
SURFACE CHEMISTRY

LECTURE 1

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting into a higher concentration of molecules on the surface is called *adsorption*. The substance adsorbed on the surface is called *adsorbate* and the substance on which it is adsorbed is called *adsorbent*.

Examples :

1. Dyes get adsorbed on cotton fibres, activated carbon, etc.
2. Ammonia gas placed in contact with charcoal gets adsorbed on it.
3. Oxalic acid placed in contact with activated carbon gets adsorbed on it.

Mechanism of adsorption process :

Adsorption is spontaneous process, so for the process ΔG is negative. According to Gibbs equation.

$$\Delta G = \Delta H - T\Delta S$$

For adsorption ΔS (Change in entropy) is always negative because adsorption of molecules on the surface lowers the disorder. So, for value of ΔG to be negative, ΔH must necessarily be negative and $|\Delta H| > |T\Delta S|$. The process is exothermic because it involves forces of attraction between adsorbate and adsorbent.

As the process of adsorption proceeds further ΔH becomes less and less after certain time period. When ΔH becomes equal to $T\Delta S$, $\Delta G = 0$ and system attains equilibrium. At equilibrium,

Factors Affecting Adsorption**1. Surface area of the adsorbent**

if the surface area of the adsorbent is large, the amount of adsorption would be more.

That is why finely divided substances have a larger adsorption power than when they are present in a compact form.

2. Nature of adsorbent gas

Easily liquifiable gases, possess high critical temperature (Carbon dioxide, Sulphur dioxide, Methane....) adsorb to the more extent in comparison to the normal gases (Oxygen, Nitrogen, Helium ...)

3. Temperature

Normally, adsorption decreases with an increase in temperature; however, it can be vice versa as well.

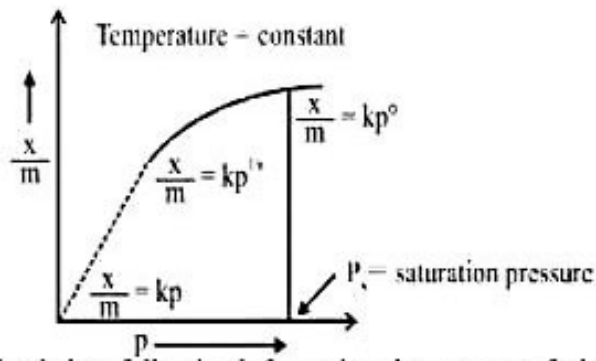
4. Pressure

A relation between x/m (amount adsorbed per unit weight of adsorbent) and the equilibrium pressure can be given in the form of Freundlich adsorption Isotherm.

1. Freundlich Adsorption Isotherm : It is represented as

$$\frac{x}{m} = kP^{1/n}, \text{ depending on whether the adsorbate is a solution or a gas.}$$

Where x = amount of adsorbate, m = amount of adsorbent P = pressure, k and n are constants which depend on the nature of the adsorbent and the gas at given temperature.



The graph obtained gives following information about extent of adsorption.

(a) **At very low pressure :** At very low pressures, the graph is nearly straight line and at these pressures.

$$\frac{x}{m} \propto P \quad \text{or} \quad \frac{x}{m} = k.P$$

(b) **At intermediate range of pressure :** At these pressures graph is curved and

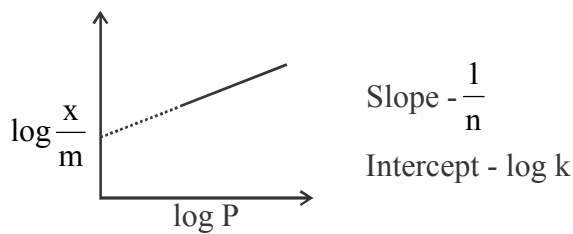
$$\frac{x}{m} \propto P^{1/n} \quad \text{or} \quad \frac{x}{m} = k.P^{1/n} \quad (\text{probable 'n' value is } 0.1 - 0.5)$$

(c) **At very high pressure :** The graph becomes parallel to x-axis which indicates that extent of adsorption is independent to the pressure i.e.,

$$\frac{x}{m} \propto P^0 \quad \text{or} \quad \frac{x}{m} = k$$

Taking logarithm form

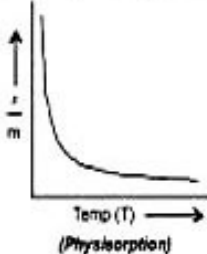
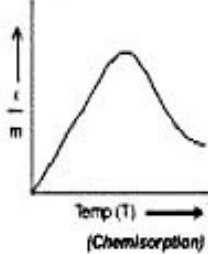
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$



There are two main types of adsorption

1. Physical adsorption (or) Physisorption
2. Chemical adsorption (or) Chemisorption

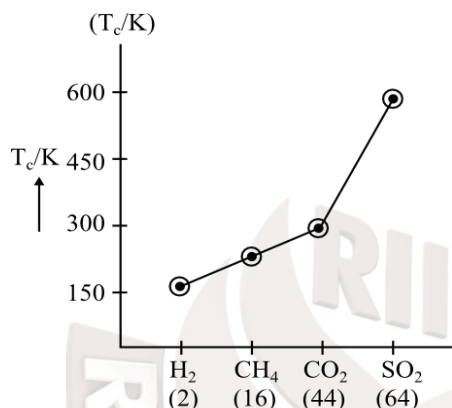
COMPARISON OF PHYSI-SORPTION AND CHEMISORPTION

S.No.	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemisorption.
5.	Heat of adsorption is low due to weak forces. (20-40kJ/mole)	Heat of adsorption is high due to strong attractive forces (80-240kJ/mole)
6.	Low temperature is favourable. It decreases with increase of temperature.	High temperature is favourable. It increases with increase of temperature.
	 <p style="text-align: center;">(Physisorption)</p>	 <p style="text-align: center;">(Chemisorption)</p>
7.	No appreciable activation energy is involved.	High activation energy is involved.
8.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does not cause desorption.
9.	It depends on the surface area. It increases with increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
10.	It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

Chemistry

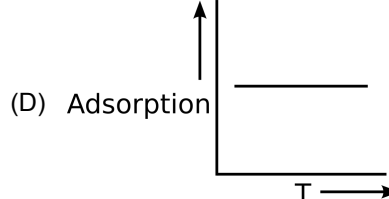
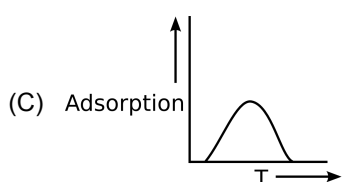
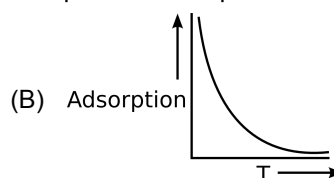
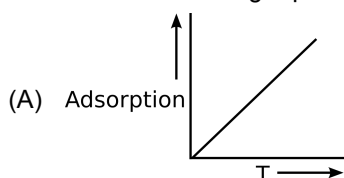
Single Correct Questions

1. According to Freundlich adsorption isotherm, which of the following is correct?
 (A) $\frac{x}{m} \propto p^1$ (at high pressure range) (B) $\frac{x}{m} \propto p^{1/n}$ (at intermediate pressure range)
 (C) $\frac{x}{m} \propto p^0$ (at low pressure range) (D) All of these are correct
2. The heat of physisorption lies in the range of
 (A) 1 to 10 kJ mol⁻¹ (B) 20 to 40 kJ mol⁻¹ (C) 40 to 200 kJ mol⁻¹ (D) 200 to 400 kJ mol⁻¹
3. Critical temperature (T_c /K) of different gases (molar masses shown) are shown below:



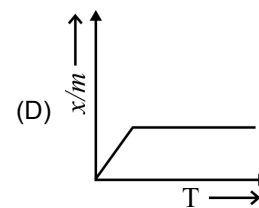
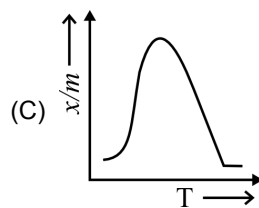
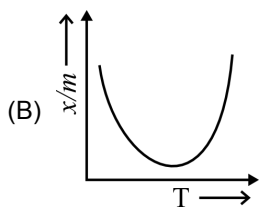
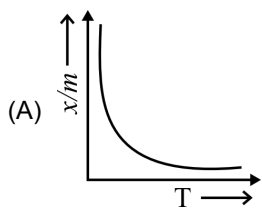
Maximum and minimum adsorption is for gases.

- (A) SO₂ (Maximum) - H₂ (Minimum) (B) CO₂ (Maximum) - H₂ (Minimum)
 (C) H₂ (Maximum) - SO₂ (Minimum) (D) independent of T_c
4. During adsorption, which of the following is positive?
 (A) ΔG (B) ΔS (C) ΔH (D) None of these
5. At the equilibrium position in the process of adsorption _____
 (A) $\Delta H > 0$ (B) $\Delta H = T\Delta S$
 (C) $\Delta H > T\Delta S$ (D) $\Delta H < T\Delta S$
6. Which of the following represents the variation of physical adsorption with temperature ?

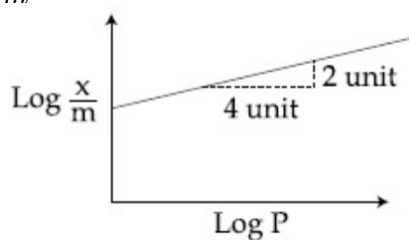


7. Which of the following is not a characteristic of chemisorption?
 (A) Ir-reversible (B) It is specific
 (C) It is multi-layered phenomenon (D) Heat of adsorption is about -400 KJ.

8. Which plot is the adsorption isobar for chemisorption where x is the amount of gas adsorbed on mass m (at constant pressure) at temperature T :



9. Adsorption of a gas follows Freundlich adsorption isotherm. In the given plot, x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p . $\frac{x}{m}$ is proportional to :



- (A) $p^{1/2}$ (B) p^2 (C) p (D) $p^{1/4}$
10. Which of the following is absorbed to maximum extent on chaycoal
- (A) H_2 (B) N_2 (C) CO_2 (D) O_2

