

## Adsorption:

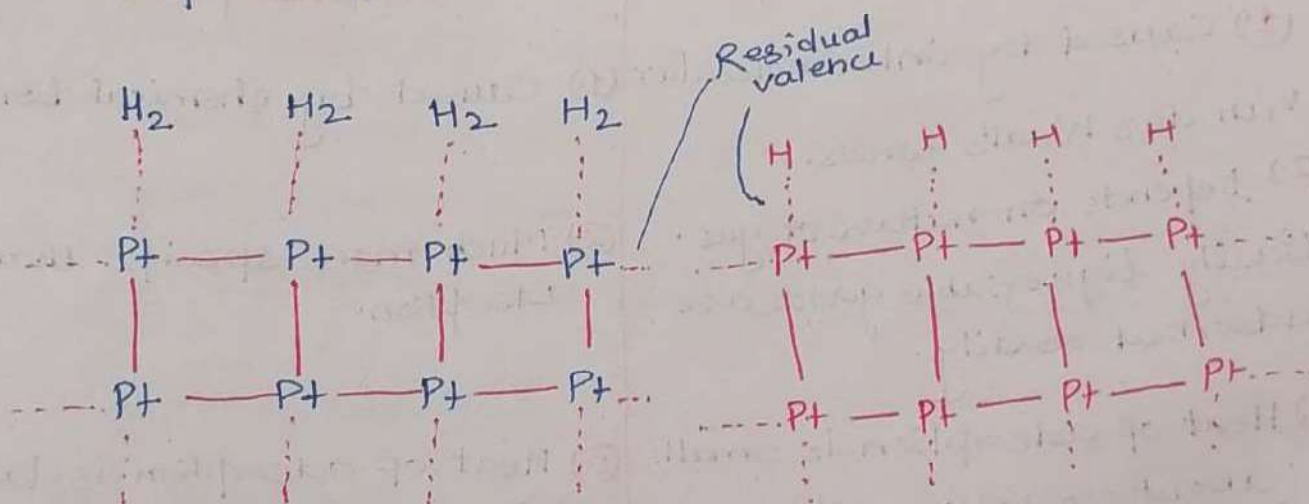
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The phenomenon of concentration of molecule of a gas or liquid at a solid surface is called adsorption.

- The substance that deposits at the surface is called Adsorbate and the solid on whose surface the deposition occurs, is called the Adsorbent.

### \* Mechanism of Adsorption:

Atoms or molecules of a solid surface behave like the surface molecules of a liquid. These are not surrounded by atoms or molecules of their kind. Therefore, they have unbalanced or residual attractive forces on the surface which can hold adsorbate particles.



The absorbed atoms or molecules can be held on the surface of a metal such as platinum (Pt) by physical van der Waal's force or chemical forces due to residual valance bonds. Thus the adsorption of hydrogen on platinum may take place in two ways (molecularly or atomically)

### \* Types of Adsorption

The adsorption of a gas into solid surface is mainly of two types

- Physical Adsorption:  $\Rightarrow$  This is due to the gas molecules being held to the solid surface by van der Waal's



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attractive forces. It is also referred to as Van der Waal's Adsorption.  
e.g. adsorption of hydrogen or oxygen on charcoal is Physical Adsorption.

### ④ Chemical Adsorption or Chemisorption:

In this kind of adsorption, the gas molecules or atoms are held to the solid surface by chemical bonds. These bonds may be covalent or ionic in nature.

e.g. hydrogen is chemisorbed on nickel.

### Comparison of Physical adsorption and chemisorption

#### Physical adsorption

- (1) Caused by intermolecular Van der Waal's forces.
- (2) Depends on nature of gas. Easily liquefiable gases are adsorbed readily.
- (3) Heat of adsorption is small (about  $20.93 \text{ kJ mol}^{-1}$ )
- (4) It is reversible
- (5) Occurs rapidly at low temperature; decreases with increasing temperature.
- (6) Increase of pressure increases adsorption; decrease of pressure causes desorption
- (7) Forms multimolecular layers on adsorbent surface.

#### Chemisorption

- (1) Caused by chemical bond formation.
- (2) Much more specific than physical adsorption.
- (3) Heat of adsorption is large ( $83.74 - 418.68 \text{ kJ mol}^{-1}$ )
- (4) It is irreversible
- (5) Increases with increase of temperature.
- (6) Change of pressure has no such effect
- (7) Forms unimolecular layer



## Factors affecting the extent of gas-solid adsorption: ③

The extent to which adsorption will happen on a solid surface depends on following factors.

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### (1) Nature of adsorbent: $\Rightarrow$

The adsorption of the gas depends on the nature of the adsorbent. A gas can be adsorbed on different adsorbent surfaces in different amounts. e.g. Hydrogen is weakly adsorbed on the alumina surface whereas it is strongly adsorbed on the nickel surface under certain conditions.

### (2) Surface Area: Adsorption being a surface phenomenon, the extent of adsorption depends on the surface area. Increase in the surface area of the adsorbent, increases the total amount of gas adsorbed. So finely divided solids and some porous substances are good adsorbents.

### (3) Nature of the gas: In general, if a gas is more liquefiable it will be more easily absorbed. For example like $\text{NH}_3$ , $\text{HCl}$ , $\text{Cl}_2$ , $\text{CO}_2$ which can be liquefied easily are more readily adsorbed on the solids surface, rather than permanent gases like $\text{O}_2$ , $\text{H}_2$ etc

### (4) Heats of Adsorption:

Heat of adsorption is defined as the energy liberated when 1 gm mole of a gas is adsorbed on the solid surface. In Physical adsorption, gas molecules concentrate on the solid surface. Thus it is similar to the condensation of a gas to liquid. Therefore, adsorption like condensation is an exothermic process. When the temperature increases the kinetic energy of the gas molecules also increases which results in more number of collisions between the molecules.



and the gas.

### (5) Effect of Pressure:

on the solid surface, there is a fixed number of adsorption sites where gas molecules can be adsorbed. Initially when the pressure has increased the rate of adsorption increases due to an increase in the gas molecules striking on the surface. Thus, an increase in the pressure increases the rate of adsorption linearly. But after sometime, it will reach a point when the pressure has no effect on the rate of adsorption as the number of adsorption sites is fixed and no more adsorption can happen in those sites. Hence, at that point, the extent of adsorption will be independent of the pressure.

### (6) Effect of Temperature:

Physical adsorption occurs rapidly at low temperature and chemisorption like most chemical changes, generally with temperature. Thus a rise of temperature can often cause physical adsorption to change to chemisorption. Nitrogen for example is physically adsorbed on iron at 463 K but chemisorbed to form a nitride at 773 K.



## ADSORPTION ISOTHERMS

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An adsorption isotherm is a graph that represents the variation in the amount of adsorbate ( $x$ ) adsorbed on the surface of the adsorbent with the change in pressure at a constant temperature.

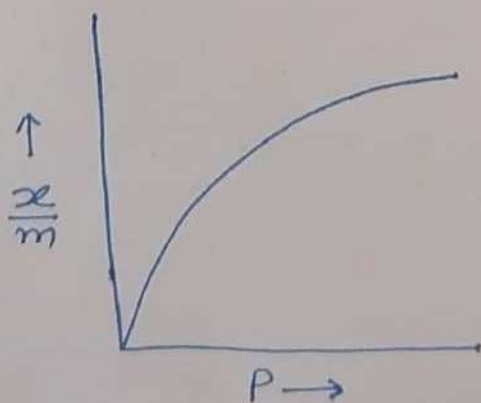
### Freundlich Adsorption Isotherm

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

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

where ' $x$ ' is the mass of the gas adsorbed on mass ' $m$ ' of the adsorbent at pressure ' $P$ '. ' $k$ ' and ' $n$ ' are constants that depend on the nature of the adsorbent and the gas at 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 curve reaches saturation at high pressure.



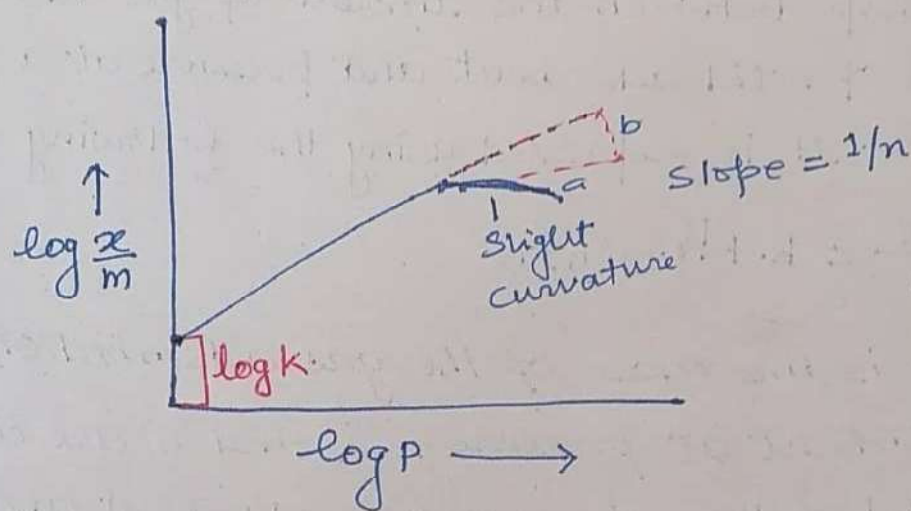
• Freundlich isotherm: a plot of mass of adsorbed gas per unit mass of adsorbent

Now if we 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, 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  $\log K$ .



It is actually found that the plots were straight lines at low pressure, while at higher pressure they showed a slight curvature, especially at low temperature. This indicated that Freundlich equation is approximate and does not apply to adsorption of gases by solid at higher pressure.



## LANGMUIR ADSORPTION ISOTHERM

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In 1916 Langmuir derived a simple adsorption isotherm based on theoretical consideration. It was named after him.

### Assumption:

Langmuir made the following assumptions.

- (1) The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.
- (2) The adsorbed layer is uniform all over the adsorbent.
- (3) There is no interaction between the adjacent adsorbed molecule.

### Derivation of Langmuir Isotherm:

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some of these molecules then evaporate and are 'desorbed' rapidly. A dynamic equilibrium is eventually established between the two opposing processes, adsorption and desorption.

If  $\theta$  is the fraction of total surface covered by the adsorbed molecules, the fraction of the naked area is  $(1-\theta)$ . The rate of desorption ( $R_d$ ) is proportional to the covered surface  $\theta$ . Therefore

$$R_d = k_d \theta$$

where  $k_d$  is the rate constant for the desorption process. The rate of adsorption ( $R_a$ ) is proportional to the available naked  $(1-\theta)$  and the pressure ( $P$ ) of the gas.

$$R_a = k_a (1-\theta) P$$

where  $k_a$  is rate constant for the adsorption process.

At equilibrium the rate of desorption is equal to the rate of adsorption. That is

$$K_d \theta = K_a (1 - \theta) P$$

$$\theta = \frac{K_a P}{K_d + K_a P}$$

or

$$\theta = \frac{(K_a/K_d)P}{1 + (K_a/K_d)P}$$

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

Where  $K$  is the equilibrium constant and is referred to as the adsorption coefficient.

The amount of the gas adsorbed per gram of the adsorbent  $x$  is proportional to  $\theta$

Hence

$$x \propto \frac{KP}{1 + KP}$$

$$x = K' \frac{KP}{1 + KP}$$

$$x = K' \frac{KP}{1 + KP} \quad \text{----- (1)}$$

where ' $K$ ' is a new constant. Equation (1) gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as Langmuir Adsorption Isotherm.

In order to test the Langmuir isotherm, equation (1) is rearranged so that

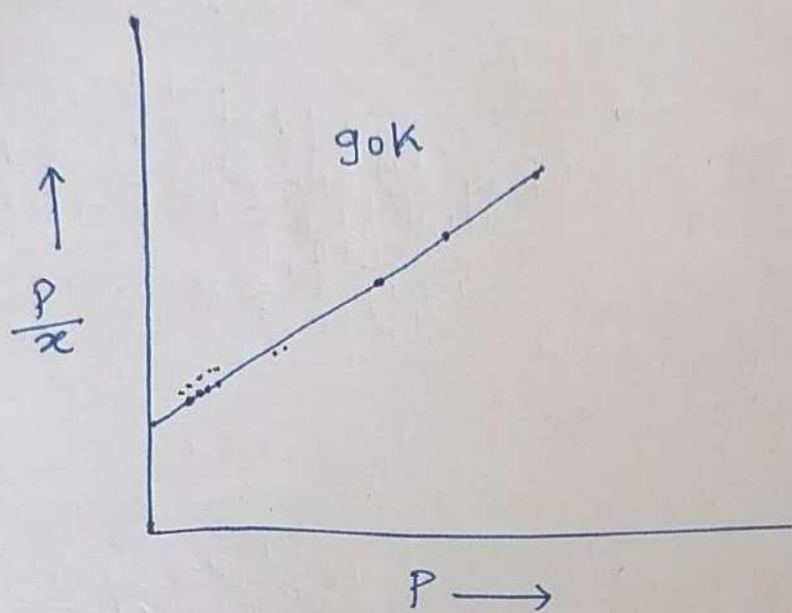
$$\boxed{\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}} \quad \longrightarrow (2)$$

where  $K''$  constant =  $K'/K$

The equation (2) is similar to an equation for a straight line. Thus if  $P/x$  is plotted against  $P$ , we should get a straight line with slope  $1/K''$  and intercept  $1/K'$ . It was found in



most cases that the actual curves were straight line. ⑨  
Thus Langmuir isotherm stood verified.



Verification of Langmuir isotherm for adsorption of  $N_2$  on mica at 30K.

Langmuir isotherm holds at low pressures but fails at high pressures.

As stated above, Langmuir Adsorption isotherm may be written as

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}$$

if Pressure is very low then the factor  $P/K''$  may be ignored.

$$x = K'P$$

if the pressure is very high  $1/K'$  may be ignored.

$$x = K''$$

Hence at low pressure the amount of gas adsorbed ( $x$ ) is directly proportional to pressure. At high pressure the mass adsorbed reaches a constant value  $K''$  when the adsorbent surface is completely covered with a unimolecular layer of the gas. At this stage adsorption is independent of pressure.