Surface chemistry deals with phenomena that occur at the surfaces or interfaces. Due to complete miscibility, there is no interface between the gases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallization occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

To accomplish surface studies accurately, it becomes imperative to have a really clean surface. Under very high vacuum of the order of 10^{-8} to 10^{-9} pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

Adsorption

Adsorption is essentially a surface phenomenon. 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***.

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.

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

The process of removing an adsorbed substance from a surface on which it is adsorbed is called ***desorption***. In flash desorption the sample is suddenly heated (electrically) and the resulting rise of pressure is interpreted in terms of the amount of adsorbate originally on the sample.

Thermodynamics of Adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.

During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative.

The enthalpy of adsorption depends on the extent of surface coverage, mainly because the adsorbate particles interact. If the particles repel each other (as for CO on palladium) the adsorption becomes less exothermic (the enthalpy of adsorption less negative) as coverage increases.

When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative.

Exceptions may occur if the adsorbate dissociates and has high translational mobility on the surface. For example, H_2 *adsorbs endothermically on glass because there is a large increase of translational entropy accompanying the dissociation of the molecules into atoms that move quite freely over the surface. In its case, the entropy changes in the process* $H_2(g) \rightarrow 2\ H(glass)$ *is sufficiently positive to overcome the small positive enthalpy change.*

Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $- T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

Types of adsorption

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

Characteristics of physisorption

- It arises because of van der Waals’ forces
- It is not specific in nature
- It is reversible in nature
- It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.
- Enthalpy of adsorption is low (20-40 kJ mol $^{-1}$) in this case
- Low temperature is favourable for adsorption. It decreases with increase of temperature.
- No appreciable activation energy is needed
- It depends on the surface area. It increases with an increase of surface area
- It results into multimolecular layers on adsorbent surface under high pressure

Since the van der Waals forces are the same as those that produce liquefaction, adsorption does not occur at temperatures that are much above the critical temperature of the gaseous adsorbate. Also, if the pressure of the gas has values near the equilibrium vapor pressure of the liquid adsorbate, then a more extensive adsorption multilayer adsorption occurs

Characteristics of chemisorption

- It is caused by chemical bond formation
- It is highly specific in nature
- It is irreversible

- Since chemical bonds are broken and formed in the process of chemisorption, enthalpy of adsorption is high (40- 400 kJ mol^{-1}).
- High temperature is favorable for adsorption. It increases with the increase of temperature.
- High activation energy is sometimes needed
- It also depends on the surface area. It too increases with an increase of surface area
- It results into unimolecular layer

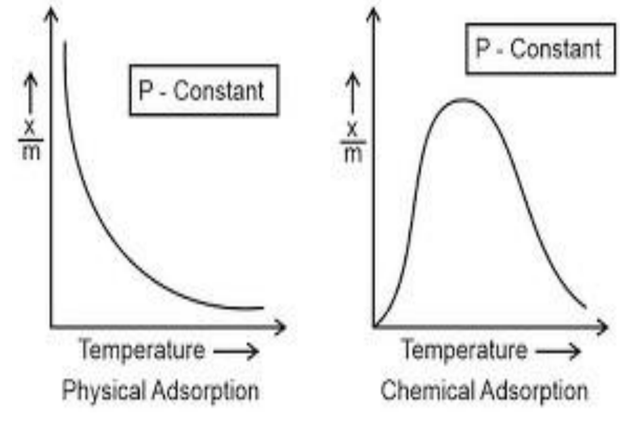
The difference between physical and chemisorption is typified by the behavior of nitrogen on iron. At the temperature of liquid nitrogen, -190 °C, nitrogen is adsorbed physically on iron as nitrogen molecules, N_2. The amount of N_2 adsorbed decreases rapidly as the temperature rises. At room temperature iron does not adsorb nitrogen at all. At high temperatures, ~ 500 °C, nitrogen is chemisorbed on the iron surface as nitrogen atoms.

Factors influencing adsorption

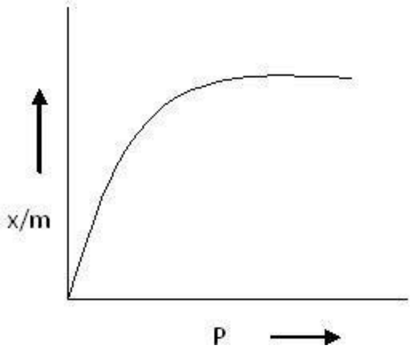
1. **Nature of adsorbent & adsorbate**: Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

   Easily liquefiable gases such as ammonia, hydrochloric acid, chlorine, Sulphur dioxide etc. are adsorbed more readily than permanent gases

2. **Temperature**
   Low temperature is favorable for physisorption and it decreases with increase of temperature. Chemisorption increases with the increase of temperature and reaches a maximum and then decreases with temperature. The plots which shows the variation of the extent of adsorption with temperature at constant pressure is known as ***adsorption isobar.***



3. **Pressure**
   The extent of adsorption increases with pressure and reaches a maximum value and then becomes independent of pressure. The pressure at which the extent of adsorption becomes independent of pressure is known as saturation pressure.



The plots which shows the variation of the extent of adsorption with pressure at constant temperature is known as ***adsorption isotherm***

Freundlich adsorption isotherm

Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

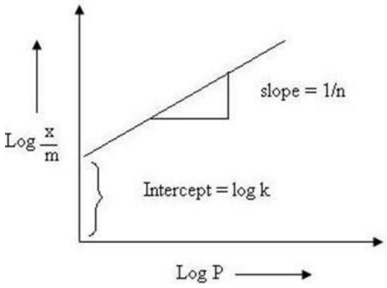
$$x/m = k.P^{1/n} \quad (n > 1)$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P. k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature

Taking logarithm of the above equation gives

$$\log (x/m) = \log k + 1/n \log P$$

The validity of Freundlich isotherm can be verified by plotting log (x/m) on y-axis (ordinate) and log p on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid



The factor 1/n can have value between 0 and 1 (probable range 0.1 to 0.5).

When1/n = 0, x/m = constant, the adsorption is independent of pressure.

When 1/n = 1, x /m = k p, i.e. x /m ∝ p, the adsorption varies directly with pressure

The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

Adsorption from solution phase

When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. The precipitate of

$Mg(OH)_2$ attains blue color when precipitated in presence of Magneson reagent. The color is due to adsorption of Magneson

The following observations have been made in the case of adsorption from solution phase:

The extent of adsorption from solution phase

- decreases with an increase in temperature
- increases with an increase of surface area of the adsorbent
- depends on the concentration of the solute in solution
- depends on the nature of the adsorbent and the adsorbate

Freundlich adsorption isotherm

$$x/m = k\,C^{1/n} \quad (n > 1)$$

where C is the equilibrium concentration, i.e., when adsorption is complete

On taking logarithm of the above equation, we have

$$\log (x/m) = \log k + 1/n \log C$$

Plotting log x m against log C a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations give the value of x. Using the above equation, validity of Freundlich isotherm can be established.

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