Adsorption and Catalysis

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- **What is adsorption?**

Adsorption is deposition or sticking or adhesion of atoms, ions or molecule from a substance (it could be gas, liquid or dissolved solid) to a surface of the adsorbent. It is a surface phenomenon.

*Adsorbate***:** The molecular species that gets adsorbed on the surface is known as adsorbate.

Adsorbents: The surface on which adsorption occurs is known as adsorbent. Common examples of adsorbents are clay, silica gel, colloids, metals.

- **What is absorption?**

Absorption is the process in which a fluid is dissolved by a liquid or a solid (absorbent). It is bulk phenomenon.

Adsorption   Absorption
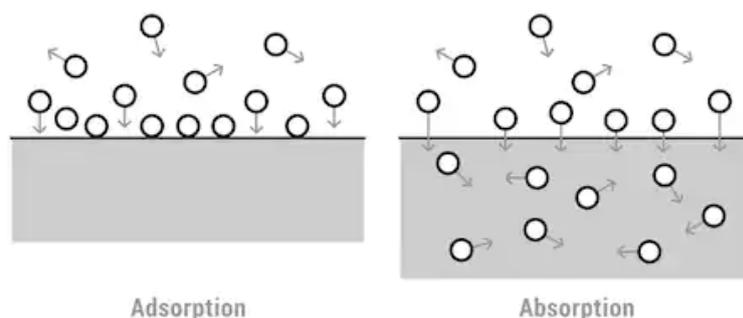
Thermodynamics of adsorption:

As adhesive force drives the process the energy i.e. enthalpy change (ΔH) of the process is negative i.e. exothermic. In this process particles adhere to the surface and there degree of freedom of the particles decreases. So the entropy change (ΔS) is negative. As per above discussion we can reach to a conclusion that adsorption is an enthalpy driven process. If the magnitude of enthalpy is excess over the magnitude of entropy change then adsorption would be spontaneous only.

$\Delta H < 0$, $\Delta S < 0$

Factors Affecting Adsorption

- Adsorption occurs on the surface of almost all solids.
- (i) Nature and surface area of the adsorbent.
- (ii) Nature of the adsorbed gas.

- (iii) Temperature.

- (iv) Pressure of the gas.

Let us now discuss these factors briefly.

(i) Nature and surface area of the adsorbent

Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents.

The extent of adsorption also depends upon the surface area of the solid. Greater the surface area, more is the surface available for adsorption and greater is the adsorption. The surface area depends upon the particle size of the substance. A cube of each side equal to 1cm has six faces. Each of them is a square with surface area of $1cm^2$. Thus, the total surface area of this cube is 6 cm^2 Fig. 17.3 (a). If its each side is divided into two equal halves, ½ cm long, and the cube is divided into two equal halves, ½ cm long, and the cube is cut along the lines indicated in the Fig (b), the cube would be divided into 8 smaller cubes with each side 0.5 cm long [Fig. 17.3 (b)]. Surface area of each small cube would be (6 ´ 0.5 ´ 0.5) = 1.5 cm^2 and the total surface area of all the 8 smaller cubes would be 12 cm^2 which is double the surface area of the original cube. If it is subdivided into smaller cubes, each of side equal to $1 ´ 10^{-6}$ cm the surface area will increase to $6 ´ 10^6$ cm^2 or 600 m^2. The increase in surface area would result in greater adsorption.

1 cm
1 cm
1 cm
(a)   (b)
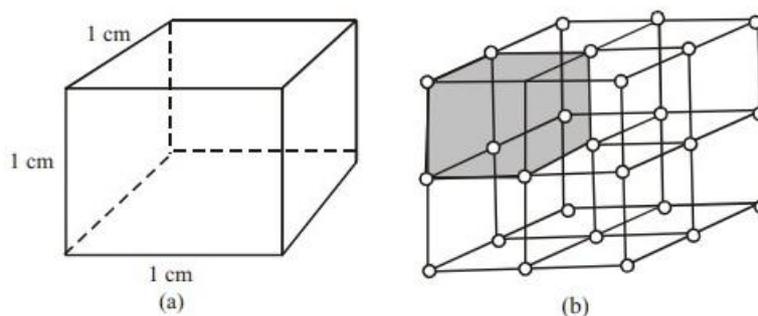
Now we can explain why the solids that are porous in nature and have rough surfaces are better adsorbents. It is so because each of these features increases the surface area.

Fact Check: Raney Nickel is more active than normal one.

In hydrogenation reaction H_2 gas is adsorbed on the surface area of Ni. Raney nickel is finely divided Ni metal and we get more surface area if we use Raney Ni rather than regular one. So Raney Ni is more effective and it takes lower temperature to carry out the hydrogenation reaction.

(ii) The Nature of the Adsorbed Gas

The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquifiable or are more soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of SO_2 or NH_3 adsorbed by charcoal is much more than that of H_2 or O_2 gases. It is because the intermolecular forces are stronger in more easily liquifiable gases, therefore, they get adsorbed more strongly.

(iii) Temperature

The extent of adsorption decreases with rise in temperature. For example, under one atmosphere pressure, one gram of charcoal adsorbs about 10 cm^3 of N_2 gas at 272 K, 20 cm^3 at 248 K and 45 cm^3 at 195 K.

Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed, is called **enthalpy of adsorption**. The adsorption process is similar to the condensation process. The reverse process is called **desorption** and is *endothermic* in nature. It is similar to the evaporation process. When a gas is kept in contact with a solid adsorbent in a closed container, a dynamic equilibrium is established in due course of time.

gas adsorbate + solid adsorbent ↔ gas adsorbed on the solid + *heat*

Since the forward process (adsorption) is exothermic in nature, according to the Le Chatelier's principle, it would be favoured at low temperature. Therefore, the extent of adsorption would increase on decreasing the temperature and would decrease on increasing the temperature.

(iv) Pressure of the Gases:

Extent of adsorption with pressures are plotted at constant temperature, known as absorption isotherm.

Freundlich Adsorption Isotherm

In 1909, German scientist Freundlich provided an empirical relationship between the amount of gas adsorbed by a unit mass of solid adsorbent and pressure at a particular temperature. It is expressed using the following equation –

$x/m = k.P^{1/n}$ (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 that depend on the nature of the adsorbent and the gas at a particular temperature.

The mass of the gas adsorbed per gram of the adsorbent is plotted against pressure in the form of a curve to show the relationship. Here, at a fixed pressure, physical adsorption decreases with increase in temperature. The curves reach saturation at high pressure. Now, if you take the log of the above equation –

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

To test the validity of Freundlich isotherm, we can plot log x/m on the y-axis and log P on the x-axis. If the plot shows a straight line, then the Freundlich isotherm is valid, otherwise, it is not. The slope of the straight line gives the value of 1/n, while the intercept on the y-axis gives the value of log$k$.
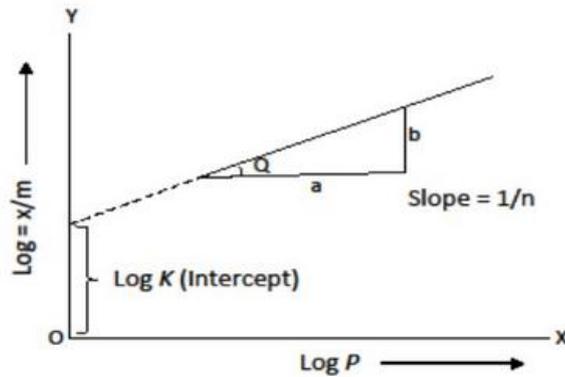
Limitations of Freundlich Isotherm

Freundlich isotherm only approximately explains the behaviour of adsorption. The value of 1/n can be between 0 and 1, therefore the equation holds good only over a limited range of pressure.

- When 1/n = 0, x/m is constant, the adsorption is independent of pressure.

- When 1/n = 1, x/m = kP, i.e. x/m $\propto$ P, adsorption is directly proportional to pressure.

Experimental results support both of the above mentioned conditions. At high pressure, the experimental isotherms always seem to approach saturation. Freundlich isotherm does not explain this observation and therefore, fails at high pressure.

The Freundlich isotherm was followed by two other isotherms – Langmuir adsorption isotherm and BET adsorption isotherm. Langmuir isotherm assumed that adsorption is monolayer in nature whereas BET isotherm assumed that it is multi-layer.
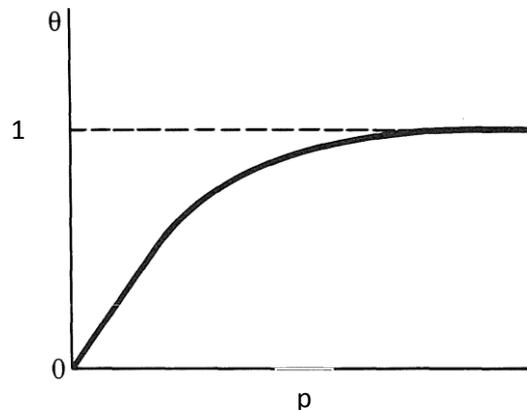
Langmuir Adsorption Isotherm

The Langmuir adsorption model explains adsorption by assuming an adsorbate behaves as an ideal gas at isothermal conditions. According to the model, adsorption and desorption are reversible processes.

$$A(g) + S \rightleftharpoons AS$$

where A is the gaseous adsorbate, S is a vacant site on the surface, and AS represents an adsorbed molecule of A or an occupied site on the surface. The equation of this model is given by

$$\theta = \frac{Kp}{1 + Kp}$$

where θ is the mole fraction of occupied sites on the surface, K is equilibrium constant and p is pressure.

Langmuir Isotherm

Physical and Chemisorption

If the adsorbate and the surface of the adsorbent interact only by van der Waals forces, then we speak of physical adsorption, or van der Waals adsorption. The adsorbed molecules are weakly bound to the surface and heats of adsorption are low (a few kilojoules at most) and are comparable to the heat of vaporization of the adsorbate. Increase in temperature markedly decreases the amount of adsorption. 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 vapour pressure of the liquid adsorbate, then a more extensive adsorption multilayer adsorption occurs. If the adsorbed molecules react chemically with the surface, the phenomenon is called chemisorption. Since chemical bonds are broken and formed in the process of chemisorption, the heat of adsorption has the same range of values as for chemical reactions : from a few kilojoules to as high as 400 kJ. Chemisorption does not go beyond the formation of a monolayer on the surface. For this reason an isotherm of the Langmuir type, which predicts a monolayer and nothing more, is well suited for interpreting the data. The Langmuir adsorption isotherm predicts a heat of adsorption that is independent of θ, the fraction of the surface covered at equilibrium. For many systems the heat of adsorption decreases with increasing coverage of the surface. If the heat adsorption depends on the coverage, then we must use an isotherm more elaborate than the Langmuir isotherm. 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.

*Comparison between Physisorption and Chemisorption*

Physisorption	Chemisorption
Low heat of adsorption usually in the range of 20-40 kJ mol^{-1}	High heat of adsorption in the range of 40-400 kJ mol^{-1}
Force of attraction are Van der Waal's forces	Forces of attraction are chemical bond forces
It usually takes place at low temperature and decreases with increasing temperature	It takes place at high temperature
It is reversible	It is irreversible
It is related to the ease of liquefaction of the gas	The extent of adsorption is generally not related to liquefaction of the gas
It is not very specific	It is highly specific
It forms multi-molecular layers	It forms monomolecular layers
It does not require any activation energy	It requires activation energy

Physical adsorption   Chemical adsorption
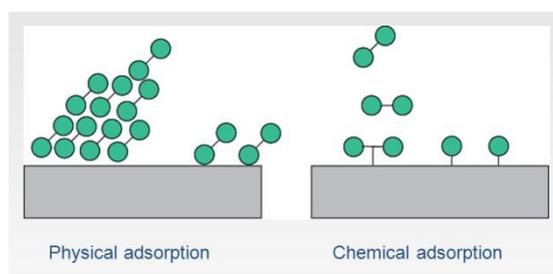
Adsorption in Biological System

N-COVID 19 is the most recent pandemic disease throughout the whole world. Novel corona (a RNA virus) virus is the main culprit. This is very dangerous because its infect human being through surface to surface contamination process. At first it adhere to the membrane by chemisorptions through its protein envelope and then the genomic material i.e. RNA transferred to human cell.
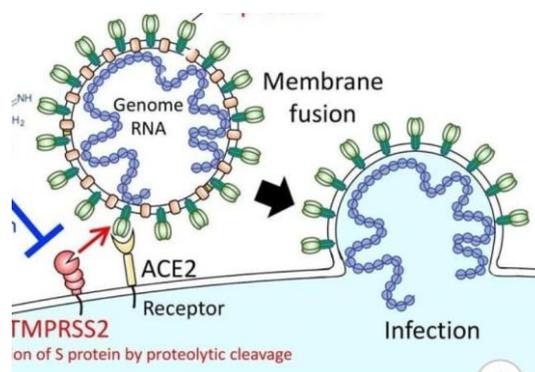
<center>**Catalysis**</center>

What is Catalysis?

Catalysisis the increase in the rate of a chemical reaction due to the participation of an additional substance called a *catalyst*.which is not consumed in the catalyzed reaction and can continue to act repeatedly. Usually, even a small amount of catalyst is sufficient to bring about this effect.In catalyzed mechanisms, the catalyst usually reacts to form a temporary intermediate which then regenerates the original catalyst in a cyclic process.

Mechanism of Catalysis

In the presence of a catalyst, less free energy is required to reach the transition state, but the total free energy from reactants to products does not change. A catalyst may participate in multiple chemical transformations. The effect of a catalyst may vary due to the presence of other substances known as inhibitors (which reduce the catalytic activity) or promoters (which increase the activity and also affect the temperature of the reaction).

Catalyzed reactions have a lower activation energy (rate-limiting free energy of activation) than the corresponding uncatalyzed reaction, resulting in a higher reaction rate at the same temperature and for the same reactant concentration. As in the case of any other chemical reaction, the reaction rate depends upon the frequency of contact of the reactants in the rate-determining step.

Usually, the catalyst participates in this slowest step. The rate of the reaction depends upon the amount of catalyst.Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated, or destroyed by secondary processes.

Types of Catalysts

Depending upon whether a catalyst exists in the same phase as the substrate catalysts can be classified as Heterogenous and Homogenous catalysts. Biocatalysts (enzymes) are often seen as a separate group.

Heterogeneous Catalysts

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on the surface are known, depending on how the adsorption takes place.

The total surface area of solid has an important effect on the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles. A heterogeneous catalyst has active sites, which are the atoms or crystal faces where the reaction actually occurs. Most of the surface of the catalyst is catalytically inactive.

Homogeneous Catalysts

Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles involved in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates. One example of homogeneous catalysis involves the influence of H^+ on the esterification of carboxylic acids, such as the formation of methyl acetate from acetic acid and methanol.

Enzymes and Biocatalysts

In biology, enzymes are protein-based compounds that catalyze metabolism as well as other biochemical reactions. Though enzymes are the most commonly known biocatalysts, certain non-protein-based classes of biomolecules also exhibit catalytic properties. These include ribozymes as well as synthetic deoxyribosymes.

Biocatalysts are considered to be an intermediate between homogeneous and heterogeneous catalysts, strictly speaking, soluble enzymes can be considered to be homogeneous catalysts whereas membrane-bound enzymes can be put under the category of heterogeneous enzymes.

Several factors affect the activity of enzymes (as well as other catalysts). Some of these include temperature, pH, the concentration of enzyme, substrate, and products. An important reagent that acts as a catalyst is water. It acts in various bonds forming as well as bond breaking reactions.