(vi) **Effect of Pressure.**

It is a known fact that there is a dynamic equilibrium (حرکی توازن) between the adsorbed gas and that which is present in the bulk of gas. It is found that the increase of pressure leads to the increase of adsorption. When the pressure is decreased, then it causes desorption (سطح سے چھوٹ جانا).

(vii) **Thickness of Adsorbed Layer:**

It was determined by Langmuir that the layer of the adsorbed gas has a thickness of one molecule at low pressure in the case of physical adsorption. If the pressure is high, then multi-molecular thick layer (زیادہ سالمے کی موٹی تہہ) is formed.

12.2 ADSORPTION ISOTHERMS (درجہ حرارت مستقل رکھ کر سطح پر جذب ہونے کا عمل)

12.2.1 Introduction:

As we have discussed above that the adsorption of a gas on solid surface in a closed vessel is a reversible process. There is a sort of **dynamic equilibrium** (حرکی توازن) **between the adsorbed molecules and the gaseous molecules free in the vessel.** This concept can help us to say that the amount of gas adsorbed depends upon pressure and temperature at equilibrium stage.

12.2.2 What Is Adsorption Isotherm?

The word isotherm means same temperature. By keeping temperature constant we can study the change of adsorption of gas by change of pressure. ***"Hence the relationship between equilibrium pressure of a gas and the weight of the gas adsorbed on the solid surface is called adsorption isotherm."*** Adsorption isotherms are given in the form of an equation (مساوات) which can be further depicted in the form of a graph. This graph is mostly a curve.

Various Types Of Adsorption Isotherms:

Different scientists have proposed different adsorption isotherms. Two of such isotherms are discussed as follows.

12.2.3 Freundlich Adsorption Isotherm:

Freundlich adsorption isotherm has been proposed by the concerned scientists in the shape of an empirical relationship (عملی تجربے پر مبنی مساوات) which is as follows:

$$\boxed{\frac{w}{m} = k\,P^{1/n}} \qquad \cdots\cdots \ (1)$$

w = Mass of the gas adsorped on the surface of the solid.

m = Mass of the adsorbent at a pressure P.

k = Constant depending upon the nature of the gas and the absorbent. It also depends upon the temperature.

n = Constant, depending upon the nature of the gas, pressure and temperature.

12.2.4 Graphical Representation:

If we plot a graph between pressure on x-axis and $\frac{w}{m}$ on y-axis, then a rising curve is obtained as shown below Fig. (12.1)

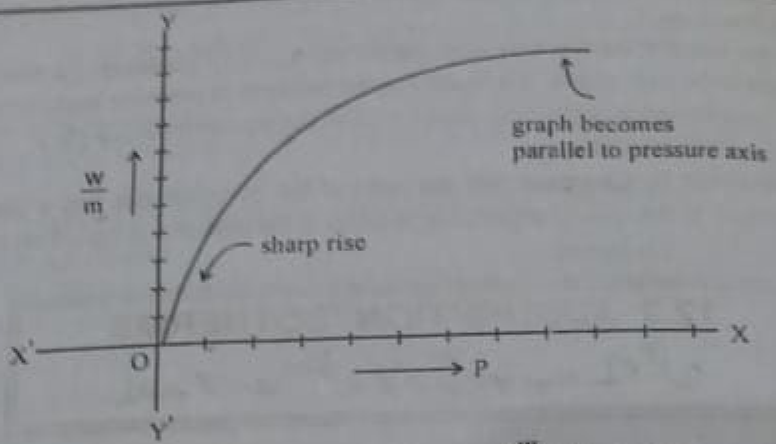

Fig. (12.1) Plot of pressure of gas and $\frac{w}{m}$ of the system.

According to the shape of the graph, there is a sharp rise of the curve at low pressures and ultimately (آخر کار), it becomes parallel (متوازی) to the pressure axes. It means that when the pressure exceeds the certain limit, then $\frac{w}{m}$ becomes constant, which means that the further adsorption of the gas stops.

This equation can be converted into the equation of a straight line by taking the log on both sides. Let us take common log with base 10.

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

$$\log\frac{w}{m} = \log k\, p^{\frac{1}{n}}$$

or $$\log\frac{w}{m} = \log k + \frac{1}{n}.\log P$$

or $$\boxed{\log\frac{w}{m} = \frac{1}{n}\log P + \log k} \quad \text{......} \quad (2)$$

Equation (2), is of straight line (y = mx + c). $\log\frac{w}{m}$ corresponds to y, log P correspond to x, log k corresponds to intercept and $\frac{1}{n}$ will be the slope of straight line. We plot a graph between $\log\frac{w}{m}$ on axis and log P on x-axis and a straight line is obtained Fig. (12.2). From the slope and the intercept the straight line, we can calculate the value of 'k' and 'n'. These two constants are the characteristics the system under consideration.

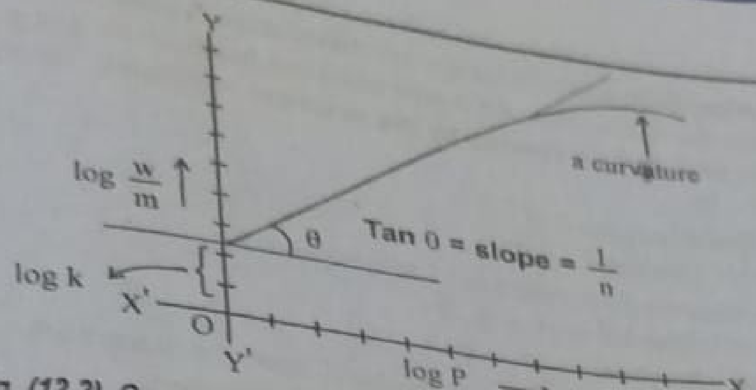

Fig. (12.2) Graph of log $\frac{w}{m}$ and log P to calculate n and k of system.

This graph also shows that the straight line is converted to curve at higher values of log P. It means that, Freundich equation is an approximation and does not apply to the adsorption of gases by solids at high pressures.

12.2.5 Langmuir Adsorption Isotherm:

The basic (بنیادی) assumptions (ابتدائی دلیل تسلیم کردہ باتیں) of Langmuir adsorption isotherm are as follows.

(i) The gas which is adsorbed on the surface of the solid has a layer of one molecule thickness (ایک مالیکول جتنی موٹی ہوتی ہے).

(ii) This unimolecular layer on the surface of the solid is uniform (یکساں) throughout.

(iii) There is no interaction (باہمی تعاون) between the molecules of the absorbed gas which are adjacent to each other.

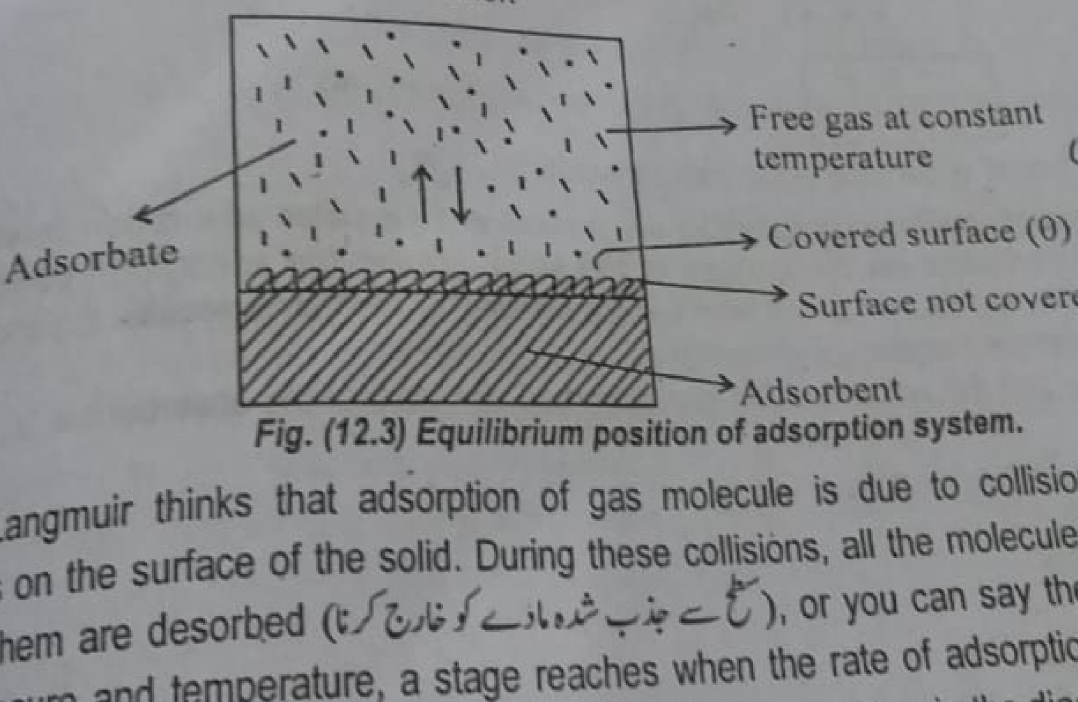

Fig. (12.3) Equilibrium position of adsorption system.

Langmuir thinks that adsorption of gas molecule is due to collisions (تصادم) of the ga[s] molecules on the surface of the solid. During these collisions, all the molecules are not adsorbed b[ut] some of them are desorbed (جذب شدہ مادے کو خارج کرنا), or you can say they are evaporated. A[t] given pressure and temperature, a stage reaches when the rate of adsorption becomes equal to rate of desorption. This is the state of dynamic equilibrium as shown in the diagram. Fig. (12.3).

12.2.6 Mathematical Derivation Of Langmuir Adsorption Isotherm:

Suppose that the total surface of the solid which has to adsorb the gas is unity and 'θ' is the fraction (کسر) of the total surface covered by the absorbed molecules. The fraction of the naked surface (ننگی سطح) is $(1-\theta)$.

Rate of desorption $\propto \theta$

or Rate of desorption $= k_d\theta$ ...... (1)

Rate constant for the process of desorption $= k_d$

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

Rate of adsorption $= k_a(1-\theta) \cdot P$ ...... (2)

In equation (2), the rate of adsorption depends upon the **bare surface** (ننگی سطح) and the external pressure P. k_a is the rate constant for the process of adsorption.

At the stage of dynamic equilibrium (حرکی توازن), these two rates are equal, so

$$k_d\theta = k_a(1-\theta) \cdot P$$

$$k_d\theta = k_a \cdot P - k_a\,\theta.P$$

$$k_d\theta + k_a\theta.P = k_a.P$$

$$\theta(k_d + k_a.P) = k_a.P$$

$$\boxed{\theta = \frac{k_a \cdot P}{k_d + k_a \cdot P}} \quad \text{...... (3)}$$

Divide the numerator and the denominator on the R.H.S by k_d.

$$\theta = \frac{k_a/k_d \cdot P}{k_d/k_d + k_a \cdot P/k_d}$$

$$\boxed{\theta = \frac{K.P}{1+K.P}} \quad \text{...... (4)}$$

Remember that 'K' is the ratio of two rate constants i.e., k_a/k_d.

This K is a sort of equilibrium constant for this process and it is called **adsorption co-effic**
Greater the rate of adsorption on the surface of the solid, greater the adsorption co-effic
According to equation (4), the fraction of the total surface covered by the gas molecules depends
the pressure of the gas and adsorption co-efficients.

Let us suppose that the amount of the gas adsorbed per gram of the absorbent is 'x'. T
proportional to θ.

$$x \propto \theta$$

$$x \propto \frac{KP}{1+KP}$$

$$\boxed{x = k'\frac{KP}{1+KP}} \quad \text{...... (5)}$$

k' = Proportionality constant

Equation (5), gives us relationship (تعلق) between the amount of the gas adsorbe
essure of the gas at constant temperature. This equation (5) is called **Langmuir ads**
therm.

Let us change the shape of equation (5) to have an equation of straight line.

$$x = k' \cdot \frac{KP}{1+KP}$$

$$\frac{1}{x} = \frac{1}{k'} \cdot \left(\frac{1+KP}{KP}\right)$$

$$\frac{P}{x} = \frac{1}{k'} \cdot \left(\frac{1+KP}{K}\right)$$

$$\frac{P}{x} = \frac{1}{k'} \cdot \left(\frac{1}{K} + P\right)$$

$$\boxed{\frac{P}{x} = \frac{1}{k''} + \frac{P}{k'}} \quad \ldots\ldots (6)$$

When $k'' = k'/K$

Equation (6) is of straight line. When a graph is plotted between P/x on y-axis and pressure of the system an x-axis, then a straight line is obtained Fig. (12.4).

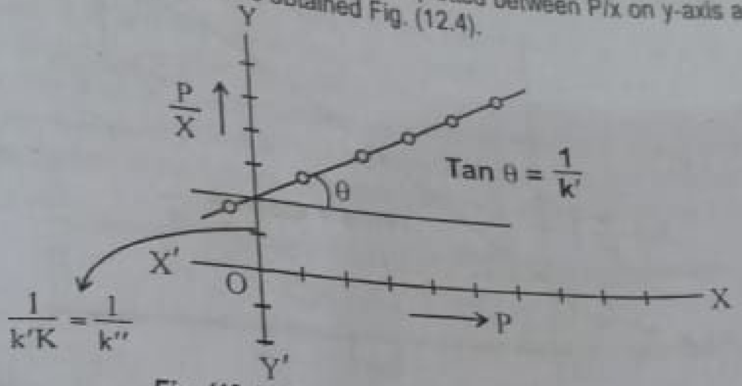

Fig. (12.4) Langmuir adsorption isotherm.

From the slope of the straight line, we can get the value of $\frac{1}{k'}$ and intercept of the straight gives the value of $\frac{1}{k''}$. Langmuir adsorption isotherm also holds at low pressures, but fails at pressures.

12.2.7 Adsorption Of the Solutes From Solutions:

It is a well known observation the **activated charcoal** can remove the **coloured im** (رنگ دار آلودگی) from the solutions. It can also adsorb many **dye stuffs** (رنگ دار چیزیں). When a s acetic acid is shaken with activated charcoal, then the certain amount of the acid is re adsorption. The concentration of the acetic acid in the solution decreases. We should keep that the adsorption for the solution mostly follows the same principles as are true for the ad gases by the solides.

Anyhow (البتہ), the factors which are responsible (ذمہ دار ہوتا) for the adsorption adsorption of solute should be of the same states.

Freundlich has given an empirical mathematical relationship (تجرباتی ہوئی حسابی مساوات amount of the solute adsorbed related to the concentration of the solution.