SURFACE CHEMISTRY

Surface chemistry deals with phenomena that occur at the surfaces or interfaces.In this Unit, we are studying some important features of surface chemistry such as adsorption, catalysis and colloids

1.Adsorption

The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption.

The molecular species or substance, which concentrates or accumulates at the surface is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent.
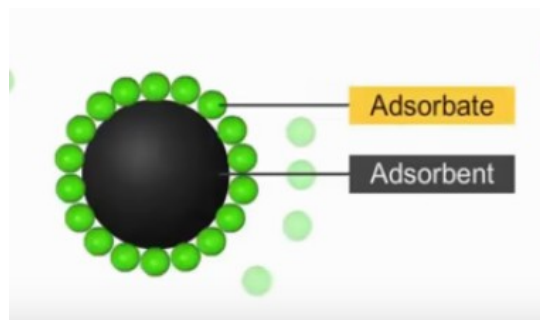
Examples

(i) If a gas like O_2 , H_2 , CO, Cl_2 , NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.

(ii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.

(iii) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption.

Desorption:-The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

2.Distinction between Adsorption and Absorption

In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in

absorption, the substance is uniformly distributed
throughout the bulk of the solid.

So absorption is the the phenomenon of uniform distribution of particles through out another particle It is a bulk phenomenon.

Examples are:-

1) $CaCl_2$ is placed in humid atmosphere, Water molecules enter throughout the body of $CaCl_2$ and it become deliquescent.

2) When chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption.

**Water vapours are absorbed by
anhydrous calcium chloride but adsorbed by silica gel.**

In other words,

**in adsorption the concentration of the adsorbate
increases only at the surface of the adsorbent, while in absorption the
concentration is uniform throughout the bulk of the solid.**

Sorption :-If both adsorption and absorption can take place simultaneously then it is called as Sorption

5.Types of Adsorption

There are mainly two types of adsorption of gases on solids.

a.Physisorption.:-If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as physical adsorption or physisorption.

b.chemisorption :-When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption.

Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased.

For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

6.Comparison of Physisorption and Chemisorption

Physisorption	Chemisorption
1. It arises because of van der Waals' forces.	1.It is caused by chemical bond formation.
2. It is not specific in nature. van der Waals' forces have no preference for adsorbate	2.It is highly specific in nature. oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.
3.It is reversible in nature.	3.It is irreversible.
4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily. 1g of activated charcoal adsorbs more sulphur dioxide (Tc 630k)than methane (Tc 190 k) and dihydrogen(Higher the critical temp higher the Vander waal's force)	4.It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ mol $^{-1}$)in this case.	5.Enthalpy of adsorption is high (80-240 kJ mol $^{-1}$) in this case.
6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	6. High temperature is favourable for adsorption. It increases with with increase of temperature.
7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	8. It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure	9It results into unimolecular layer.

6.Adsorption Isotherms

The graph showing extend of adsorption against pressure at constant temperature is called adsorption isotherm
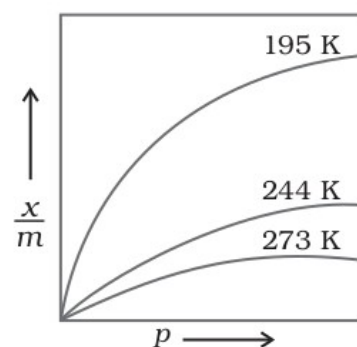
Freundlich adsorption isotherm:-

Freundlich conducted a study on the variation of extend of adsorption(x/m) with pressure(p) by plotting a graph

These curves indicate that
a) at a fixed pressure, there is a
decrease in physical adsorption with
 increase in temperature.

b) curves always seem to approach
saturation a t high pressure.

On the basis of his observation, he derived the mathematical expression for it.

At low pressure, $x/m \ \alpha \ P^1$
At high pressure, $x/m \ \alpha \ P^0$
At saturation pressure Ps,   x/m is directly proportional to P
    raised to a power that has value b/w one and zero.
        At Ps, $x/m \ \alpha \ P^{1/n}$, were   n › 1
Therefore in general,

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

It is the mathematical expression of Frendlich adsorption isotherm.

7.Graphical method of calculation of x/m

x/m can be calculated graphically.
Consider the eqn. $x/m = KP^{1/n \cdot}$
Taking logarithm on both sides,
$$\log x/m \quad = \log KP^{1/n}$$
$$= \log K + \log P^{1/n}$$
$$= \log K + 1/n \log P$$

Or by rearranging,   **$\log x/m \quad = \ 1/n \log P + \log K$**
    The above equation is of the form y = mx+c

so a plot of log x/m against
log P gives a straight line whose
slop is 1/n and y intercept is log K.
From the slop n can be
calculated and from y intercept,
k can be calculated By substituting
n ,k and p , x/m can be calculated