- F.Y.B.Sc. CBCS COURSE IN CHEMISTRY CH: 101 Physical and Inorganic Chemistry -I (Section A) Core Course-A-1(Semester I)
- Chapter 1: Surface Chemistry (L: 6, M: 8)

- A POWERPOINT PRESENTATION FOR F. Y. B. Sc. CBCS COURSE IN CHEMISTRY ON THE TOPIC

ENTITLED

"Surface Chemistry"

BY

Dr. R. K. Chaudhari

Associate Professor, S.V.S.'s Dadasaheb Rawal College, Dondaicha.

Dondaicha. Dist- Dhule. **(M. S.)**

----- August 2020 -----

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 1

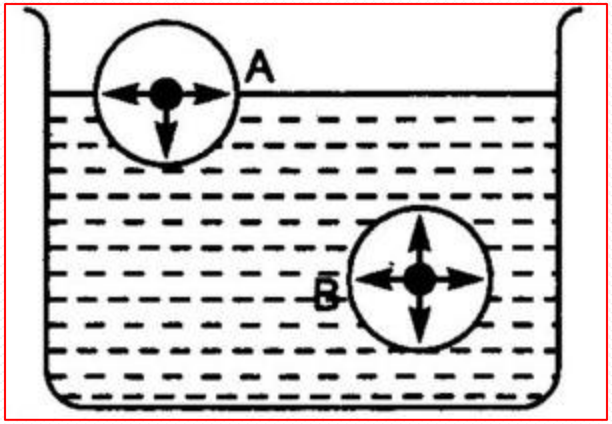
TOPIC: - SURFACE CHEMISTRY

DATE: -3, OCTOBER, 2020

TIME: 9.00 A.M.

"Surface Chemistry"

Introduction: - Consider a liquid in a container. There are two types of molecules.



Interior molecules (B)

↓

Symmetric distribution

↓

No surface tension

Surface (A)

↓

Unbalanced

↓

In a state of strain

Surface tension

(Free energy)

Solid 

outer layer of solids have residual forces

There is a tendency for the free energy of any surface to decrease and it is this tendency which is ultimately responsible for the phenomena of adsorption. So, adsorption is a surface phenomenon.

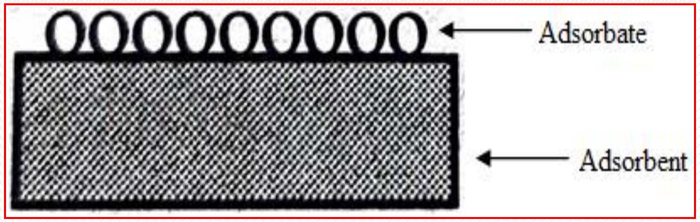
Formation of a kind of bond restricts the freedom of movement of molecules and hence, decreases free energy.

Adsorption: - "The collection or deposition of a substance on the surface of another substance is known as adsorption".

Or "The change in concentration at the interfacial layer between two phases of a system is called adsorption".

Adsorbent: - 'The substance which adsorbs the other substance is called the adsorbent."

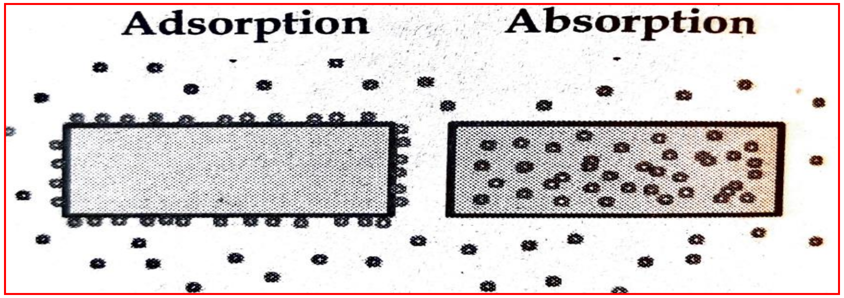
Adsorbate: - "The substance which gets adsorbed on the surface of other substance is called adsorbate."



Desorption: - "The process of removal of adsorbate from the surface of an adsorbent is known as desorption." i.e Reverse process of adsorption is called desorption.

Absorption: - "The phenomena in which, a substance is uniformly distributed throughout the body of solid or liquid is called as absorption."

Or "The penetration of one substance in the body of other substance is called as absorption." e.g. Sponge dipped in water.



Difference between Adsorption and Absorption:

Adsorption	Absorption
1) It is a surface phenomenon	1) It is a bulk phenomenon
2) It is the accumulation of substance on the surface of another substance.	2) It is the uniform distribution of substance throughout the body of other substance.
3) It is due to strain at the surface layer.	3) It is due to porous nature of the material.
4) It depends upon temperature and pressure.	4) It is independent on temperature and pressure.
5) It is reversible and dynamic equilibrium is attained in short time.	5) It is irreversible and static equilibrium is attained very slowly.
6) It depends upon surface area of adsorbent.	6) It is independent on surface area.
7) It is an exothermic process.	7) It is neither exothermic nor endothermic process.
8) Increase in surface area increases the adsorption.	8) Absorption increases by increasing volume bulk of material.
9) The extent of adsorption depends upon active centers or free valencies.	9) It depends upon porosity of the material.
10) Number of layers can be formed.	10) Formation of layers is not possible.
11) e.g. Adsorption of H_2 gas on Nickel or Palladium metal.	11) e.g. Blotting paper in contact with ink.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 2

TOPIC: - SURFACE CHEMISTRY

DATE: -9, OCTOBER, 2020

TIME: 9.00 A.M.

Factors affecting adsorption:-

1) Surface area of an adsorbent:- At a given temperature and pressure, larger the surface area of an adsorbent, more will be the adsorption.

2) Nature of an adsorbent:- The rate of adsorption is more on rough surface, porous solid, Colloidal particles and finely divided form of the substance.

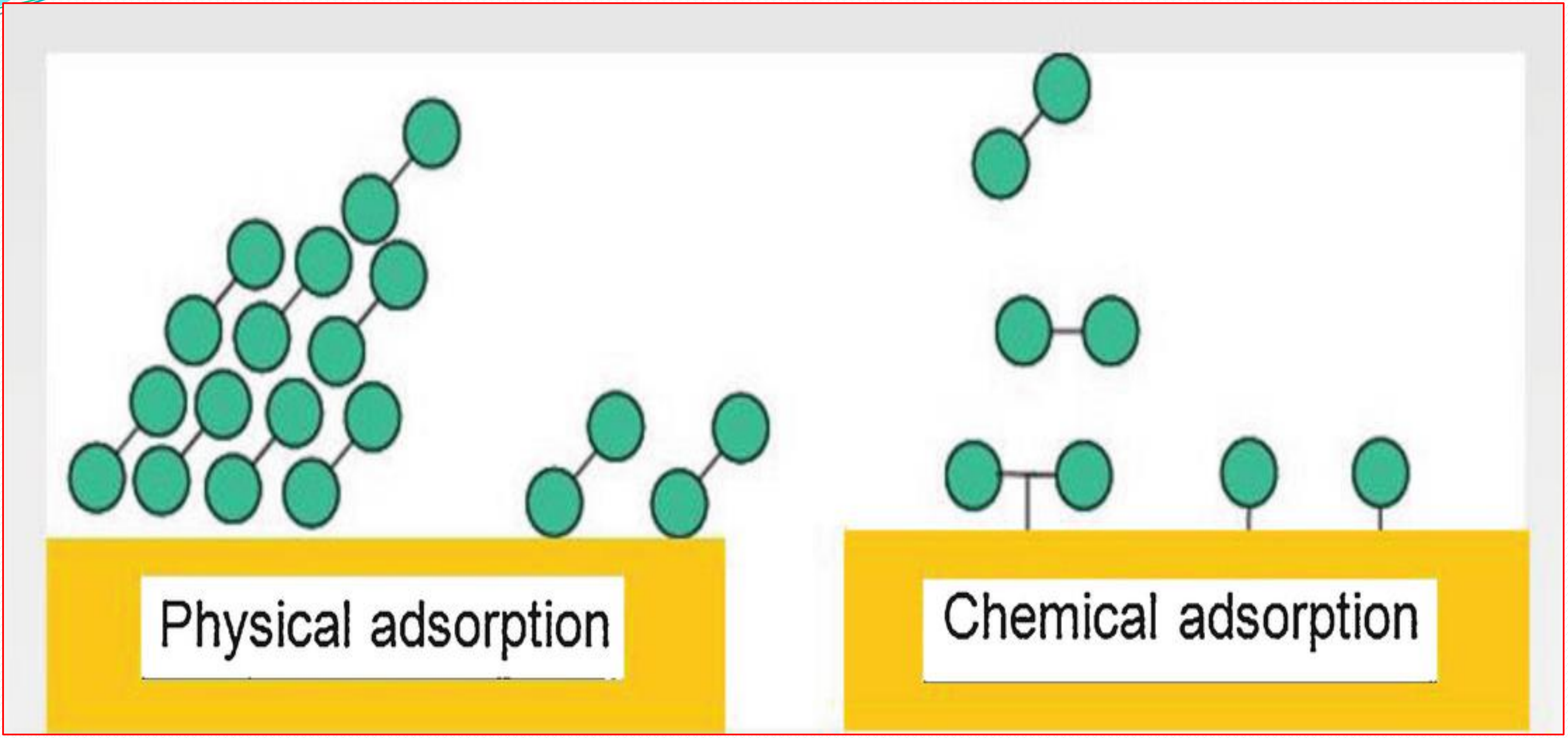
3) Temperature: - The rate of adsorption is decreases with the increase in temp.

4) Pressure: - In case of gases, the rate of adsorption increases with increase in pressure on adsorbate untill saturation is reached.

5) Nature of gas: - All the gases get adsorbed on solid surfaces. But, the gases which can be easily liquefied and which are highly soluble in water get adsorbed to a greater extent. Hence, vapours adsorbed more readily than gases.

Types of Adsorption: - Depending upon the nature of forces involved in adsorption, the adsorption process is classified into two types; Physical and Chemical adsorption.

Physical adsorption (Physiosorption)	Chemical adsorption (Chemisorption)
1) This is due to the gas molecules being held on solid surface by weak Van der walls forces of attraction.	1) The gas molecules are held on solid surface by chemical bonds or chemical forces i.e. Covalent bonds.
2) Heat of adsorption is low.	2) Heat of adsorption is high.
3) It occurs at low temperature.	3) It occurs at high temperature.
4) Rate of adsorption is fast.	4) Rate of adsorption is slow.
5) It is reversible.	5) It is irreversible.
6) It is not specific. Every gas is adsorbed.	6) It is highly specific.
7) Forms multimolecular layers on adsorbent surface.	7) Forms unimolecular layer.
8) It does not require activation energy.	8) It requires activation energy.
9)e.g. Adsorption of acetic acid on charcoal.	9) e.g. Adsorption of H_2 gas on Nickel.


Physical adsorption
Chemical adsorption

Adsorption Isotherm: -

"The relation between the amount of the substance adsorbed by an adsorbent and the equilibrium pressure or concentration at a constant temperature is called as adsorption isotherm."

There are two types of adsorption isotherms: -

1) Freundlich Adsorption isotherm
2) Langmuir Adsorption isotherm

1) Freundlich Adsorption isotherm: -

"The relation between amount of the gas adsorbed on the adsorbent and equilibrium pressure at constant temperature is known as Freundlich's Adsorption isotherm."

Mathematically, it is

$$\frac{x}{m} \; \alpha \; P^{1/n}$$

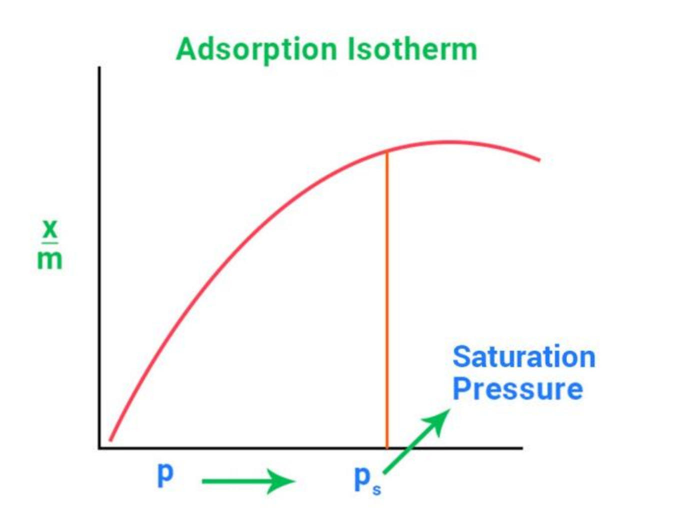
$$\frac{x}{m} = kP^{1/n}$$

Where, $x \rightarrow$ Amount of gas adsorbed

$m \rightarrow$ Mass of the adsorbent

$P \rightarrow$ Equilibrium pressure

k and n are constants depending on the nature of adsorbent, adsorbate and temperature.



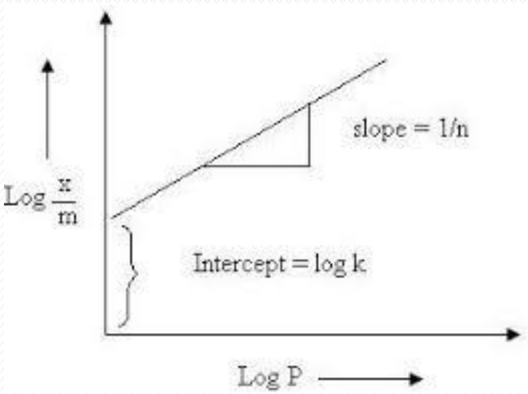
Taking logarithm of both sides of eqn. (1)

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

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

log (m ×n) = log m +log n
(log m^n = n× log m)

This eqn. is similar to the eqn. of straight line y= mX+C. When log of x/m is plotted against log P, then the nature of graph is as shown below:



Slope gives 1/n and intercept gives log k. The value of 1/n varies from 0 to 1.

If 1/n is 0, adsorption is independent of pressure.

If 1/n is 1, adsorption changes with pressure.

At low pressure, the graph is st. line. But, at high pressure, it deviates from st. line and shows slight curvature. This indicates that, Freundlich's adsorption isotherm is approximate and it is not applicable at high pressure.

Solids also adsorb from solutions. For example, when a solution of acetic acid in water is mixed with charcoal, some of the acid is adsorbed by the charcoal In the case of adsorption of a solid by a liquid, the Freundlich's adsorption isotherm can be given as

$$\frac{x}{m} \alpha C^{1/n} \quad \text{OR} \quad \frac{x}{m} = K C^{1/n}$$

Where, C is the equilibrium concentration of the adsorbed substance.

2) Langmuir's Adsorption isotherm: -

Langmuir derived the isotherm, on the basis of following assumptions:-

1) The solid surface has uniform adsorption properties.

2) Adsorbed layer is unimolecular in thickness.

3) Molecules of the gas will strike the surface and will adhere for an appreciable time, while, other gas molecules will try to evaporate from the surface (desorption).

4) A dynamic equilibrium is set up between the two opposing processes (adsorption and desorption). At equilibrium, the rate of adsorption is equal to the rate of evaporation.

5) The adsorbed molecules are dissociated i.e. Langmuir's isotherm is applicable to chemical adsorption.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 3

TOPIC: - SURFACE CHEMISTRY

DATE: -10, OCTOBER, 2020

TIME: 9.00 A.M.

Solids also adsorb from solutions. For example, when a solution of acetic acid in water is mixed with charcoal, some of the acid is adsorbed by the charcoal In the case of adsorption of a solid by a liquid, the Freundlich's adsorption isotherm can be given as

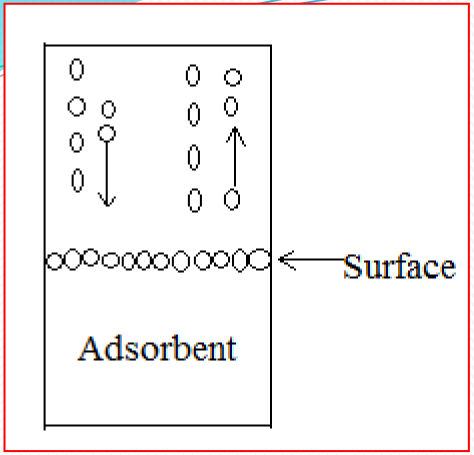
$$\frac{x}{m} \alpha \, C^{1/n} \quad \text{OR} \quad \frac{x}{m} = K \, C^{1/n}$$

Where, C is the equilibrium concentration of the adsorbed substance.

2) Langmuir's Adsorption isotherm: -

Langmuir derived the isotherm, on the basis of following assumptions:-

1) The solid surface has uniform adsorption properties.
2) Adsorbed layer is unimolecular in thickness.
3) Molecules of the gas will strike the surface and will adhere for an appreciable time, while, other gas molecules will try to evaporate from the surface (desorption).
4) A dynamic equilibrium is set up between the two opposing processes (adsorption and desorption). At equilibrium, the rate of adsorption is equal to the rate of evaporation.
5) The adsorbed molecules are dissociated i.e. Langmuir's isotherm is applicable to chemical adsorption.



Derivation of Langmuir's adsorption isotherm: -

Let, θ be the fraction of the total surface covered by the adsorbed molecule at any instant. Then the fraction $(1-\theta)$ of the surface will be free and available for adsorption.

According to Kinetic theory of gases at constant temperature, the rate at which molecules strike unit area of the surface is proportional to pressure (P) of the gas.

The rate of adsorption of molecules is determined by both pressure and fraction of the free surface area.

i.e. Rate of adsorption α $P(1-\theta)$

$$= K_1 P (1-\theta)$$

Where, K_1 is proportionality constant.

The rate of evaporation will be proportional to the fraction θ of the surface already covered by the molecules.

Rate of evaporation α θ

$$= K_2 \theta \text{ ----------(2)}$$

Where, K_2 is proportionality constant.

At equilibrium, rate of adsorption becomes equal to rate of evaporation,

i.e. Rate of adsorption = Rate of evaporation

$$K_1\, P\, (1 - \theta) = K_2\, \theta$$

$$K_1\, P - K_1\, P\, \theta = K_2\, \theta$$

$$K_1\, P = K_2\, \theta + K_1\, P\, \theta$$

$$K_1\, P = (K_2 + K_1\, P)\, \theta$$

$$\theta = \frac{K_1\, P}{K_2 + K_1\, P}$$

Now, the amount of gas adsorbed per unit mass of the adsorbent $(\frac{x}{m})$ is directly proportional to the fraction θ of the surface covered.

$$\frac{x}{m}\, \alpha\, \theta$$

$$\frac{x}{m} = k\, \theta.$$

On substituting the value of θ,

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

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

Divide numerator and denominator by K_2

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

$$\frac{x}{m} = \frac{aP}{1+bP} \qquad \left(\text{where } \frac{k\,K_1}{K_2} = a \;\&\; \frac{K_1}{K_2} = b\right)$$

This equation is known as Langmuir's adsorption isotherm. It gives the relation between the amount of gas adsorbed per gram of adsorbent and the pressure of the gas at constant temperature.

Divide this equation by P

$$\frac{x/m}{P} = \frac{a}{1+bP}$$

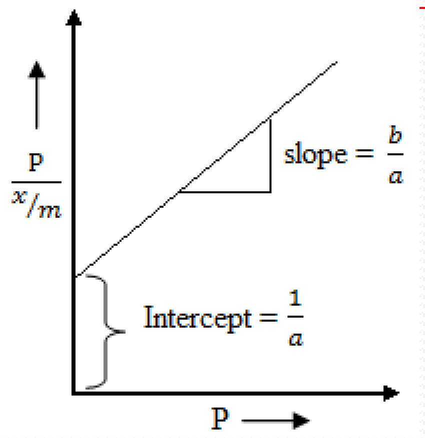
Changing numerator and denominator,

$$\frac{P}{x/m} = \frac{1+bP}{a}$$

$$\frac{P}{x/m} = \frac{1}{a} + \frac{bP}{a}$$

$$\frac{P}{x/m} = \frac{b}{a}P + \frac{1}{a}$$

This equation is similar to the equation of straight line y=mx+c. If the graph of $\left(\frac{P}{x/m}\right)$ is plotted against (P), then a straight line is obtained.



The excellent straight line is obtained by Langmuirs equation confirms that, it is superior to Freundlich's adsorption isotherm.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 4

TOPIC: - SURFACE CHEMISTRY

DATE: -16, OCTOBER, 2020

TIME: 3.00 P.M.

Problems:-

1) Find out the equilibrium pressure during adsorption of 75 cc of carbon monoxide by wood charcoal weighing 3.0 gms. Adsorption follows Freundlich's adsorption isotherm. (Given: k = 0.088 cc and n = 1.25).

Answer:

$$\frac{x}{m} = k\ P^{1}/_{n}$$

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

$$\log \frac{75}{3} = \log 0.088 + \frac{1}{1.25} \log P$$

$$\log 25 - \log 0.088 = \frac{\log P}{1.25}$$

$$1.3979 - \bar{2}.\ 9445 = \frac{\log P}{1.25}$$

$$2.4554 = \frac{\log P}{1.25}$$

$$2.4554 \times 1.25 = \log P$$

$$\log P = 3.0692$$

P = Antilog of (3.0692)

P = 1173 cm.

2) Calculate the amount of the substance (X) adsorbed by 2.7 gm of the activated charcoal in the solution containing 1.98 gms/lit. of the solution at 298 K. The value of K and n for the given system are 0.52 and 3 resectively.

Answer: Freundlich's adsorption isotherm is $\frac{x}{m} = K\, C^{1/n}$

Where, m = Mass of the adsorbent = 2.7 gm

C = Concentration = 1.98 gms/lit., n = 3 and K = 0.52

Amount adsorbed = x = ?

$$\frac{x}{2.7} = 0.52 \times (1.98)^{\frac{1}{8}}$$

$$x = 2.7 \times 0.52 \times (1.98)^{\frac{1}{8}}$$

$$\log x = \log 2.7 + \log 0.52 + \frac{1}{8}\log 1.98$$

$$\log x = 0.4313 + \bar{1}.7160 + \frac{1}{8} \times (0.2966)$$

$$\log x = 0.1473 + 0.0988$$

$$\log x = 0.2461$$

$$x = \text{Antilog of } (0.2461)$$

$$x = 1.76 \text{ gm.}$$

3) The mass x of a solute adsorbed per gm of solid adsorbent is given by Freundlich's adsorption isotherm. Where K and n are 0.160 and 0.431 resply. Calculate amount of acetic acid (m = 60.05 gm/mole) that 1 kg of charcoal adsorbed from 0.837 M vinegar solution.

Answer:

x = Amount adsorbed =?

K = 0.160, n = 0.431, m = 1gm

$$\frac{x}{m} = K\,C^{1/n}$$

$$x = m\,K\,C^{1/n}$$

$$x = 1 \times 0.160 \times (0.837)^{\frac{1}{0.431}}$$

$$x = 0.160 \times (0.837)^{2.320}$$

$$x = 0.160 \times 0.6618$$

$x = 0.1058$ gm per gm of charcoal.

$x = 105.8$ gm of acetic acid per kg of charcoal.

$x = \frac{105.8}{60.05} = 1.76$ mole of acetic acid per kg charcoal.

2.320 × 0.837

= 2.320 × $\bar{1}.9227$

= 2.320 × (-1.0 + 0.9227)

= 2.320 × (-0. 0773)

= - 0.1793 (Antilog of)

=-0.0 -0. 1793

= -0.0-1.0 +1.0- 0.1793)

= -1 + 0.8207

= $\bar{1}.$ 8207 (Antilog of)

= 0.6618

4) For adsorbent adsorbate system obeying Langmuir's adsorption isotherm a = 0.52 bar^{-1} and b = 0.15 bar^{-1} . Calculate at what pressure 25% of the surface covered.

Answer: Langmuir's adsorption isotherm is $\frac{x}{m} = \frac{aP}{1+bP}$

a =0.52 bar^{-1} and b = 0.15 bar^{-1}

The surface covered 25% means $\frac{x}{m} = \frac{25}{100}$ =0.25

$$\frac{x}{m}(1 + bP) = aP$$

$$\frac{x}{m} + \frac{x}{m}bP = aP$$

$$\frac{x}{m} = aP - \frac{x}{m}bP$$

$$\frac{x}{m} = (a - \frac{x}{m}b)P$$

$$P = \frac{x/m}{a - x/mb}$$

$$P = \frac{0.25}{0.52 - 0.25 \times 0.15}$$

$$P = \frac{0.25}{0.52 - 0.0375}$$

$$P = \frac{0.25}{0.4825}$$

P = 0.5181 bar.

Thank You.

Stay Home, Stay Safe