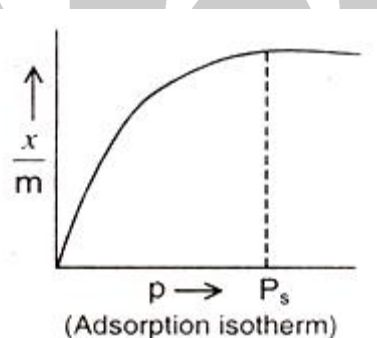
Activated charcoal is the most common adsorbent for easily liquefiable gases. Poisonous gases such as CH_4 and CO fall in this group. Therefore, it is used in gas masks. Other gases such as O_2 , H_2 and N_2 adsorb more on metals such as Ni , Pt and Pd .

(iii) Specific area of solid:

Specific area of an adsorbent is the surface area available for adsorption per gm of adsorbent. Greater the specific area of an adsorbent, greater will be the adsorption. The specific area of an adsorbent can be increased by making the surface rough. The pores must be large enough to allow penetrations of gas molecules.

(iv) Pressure of a gas:

As physical adsorption is reversible, it is accompanied by decrease in pressure. Therefore, it is expected that at a given temperature the extent of adsorption will increase with the increase of pressure of the gas. The extent of adsorption is measured as x/m where m is the mass of adsorbent and x that of adsorbate. If the physical adsorption is limited to uni molecular layer, the plot of x/m vs. equilibrium pressure at a constant temperature is as shown.



It is evident from the graph that at a certain pressure the adsorption reaches a maximum value i.e. the adsorption becomes saturated and the corresponding pressure is called saturation pressure (P_s). Beyond this pressure the adsorption remains constant.

At low pressures, x/m varies linearly with p
 $x/m \propto p^1$ or $x/m = kp^1$

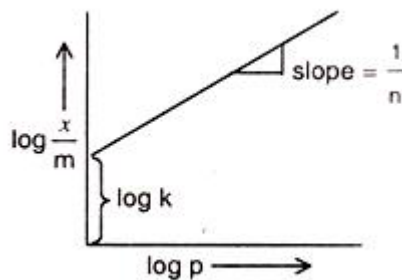
At high pressures, x/m is independent of p
 $x/m \propto p^0$ or $x/m = kp^0$

At intermediate pressures, the variation of x/m vs p can be expressed as $x/m \propto p^{(1/n)}$ where

$$n > 1.$$

$$\text{or } x/m = k p^{(1/n)}$$

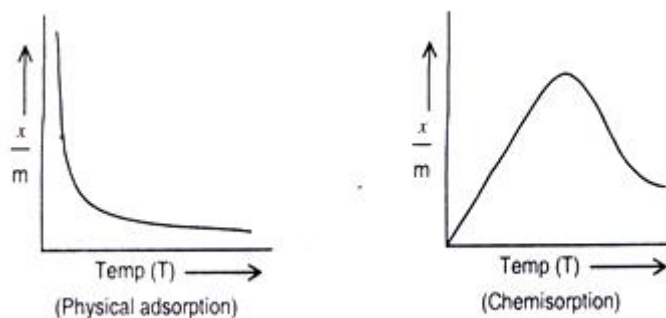
$$\text{or } \log x/m = \log k + 1/n \log p$$



This is called **Freundlich adsorption isotherm**.

(v) Temperature

As adsorption is accompanied by release of heat energy, so in accordance with Le-Chatelier's principle, the increase of temperature should decrease the extent of adsorption. This has indeed been found to be so. A plot of x/m vs. temperature at constant pressure is called adsorption isobar. In the case of physical adsorption x/m decreases with increase of temperature. However, in the case of chemisorption x/m initially increases with temperature and then decreases as shown below. The initial increase is due to the fact that chemisorptions require activation energy.



(vi) Activation of solid:

Activation of adsorbent means increasing its adsorbing power. This is increased by increasing specific area either by making the surface rough or by breaking the solid into smaller particles. But care must be taken so that particles do not become very

small, otherwise the inter-particle spaces will be too small to allow penetration of gas molecules.

3. Give an account of Langmuir adsorption isotherm.

Langmuir Isotherm

Langmuir adsorption isotherm is based on the following assumptions.

- i) Adsorption does not proceed beyond monolayer coverage.
- ii) All the sites available on the adsorbent surface are equivalent and the surface is perfectly uniform, that is flat.
- iii) The ability of a gas molecule to get adsorbed at a particular site is independent of the occupation of neighboring sites. This implies that there is no interaction between adjacent adsorbed molecules.
- iv) A dynamic equilibrium exists between the adsorbed molecules and the free gas molecules.

Initially, since the surface is completely bereft of any gas molecules, every molecule of the gas that strikes the surface of solid may get adsorbed. After some time, only those gas molecules may get adsorbed which strike the part of the surface that is not already covered. This means, that initially the rate of adsorption is high and then decreases as less surface is available for adsorption.

Since a dynamic equilibrium exists between the adsorbed molecules and the free gas molecules, it implies that the adsorbed molecules also undergo desorption, probably due to thermal agitation. When the rate of adsorption equals the rate of desorption, dynamic equilibrium is attained.

If q is the fraction of the total available surface covered with gas molecules, at any instant, then $(1-q)$ is the fraction of the surface of the solid which is empty. From kinetic theory of gases, it is known that the rate at which gas molecules collide per unit area of a surface is directly proportional to the pressure of the gas. The rate of adsorption depends on both the pressure of the gas and fraction of surface available for adsorption. Hence,

$$\text{Rate of adsorption} = K_a (1-q) P \dots\dots(3)$$

$$\text{Rate of desorption} = K_d (q) \dots\dots(4)$$

At equilibrium, the rate of adsorption is equal to the rate of desorption i.e.,

$$K_a (1-q) P = K_d (q)$$

$$\text{or, } \theta = \frac{K_a P}{K_d + K_a P}$$

$$\text{or, } \theta = \frac{KP}{1 + KP} \quad \dots (5)$$

$$\text{where } K = \frac{K_a}{K_d}$$

Now, the extent of adsorption (x/m) is proportional to the fraction of surface covered. Therefore,

$$\frac{x}{m} = k\theta = \frac{kKP}{1 + KP} \quad \dots (6)$$

$$\text{or, } \frac{x}{m} = \frac{aP}{1 + KP} \quad \dots (7) \quad (a = kk)$$

This is the equation which describes the Langmuir adsorption isotherm. Here a and K are the Langmuir parameters and are characteristic of a particular system at a particular temperature.

At very high pressure, the Langmuir isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{k} \quad \dots (8)$$

At very low pressure,

$$\frac{x}{m} = aP \quad \dots (9)$$

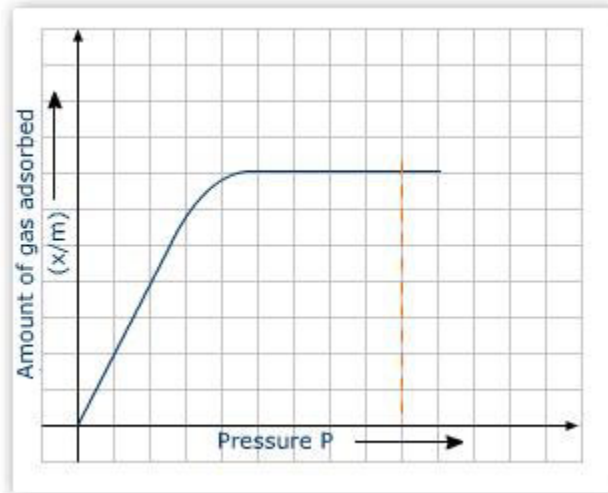
i.e., the extent of adsorption is proportional to pressure.

The parameters a and K can be determined by taking the inverse form of equation 7.

$$\frac{m}{x} = \frac{1}{ap} + \frac{K}{a} \quad \dots (10)$$

A plot of m/x against $1/P$ gives a straight line with slope and intercept equal to $1/a$ and K/a respectively.

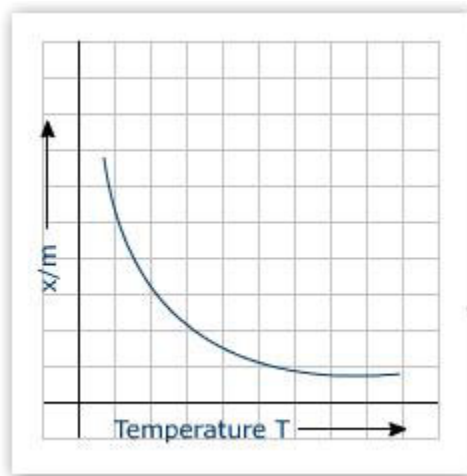
Langmuir isotherm shows that at low pressures of the adsorbate, the extent of adsorption is linear and at high pressure the extent of adsorption is a constant. This form of isotherm is shown in figure 7.4.



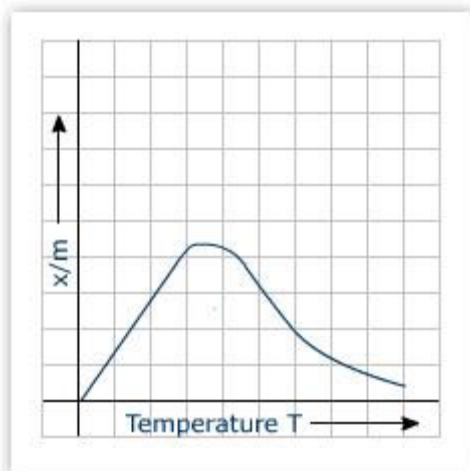
Langmuir adsorption isotherm

v) Effect of temperature

Most adsorption processes are exothermic; hence adsorption decreases with increasing temperature. This is especially true for physisorption. For chemisorption, extent of adsorption initially increases with temperature and then decreases. The plot of extent of adsorption versus temperature T at a constant pressure is called the adsorption isobar. How the extent of adsorption (x/m) varies with temperature for physisorption and chemisorption as shown in figures 7.5 (a) and 7.5 (b).



Physical adsorption at a given pressure



Chemical adsorption at a given pressure

In chemisorption, the initial increase of x/m with temperature is due to the fact that like chemical reactions, chemisorption also requires activation energy.

(vi) Activation of adsorbent

Activation of an adsorbent implies enhancing the adsorptive powers of an adsorbent. This is done by either increasing the specific area of the adsorbent by breaking the solid adsorbent into fine pieces or activating the surface of the adsorbent by specific treatments. How charcoal is activated is already discussed in the section pertaining to nature of the adsorbent.

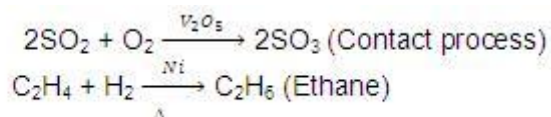
4. What is catalysis? How catalysis is classified? Give two examples for each.

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

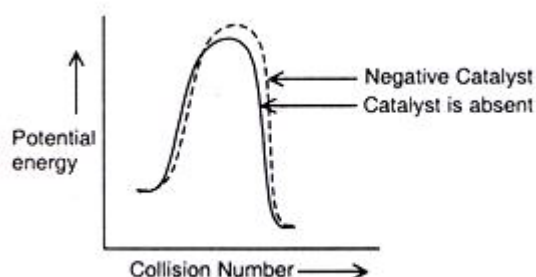
Types of Catalysts

(i) **Positive catalysis:** The catalyst increases the rate of a reaction.

Example:



(ii) **Negative catalysis (Inhibitor or retarder):** Chemical reactions are sometimes retarded by the presence of a foreign substance the substance is known as a negative catalyst.



Examples

Alcohol, Acetanilide: Prevents oxidation of Na_2SO_3 by air

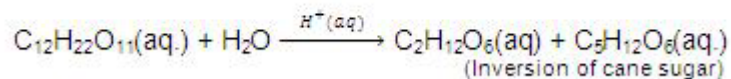
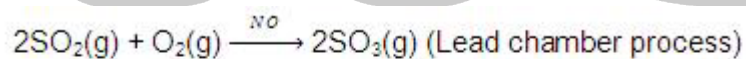
H_3PO_4 : Prevents decomposition of H_2O_2

(iii) Auto catalysis: In this type of catalysis, one of the products of the reaction catalyses the reaction. In the oxidation of oxalic acid by KMnO_4 , Mn^{2+} ion formed is known to accelerate the reaction. So, when KMnO_4 solution is run into warm solution of oxalic acid (+ dil. H_2SO_4), initially there is a time lag before decolourisation occurs; as more KMnO_4 is added, the decolourisation becomes almost instantaneous.

5. Explain Homogeneous and Heterogeneous catalysis. Give two examples for each.

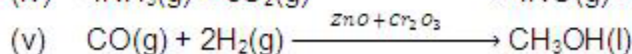
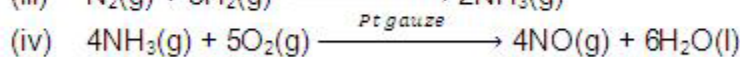
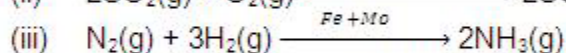
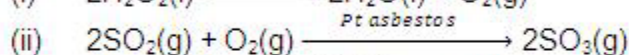
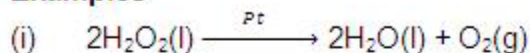
Types of Catalysts

(iv) Homogeneous catalysis: A catalytic process in which the catalyst is in the same phase as the reactant is called homogenous catalysis.



(v) Heterogeneous catalysis: A catalytic process in which the catalyst and the reactants are in different phases is called heterogeneous catalysis. This process is also called contact or surface catalysis.

Examples



(vi) Induced catalyst: When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

Examples of induced catalysis:

(1) Sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

(2) The reduction of mercuric chloride (HgCl_2) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of KMnO_4 and HgCl_2 , both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of HgCl_2 .

6. What are the characteristics of a catalyst?

Characteristics of Catalytic Reactions

(i) The catalyst remains unchanged in amount and chemical composition at the end of the reaction; it may, however, undergo considerable change in physical form.

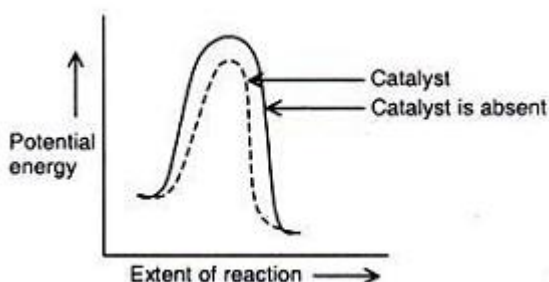
(ii) A small quantity of the catalyst is capable of producing the desired effect.

(iii) The action of a catalyst is specific to a large extent. Thus, the decomposition of KClO_3 is catalyzed by MnO_2 but not by platinum.

(iv) The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring.

(v) A catalyst does not alter the final state of equilibrium in a reversible reaction.

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 is said to lower the activation energy and thus increase the rate of the reaction.

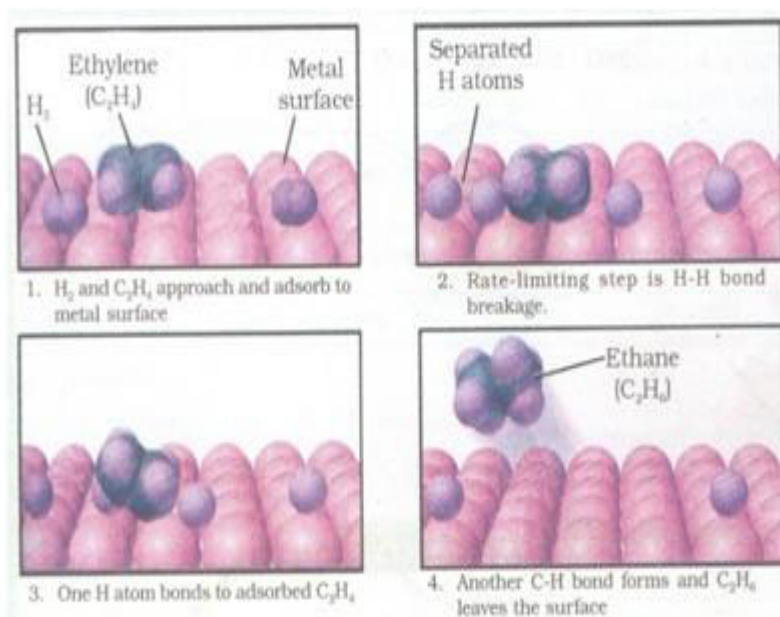


Thus, a catalyst increases the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalysed reaction.

7. Explain the nature of Solid catalysts.

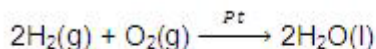
Nature of Solid Catalysts

Solid catalysts may be metals, metal oxides, metal sulphides, clays etc. These materials may be used in their pure form or in the form of their mixtures. Further, they may be crystalline, microcrystalline (in the form of fine particles) or amorphous.

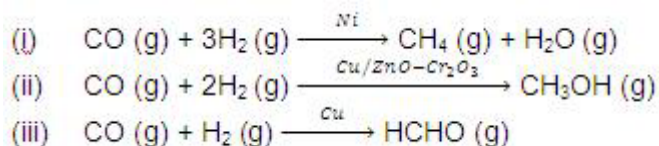


Important features of solid catalysts:

1. Activity: The activity of a catalyst depends upon the strength of chemisorptions to a large extent. The reactant must adsorb reasonably strongly for the catalyst to be active but must not adsorb so strongly that they are immobilized and other reactants are left with no space on the catalyst surface adsorption. It has been found that for hydrogenation the catalytic activity increases as we go from group 5 metals to group 11 with maximum activity shown by group 7-9 elements of the periodic table.



2. Selectivity: The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example, starting with H₂ and CO using different catalysts we get different products.



Action of a catalyst is highly specific (selective) in nature i.e., a given substance can act as a catalyst only in a particular reaction and not for all the reactions. It means a substance which acts as a catalyst in one reaction may fail to catalyze other reaction i.e., a catalyst is highly selective in nature.

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