

Unit II SURFACE CHEMISTRY & CATALYSIS

SURFACE CHEMISTRY

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SURFACE CHEMISTRY

2.1 INTRODUCTION

Surface chemistry is referred to as the study of the phenomenon occurring on the surfaces of substances. This is very applicable in industries and day to day lives. In other words, surface chemistry deals with all types of surface phenomenon.

What is Surface Chemistry?

It is the study of the chemical phenomena that occur at the interface of two surfaces which can be solid-liquid, solid-gas, solid-vacuum, liquid-gas, etc. Some applications of surface chemistry are known as surface engineering. There are various phenomena taking place on the surface of substances and some of them are:

- Adsorption
- Heterogeneous Catalysis
- Corrosion
- Crystallization

Applications of Surface Chemistry

In a wider perspective, surface chemistry deals with the interaction of surfaces of one system with that of the other system. Some phenomena work on this principle such as:

- Catalysis
- Colloid Formation
- Electrode Reactions
- Chromatography

Surface Chemistry has a major role in various chemical processes such as:

- Enzymatic reactions at the biological interfaces found in the cell walls and membranes.
- In the electronics industry, they are used in the surface and interface of microchips found in computers.
- In automobile exhausts, the heterogeneous catalysts found in the catalytic converter for cleaning emissions.

Role of Adsorption in Surface Chemistry

Accumulation of species on higher concentration on the surface of a substance due to intermolecular force is known as adsorption. For Example, gases such as H₂, O₂, N₂ adsorbs on the surface of activated charcoal.

IMPORTANT TERMS IN SURFACE CHEMISTRY

ADSORPTION

It is a surface phenomenon. It is defined as the accumulation of a substance on the surface of a solid or liquid”.

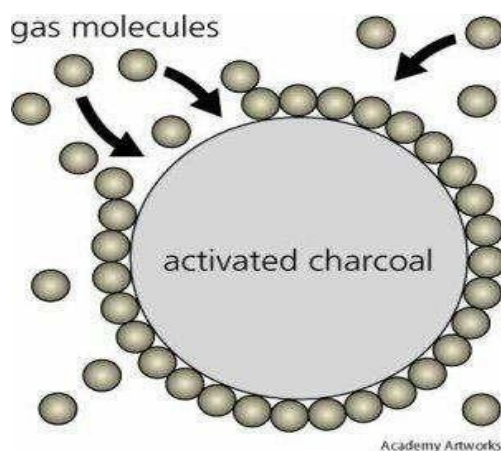


Figure 2.1.1 Illustration of adsorption

[Source: <https://www.emedicalprep.com/study-material/chemistry/surface-chemistry/adsorption/>]

Examples

- Activated charcoal adsorbs gases like CO₂, SO₂, Cl₂ etc.
- Pt or Ni metal kept in contact with a gas adsorbs the gas - Hydrogenation of oils.
- Animal charcoal, when added to acetic acid solution and shaken vigorously, adsorbs acetic acid.
- Molasses is decolorized by activated charcoal.

ADSORBATE

The substance held on the surface of the solid is called adsorbate.

Example: Various gases (NH₃, water vapour, CO₂, etc)

Substances in solution (NaCl, dye, etc.)

ADSORBENT

The substance on which adsorption occurs. (OR) The solid that takes up a gas or a solute from the solution is called adsorbent.

Example: Silica gel, charcoal, Pd, Pt, Ni, alumina gel, etc.

EXAMPLES OF ADSORPTION

- In the adsorption of acetic acid by charcoal, “acetic acid is adsorbate and the charcoal is adsorbent”.
- In the adsorption of H_2 gas on platinum or nickel, “ H_2 gas is adsorbate and Pt or Ni is adsorbent”.

ABSORPTION

It is a bulk phenomenon. It is defined as “process in which a substance is uniformly distributed throughout the body of the solid or liquid”.

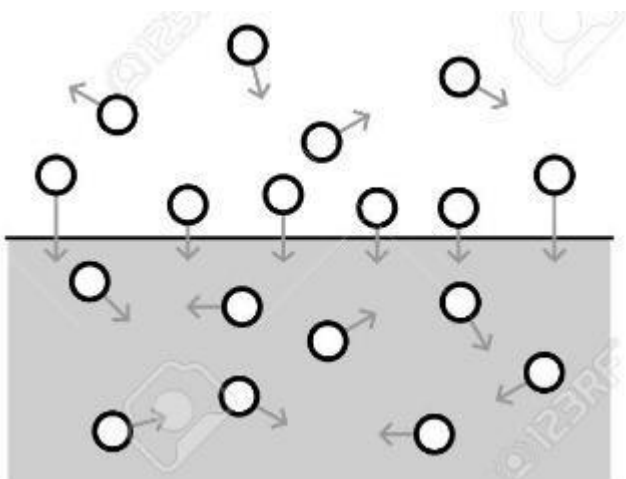


Figure 2.1.2 Illustration of absorption

[Source: https://www.123rf.com/photo_93069281_stock-vector-scheme-of-absorption-and-adsorption.html]

Examples:

- If a chalk piece is dipped into a solution of coloured ink and kept for some time, the chalk piece absorbs the coloured substance.
- A sponge placed in water absorbs water into it.
- H_2 gas kept in contact with finely divided palladium metal is absorbed by Pd metal. This absorption of H_2 gas by Pd is known as occlusion.

OCCLUSION

The adsorption of gas on a solid surface is called occlusion.

SORPTION

It is a process in which both adsorption and absorption takes place simultaneously.

DESORPTION

The removal of adsorbed substance from the surface is called desorption.

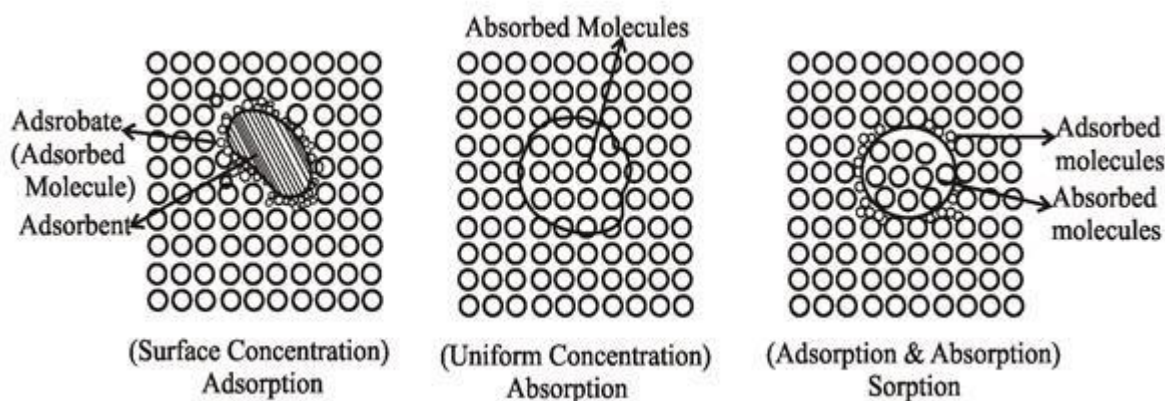


Figure 2.1.3 Illustration of adsorption, absorption and sorption

[Source: <https://chemistry-desk.blogspot.com/2012/10/adsorption.html>]

Examples of Adsorption and Absorption

- ❖ When a sponge is put into water, the water enters into the whole body of sponge – it is an example of absorption.
- ❖ When a solution of methylene blue (dye-coloured substances) in water is stirred with solid carbon, the dye gets adsorbed by charcoal and thus decolourises the water – it is an example of adsorption.
- ❖ Ammonia is adsorbed on charcoal while it is absorbed by water.
- ❖ Water vapours are adsorbed on silica gel while they are adsorbed by anhydrous CaCl_2 .
- ❖ NH_3 can undergo adsorption and absorption. When ammonia is passed through water in contact with charcoal. Water dissolves NH_3 (absorption) which is then adsorbed by charcoal crystals.

Exothermic nature of adsorption

The amount of heat evolved when 1 mole of any gas is adsorbed on a solid adsorbent surface is called enthalpy or molar heat of adsorption”.

DIFFERENCES BETWEEN ADSORPTION AND ABSORPTION

S.No	Adsorption	Absorption
1.	It is a surface phenomenon i.e. higher concentration of a liquid or gas molecules over the surface of a solid.	It is a bulk phenomenon i.e. accumulation of substrate on the surface of the solid, in which the substrate is uniformly distributed throughout the body of the solid substance.
2.	It is a fast process.	It is a slow process.
3.	Equilibrium is attained easily.	Equilibrium is attained slowly.
4.	It depends upon the surface area of the adsorbent. Adsorption is more rapid when the surface of adsorbent is more.	No such effect is observed.
5.	Example: Ammonia is adsorbed on charcoal.	Example: When a sponge is put into water, the liquid enters into the whole body of the sponge.

Table 2.1.1 Differences between adsorption and absorption

TYPES (OR) CLASSIFICATION OF ADSORPTION

Adsorption is classified into two types:

- Physical adsorption (or) Physisorption (or) Vander Vaal's Adsorption
- Chemical adsorption (or) Chemisorption (or) Activated Adsorption

PHYSICAL ADSORPTION (OR) PHYSISORPTION

It is a process in which the adsorbed molecules are held to the surface of the adsorbent by weak physical or Vander Vaal's forces.

(e.g.) Adsorption of H₂ on charcoal

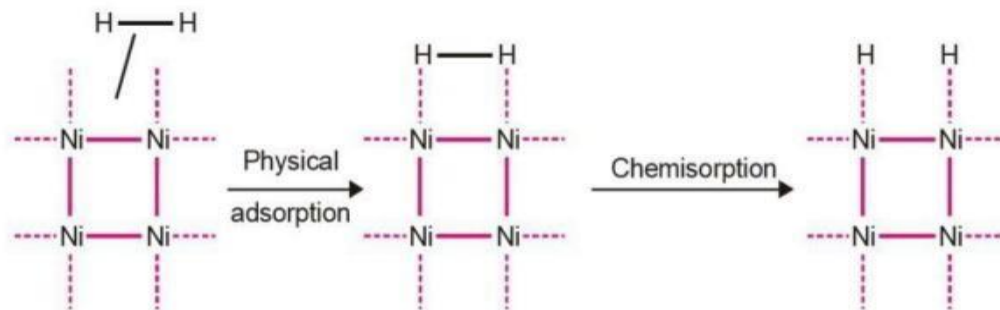
CHEMICAL ADSORPTION (OR) CHEMISORPTION

It is a process in which the adsorbed molecules are held to the surface of the adsorbent by strong chemical bonds.

(e.g) Adsorption of H_2 on Ni, adsorption of O_2 on tungsten

Example: Adsorption of H_2 on Ni

H_2 molecule is first adsorbed by Vander Vaal's forces and then undergoes dissociation to hydrogen atoms. Then the H-atoms are chemisorbed on Ni.



Hydrogen dissociates before it is chemisorbed on nickel.

Figure 2.1.4 Adsorption of H_2 on Ni

[Source: <https://www.slideshare.net/aminul308/adsorption-83054943>]

DIFFERENCES BETWEEN PHYSISORPTION AND CHEMISORPTION

S.No.	Property	Physical adsorption	Chemical adsorption
1.	Nature of adsorption	Weak	Strong
2.	Enthalpy of adsorption	Low. (20-40 Kcal/mol)	High. (40 – 400 Kcal/mole)
3.	Reversibility of adsorption process	Reversible and occurs rapidly.	Irreversible and occurs slowly.
4.	Temperature at which adsorption is more pronounced	Low temperatures (below the B.pt of the adsorbate gas)	High temperatures (generally above the B.pt. of the adsorbate gas)
5.	Effect of change in temperature	Decreases with rise in temperature.	Increases with rise in temperature.
6.	Specificity of adsorption	Not specific. Generally takes place on all surfaces.	Highly specific. Takes place on specified surfaces only.
7.	Nature of adsorbate layers formed	Multilayered	Unilayered

8.	Effect of pressure on adsorption	Increases with rise in pressure of adsorbate gas and finally attains a limiting value.	Pressure of the adsorbate has a negligible effect.
9.	Energy of activation	Insignificant i.e. very low.	Significant i.e. relatively high.
10.	Dependence on the nature of the adsorbate & adsorbent	Depends on the adsorbate (gas) only. Easily liquefiable gases are more readily adsorbed.	Depends on the adsorbate as well as adsorbent. No correlation can be given.
11.	Ease of desorption	Easy since Vander Waals forces are involved.	Not easy since chemical forces are involved.

Table 2.1.2 Differences between Physisorption and chemisorption

CHARACTERISTICS OF ADSORPTION

- Adsorption is a highly selective process.
- It is a physical phenomenon accompanied by a chemical change.
- It depends on the nature of the adsorbent and adsorbate.
- It is always spontaneous.
- It is always accompanied by evolution of heat.
- The rate of adsorption depends on temperature, pressure and concentration.

2.2 ADSORPTION OF GASES ON SOLIDS

Most of the surface reactions takes place by chemisorption and solids adsorb gases to some measurable extent. The adsorption of gases on solid surfaces of finely divided metals like Fe, Ni, Pt, Pd, etc. depends on the following factors:

- Nature of gases
- Nature and surface area of adsorbents
- Enthalpy of adsorption
- Reversible character of adsorbed gases
- Effect of pressure and temperature
- Thickness of adsorbed layer of gas
- Activation of adsorbent

FACTORS INFLUENCING THE ADSORPTION OF GASES ON SOLIDS

NATURE OF GASES

Gas molecules with high polarity, which is soluble and easily liquefied, will be easily adsorbed. Easily liquefiable gases (HCl, NH₃, Cl₂, SO₂, etc.) are adsorbed more easily than the permanent gases (H₂, N₂, O₂, etc.).

Reasons

They are having high critical temperature (i.e. the minimum temperature above which a gas cannot be liquefied) and greater \uparrow intermolecular forces. The higher the critical temperature (T_c), the more easily the gas is liquefied and more readily it is adsorbed.

Example: Adsorption of various gases on 1 g of activated charcoal

Gases	SO ₂	NH ₃	CO ₂	CO	N ₂	H ₂
Critical temperature (T _c) (K)	403	406	304	134	126	33
Amount of gas adsorbed (mL)	380	180	48	9.3	8.0	4.5

Table 2.1.3 Adsorption of various gases on 1 g of activated charcoal

NATURE OF THE ADSORBENT

Since adsorption is a surface phenomenon, it is evident that

Highly porous substances undergo adsorption to a greater extent because pores permit the diffusion of gases.

Example

Activated charcoal at 24°C adsorbs 1.47 gm of CCl₄ per gram of charcoal whereas before activation it would adsorb only 0.011 gm of charcoal.

SURFACE AREA OF THE ADSORBENT

Adsorption involves concentration of a substance on the surface. Hence, the extent of adsorption depends on the surface area of the adsorbents.

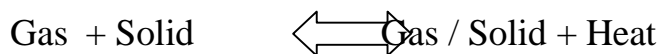
Larger the surface area of the adsorbent, the greater is its adsorption capacity under the given conditions of temperature and pressure.

Example:

Finely divided metals like Ni, Pt, etc. and porous substances like charcoal, fuller's earth, silica gel, etc. provide large surface area and are excellent solid adsorbents.

EFFECT OF PRESSURE

According to Le-Chatlier's Principle, since dynamic equilibrium exists between the adsorbed gas and the gas in contact with the solid, the amount of gas adsorbed by a given solid is directly proportional to pressure.



(i.e.) increase of pressure increases the adsorption and decrease of pressure causes desorption (decreases the adsorption).

EFFECT OF TEMPERATURE

Physical adsorption: It occurs rapidly at lower temperature and decreases with increase of temperature.

Chemical adsorption: Initially it increases with increase of temperature to some extent and then decreases with temperature because chemisorption like an ordinary chemical change requires some activation energy.

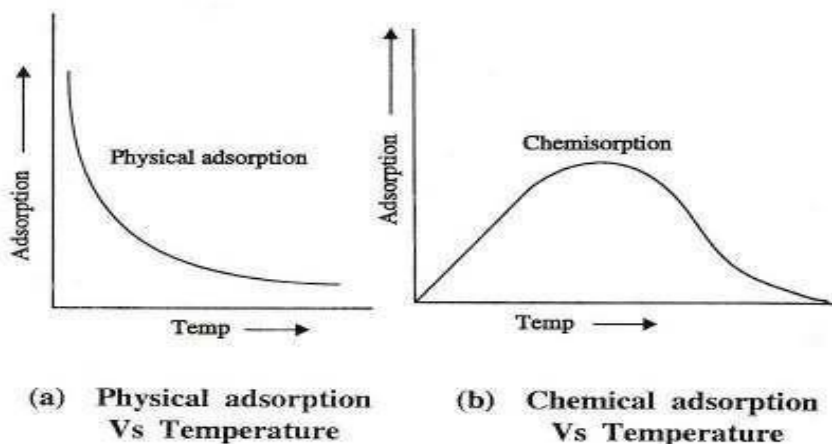


Figure 2.2.1 Variation of Physisorption & Chemisorption with temperature

[Source: <https://www.sarthaks.com/900304/explain-graphical-representation-of-chemical-adsorption-and-physical-adsorption>]

Example

At 60 mm pressure, 1 gm of charcoal adsorbs about 10 cc of N₂ at 0°C, about 20cc of N₂ at -30°C and about 45cc of N₂ at -80°C.

THICKNESS OF ADSORBED LAYER OF GAS

In Physisorption, the adsorbed gases form a unimolecular thick layer at low pressure. But, above a certain pressure, a multimolecular thick layer is formed.

In chemisorption, only a unimolecular thick layer is formed, since adsorbed gases combine directly with the adsorbent surface.

EFFECT OF ACTIVATION OF ADSORBENT

In order to increase the rate of adsorption, activation (i.e. increasing the adsorbing power of the adsorbent) is necessary. Activation can be done by:

- ✓ **Creation of rough surface**
 - Mechanical rubbing of metallic or solid adsorbents.
 - Subjecting to some chemical reactions on the solid adsorbent.
- ✓ **Increasing effective area of the surface**
 - By sub-dividing the solid adsorbents into finer particles.
 - Strong heating of solid adsorbent in superheated steam opens the pores and thereby adsorption activity increases.

ENTHALPY OF ADSORPTION

Adsorption is always exothermic.

In **physical adsorption**, enthalpy of adsorption is about 5 kcal/mole due to weak Vander Waal's forces. Hence, such gases are adsorbed to a smaller extent on solid adsorbent.

In **chemical adsorption**, enthalpy of adsorption is about 100 kcal/mole due to relative formation of chemical bond between gas and the adsorbent. Hence, such gases are adsorbed to a larger extent on solid adsorbent.

REVERSIBLE CHARACTER OF ADSORPTION

Physical adsorption: It is a reversible process. The gas adsorbed on a solid can be removed (desorbed) under reverse conditions of temperature and pressure.



Chemical adsorption: It is an irreversible process, because surface compound is formed and desorption is quite difficult.

2.3 ADSORPTION OF SOLUTES FROM SOLUTIONS

A solution is made up of two basic components – solute and solvent.

When an adsorbent is dropped into a solution, either the solute or the solvent may become adsorbed. Adsorption of solvent is very rare. Adsorption of solutes from the solution follows two mechanisms.

➤ **An adsorbent adsorbs dissolved substances (solutes) from solutions.**

Example: Activated animal charcoal (i.e. charcoal from which pre-adsorbed gases have been removed completely)

- It adsorbs colouring matter present in sugar solutions thereby making the latter colourless.
- It adsorbs certain acids like acetic acid and oxalic acid present in water, thereby acid concentration in water decreases.
- It also adsorbs ammonia from the solution of ammonium hydroxide.
- It adsorbs Cl^- ions from NaCl or AgCl solution.

➤ **An adsorbent adsorbs certain substance from the solution in preference to other substances.**

Examples:

- **Charcoal:** It adsorbs non-electrolytes more readily than electrolytes from a solution.
- **Alumina:** It adsorbs electrolytes in preference to non-electrolytes.

FACTORS INFLUENCING ADSORPTION OF SOLUTES FROM SOLUTION

The amount of solute adsorbed by a solid from the solution depends on the following factors:

Surface area of the adsorbent: If the surface area of the adsorbent is greater, the rate of adsorption is also greater.

Nature of the adsorbent: Some adsorbents are specifically more effective in attracting certain substances to their surface than the other.

Nature of the solute adsorbed: If the molecular weight of the solute is high, the extent of rate of adsorption is also high.

Effect of temperature and concentration

Adsorption of substances from the solution depends on temperature and concentration of the solution. An increase in temperature decreases the extent of adsorption and vice versa. Freundlich adsorption isotherm is suitable to explain the effect of concentration.

When an adsorbent is dropped into a solution, either the solute or solvent may be adsorbed.

- ✓ If the solute is adsorbed by the adsorbent, it is known as **positive adsorption**.
- ✓ If the solvent is taken up by the adsorbent, it is known as **negative adsorption**.

NEGATIVE ADSORPTION:

Adsorption from a solution decreases with rise of temperature and decrease in concentration of the solution. This type of adsorption is known as negative adsorption.

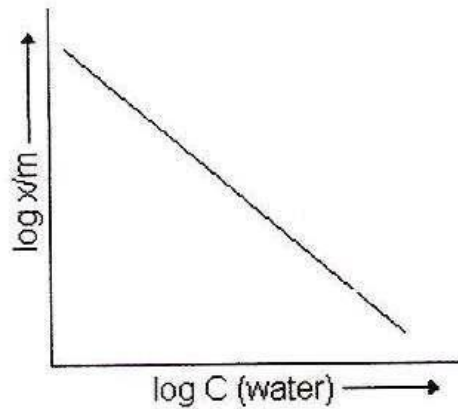


Figure 2.3.1 Negative Adsorption

[Source: "Engineering Chemistry" by Dr. Ravikrishnan, Page 2.26]

Example: From the dilute solution of KCl, charcoal adsorbs water thereby the salt concentration is increased.

POSITIVE ADSORPTION

Adsorption from a solution increases with decrease of temperature and increases in concentration of the solution. This type of adsorption is known as positive adsorption.

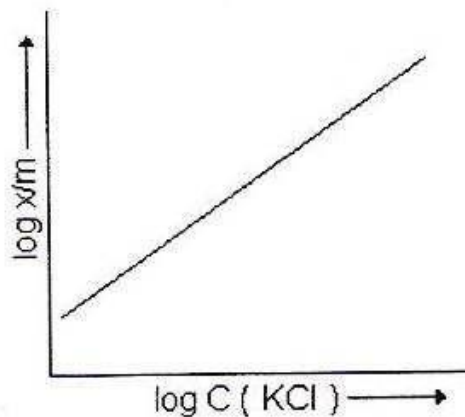


Figure 2.3.2 Positive Adsorption

[Source: "Engineering Chemistry" by Dr. Ravikrishnan, Page 2.26]

Example: From the concentrated solution of KCl, charcoal adsorbs KCl rather than water thereby the salt concentration gets decreased.

2.4 ADSORPTION CURVES

The amount of gas molecules adsorbed on the surface of the adsorbent depends on pressure and

temperature (i.e) the amount of gas adsorbed is a function of the T and P only.

If, “x” is the amount of gas adsorbed on mass, “m” of the adsorbent at pressure (P) and temperature (T), then it can be represented as

$$x/m = f (P, T) \dots\dots\dots (1)$$

This mathematical equation is called adsorption curve.

This equation (1) gives three types of adsorption curves under different conditions of P, T and x/m.

ADSORPTION ISOTHERM

If T is kept constant, then equation (1) becomes

$$x/m = f (P)\dots\dots\dots(2)$$

Equation (2) explains the variation of adsorption with P at constant T.

ADSORPTION ISOBAR

If P is kept constant, then equation (1) becomes

$$x/m = f (T)\dots\dots\dots(3)$$

Equation (3) explains the variation of adsorption with T at constant P.

ADSORPTION ISOSTERE

If the amount of adsorbed gas is kept constant, then

$$P = f (T)\dots\dots\dots(4)$$

Equation (4) explains the variation of P with T when x/m is kept constant.

2.5 ADSORPTION ISOTHERMS

The extent of adsorption (x/m) [where “x” is the mass of the adsorbate and „m” is the mass of the adsorbent] depends on pressure. This can be understood by plotting a graph between x/m against P.

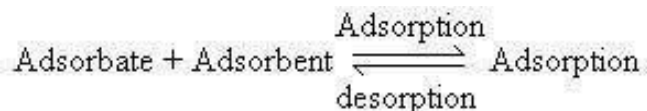
DEFINITION

The process of Adsorption is usually studied through graphs know as adsorption isotherm.

It is “the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature”.

BASIC ADSORPTION ISOTHERM

In the process of adsorption, adsorbate gets adsorbed on adsorbent.



According to Le-Chatlier's principle, the direction of equilibrium would shift in that direction where the stress can be relieved.

In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases.

Since number of molecules decreases in forward direction, with the increase in pressure, forward direction of equilibrium will be favoured.

From the graph, it is clear that the extent of adsorption (x/m) increases with increasing pressure (P) and becomes maximum at P_s , called the saturation pressure.

At P_s , the rate of adsorption becomes equal to the rate of desorption i.e. dynamic equilibrium is reached and further increase of P does not alter this equilibrium.

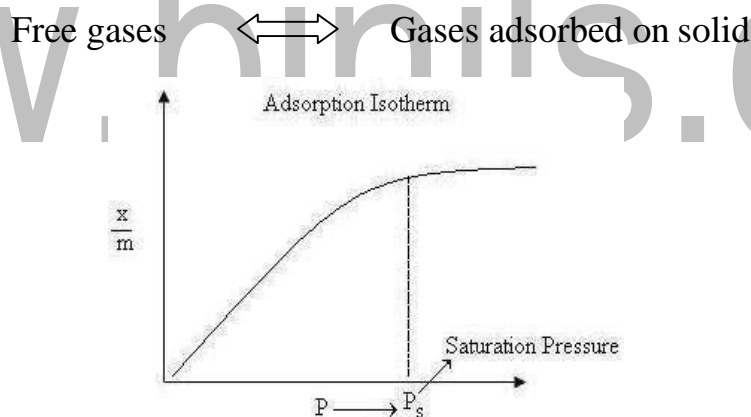


Figure 2.5.1 Basic Adsorption Isotherm

[Source: [https://www.semanticscholar.org/paper/Stability-Study-of-Important-Metal-Organic-\(MOFs\)-a-Agarwal/4c4630f42777deaf492736035be627c6be79090a/figure/5](https://www.semanticscholar.org/paper/Stability-Study-of-Important-Metal-Organic-(MOFs)-a-Agarwal/4c4630f42777deaf492736035be627c6be79090a/figure/5)]

From the graph, we can predict that after saturation pressure P_s , adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure.

TYPES OF ADSORPTION ISOTHERMS

Adsorption isotherms are divided into five different types. A large number of adsorption isotherms of gases on a variety of adsorbents at different temperatures have been studied. In each type, the saturation pressure, where the maximum adsorption occurs, is indicated by P_s .

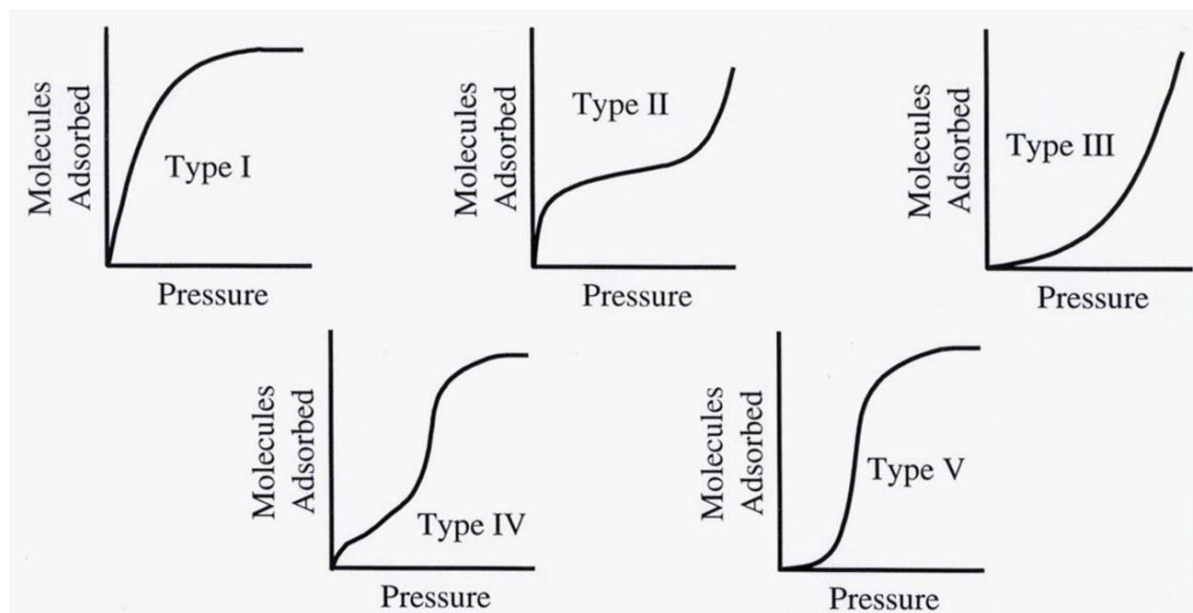


Figure 2.5.2 Different types of adsorption isotherms

[Source: [https://www.semanticscholar.org/paper/Stability-Study-of-Important-Metal-Organic-\(MOFs\)-a-Agarwal/4c4630f42777deaf492736035be627c6be79090a/figure/5](https://www.semanticscholar.org/paper/Stability-Study-of-Important-Metal-Organic-(MOFs)-a-Agarwal/4c4630f42777deaf492736035be627c6be79090a/figure/5)]

TYPE I ADSORPTION ISOTHERM

The above graph depicts Monolayer adsorption. This graph can be easily explained using Langmuir Adsorption Isotherm. The amount of gas adsorbed approaches a limiting value „ P_s “, which is just enough to complete a monomolecular layer, even when the gas pressure is high. Further increase in pressure will not increase the amount of adsorption. **Examples:** Adsorption of Nitrogen (N_2) or Hydrogen (H_2) on charcoal at temperature near to $-180^\circ C$.

TYPE II ADSORPTION ISOTHERM

Type II Adsorption Isotherm shows large deviation from Langmuir adsorption model. The graph represents a case of multi-molecular layer physical adsorption on non-porous materials. It has been suggested that, the gas molecules adsorbed in the first layer may hold a second layer by weak Vander Vaal's forces, which in turn, may hold a third layer and so on. The intermediate flat region in the isotherm corresponds to monolayer formation. So, this represents the transition of monomolecular layer to multimolecular layer. Thus the curve shows that, there is a transition point „B“ which

represents the P at which the formation of monolayer is complete and that of multilayer is being started. **Examples:** Nitrogen [N_2 (g)] adsorbed at -195°C on Iron (Fe) catalyst and Nitrogen [N_2 (g)] adsorbed at -195°C on silica gel.

TYPE III ADSORPTION ISOTHERM

Type III Adsorption Isotherm also shows large deviation from Langmuir model. This isotherm explains the formation of multilayer. Examples: Bromine (Br_2) at 79°C on silica gel or Iodine (I_2) at 79°C on silica gel. It represents a case of physical adsorption on porous materials. There is no flat portion in the curve which indicates that monolayer formation is missing. The curve represents that multilayer formation starts even before the completion of monolayer formation.

TYPE IV ADSORPTION ISOTHERM

Adsorption isotherm represents a case of physical adsorption on porous materials accompanied by capillary condensation. Examples: Adsorption of Benzene on Iron Oxide (Fe_2O_3) at 500°C and adsorption of Benzene on silica gel at 500°C . At lower pressure region the graph is quite similar to Type II. This explains formation of monolayer followed by multilayer. The saturation level reaches at a pressure below the saturation vapour pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at the pressure even below the saturation pressure (P_s) of the gas. This is only due to the formation of multimolecular adsorption layers of the gas molecules but also due to condensation of some of the gas molecules within the capillary pores of the adsorbent. This is known as capillary condensation of the gas.

TYPE V ADSORPTION ISOTHERM

It also represents a case of physical adsorption on porous materials. It indicates that the formation of multi molecular layer starts at the beginning of adsorption. Example: Adsorption of Water vapours at 1000°C on charcoal. Explanation of Type V graph is similar to Type IV. Type IV and V shows phenomenon of capillary condensation of gas.

FREUNDLICH'S ADSORPTION ISOTHERM

The amount of gas adsorbed for a given quantity of adsorbent (substrate) increases rapidly as pressure increases and the rate decreases as the surface covered is more and more.

The relationship between the magnitude of adsorption (x/m) and pressure (P) can be expressed mathematically by an empirical equation known as Freundlich adsorption isotherm.

$$\frac{x}{m} = K P^{1/n}$$

DERIVATION OF FREUNDLICH'S ADSORPTION ISOTHERM

The equation for Freundlich adsorption isotherm may be derived from the result obtained from the graph.

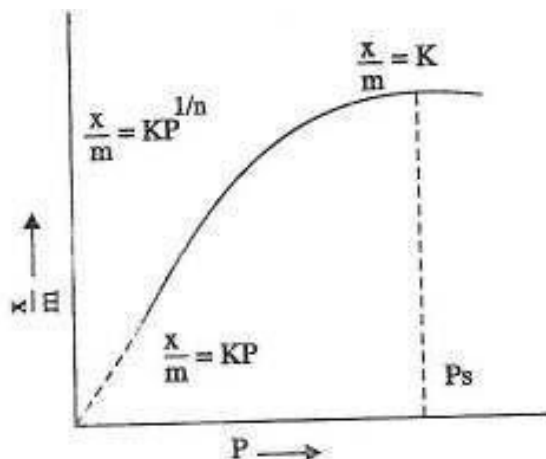


Figure 2.5.9 Adsorption isotherm

[Source: "Chemistry for Technologists, by Dr. Ravikrishnan A, Page 2.12]

(i) At low pressure: Adsorption increases with pressure. The adsorption isotherm is almost a straight line indicating a direct relationship between the extent of adsorption and pressure.

$$x/m \propto P \text{ (OR) } x/m = KP \dots\dots (1)$$

(ii) At high pressure: The adsorption is almost constant. The adsorption isotherm is parallel to the X - axis indicating that the extent of adsorption is independent of the pressure.

$$x/m = \text{constant (OR) } x/m = K \dots\dots (2)$$

(iii) At intermediate (normal) pressure: The extent of adsorption should be proportional to fractional power of pressure.

$$x/m \propto P^{1/n} \text{ (OR) } x/m = KP^{1/n} \dots\dots (3)$$

where, n is a whole number, whose values lies between 0 and 1.

Equation (3) is known as Freundlich Adsorption isotherm.

Taking logarithm on both sides, equation (3) becomes

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

On plotting $\log x/m$ versus $\log P$, a straight line is obtained with a slope of $1/n$ and intercept $\log K$.

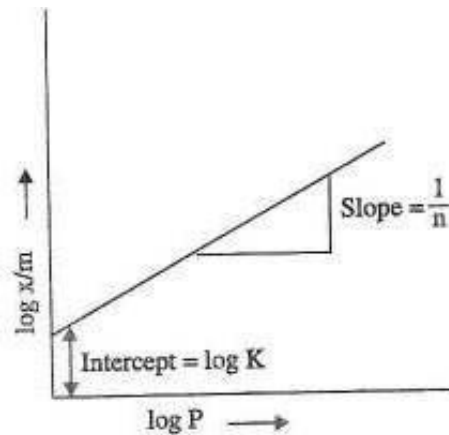


Figure 2.5.10 Freundlich Adsorption isotherm
[Source: “Chemistry for Technologists, by Dr. Ravikrishnan A, Page 2.16]

LIMITATIONS OF FREUNDLICH’S ADSORPTION ISOTHERM

- Freundlich equation is purely empirical and has no theoretical basis.
- The equation is valid only up to a certain pressure and invalid at higher pressure.
- The constant K and n vary with T .
- It fails when the concentration of adsorbate is very high.

LANGMUIR’S ADSORPTION ISOTHERM

Irving Langmuir (1916) has shown that there is an equilibrium established between adsorption and desorption. He has derived an isotherm equation on the basis of the following assumptions.

- The adsorbed molecules form only unimolecular layer on the solid adsorbent surface.
- The adsorbed molecules on the surface do not interact with each other.
- The molecules of a gas are adsorbed only on vacant sites of adsorbent surface. Each site can hold only one molecular species of the adsorbate.
- The adsorption process consists of two opposing processes (i) condensation of the adsorbate molecules on the adsorbent surface (ii) desorption of molecules from the adsorbent surface.
- The adsorbed gas molecule behaves ideally in the vapour phase.

DERIVATION OF LANGMUIR ADSORPTION ISOTHERM

Consider an adsorbing surface of area 1 sq.cm on which the molecules of a gas are condensing and evaporating. When the adsorption starts, the rate of adsorption or condensation is highest initially while the rate of desorption is very small. As the adsorption proceeds, the two rates gradually approach each

other until a dynamic equilibrium is obtained when the rate of adsorption is equal to the rate of desorption.

If, A is gas molecule and M is solid surface, then

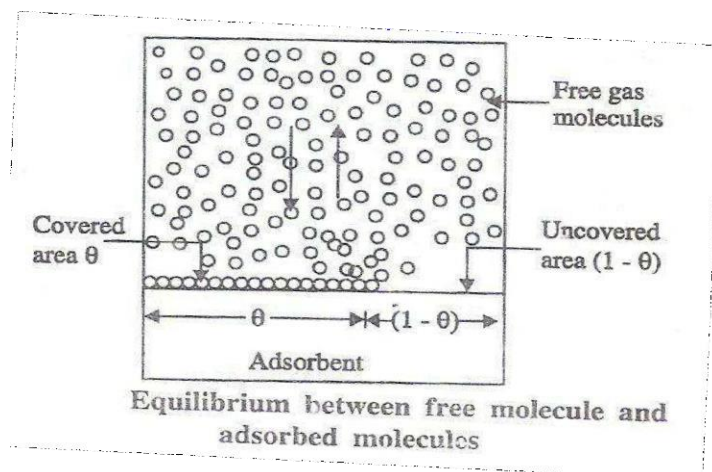
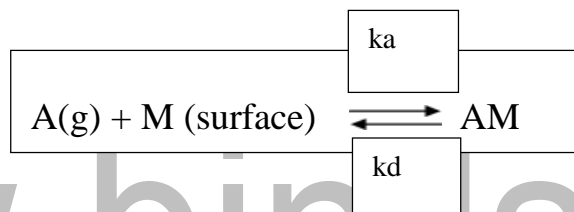


Figure 2.5.11 Equilibrium between free molecules and adsorbed molecules
[Source: "Chemistry for Technologists, by Dr. Ravikrishnan A, Page 2.16]



K_a – rate constant for adsorption
 K_d – rate constant for desorption

Let the,

Fraction of the total surface area covered by

the adsorbed gas molecule = θ

If the total area is 1 sq.cm.,

then fraction of the remaining surface available

for adsorption i.e.uncovered area = $1 - \theta$

If P is the pressure of the gas,

The rate of adsorption is proportional to the pressure and fraction ofuncovered area ($1 - \theta$)

The rate of adsorption, $R_a = k_a (1 - \theta) P$

The rate at which gas molecules evaporate from the surface (desorption) will depend on the fractionof the surface covered by gas molecules (θ).

Hence, The rate of desorption, $R_d = k_d \theta$

At equilibrium,

$$R_a = R_d$$

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

Solving for θ ,

$$k_a P - k_a P \theta = k_d \theta$$

$$k_a P = k_a P \theta + k_d \theta$$

$$k_a P = (k_d + k_a P) \theta$$

$$\theta = \frac{k_a P}{k_d + k_a P}$$

Divide the numerator & denominator on RHS by k_d , and considering $K = \frac{k_a}{k_d}$ we get,

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

where, $k_a / k_d = K$, is adsorption co-efficient

But, the amount of gas adsorbed per unit mass of the adsorbent, x is proportional to the fraction of the surface covered, θ

$$x \propto \theta \text{ (OR) } x = K' \theta$$

Hence,

$$X = \frac{K'KP}{1 + KP} \dots\dots\dots(1)$$

where, K' = new constant

The above equation gives the relation between the amounts of gas adsorbed to the pressure of the gas at constant temperature which is called as Langmuir's Adsorption Isotherm.

Equation (1) can be re-written as

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

Dividing both sides by $K'K$

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

$$\frac{1}{K'K} + \frac{KP}{K'K} = \frac{P}{x} \dots\dots\dots(2)$$

K'K

K'K

x

Equation (2) is similar to an equation for a straight line $y = mx + c$

Thus, if the graph is plotted between P/x versus P , we should get a straight line with slope $K / K'K$ and intercept $1 / K'K$.

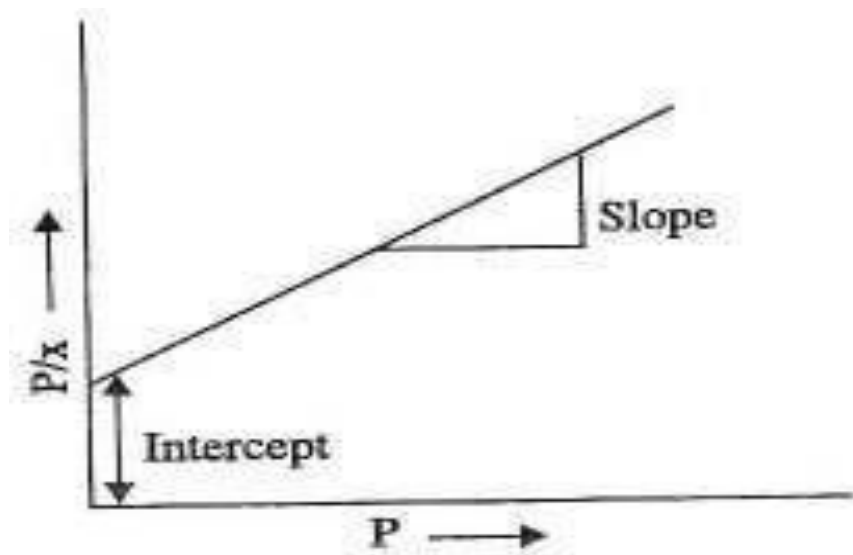


Figure 2.5.12 plot of P/x Vs P

[Source: "Chemistry for Technologists, by Dr. Ravikrishnan A, Page 2.21]

Case 1: At low pressure, $(K / K'K) P$ term is negligible. (i.e.) $1 / K'K \gg (K / K'K) P$.

Hence equation (2) becomes

$$1 / K'K = P / x \text{ (OR) } x = P K'K \dots\dots (3)$$

i.e. the amount of adsorption per unit mass of adsorbent is directly proportional to P at low pressure.

Case 2: At high pressure, $1 / K'K$ term is negligible. (i.e.) $(K / K'K) P \gg 1 / K'K$.

Hence equation (5) becomes

$$(K / K'K) P = P / x \text{ (OR) } x = K'(\text{constant}) \text{ (OR) } x = K' P^0 \dots\dots\dots (4)$$

i.e. at high pressure, the extent of adsorption at a given temperature is independent of pressure of the gas, because the surface becomes completely covered.

Case 3: At normal pressure, equation (7) becomes

$$x = K' P^n \dots\dots\dots (5)$$

where, n lies between 0 and 1.

Equation (5) is Freundlich adsorption isotherm.

Limitations of Langmuir adsorption equation

1. The solid surface is heterogeneous.
2. This equation is valid only at low pressure conditions.
3. At high pressure multilayer adsorption takes place.
4. Langmuir assumed that the molecules do not interact with each other. This is impossible as weak force of attraction exists between molecules of same type.

From the above facts it can be concluded that the Langmuir equation is valid under low pressure conditions and fails at high pressure.