CHAPTER

10

SURFACE CHEMISTRY

10.1.0 INTRODUCTION

It is that branch of chemistry, which deals with the interaction of a certain substance at the surface of a solid substance. When a solid surface is exposed to a gas or a liquid, the molecules from the gas or a solution phase concentrate at the surface of solid. We can also say that molecules of gas are accumulated on the surface of the solid.

"This phenomenon of accumulation of the molecules of a gas or a liquid at a solid surface is called adsorption."

10.1.1 Adsorbate and Adsorbent:

"That substance which concentrates upon the surface of a solid is called adsorbate and the solid is called adsorbent."

Examples:

(i)   Methylene blue is on organic dye. When finally divided charcoal is stirred into the dilute solution of methylene blue, then the molecules of dye are adsorbed by the particles of charcoal. The process of adsorption is noted by the effect, that intensity of the colour of solution decreases.

(ii)   It has also been observed that the pressure of the gases like SO_2, Cl_2 and NH_3 are decreased, when powdered charcoal is placed in the vessels of these gases. Actually, the molecules of these gases concentrate on the charcoal surface and we say that gas has been adsorbed on the surface of charcoal.

10.1.2. Difference between adsorption and absorption:

As we have discussed above, that in case of adsorption the concentration is present on the surface of solid. In the case of absorption, the outer substance penetrates into the body of absorbent. Anyhow, absorption and adsorption take place side by side. For this purpose, a new term has been introduced which is called sorption. This phenomenon includes both adsorption and absorption.

10.1.3 Why absorption takes place?

The atoms and molecules of solid substance present in the bulk of a solid are satisfied due to surrounding atoms and molecules. Their valencies are fulfilled.

The atoms and molecules at the surface of solid are unbalanced. There are residual attractive forces on the solid surface. These residual forces are responsible to hold the molecules of adsorbate.

10.1.4 Types of adsorption:

When a gas is adsorbed on the surface of a solid, then two types of adsorptions can be thought of

(a)   Physical adsorption   (b) Chemical adsorption

(i)   Physical adsorption

"It is that type of adsorption, which is due to presence of Van der Waal's attractive forces between the gas molecules and the solid surface." The adsorption of H_2 and O_2 on the surface of charcoal is physical adsorption. This is also called Van der Waal's adsorption.

(ii)   Chemical adsorption

"When the molecules of a gas are held by the solid substance by chemical bonds, then it is called chemical adsorption." It is also called chemisorption.

Hydrogen is chemisorbed on nickel. Hydrogen has physical adsorption on nickel and the after dissociation of H_2 it gets chemisorption on the surface of nickel. It means that process of adsorption is a combination of two types of adsorptions i.e. physical and chemical.

10.1.5 Difference of physical and chemical adsorption:

When the gases are adsorbed on the solid surface then, there can be physical or chemical adsorption. These two types of adsorptions differ in many respects. Let us discuss some of them.

1.   Surface area:

The extent of adsorption depends upon surface area. Greater the surface area of adsorbent, greater the amount of the gas adsorbed. If nickel and platinum metals are finally divided, then they adsorb the hydrogen gas to greater extent just like charcoal and silica gel.

2.   Nature of gas:

Greater the critical temperature of gas, greater the possibility of adsorption. Critical temperature of SO_2 is 157°C and 1 g of activated charcoal adsorbs 380 cm^3 of SO_2. But adsorption of CH_4 and H_2 is less.

3.   Heat of adsorption:

It is the amount of heat evolved when 1g mole of a gas is adsorbed on the solid surface. This heat of adsorption is less for physical adsorption and is in the range of 5 kcal mol^{-1}. It varies from 20 – 100 kcal mol^{-1} for chemisorption.

4.   Reversible process:

The gas which is adsorbed on the solid surface, can be desorbed under reverse conditions of temperature and pressure. Anyhow, chemisorption is not a reversible process because a compound is produced upon the surface of the solid.

5.   **Effect of temperature:**

Low temperature favours the physical adsorption while chemisorption generally increases with temperature. For example, nitrogen shows physical adsorption on the surface of iron at 190°C, but at 900°C chemisorption takes place to form nitride.

6.   **Effect of pressure.**

It is a known fact that there is a dynamic equilibrium 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.

7.   **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 is formed.

10.2.0 ADSORPTION ISOTHERMS

10.2.1. 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 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.

10.2.2 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 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.

10.2.3 Freundlich adsorption isotherm:

Freundlich adsorption isotherm has been proposed by the concerned scientists in the shape of an empirical relationship which is as follows:

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

w = Mass of the gas adsorbed 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.

10.2.4 Graphical representation:

If we plot a graph between pressure on x-axis and $\dfrac{w}{m}$ on y-axis, then a rising curve is obtained as shown below. Fig. (1)
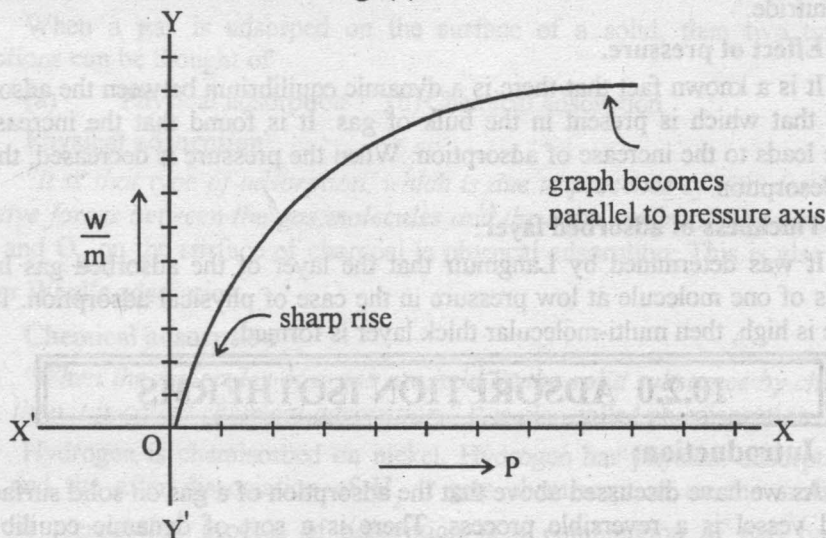

Fig. (1) Plot of pressure of gas and $\dfrac{w}{m}$ of the system.

According to the shape of the graph, there is a sharp rise of the curve at low pressures and ultimately, it becomes parallel to the pressure axes. It means that when the pressure exceeds the certain limit, then $\dfrac{w}{m}$ 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 $\quad \log \dfrac{w}{m} = \log k + \dfrac{1}{n} \cdot \log P$

or $\quad \log \dfrac{w}{m} = \dfrac{1}{n} \log P + \log k \quad \ldots\ldots (2)$

Equation (2), is of straight line. (See page 583, 11.2.0) $\log \dfrac{w}{m}$ corresponds to y, $\log P$ correspond to x, $\log k$ corresponds to intercept and $\dfrac{1}{n}$ will be the slope of straight line. We plot a graph between $\log \dfrac{w}{m}$ on *y*-axis and $\log P$ on x-axis and a

straight line is obtained Fig. (2). From the slope and the intercept of the straight line, we can calculate the value of 'k' and 'n'. These two constants are the characteristics to the system under consideration.
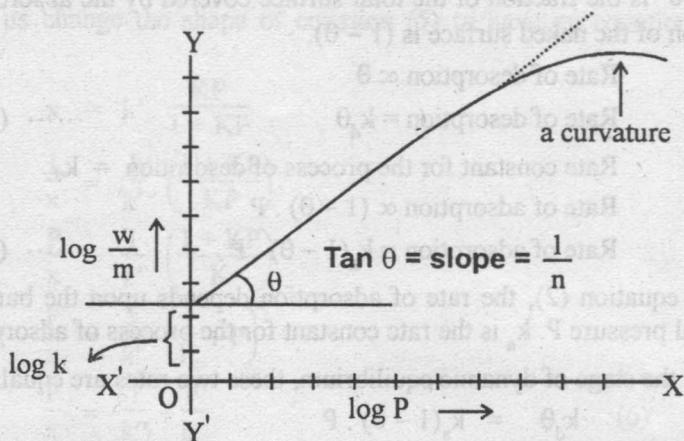

Fig. (2) Graph of $\log \frac{w}{m}$ and $\log P$ to calculate n and k of system.

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.

10.2.5 Langmuir adsorption isotherm:

The basic assumptions 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.

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

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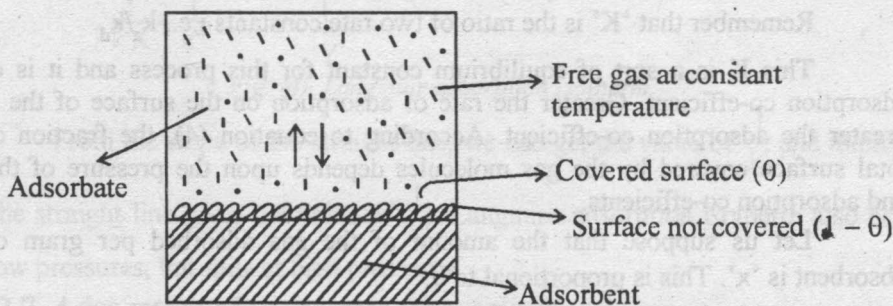

Fig. (3). Equilibrium position of adsorption system.

Langmuir thinks that adsorption of gas molecule is due to collisions of the gas molecules on the surface of the solid. During these collisions, all the molecules are not adsorbed but some of them are desorbed, or you can say they are evaporated. At a given pressure and temperature, a stage reaches when the rate of adsorption becomes equal to the rate of desorption. This is the state of dynamic equilibrium as shown in the diagram. Fig. (3).

10.2.6 Mathematical derivation of Langmuir adsorption ioshterm:

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

$$\text{Rate of desorption} \propto \theta$$

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

Rate constant for the process of desorption $= k_d$

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

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

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

At the stage of dynamic equilibrium, these two rates are equal, so

$$k_d\theta \quad = \quad k_a(1 - \theta) . P$$

$$k_d\theta \quad = \quad k_a . P - k_a \theta . P$$

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

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

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

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

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

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

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-efficient. Greater the rate of adsorption on the surface of the solid, greater the adsorption co-efficient. According to equation (4), the fraction of the total surface covered by the gas molecules depends upon 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'. This is proportional to θ.

$$x \propto \theta$$

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

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

$$k' = \text{Proportionality constant}$$