

CHEMISTRY STUDY MATERIALS FOR CLASS 12

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Surface Chemistry

It is the branch of chemistry that deals with the study of nature of surfaces and the different processes taking place at the surface. The important surface phenomena are adsorption, corrosion, electrode process, heterogeneous catalysis, dissolution etc.

ADSORPTION

It is the process of concentration or accumulation of a substance on the surface of another substance. The substance which is adsorbed is called adsorbate and the substance whose surface on which adsorption takes place is called adsorbent. The commonly used adsorbents are charcoal, silica gel, alumina gel, clay, colloids, and metals in finely divided state etc.

Adsorption is a surface phenomenon. Some examples of adsorption are:

1. Powdered charcoal adsorbs gases like H_2 , O_2 , CO , Cl_2 , NH_3 , SO_2 etc.
2. Silica gel adsorbs moisture
3. Animal charcoal adsorbs colouring material from sugar solutions

Desorption: The process of removal of an adsorbed substance from the surface of adsorbent is called desorption. i.e. it is the reverse of adsorption.

Distinction between adsorption and absorption

In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the solid. So adsorption is a surface phenomenon while absorption is a bulk phenomenon.

Sorption: If adsorption and absorption occur simultaneously, the process is called sorption.

Mechanism of Adsorption

The surface particles of the adsorbent are not in the same environment as the particles inside the bulk (inner part). Inside the adsorbent, all the forces are mutually balanced. But at the surface, there is always some unbalanced or residual forces. These forces of the adsorbent are responsible for adsorption.

Heat of adsorption (Enthalpy of Adsorption)

Adsorption is an exothermic process. i.e. some heat is always evolved during adsorption. The amount of heat evolved when 1 mole of an adsorbate is adsorbed on the surface of an adsorbent is called heat of adsorption.

Thermodynamic aspects of adsorption

Adsorption is an exothermic process. When a gas is adsorbed, the degree of freedom (randomness) of its molecules decreases and hence the entropy decreases. i.e., ΔS becomes negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, ΔG must be negative. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if $\Delta H > T\Delta S$. 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

Depending on the force of attraction between adsorbent and adsorbate, adsorption is of two types – physical adsorption or physisorption and chemical adsorption or chemisorption.

If the force of attraction between adsorbent and adsorbate is weak van der Waals force, it is called physical adsorption or physisorption. For physisorption, the heat of adsorption is low and it is not specific since the van der Waals forces are universal. That is any substance can form van der Waals force with any surface.

In chemisorptions, the force of attraction between adsorbent and adsorbate is chemical bond. It is also called activated adsorption since it involves some activation energy. For chemisorption, the enthalpy of adsorption is high and it takes place at high temperature. It is highly specific in nature and it will occur only if there is some possibility of chemical bonding between adsorbent and adsorbate.

A physisorption at low temperature may pass into chemisorption at high temperature. For e.g. Hydrogen gas is first adsorbed on nickel by Vander Waals force. But at high temperature, the molecules of H_2 dissociate to form H atoms and they are adsorbed on the surface of Ni by chemical bond.

Both physisorption and chemisorption increases with increase in surface area of the adsorbent. Surface area can be increased by powdering the adsorbent.

Distinction between physisorption and chemisorption

	Properties	Physisorption	Chemisorption
1	Force of attraction	Weak van der Waals force	Strong chemical bond
2	Specificity	Not specific in nature	Highly specific
3	Reversibility	Reversible	Irreversible
4	Extend of adsorption and nature of gas	Easily liquefiable gases (e.g. CO ₂ , HCl, NH ₃ etc) are easily adsorbed than permanent gases (e.g. H ₂ , N ₂ , O ₂ etc)	Gases which can react with the adsorbent show chemisorption
5	Heat of adsorption	Low (20-40 kJ/mol)	High (80-240 kJ/mol)
6	Temperature	Low temperature is favourable. It decreases with increase in temperature	High temperature is favourable. It increases with increase in temperature
7	Activation energy	No appreciable activation energy is needed	High activation energy is required
8	Nature of layer	Multimolecular layer of adsorption occurs	Only unimolecular layer of adsorption occurs

Adsorption Isotherms

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a graph called adsorption isotherm.

Freundlich adsorption isotherm:

Freundlich 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:

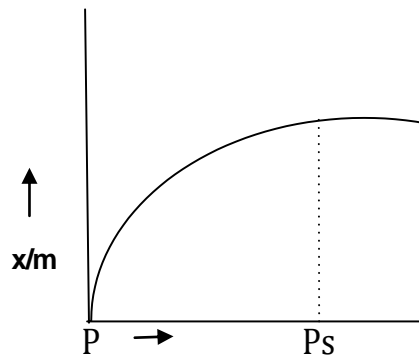
$x/m = k.P^{1/n}$ (where $n > 1$) where x is the mass of the gas adsorbed, m is the mass of the adsorbent, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

The above relationship can be represented in the form of a graph as follows:

From the graph it is clear that x/m (extend of adsorption) increases with pressure upto a certain pressure called *saturation pressure* (P_s) and after that it becomes constant. If we take logarithm of the above equation,

we get

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



This equation is of the form $y = mx+c$, equation for a straight line. So if we plot $\log x/m$ against $\log P$, we get a straight line, which verifies Freundlich isotherm.

The value of $1/n$ in Freundlich isotherm ranges from 0 to 1

When $1/n = 0$, $x/m = a$ constant. i.e. the adsorption is independent of pressure. When $1/n = 1$, $x/m = k.p$, the adsorption varies linearly with pressure.

Freundlich adsorption isotherm failed to explain adsorption at very high pressures.

Adsorption from solution

Certain solid adsorbents can adsorb solute particles from solution. This is known as adsorption from solution. E.g.:

1. 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.
2. Animal charcoal adsorbs colouring materials from sugar solution. So it is used for the purification of sugar. The important characteristics of adsorption from solution are:
 - (i) The extent of adsorption decreases with an increase in temperature.
 - (ii) The extent of adsorption increases with an increase of surface area of the adsorbent.
 - (iii) The extent of adsorption depends on the concentration of the solute and the nature of the adsorbent and the adsorbate.

Freundlich adsorption isotherm is applicable to adsorption from solution also. Here instead of pressure, concentration of the solution is used.

i.e., $x/m = kC^{1/n}$ (where C is the equilibrium concentration).

On taking logarithm of the above equation, we have $\log x/m = \log k + 1/n \log C$

On plotting $\log x/m$ against $\log C$, a straight line is obtained which verifies Freundlich isotherm.
