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# SURFACE CHEMISTRY AND COLLOIDS

19 + 21 Marks
PRAC-KKD

V.V.Imp

***① (a) What is adsorption? Explain the types of adsorption?

June-2010 (b) Write the differences between physical adsorption and chemical

July-2009 adsorption. (chemisorption)?

(c) Explain the factors effecting the adsorption?

Ans: **Adsorption :-**

The process of concentration of molecules of a gas (or) a liquid on the surface of a solid is called Adsorption.

Adsorption occurs on the surface only.

i.e. Adsorption is a surface phenomenon.

The substance adsorbed on the surface of a solid (or) a liquid is called adsorbate. (అధిశోషితం)

The substance on whose surface the adsorption occurs is called adsorbent.

Example: In the adsorption of acetic acid by charcoal, acetic acid is called adsorbate and the charcoal is called adsorbent.

Adsorption is of two types:

① physical adsorption ② chemical adsorption.

① **physical adsorption :-**

If the molecules of adsorbate are held on the surface of adsorbent by vander Waal's forces, this process is called physical Adsorption.

Example: Adsorption of "$H_2$" on coconut charcoal

② **chemical adsorption (chemisorption) :-**

If the molecules of the adsorbate are held on the surface of adsorbent by chemical forces, this process is called chemical adsorption.

Example: Adsorption of "$H_2$" on nickel.

## Differences between physical adsorption and chemical adsorption :-

| physical adsorption | chemical adsorption |
|---|---|
| 1. physical adsorption is a weak process. | 1. chemical adsorption is strong. |
| 2. This occurs rapidly | 2. chemical Adsorption takes place slowly. |
| 3. This is a multilayered process. | 3. This is a unilayered process. |
| 4. This process is reversible | 4. This process is irreversible. |
| 5. Adsorption decreases with increase in temprature. | 5. Adsorption increases with increase in temprature. |
| 6. Activation energy of adsorption is low. | 6. Activation energy of adsorption is high. |
| 7. Adsorption depends on the nature of the adsorbate. | 7. Adsorption depends on the nature of the both adsorbate and adsorbent. |
| 8. Enthalpy of adsorption is low (20-40 KJ/mole) | 8. Enthalpy of adsorption is high 40 - 400 KJ/mole. |

## Factors effecting adsorption :-

① Nature of adsorbent and adsorbate :-

Easily liquibiable gases are easily adsorbed. Gases like $SO_2$, $NH_3$, HCl and $CO_2$ are easily liquibiable and are easily adsorbed than $H_2$, $O_2$ and $N_2$.

Since adsorption is a surface phenomenon, the larger the surface area, the greater is the adsorption. Finely divided substances are good adsorbents.

② Effect of temprature :-

Adsorption is an exothermic process.
Hence the lower the temprature and the adsorption is high.
But low temptatures favour physical adsorption and high tempratures favour chemisorption.

③ Effect of pressure :-

The higher the pressure, the greater is the adsorption.
Freundlich gave an emperical relationship between the amount of gas adsorbed ($\frac{x}{m}$) by unit mass of the adsorbent and the equilibrium pressure (p) of the gas at a given temprature.

$$\frac{x}{m} = k \cdot p^{\frac{1}{n}}$$

"x" is the mass of adsorbate and "m" is the unit mass of adsorbent.
"k" and "n" are the constants.
p = gas pressure.

④ surface area of the adsorbent :-

The extent of adsorption increases by increasing the surface area of the adsorbent.
Finely divided metals (pt, Ni) provided large surface area and are useful as good adsorbents.

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Q
② ⓐ What is adsorption ?
*** ⓑ Explain the Freunddlich and Langmuir adsorption isotherms.
march-2009.
march-2010.
(OR)
Derive the Langmuir and Freundlich adsorption isotherms.
ⓒ Write any four applications of adsorption.

Ans: Adsorption :-

The process of concentration of molecules of a gas (or) a liquid on the surface of a solid is called adsorption.

Examples : ① Adsorption of "$H_2$" gas on coconut charcoal.
② Adsorption of $H_2$ on Nickel.

① Freunddlich adsorption isotherm :-

Adsorption isotherms give the relation between extent of adsorption and pressure of the gas which is in equilibrium with adsorbent.

According to Freundlich, as the temprature increases extent of adsorption decreases.

At constant temprature, as the pressure increases the extent of adsorption increases and becomes constant after a particular pressure.

From these observations Freundlich proposed the following equation.

$$\frac{x}{m} = k \cdot p^{\frac{1}{n}}$$

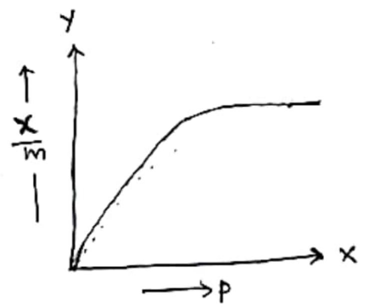
Freundlich equation showing the relationship between the amount of gas adsorbed ($\frac{x}{m}$) by unit mass of the adsorbent and the pressure (p) of the gas at a given temprature.

$\frac{x}{m}$ = Extent of adsorption.   x = mass of adsorbate
m = unit mass of adsorbent.

"k" and "n" are constants.

p = pressure of adsorbate gas at equilibrium state.

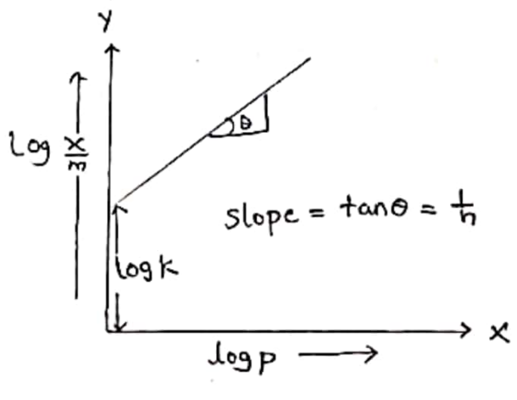
The adsorption isotherm at different pressures is shown below.




The above equation can be written as

$$\log \frac{x}{m} = \frac{1}{n} \log p + \log k$$

The graph showing the relation between $\log \frac{x}{m}$ and $\log p$ is a straight line with slope is equal to $\frac{1}{n}$ and intercept = k



Real gases deviates more at high temprature.

## Derivation of Langmuir's adsorption isotherm:-

Based upon kinetic theory, Langmuir (1916) derived an expression for the adsorption isotherm.

① According to Langmuir's, a gas adsorbed on any surface is only of unimolecular thickness.

② Adsorption of the gas on the solid surface goes on increasing until the entire surface is completely covered with one molecule thick layer.

③ Adsorption consists of two opposing processes. They are

ⓐ condensation of the gas molecules on the solid surface

ⓑ evaporation (desorption) of the gas molecules from the surface back into the gaseous phase.

④ At starting when whole of the surface is uncovered, then the rate of condensation is very high and as the surface is covered more and more.

⑤ The rate of evaporation depends upon the covered surface.

⑥ A state of equilibrium is finally reached when the rates of adsorption and desorption are equal.

Derivation of Langmuir isotherm:

Suppose at any instant,

The fraction of the surface covered by adsorbed molecules $= \theta$

$\therefore$ The fraction of the surface uncovered $= 1-\theta$

The pressure of the gas $= P$

Since the rate of adsorption is proportional to the pressure ($P$) of the gas as well as uncovered surface $(1-\theta)$.

$$\text{Rate of adsorption (condensation)} \propto P(1-\theta)$$

$$= k_1 P(1-\theta)$$

Where "$k_1$" is a proportionality constant.

$$\text{Rate of desorption (evaporation)} \propto \theta$$

$$= k_2\theta$$

Where "$k_2$" is another proportionality constant.

At equilibrium,

Rate of adsorption = Rate of desorption.

$$\therefore \quad k_1 p(1-\theta) = k_2\theta \quad \longrightarrow (1)$$

$$k_1 p - k_1\theta p = k_2\theta$$

$$k_1 p = (k_2\theta + k_1\theta p)$$

$$k_1 p = \theta(k_1 p + k_2)$$

$$\theta = \frac{k_1 p}{k_1 p + k_2}$$

multiplying and divided by "$k_2$"

$$\theta = \frac{\frac{k_1 p}{k_2}}{\frac{k_1 p}{k_2} + \frac{k_2}{k_2}}$$

$$\theta = \frac{ap}{1+ap}$$ Where $\frac{k_1}{k_2} = a$, which is another constant.

Since adsorption is of unimolecular thickness "$\theta$" is proportional to the amount of gas adsorbed per unit mass of the adsorbent i.e. $\frac{x}{m}$.

Where "x" is the amount of gas adsorbed on "m" gms of adsorbent.

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

$$\frac{x}{m} = k_3\theta$$ "$k_3$" is the proportionality constant

substituting the value of "$\theta$" in the above equation,

$$\frac{x}{m} = k_3 \frac{ap}{1+ap}$$

$$\frac{x}{m} = \frac{bp}{1+ap}$$

Where "b" is the new constant for the product $k_3 a$.

$$\frac{x}{m} = \frac{bp}{1+ap}$$

This equation is known as Langmuir's adsorption isotherm.

The above equation may be rearranged to give

$$\frac{1}{\frac{x}{m}} = \frac{1+ap}{bp} = \frac{1}{bp} + \frac{ap}{bp}$$

$$\therefore \frac{1}{\frac{x}{m}} = \frac{1}{bp} + \frac{a}{b}$$

multiplying with "p" on both sides, we get

$$\frac{p}{\frac{x}{m}} = \frac{p}{bp} + \frac{ap}{b}$$

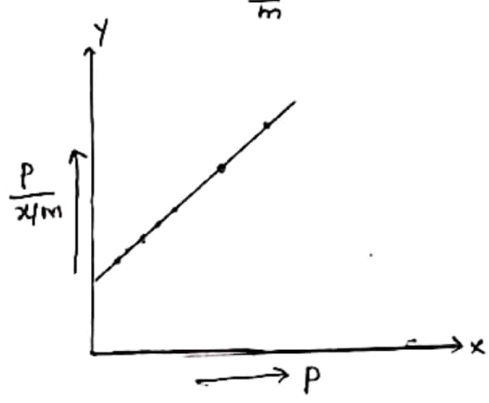
$$\boxed{\frac{p}{\frac{x}{m}} = \frac{1}{b} + \left(\frac{a}{b}\right)p}$$

"a" and "b" are constants.

A straight line graph should be obtained when $\frac{p}{\frac{x}{m}}$ is plotted against "p"

slope is equal to $\frac{a}{b}$

and intercept is equal to $\frac{1}{b}$




case-I :-

① Langmuir's equation at lower pressures :-

When adsorption is slight.

i.e. when gas pressure is low, then the value of $\theta$ is negligible.

As $(1-\theta)$ becomes equal to "1".

$$(1-\theta)k_1 p = k_2\theta$$

$$k_1 p = k_2\theta$$

$$\theta = \frac{k_1}{k_2}p$$

But "$\theta$" value depends on "$\frac{x}{m}$"

$$\therefore \frac{x}{m} = \frac{k_1}{k_2}p$$

$$\therefore \boxed{\frac{x}{m} \propto p}$$

At low pressures adsorption is directly proportional to gas pressure

② At higher pressure :-

When adsorption is high, the value of "$\theta$" becomes nearly equal to "1"

$$\therefore (1-\theta)k_1 p = k_2\theta$$

$$k_1 p - k_1\theta p = k_2 \quad (\because \theta \simeq 1)$$

$$k_1 p - k_1\theta p = k_2$$

$$k_1 p - k_2 = k_1\theta p$$

$$\frac{k_1 p}{k_1 p} - \frac{k_2}{k_1 p} = \theta$$

$$1 - \frac{k_2}{k_1 p} = \theta$$

$$\therefore \frac{x}{m} = 1 - \frac{k_2}{k_1 p}$$

As pressure increases "$\frac{K_2}{K_1 P}$" value decreases and the extent of adsorption reaches a limiting value.

## Applications of adsorption:-

① Silica and aluminium gels are used as adsorbents. These gels remove moisture.

② Activated charcoal is used in gas masks. The poisonous gas vapours are adsorbed by charcoal and pure air passes through its pores.

③ chromatography is based on selective adsorption of different substances by an adsorbent.

④ Different inert gases are adsorbed on charcoal to different extents. Extent of adsorption increases with increase in molecular weight and this fact is used to separate a mixture of inert gases by adsorption on coconut charcoal at different tempratures.

⑤ A number of drugs work by their adsorption on germs.

⑥ The colouring matter in sugar juice and vegetable oils is removed by substances like activated charcoal. coloured impurity is generally removed with animal charcoal.

## COLLOIDS

① colloidal solution:-

colloidal solution is a binary systems in which the particle size of the dispersed phase is of the order of $1m\mu - 0.1\mu$.

colloidal solution is a heterogeneous binary system.

Example: Starch paste, gelatin when added to hot water and the mixture is shaked well, colloidal solutions of the substance are formed.

② True solutions:-

The size of the particles in true solution is less than $1m\mu$ ($1m\mu = 10^{-9}m$)