Adsorption

By Dr. Vipul B. Kataria

What you must know?

- The word adsorption was first used by German physicist **Heinrich Kayser** in 1881.
- It is necessary to learn adsorption and content related to it due to its versatile applications in the field of biological chemistry, industrial chemistry, routine life, air freshener, and other branches of chemistry.
- For example: Protein in our body adsorbed by blood or other body fluid.
- Adsorption is surface phenomenon and involved both **liquid and solid surface**.
- It is closely associated with **surface tension** (another surface phenomenon). However it is only associated with liquid surface. For simple understanding of surface tension, we can look to the example of floating pin on the water if placed horizontally.
- Both adsorption and surface tension is related to **surface energy**.
- In the inner side of liquid or solid molecules experience attraction in each direction. But at the outer surface molecules have **different neighbouring molecular atmosphere**.
- Due to this, molecules at surface have more attraction to downward, and they tend to move inside.
- As a result of this, molecules at the surface of liquid or solid have **higher energy**, and are unstable due to residual force.
- So, the surface of liquid and solid has property to retain other molecules when come in contact of outer atmosphere.
- The phenomenon of increase in concentration of molecules (gas or liquid) at the interface of liquid or solid owing to the operation of surface forces is known as **adsorption**.
- **Adsorbent:** The substance (liquid or solid) on which the adsorption takes place is known as adsorbent. For example: charcoal, silica gel, activated alumina, zeolites, molecular sieves, and synthetic resins.
- **Adsorbate:** The substance (gas or liquid) which is get adsorbed is known as adsorbate. Adsorption of protein by blood. Here protein is adsorbate and blood is adsorbent.

- **Absorption:** It is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase – gas, liquid, or solid material. This is a different process from adsorption, since molecules undergoing absorption are taken up by the volume, not by the surface (as in the case for adsorption).

- **Sorption:** It is a phenomenon physical and chemical process by which one substance becomes attached to another. It is collective term for both absorption and adsorption. For example: water vapour is absorbed by calcium chloride while it is adsorbed by silica gel. In some case it is difficult to distinguish absorption and adsorption, so sorption is used to describe such phenomenon.
- **Desorption:** It is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (either adsorption or absorption). It can be achieved by various means like increasing temperature or reducing pressure.

Adsorption of gases

- The process of adsorption in case of gases owes to two different kind of operative forces. Physical and Chemical. According to this, it can be classified into physical adsorption and chemical adsorption.
- Physical adsorption (physisorption): In this kind of process, adsorbate retain on the surface of the absorbent by weak Van der Waal's attraction. For example, adsorption of oxygen or hydrogen by charcoal. A special species of lizard known as Gecko can climb vertical glass due to Van Der Waal's attraction between its toe and surface of glass.

- Chemical adsorption: in such kind of process adsorbate bind to adsorbent by some kind of chemical force. The surface molecules of both adsorbate and adsorbent, bind by chemical bond and has high energy. Therefore it is referred as activated adsorption.

Difference between physical and chemical adsorption

Physical Adsorption	Chemical Adsorption
1. The molecules of adsorbate and adsorbent are joined by weak **Van Der Waal's attraction.**	1. The molecules of adsorbate and adsorbent are joined by some kind of **chemical bond.**
2. It takes place at **low temperature.**	2. It requires **high temperature.**
3. Enthalpy of adsorption is of the order of **20 KJ/mol.**	3. Enthalpy of adsorption is of the order of **200 KJ/mol.**
4. It is **not specific**. Almost all gases adsorbed more or less on solid surface.	4. It is **highly specific**, and occurs when there is possibility of bond formation.
5. **More than one layer** of adsorbate can be formed on the surface of adsorbent.	5. **Single layer** can be formed on the adsorbent.
6. It is **reversible**.	6. It is **irreversible** in general.
7. For Example: Adsorption of ammonia or chlorine gas by charcoal.	7. For Example: Adsorption of oxygen by tungsten.

Enthalpy of Adsorption

- It is exothermic process hence energy is released.
- A spontaneous reaction requires free energy (ΔG) to be negative.
- When molecules of adsorbate bind on the surface of adsorbent, they got reduce the translational freedom.
- Entropy (ΔS) of the system is generally negative.
- In order to keep free energy (ΔG) negative, enthalpy (ΔH) must be remain negative.
- As a result of it process of adsorption remains exothermic.

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

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

Now in general

$$X = -T\Delta S$$

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$$X/\Delta S = -T$$

Now both sides have minus sign (-) so it will be cancelled. Hence value of temperature will be higher.

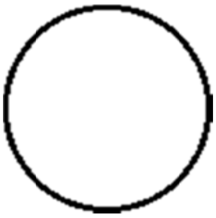
In an adsorption process, the change in enthalpy for mole of an adsorbate on an adsorbent surface is referred as **enthalpy of adsorption**.

Factors affecting adsorption of gases on solid

- **Nature of adsorbate or nature of gas:** Physical adsorption depends on the nature of gas. The operative force for adsorption is Van Der Waals' force hence it causes condensation of gas into liquid. Higher the critical temperature (T_c) of gas more easily it will be adsorbed.
- **Nature of adsorbent:** Adsorption depends upon type of adsorbent.
- **Surface Area:** higher the surface area higher the adsorption.
- **Effect of pressure:** increase in pressure facilitates condensation of gas hence it will be more physical adsorption. As the pressure approaches critical pressure (P_c) multilayer adsorption takes place hence rate of adsorption increases.
- **Effect of temperature:** Van Der Waals forces increases at critical temperature. Physical adsorption increases at low temperatures.

Critical Temperature

Gases can be converted to liquids by compressing the gas at a suitable temperature. Gases become more difficult to liquefy as the temperature increases because the kinetic energies of the particles that make up the gas also increase.



Microscopic view of a gas.

Microscopic view of a liquid.

The ***critical temperature*** of a substance is the temperature at and above which vapor of the substance cannot be liquefied, no matter how much pressure is applied. Every substance has a critical temperature. Some examples are shown below.

Substance	**critical temperature (^{o}C)**
NH_3	132
O_2	-119
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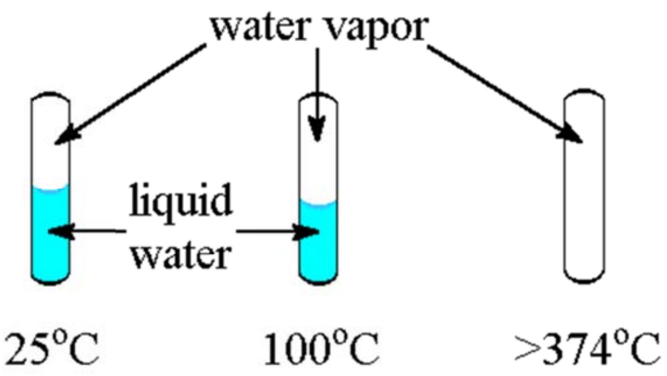

Tubes containing water at several temperatures. Note that at or above 374^{o}C (the critical temperature for water), only water vapor exists in the tube.

Critical Pressure

The ***critical pressure*** of a substance is the pressure required to liquefy a gas at its critical temperature. Some examples are shown below.

substance	**critical pressure (atm)**
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Adsorption Isotherm

- The quantity of gas adsorbed by a given amount of adsorbent depends on temperature as well as pressure.
- At given temperature adsorption of gas or vapour on a solid surface is found to increase with increase in pressure of gas.
- However we cannot say that temperature and pressure are proportional to each other in this case.
- An empirical relation can be derived from the observations.

Freundlich adsorption isotherm

- The **Freundlich equation** or **Freundlich adsorption isotherm**, an adsorption isotherm, is a curve relating the concentration of a gas on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact.
- Freundlich gave and empirical formula between the **quantity of gas adsorbed by the given amount of solid**.

$$\frac{x}{m} = KP^{1/n} \qquad (n>1) \ldots\ldots\ldots\ldots(8.1)$$

Where x is weight of gas adsorbed by m gram of adsorbent at pressure P, K & n are constant. It is only valid for solid substance. It can be modified for liquid as under.

$$\frac{x}{m} = KC^{1/n} \qquad (n>1) \ldots\ldots\ldots\ldots(8.2)$$

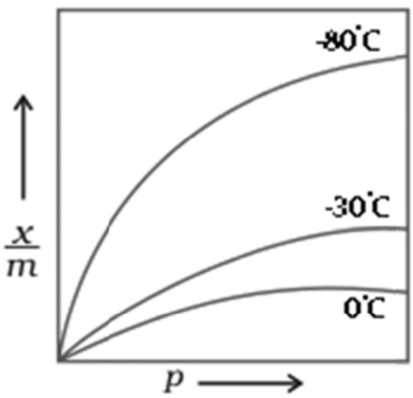
where C is concentration of Adsorbate

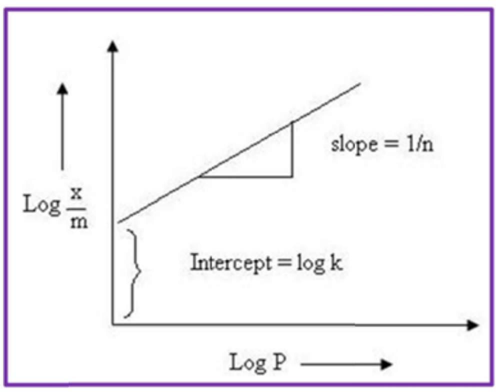
Take log of the equations 8.1 & 8.2

$$\ln\frac{x}{m} = \ln K + \frac{1}{n}\ln P \ldots\ldots\ldots\ldots(8.3)$$

$$\ln\frac{x}{m} = \ln K + \frac{1}{n}\ln C \ldots\ldots\ldots\ldots(8.4)$$

- If the relation holds true then **plots of amount of gas adsorbed against pressure** will be of the form showed in figure.





- It can be shown in figure that **adsorption decrease with increase in temperature** at constant pressure.
- The isotherm can be tested by **plotting log P against log x/m, the slope is 1/n whereas intercept is log k**.
- The plot is straight line in practical but found irregular with **high or low pressure**.

Limitations

- The equation is **empirical** and there is no theoretical basis.
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Langmuir adsorption isotherm

- Langmuir derived an adsorption isotherm based on theoretical aspects.
- The basis is kinetic theory of gases.
- It was discovered by Irving Langmuir.
- It relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature.
- It has been found in more agreement with experimental observations over wider range of pressure than Freundlich adsorption isotherm.
- The isotherm is based on assumption that (1) Fixed number of vacant or adsorption sites are available on the surface of solid. (2) All the vacant sites are of equal size and shape on the surface of adsorbent. (3) Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process. (4) Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.
- He postulated that adsorption of gases on solid surface is uni-molecular.
- He also observed that adsorption consists of two actions (1) the tendency of adsorbed molecules to evaporate back into gaseous phase. (2) the tendency of gaseous molecules to condense on the surface.
- Let us assume that 1 cm2 surface of solid (adsorbate) is exposed to gas at pressure P, and θ is the fraction of gas adsorbed then $(1- \theta)$ surface available for condensation of gaseous molecules.

- Suppose n number of molecules are striking on $(1 - \theta)$ cm2 surface and α is the fraction of molecules adsorbed on the remaining surface of solid than

$$\text{Rate of adsorption} = \alpha\, n\, (1 - \theta)$$

- The rate of evaporation will be proportional to area of surface covered by gaseous molecules. So, $\theta = K\,\theta$
- Now, for adsorption equilibrium both rate (rate of evaporation and condensation) should be equal.

$$K\,\theta = \alpha\, n\, (1 - \theta) \Longrightarrow \theta = \frac{\alpha n}{K + \alpha n}$$

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For F.Y.B.Sc. Semester-I

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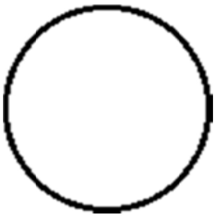

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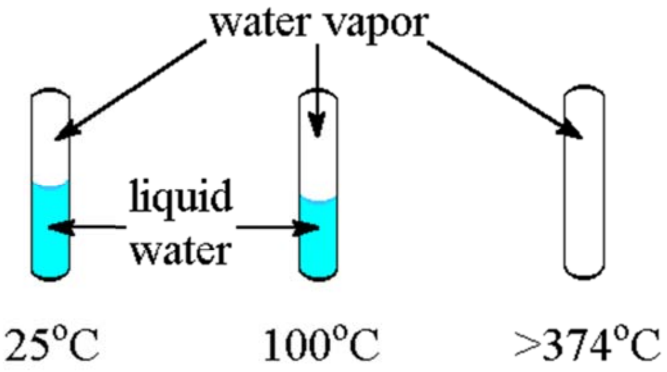

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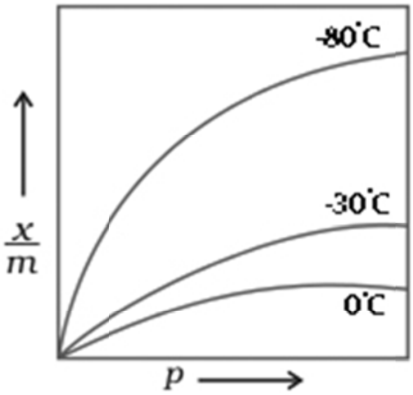

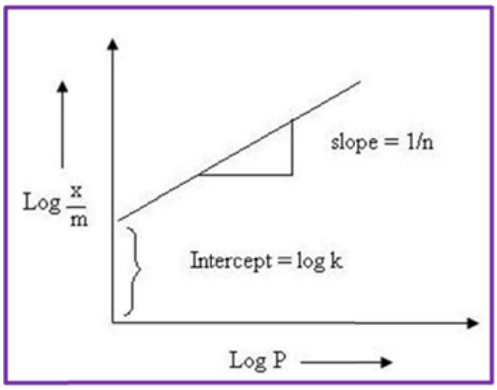

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- The rate of evaporation will be proportional to area of surface covered by gaseous molecules. So, θ = K θ
- Now, for adsorption equilibrium both rate (rate of evaporation and condensation) should be equal.

$$K\,\theta = \alpha\, n\,(1-\theta) \Longrightarrow \theta = \frac{\alpha n}{K + \alpha n} \;\ldots\ldots\ldots\ldots\ldots\; (8.5)$$

- According to kinetic theory of gas, the rate at which gaseous molecules strike is proportional to the pressure of gas.

$$n \;\boldsymbol{\alpha}\; P \text{ hence } n = \beta P \ldots\ldots\ldots\ldots\ldots\ldots (8.6)$$

From equation 8.5 and 8.6

$$\theta = \frac{\alpha\beta P}{K + \alpha\beta P} = \frac{\alpha\beta P/K}{1+\alpha\beta P/K} = \frac{K_1 P}{1+K_1 P} \text{ Where } K_1 = \alpha\beta/K \;\ldots\ldots\ldots\; (8.7)$$

Now Langmuir assumed that the adsorption is single layer then θ is proportional to amount of gas adsorbed per unit of the solid.

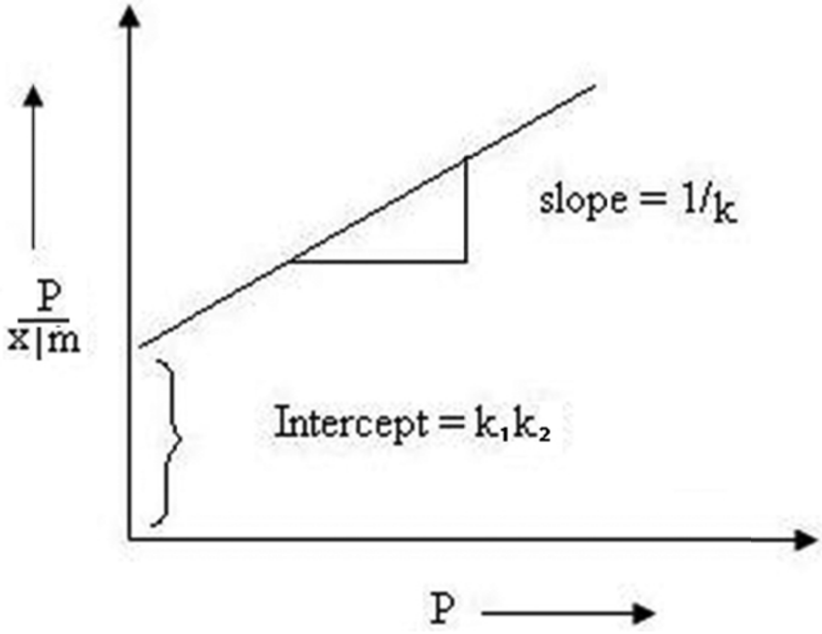
$$x/m \;\boldsymbol{\alpha}\; \theta \Longrightarrow x/m = K_2\,\theta \Longrightarrow \theta = \frac{x}{mK_2} \;\ldots\ldots\ldots\ldots\ldots\; (8.8)$$

Comparing equation 8.7 and 8.8

$$\frac{x}{m} = \frac{K_1 K_2 P}{1 + K_1 P} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8.9)$$

In order to verify this isotherm take reciprocal of equation 8.9

$$\frac{1}{x/m} = \frac{1+K_1P}{K_1K_2P} \Longrightarrow \frac{P}{x/m} = \frac{1}{K_1K_2} + \frac{P}{K_2} \text{……………………. (8.10)}$$



So the graph of $\frac{P}{x/m}$ vs P should be straight line where slope is $1/K_2$ and intercept is $1/K_1K_2$.

The straight line supports langmuir's assumption that adsorption is unilayer.

Two special cases of Langmuir isotherm

(i) At very low pressure: we can neglect K and P in the denominator in equation 8.9

$$\frac{x}{m} = K_1K_2P \Longrightarrow x/m \;\alpha\; P \text{ ………….. (8.11)}$$

Extent of adsorption is directly proportional to pressure.

(ii) At very high pressure: at very high pressure 1 <<<<<< K_1P so equation 8.9 will be

$$\frac{x}{m} = \frac{K_1K_2P}{K_1\,P} = K_2 \text{ ………………….. (8.12)}$$

Extent of adsorption does not depend upon pressure

It is evident that at very high pressure $x / m = KP^o \Longrightarrow x / m = KP^{1/n}$

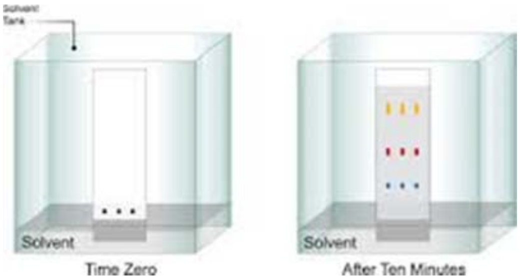
Where n should be from 0 to 1.

The theory supports Freundlich eqation.

Applications of Adsorption

- Production of high vacuum: Dewar containers are used to store liquid hydrogen or liquid. Activated charcoal placed between the walls of container, and adsorbs all the gas molecules between the walls.

- Heterogenous catalyst: The molecules of reactants are adsorbed on the surface of solid catalyst to facilitate the reaction.
- Gas masks: All the gas masks contain charcoal layer which adsorbed poisonous gases.
- Removing colour impurities: Activated charcoal is used to remove colour impurities from the reaction mixture.
- Air Freshener: It adsorbs gases of bad smell.
- Recover solvent vapour: In industrial chemistry, phenomenon of adsorption is used to recover solvent vapour.
- Chromatography: It is based upon different adsorption rate of different constituents. It is useful for isolation and purification processes.



- Adsorption indicators: it is useful in titration analysis. Titration of chlorine with $AgNO_3$ in which fluorescein is used as adsorption indicators.
- Adsorption of nutrients on soil: Soil contains minute colloidal fraction of clay. Clay can adsorb the moisture rich in nutrients like nitrogen, phosphorous, and potassium.