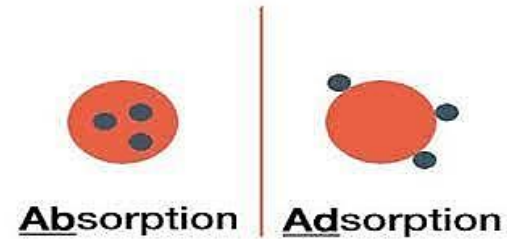


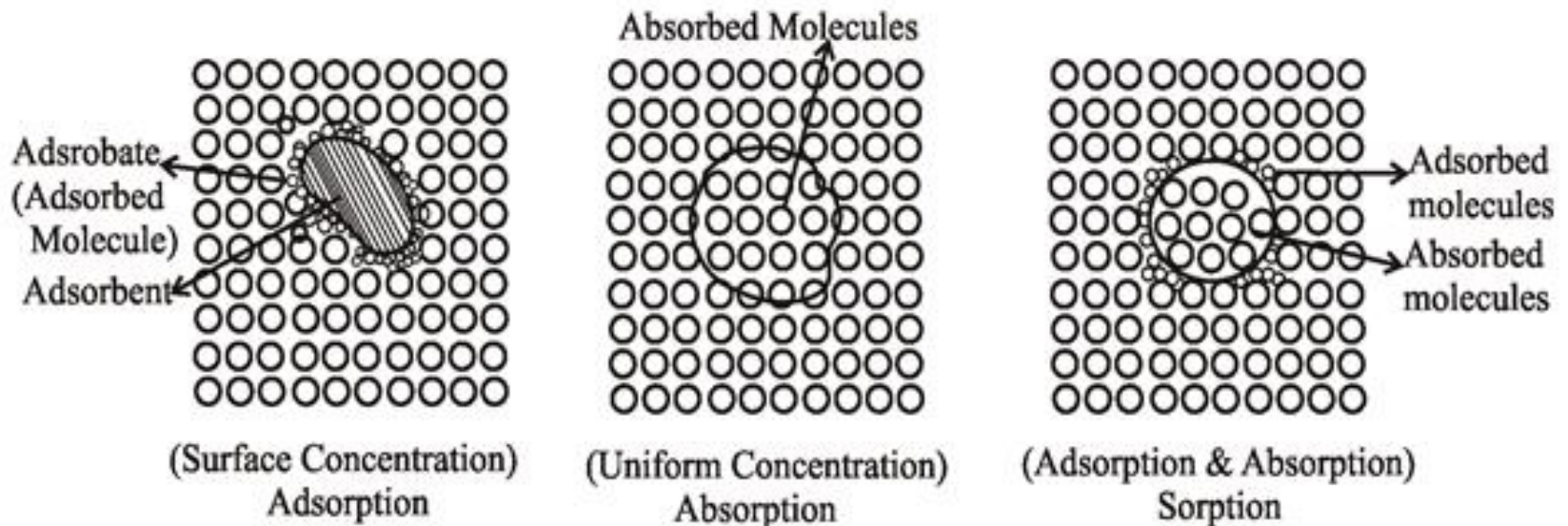
Sorption characteristics of fibers



Sorption



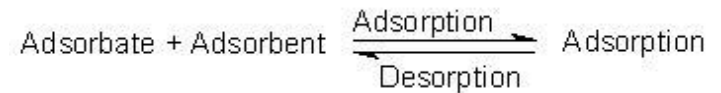
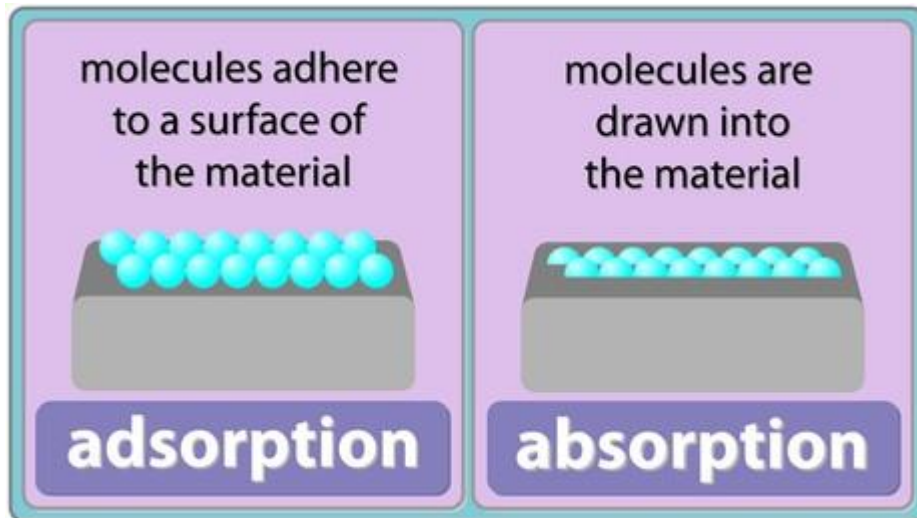
Sorption describes the actions of **absorption and adsorption**.
 Adsorption and absorption are important processes that occur in chemistry and biology.





Adsorption & Absorption

- The major difference between adsorption and absorption is that one is a surface process and the other a bulk process.
- Adsorption — takes place on the surface of a substrate



- Absorption — one substance enters the bulk, or volume, of another substance e.g. a gas absorbed by a liquid



Adsorption is a surface process, the accumulation of a gas or liquid on a liquid or solid. Adsorption can be defined further based on the strength of the interaction between the adsorbent (the substrate onto which chemicals attach) and the adsorbed molecules.

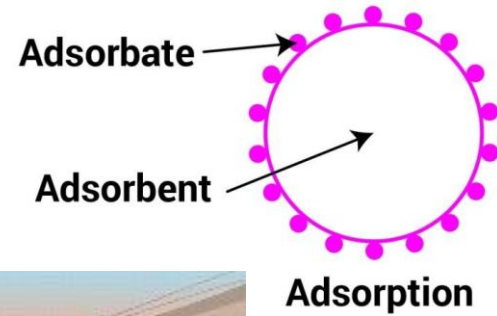
Factors affecting adsorption:

The extent of adsorption depends upon the following factors:

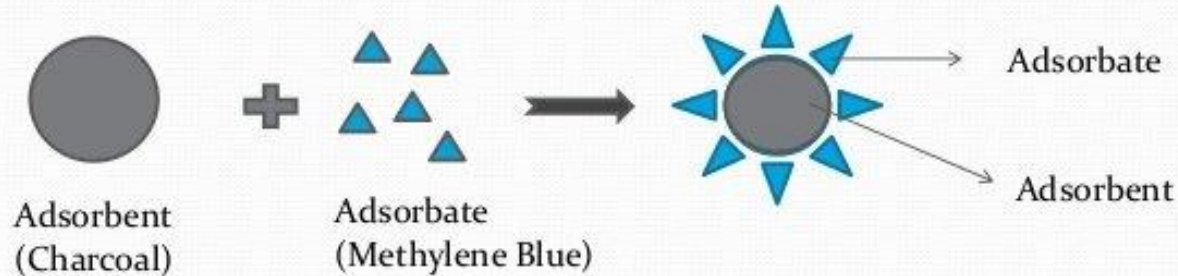
- Nature of adsorbate and adsorbent.
- The surface area of adsorbent.
- Activation of adsorbent.
- Experimental conditions. E.g., temperature, pressure, etc.



Adsorbate and Adsorbent



Mechanism of Adsorption



Adsorbent atoms or molecules are not surrounded by atoms or molecules of their kind and they have unbalanced attractive forces on the surface which can hold adsorbate particles.

Example: Silica gel, Alumina



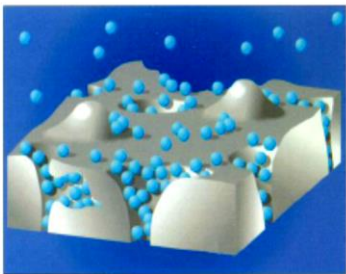


Physisorption — Van der Waals interactions between substrate and adsorbate (the molecule that is adsorbed)

Chemisorption — Chemical bonds involved (covalent bonds usually) in sticking the adsorbate to the adsorbent

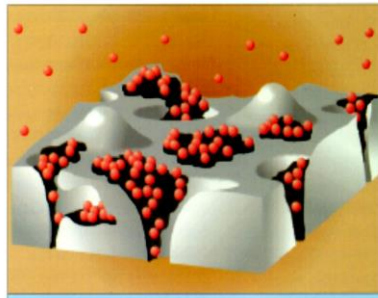
Chemisorption involves more energy than physisorption. The difference between the two processes is loosely based on the binding energy of the interaction.

Physical sorption



Example: sorption of inert gas at low temperature at surface of porous materials.

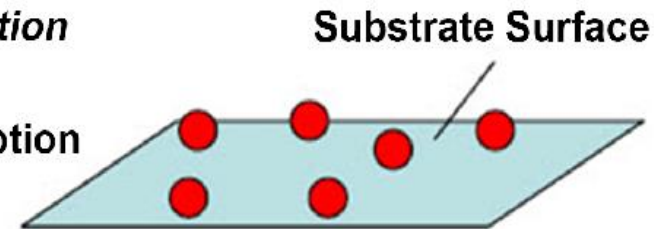
Chemisorption



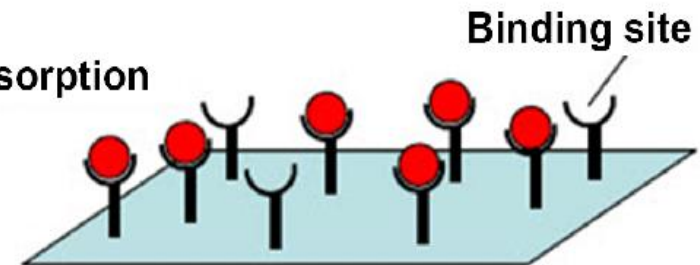
Example: reactive gas sorption on the active sites of porous materials.

(a) Adsorption

Physisorption



Chemisorption



1. Physical adsorption (physisorption): **If the force of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption.** It is also known as Vander Waal's adsorption. In physical adsorption the force of attraction between the adsorbate and adsorbent are very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure.

2. Chemical adsorption (chemisorption): **If the force of attraction existing between adsorbate and adsorbent are almost same strength as chemical bonds, the adsorption is called chemical adsorption.** It is also known as Langmuir adsorption. In chemisorption the force of attraction is very strong, therefore adsorption cannot be easily reversed.

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



Physisorption vs Chemisorption

Property	Physisorption	Chemisorption
Forces	van der Waals	Chemical bonding
ΔH_{ads} (kJ mol ⁻¹)	< 40	50-200
E_a (kJ mol ⁻¹)	Rare	60–100
Isothermal Reversibility	Complete	Slow or none
Extent	Multilayers	Monolayer

Physisorption: Surface area and porosity are physical properties that impact the quality and character of solid phase materials, Pore size distribution, Pore Volume etc.

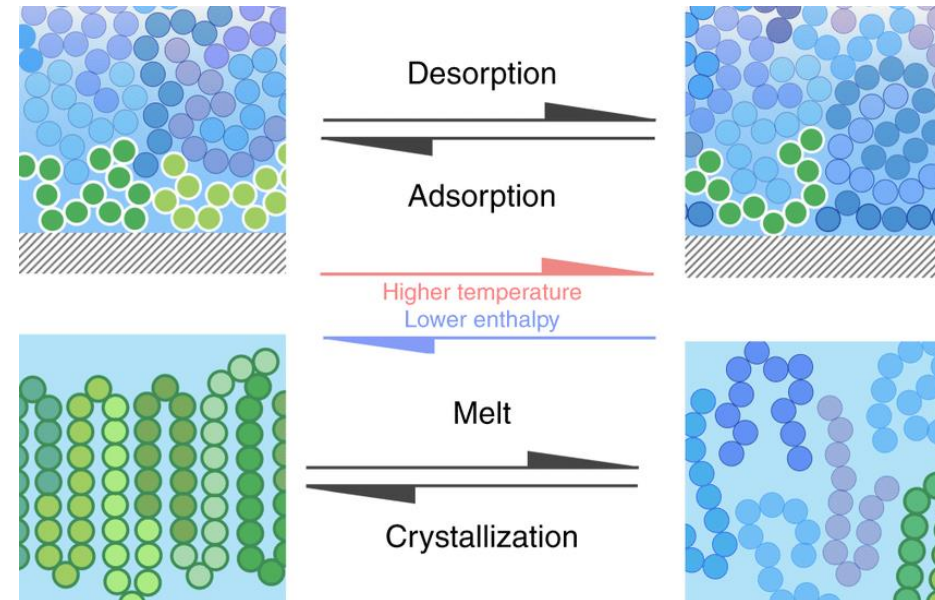
Chemisorption - measures the number of surface active sites which are used to promote a specified catalytic reaction. Critical parameters for chemisorption measurement are: the area of the active element, metal dispersion, surface acidity, exposed proportion of the active element.



Desorption

- Desorption is the release of one substance from another, either from the surface or through the surface.
- Desorption can occur when an equilibrium situation is altered.

Imagine a tank of water in equilibrium with its surroundings. The amount of oxygen entering and leaving the water from the air will be the same — and the oxygen concentration in the water will be constant. If the water temperature increases, the equilibrium and solubility are changed, and the oxygen will desorb from the water — lowering the oxygen content.

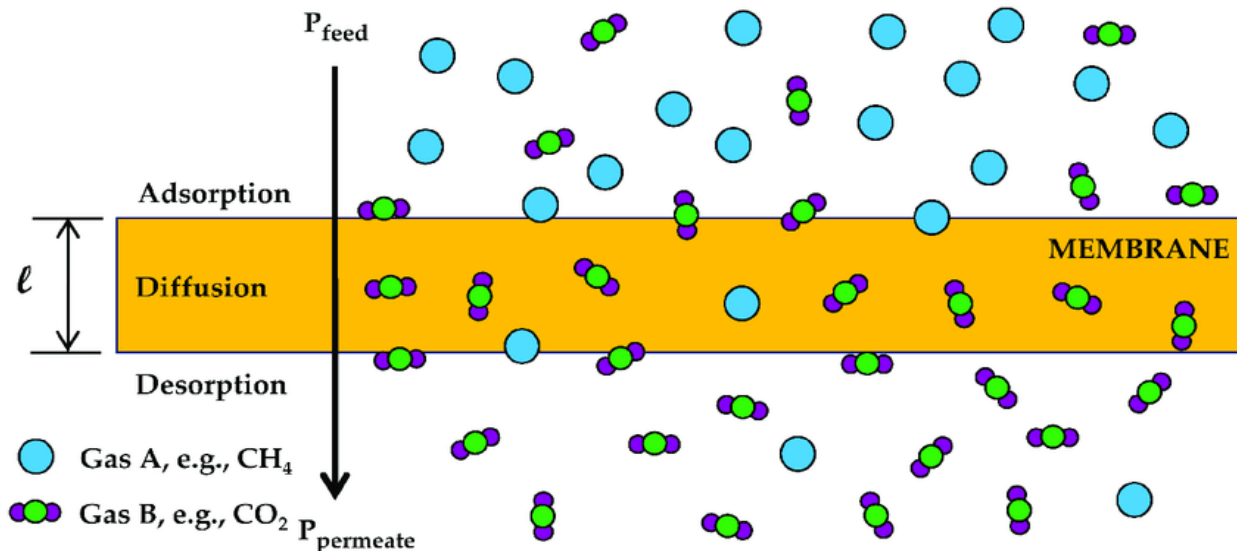


Absorption

- Absorption is a phenomenon involving the bulk properties of a solid, liquid or gas. It involves atoms or molecules crossing the surface and entering the volume of the material. As in absorption, there can be physical and chemical absorption.
- **Physical absorption** — A non-reactive process e.g. when oxygen present in air dissolves in water. The process depends on the liquid and the gas, and on physical properties like solubility, temperature and pressure.
- **Chemical absorption** — A chemical reaction takes place when the atoms or molecules are absorbed. An example is when hydrogen sulphide is removed from biogas streams and converted into solid sulphur.



Sorption- I



Fibers are surrounded by penetrants molecules or particles (water vapor, liquids, gases, or solid particles) in specific medium (air, water):

Penetrants diffusion by medium towards fiber. This process is usually very quick.

Adsorption on the fiber surface. Adsorption processes are often investigated separately because some penetrants are not able to penetrate into fibers or penetration is very slow.

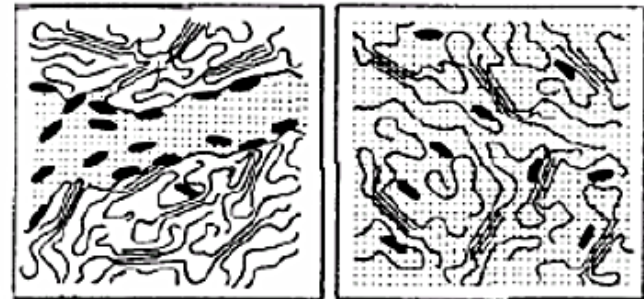
Diffusion into fiber body, where transport of penetrants occurs.

In some cases are penetrants immobilized in specific sites of fiber (creation of bond between penetrants and fiber).

Desorption of penetrants from fibers back to the medium (reverse processes)



Sorption- II



Macroscopic result can be deposition of penetrant on fiber surface (e.g. soiling by dust particles), penetrant transport into fiber and immobilization (e.g. dyeing) or penetrant transport through fibers (sweet removal)

Sorption processes have three basic features:

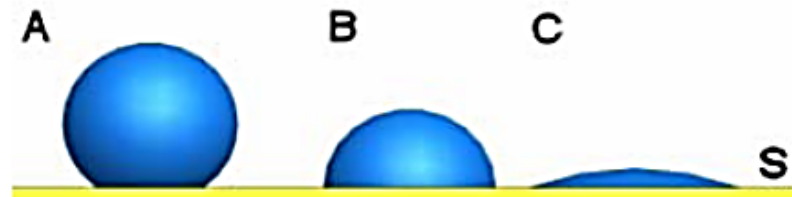
- kinetic (rate of changes),
- equilibrium (magnitude of changes),
- thermodynamic (driving force of changes).

All these features have simultaneous influence on the results of sorption. Their separate investigation is very complicated and requires often special experiments.





Nature of Fibers

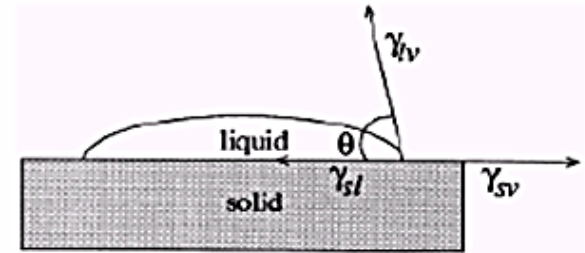
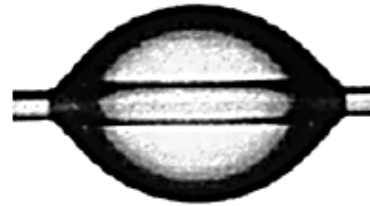


- **Hydrophobic fibers** are electrically neutral and nonpolar, and thus prefer other neutral and nonpolar solvents. Hydrophylic are natural fibers and fibers created from natural polymeres. On many hydrophilic surfaces, water droplets will exhibit contact angles of 10° to 30°
- **Superhydrophobic fibers** have surfaces that are extremely difficult to wet with water contact angles in excess of 150° . On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent.
- A **hydrophilic fiber** is typically charge-polarized and capable of hydrogen bonding creation (can transiently bond water). This is thermodynamicaaly favorable and these fibers exhibit marked swelling not only in water, but also in other polar solvents. Hydrophobic are majority of fibers created from synthetic polymers. On highly hydrophobic surfaces, which are incompatible with water, a large contact angle (70° to 90°) are observed.





Wetting - I



Fiber is in local contact with liquid (e.g. partially immersed, water drop on the fiber surface etc.). In these cases the wetting occurs.

Wetting is result of energetic interactions between three phases i.e. solid, liquid and air (gas phase) in equilibrium. The characteristic of wetting is contact angle θ

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

$\gamma_{lv} = \gamma$ Interfacial energy liquid /air.

γ_{sv} Interfacial energy solid/air.

γ_{sl} Interfacial energy solid/liquid.

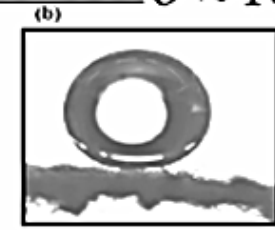
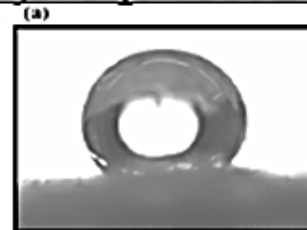
Micro rough fiber surface

Non wetting ($\theta > 90^\circ$)

Partial wetting ($\theta < 90^\circ$)

Full wetting ($\theta \approx 0^\circ$)

Ultrahydrophobic surfaces ($\theta \approx 180^\circ$)



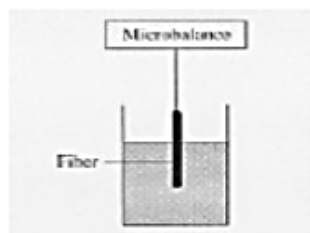


Wetting - II

Wettable liquids have adhesive forces (attraction to the solid surface) higher than cohesive forces in liquid

Wilhelmy balance

no absorption



A vertical fiber known perimeter is attached to a balance, and the force due to wetting is measured.

Wetting force

$$F_W = \gamma_{lv} * O_V * \cos \theta$$

O_V is fiber circumference

Contact angles θ [°] for ethanol and water

polymer	ethanol	water
PP	47	86
PES	26	75
PA 6.6	18	71

Wetting coefficient

thermodynamic driving force for spontaneous wetting

$$S = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl})$$

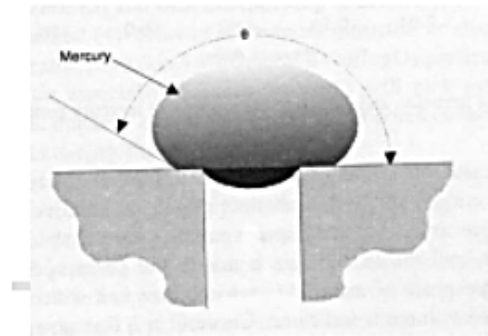
$$S = \gamma_{lv} * (\cos \theta - 1)$$

Full wetting $\theta=0^\circ$

$$O_V = F_W / \gamma_{lv}$$



Water sorption - I



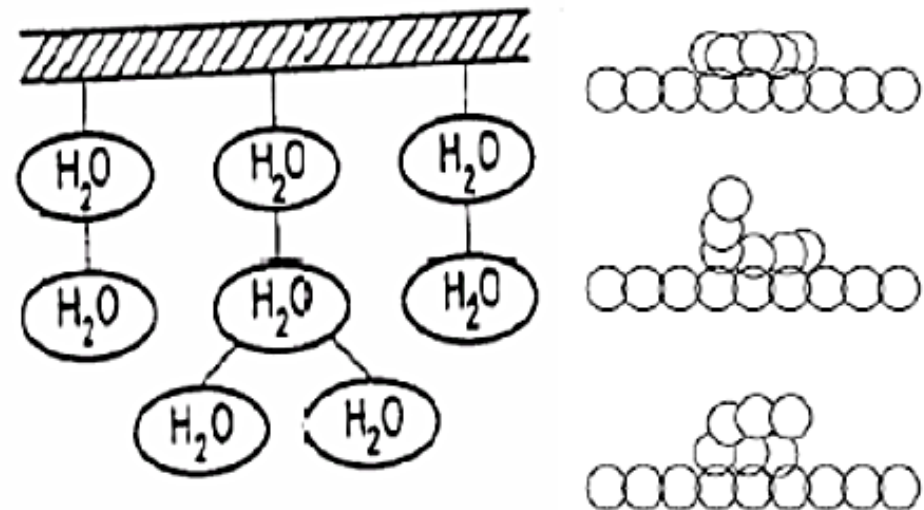
Hydrophilic fibers – porous (affinity to water) are able to link and transport water. Hydrophilic fibers are natural and chemical fibers containing hydrophilic groups (able to create hydrogen bonds).

Hydrophobic fibers – non porous (no affinity to water) are not capable to link water by specific sites and no wetting of fiber surface. Water is spread on the fiber surface and between fiber bundles by capillary forces.

Water in polymers is acting as plasticization matter lowering glass transition temperature and increasing deformability. Water has positive influence on the electric conductivity and lower density of fibers.

Water sorption is connected with chemical composition of fibers, state of their surface, accessibility of hydrophilic groups, loosening of fiber structure, pores distribution, temperature and time.

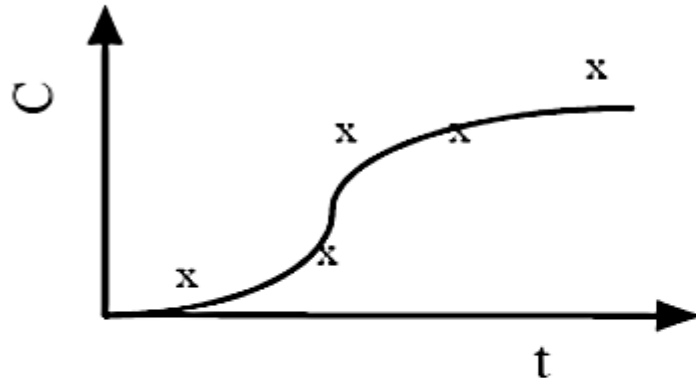
1. sorption centers existence (hydroxyl groups etc.)
2. sorption centers accessibility
3. secondary sorption centers formation





Water vapor sorption

Diffusion with reaction and immobilization



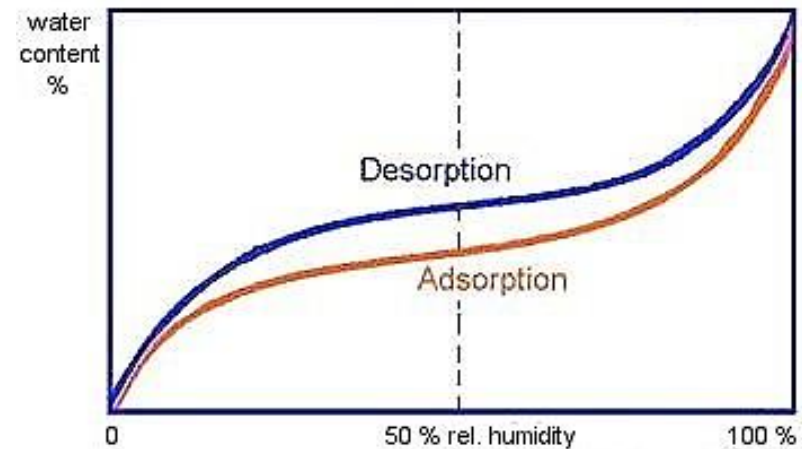
$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + k_1 * C - k_2 * S$$

S is saturation concentration of sorption centers

- For some fibers is sorption accompanied by marked swelling which increase number of accessible sites for water molecules. The water molecules are clustered and these clusters are linked on the accessible sites.
- For hydrophilic materials is clustering tendency high and water diffusion coefficient in fiber pores is high.
- For less hydrophilic materials is clustering tendency smaller and water diffusion coefficient in fiber pores is decreasing.



Sorption isotherm



- A **sorption isotherm** is the graphic representation of the sorption behavior of a substance. It describes the relationship between the water content of the substance and the relative humidity of the ambient air at a particular temperature.
- When determining the equilibrium states between the product and the ambient air, differences are found between the values which are measured during water vapor adsorption (**adsorption isotherm**) and those which are measured during water vapor release (**desorption isotherm**).
- The values for the desorption isotherm are always somewhat higher than those for the adsorption isotherm. The differences between adsorption and desorption isotherms are at their greatest at moderate relative humidities
- The profile of a sorption isotherm is characteristic of the hygroscopicity of a product.

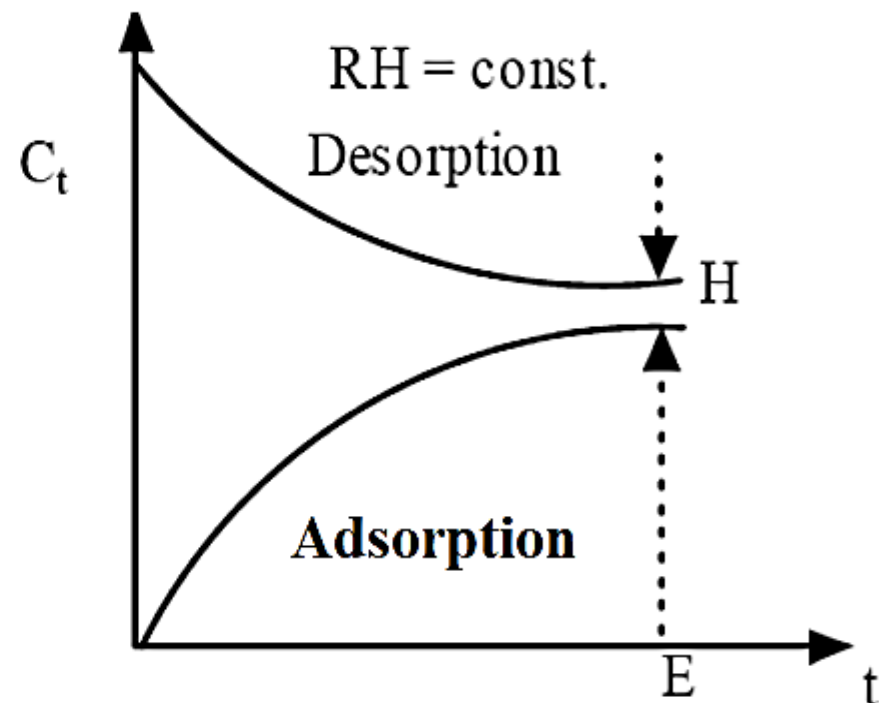
- Adsorption isotherms are basic tool for investigation of interactions between penetrants and fiber surface
- Adsorption isotherm is dependence of penetrant concentration on the fiber surface (or in the fiber) C_p on the concentration of penetrant C_o in medium (surroundings) in equilibrium (stabilization of distribution of penetrant between fiber and medium).
- Due to large volume of medium is concentration C_o practically constant during whole sorption process.
- Experiments are usually realized under isothermal conditions.



Isotherms construction

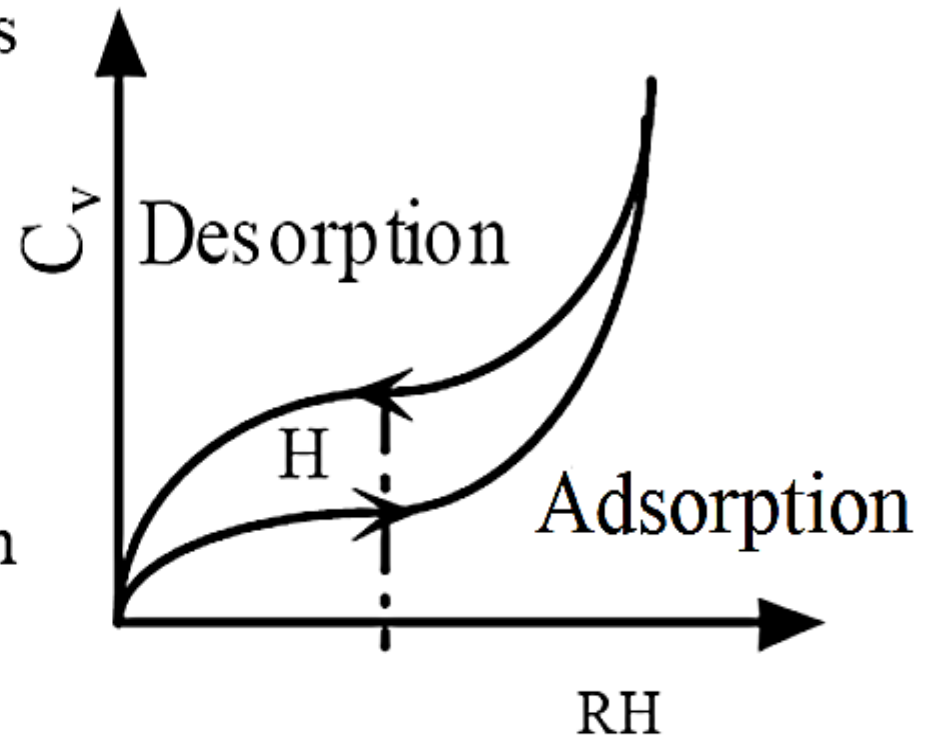
- Construction is based on the kinetic experiments, i.e. dependence of water concentration in fiber C_t on the time t (at constant relative humidity RH). Equilibrium value C_v for infinite time $t = \infty$ and corresponding RH are then one point on absorption isotherm. If the process is started from dry fiber the humidification occurs (absorption). If the process is started from wet fiber the drying occurs (desorption).

$$C_t = C_v * (1 - \exp(-K * t))$$



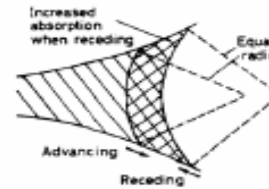
Equilibrium isotherms of water vapor

- Adsorption isotherms and desorption isotherms for water vapor are experimentally created.
- Water vapor sorption isotherm is dependence of equilibrium concentration of water in fiber C_V on the surrounding air relative humidity RH





Hysteresis



< ca. 40% RH
=> Adsorption
(BET, etc.)

> ca. 40% RH
=> Condensation
$$\ln\left(\frac{p}{p_s}\right) = -\frac{2\gamma_{lg} v}{r RT}$$

(Kelvin equation)

Fiber	Hysteresis H [%]
cotton	0,9
viscose	1,8
wool	2,0
diacetate	2,6
PA 6	0,25

RH = 65%

Hysteresis is difference between absorption and desorption isotherms at selected air relative humidity RH. Hysteresis of hydrophilic fibers is marked and for hydrophobic fibers is very low.

Hysteresis reason is various number of accessible binding sites in fibers during drying of wet fiber (more) or wetting of dry fiber (less).

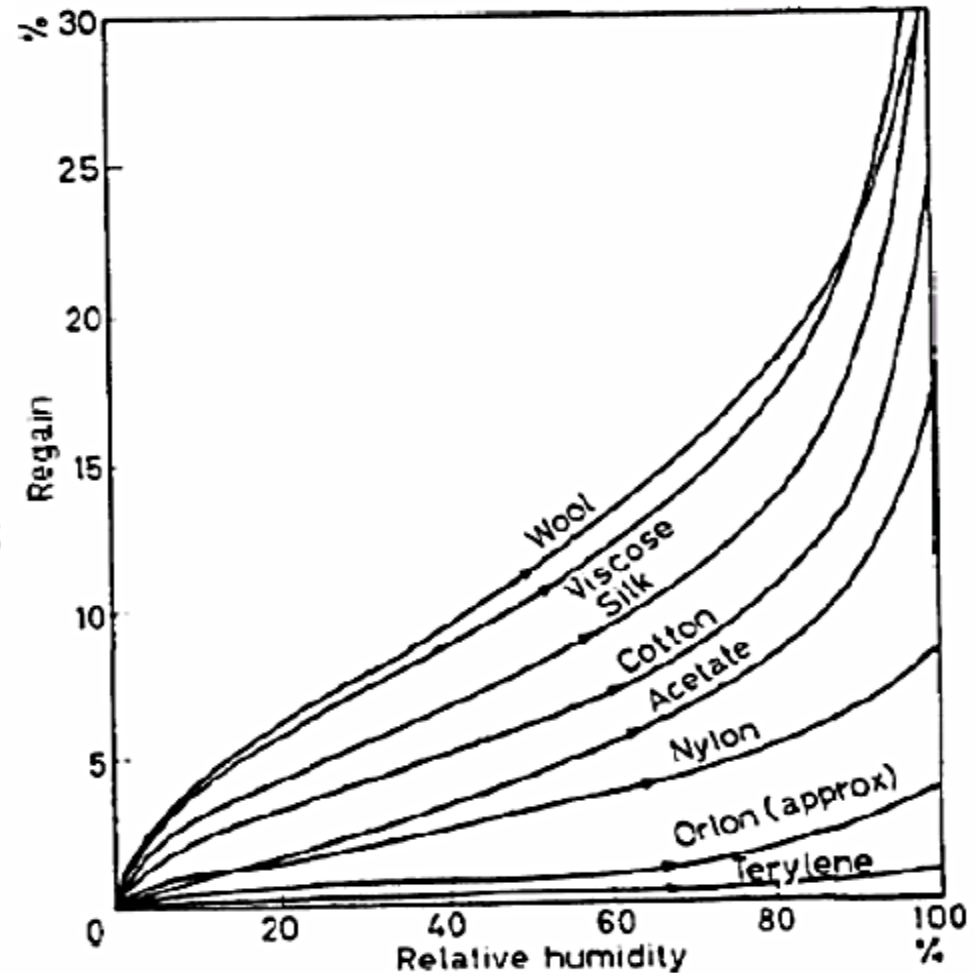
Hysteresis occurs in the cases, when pores in the fiber are open on the both sides or have so called bottle shape.

Hysteresis can occur due to capillary condensation as well.



Equilibrium isotherms of water vapor - Fibers

Hysteresis has practical importance for cases when at give air humidity the maximum (or. minimum) water content is required. In testing labs the wetting of dry fiber to required humidity (standard 65% *RH*) is used



Temperature effects - Sorption

Temperature influence on water sorption (at 70% *RH*)

Temperature [°C]	-29	4	35	71
cotton	8,5	9,7	7,8	6,7
wool	17	17,5	15	13
viscose	16	17,0	14	12

First step of water vapor absorption into fibers is the condensation of water on the their surface.

- Latent heat of condensation (heat evolved due to phase change for gas to liquid) is about 2450 Jg^{-1} water. Part of condensed water is transported into fibers (it depends on the air humidity *RH*).
- Part of condensed water is spread on fibers surface by capillary forces.
- Water presence in accessible fiber regions leads to creation of secondary bonds decreasing of system total energy.
- Excess energy is evolved as heat of sorption. Sorption is therefore characterized by heat creation.





Differential heat of sorption

Q [$\text{Jg}^{-1}\text{water}$].

It is heat evolved by sorption of 1g water on huge number of fibers at given air relative humidity RH . Less initial water content at beginning of sorption process leads to higher value of heat Q .

For dry viscose fibers is

$$Q = 1,17 \text{ [Jg}^{-1}\text{water]}$$

For viscose fibers containing 75 % RH is

$$Q = 0,24 \text{ [Jg}^{-1}\text{water]}$$

Fiber	H [kJ g^{-1}]	Q [kJ g^{-1}]
cotton	46	1,20
mercerized cotton	73	1,17
flax	55	1,2
viscose	106	1,17
wool	113	1,30
Natural silk	69	1,28
acetate	34	1,24
PA 6.6	31	1,05
PAN	7	—
PES	5	—





Integral heat of sorption

heat of swelling Q_s
heat of condensation L
total heat Q (for vapor)

$$Q = L + Q_s$$

Integral heat of sorption

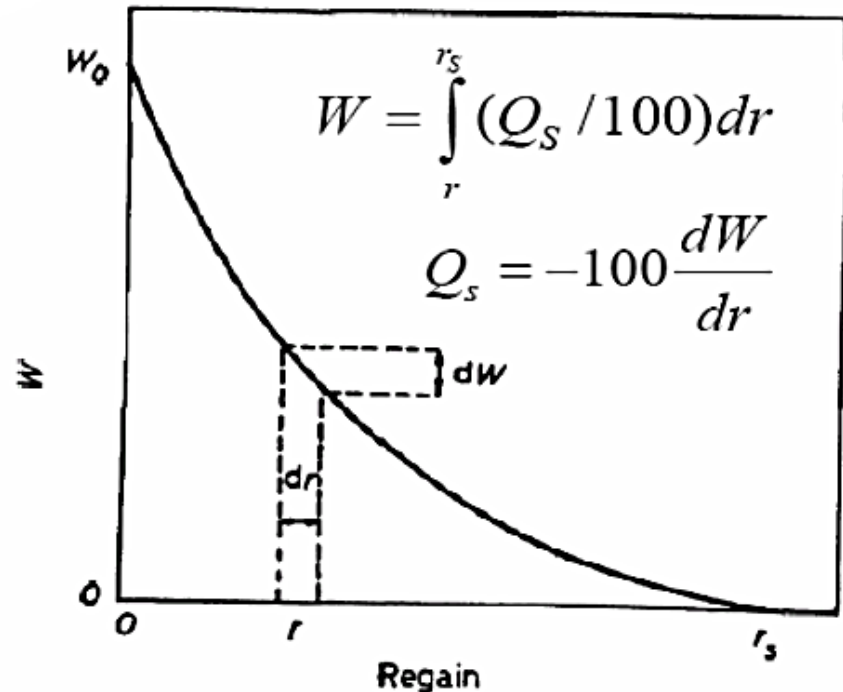
H [$\text{Jg}^{-1}\text{fiber}$].

It is heat evolved at complete saturation of 1 g fiber at given RH.

This heat is also called as wetting heat.

It is closely connected with ability of fibers to attract and link water..

Higher H indicates higher ability to link water.



Changes of integral heat of sorption due to air humidity (RH)





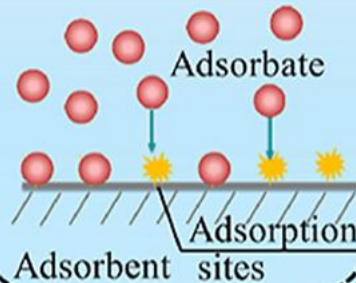
Adsorption isotherm models

Models based on Polanyi's potential theory: D-A, D-R...

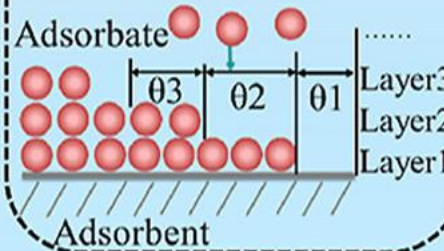
Empirical models:
Temkin, R-P, Toth

Linear ← C_0 is low
Sips ← 1 adsorbate occupies $1/n_s$ sites

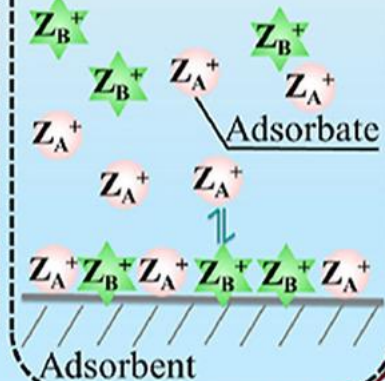
Monolayer chemical Adsorption models:
Langmuir, Volmer...



Multi-layer physical adsorption models:
Freundlich, BET, Aranovich...



Ion exchange model



Applications

The number of the optimum models in literature follows the order of: Langmuir > Freundlich, > Temkin, Sips, linear, R-P > Others

Solving methods (UI)

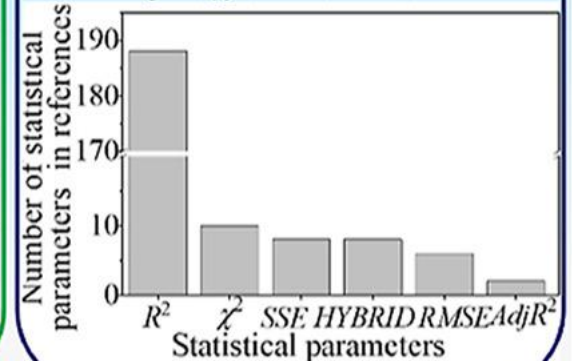
Adsorbate
Adsorbent
Adsorption equilibrium
Multi-layer Adsorption
Monolayer Adsorption

Adsorption isotherms	
Linear model	Sips model
Freundlich	Toth model
R-P model	Temkin
D-R model	D-A model
Langmuir	Volmer
BET model	Aranovich

OK

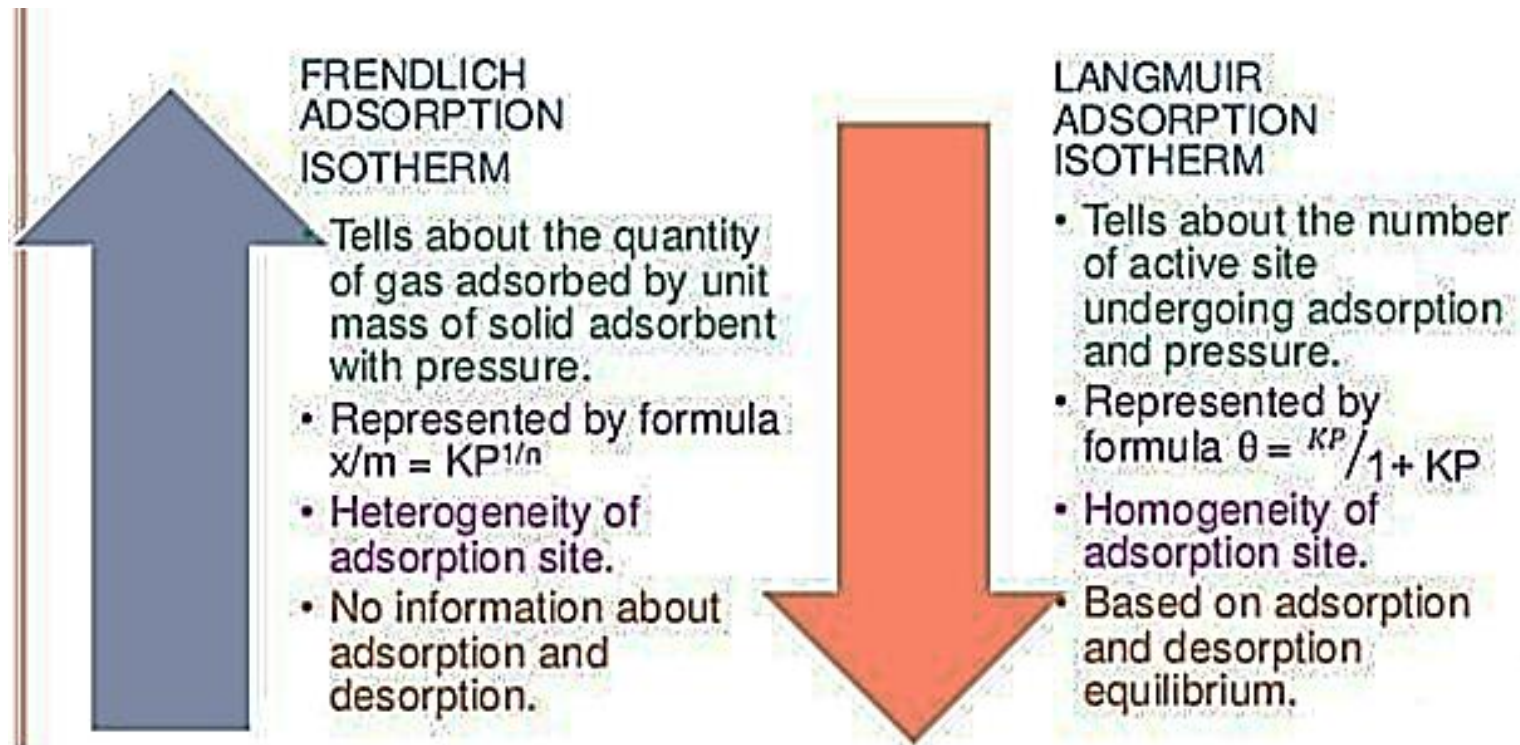
Statistical parameters

R^2 , $AdjR^2$, χ^2 , SSE , MSE , $HYBRID$



The linear isotherm model has been **used to represent the partition of adsorbates between solid and liquid phases.**

Analytical isotherm equations such as Langmuir and Freundlich isotherms are **widely used for modeling adsorption data.**



Adsorption Isotherm Models

Adsorption empirical isotherms

Examples

- Linear model (Henry's law)
- Freundlich isotherm
- Redlich–Peterson (R–P) isotherm
- Sips isotherm model
- Toth isotherm model
- Temkin isotherm

Models based on Polanyi's potential theory

Examples

- Dubinin-Radushkevich (D-R) model
- Dubinin-Astakhov (D-A) model

Chemical adsorption models

Examples

- Langmuir model
- Volmer isotherm model

Physical adsorption models

Examples

- BET model
- Aranovich model

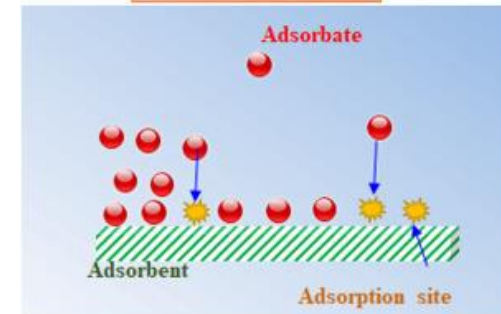
Ion exchange isotherm model

Examples

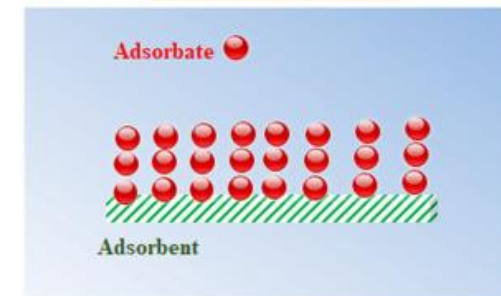
- Monovalent ions exchange
- Bivalent ions exchange
- Homovalent exchanges
- Heterovalent exchanges

Possible adsorption mechanisms

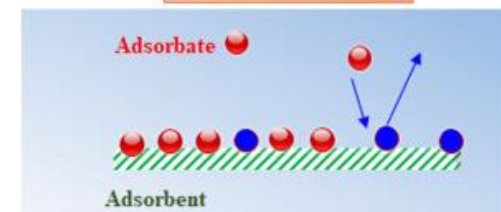
(a) Monolayer chemical adsorption models



(b) Multilayer physical adsorption models

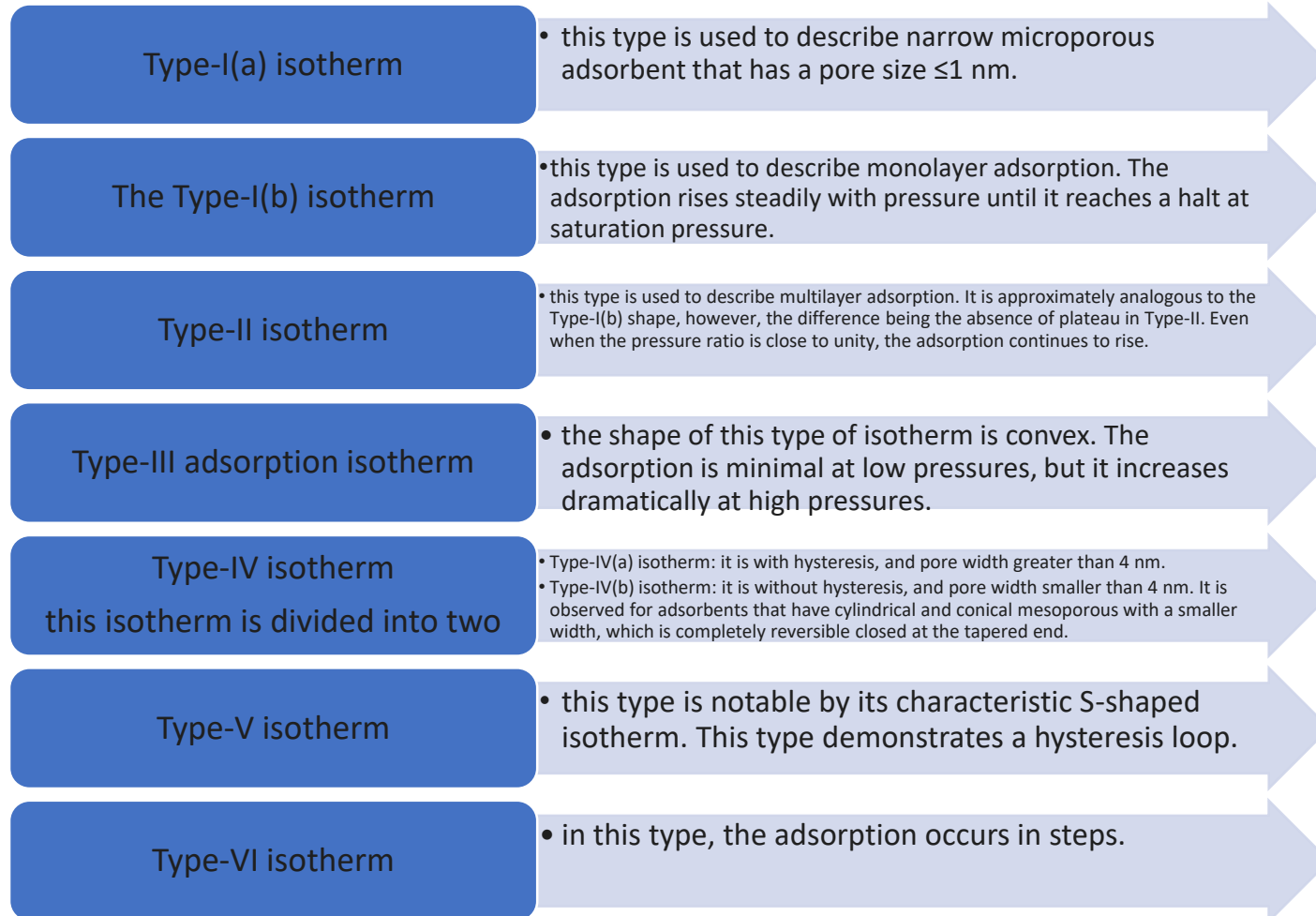


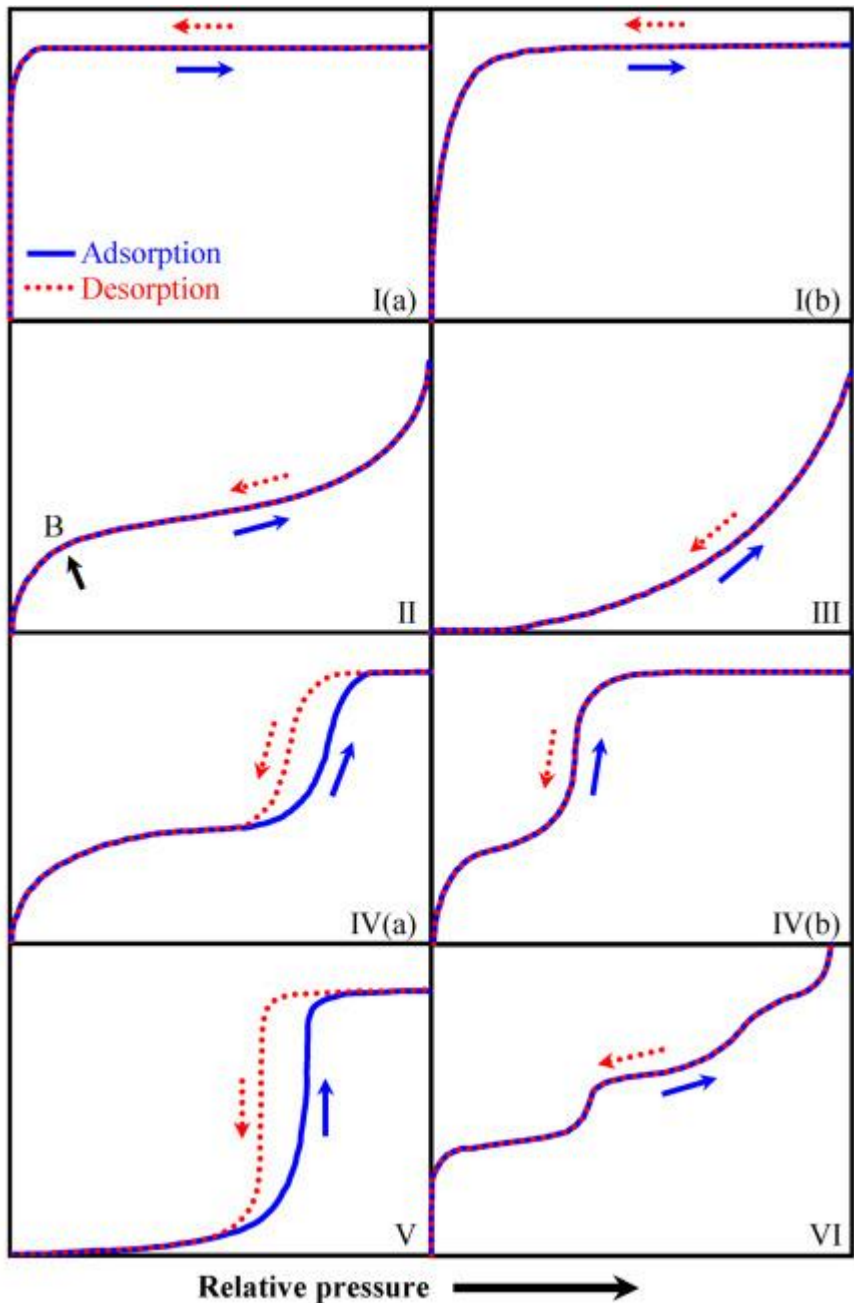
(c) Ion exchange model





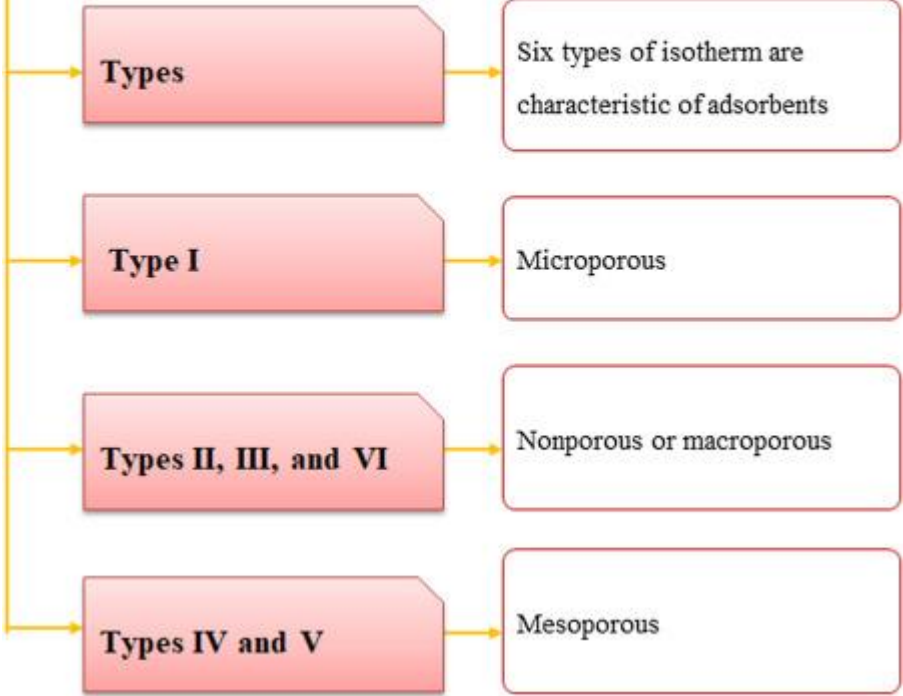
The International Union of Pure and Applied Chemistry (IUPAC) divides adsorption pairs into eight groups based on the type of adsorption isotherms



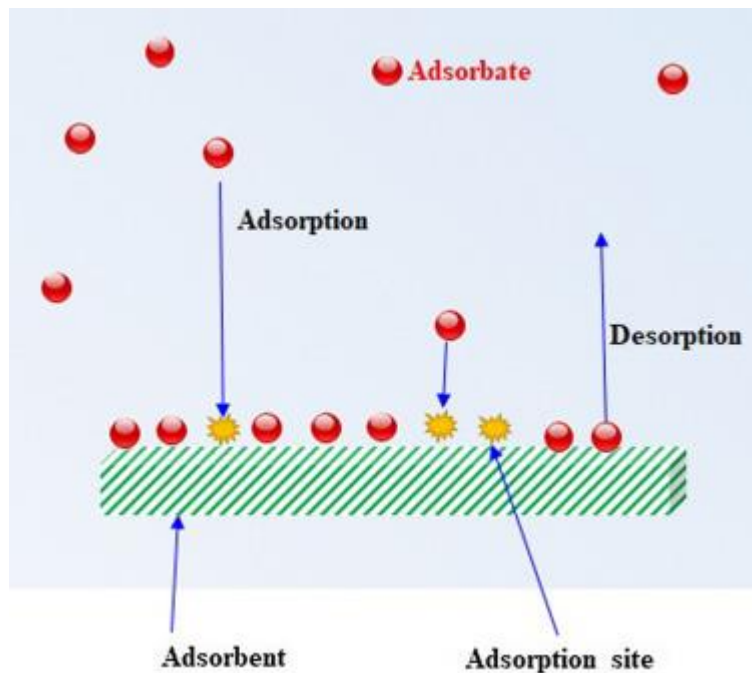


EC

Types of BET Adsorption Isotherms



Linear Isotherm Model

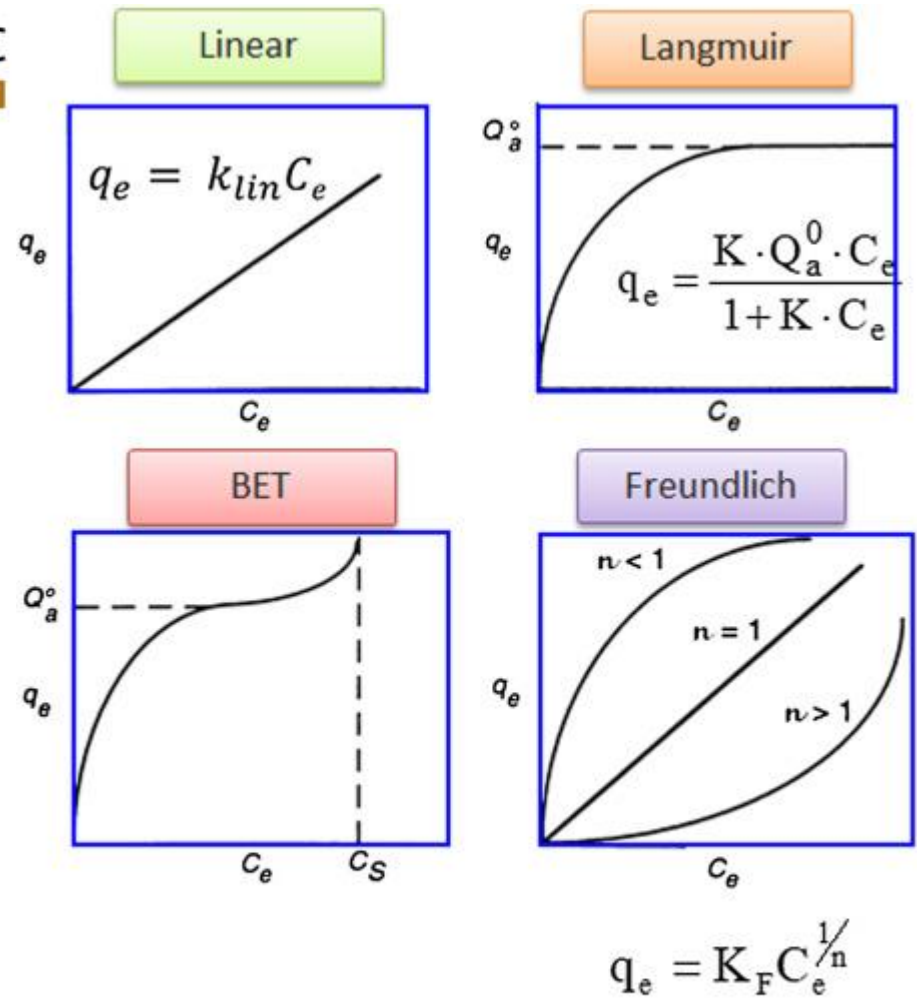


The linear isotherm model, or Henry's law, is the relation between the equilibrium concentration of adsorbate (C_e) and adsorption capacity at equilibrium (q_e in mg adsorbate/g adsorbent). The model describes the partition of adsorbates between the liquid and solid phases. Generally, the mechanisms of the partition processes include electrostatic interaction, van der Waals interaction, and hydrophobic interaction





Comparison of different linear and Langmuir models

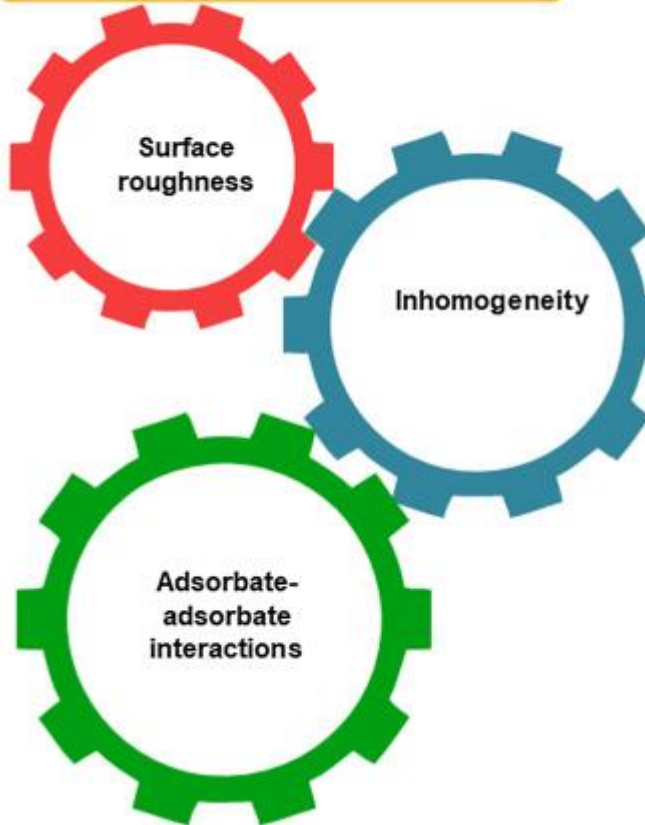


$$q_e = \frac{K_B \cdot C_e \cdot Q_a^0}{(C_S - C_e) \{1 + (K_B - 1)(C_e / C_S)\}}$$





Assumptions of Freundlich Isotherm



Limitations of Freundlich Isotherm

Freundlich equation has no theoretical foundation. It is mostly an empirical formula.

The equation is valid only upto a certain pressure. It is invalid at a higher pressure.

Freundlich's adsorption isotherm fails at high pressure. It is valid only within a limited range of pressure.

The constants K and n vary with temperature.

Freundlich's adsorption isotherm fails at high concentration of the adsorbate.

Proposed by
Herbert
Freundlich
1909

Estimate the
sorption intensity
of the adsorbent
towards the
adsorbate.

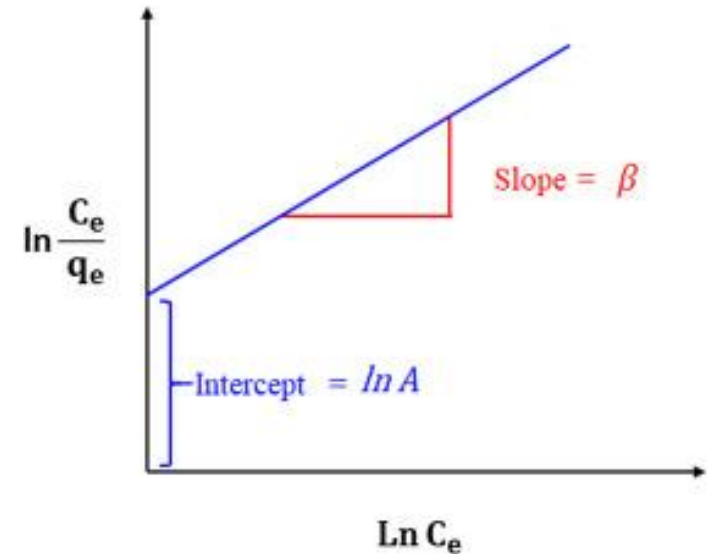
This isotherm
is an empirical
expression
that accounts
for surface
heterogeneity.



Redlich–Peterson Isotherm

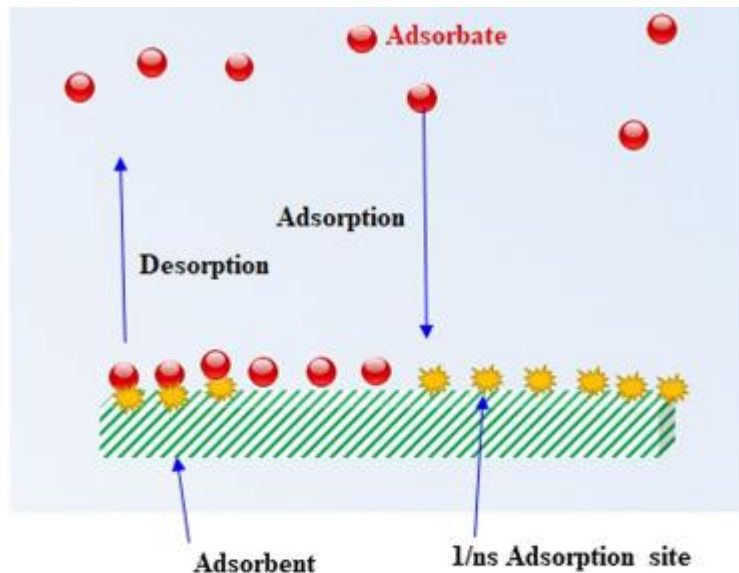
The Redlich–Peterson (R–P) isotherm is considered a three-parameter empirical adsorption hybrid model which incorporates elements from the Langmuir and Freundlich isotherms. Generally, the adsorption mechanism is unique in nature. It does not follow ideal monolayer adsorption characteristics. It has been commonly used in heterogeneous and homogeneous adsorption processes.

Redlich–Peterson adsorption capacity constant is achieved via trial and error to attain the maximum linear regression value of the isotherm plot



The **Sips isotherm** is a hybrid form of Langmuir and Freundlich models, and it is deduced to predict the adsorption in heterogeneous systems and circumvent the limitation of the rising adsorbate concentration associated with the Freundlich isotherm.

In brief, Sips model becomes the Langmuir model when $n_s = 1$ and becomes the Freundlich model at low C_0 . Nevertheless, Sips model does not satisfy Henry's law at low C_0 .



Sips model represents the monolayer adsorption of one adsorbate molecule onto $1/n_s$ adsorption sites

Temkin isotherm model

First Temkin equation

Temkin equation was proposed to describe adsorption of hydrogen on platinum electrodes within acidic solutions

Basic assumptions

- The adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface.
- Uniform distribution of binding energies
- Useful for chemisorption

Drawbacks of Temkin isotherm model

Temkin isotherm model can't be used for complex systems

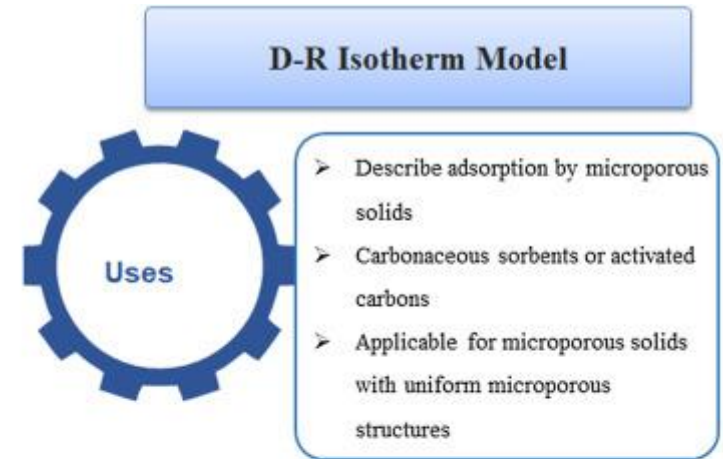
Extremely low concentration values of the adsorbate in liquid phase are ignored.

Extremely high concentration values of the adsorbate in liquid phase are ignored.

Adsorption models based on Polanyi's potential theory

Polanyi's potential theory describes that the adsorption comprises an “adsorption space,” where molecules lose potential energies. These energies are temperature independent and increase in the spaces closing to the adsorbent. Mostly, the highest potential energy is attained in the cracks or pores inside the used adsorbent.

The *D–R isotherm* is used to define the adsorption mechanisms; it helps distinguish between chemisorption and physisorption. The D–R isotherm does not reduce to Henry's law at low pressures, which is an essential for thermodynamic consistence.



Drawbacks of D-R isotherm model

The D-R isotherm does not reduce to Henry's law at low pressures isotherm

This model does not act as thermodynamically consistent adsorption





Chemical adsorption models

This class of models considers the monolayer adsorption processes where the adsorbate molecules are adsorbed onto the adsorption sites of adsorbents.

Basic assumptions of Langmuir Model

The surface is homogeneous and the distribution of adsorption sites is homogeneous

All sites are equivalent

Mono-layer adsorption only

No interactions between adsorbate molecules on adjacent sites

The interaction between adsorbate molecules is negligible.

Adsorbate molecules have a tendency to get adsorbed and desorbed from the surface

Heat of adsorption is constant and equivalent for all sites

The adsorption energy is constant

Limitations of Langmuir isotherm

Holds only at low pressure.

Multilayer adsorption is possible.

Ignores adsorbate-adsorbate interactions.

Fails to account for the surface roughness of the adsorbent.

Saturation value of adsorption depends upon temperature.

Volmer isotherm model

The Volmer model is an adsorption model with a monolayer distribution. It assumes that adsorbate molecules migrate over adsorbent surfaces. The interactions between adsorbates are, however, minimal in this model.



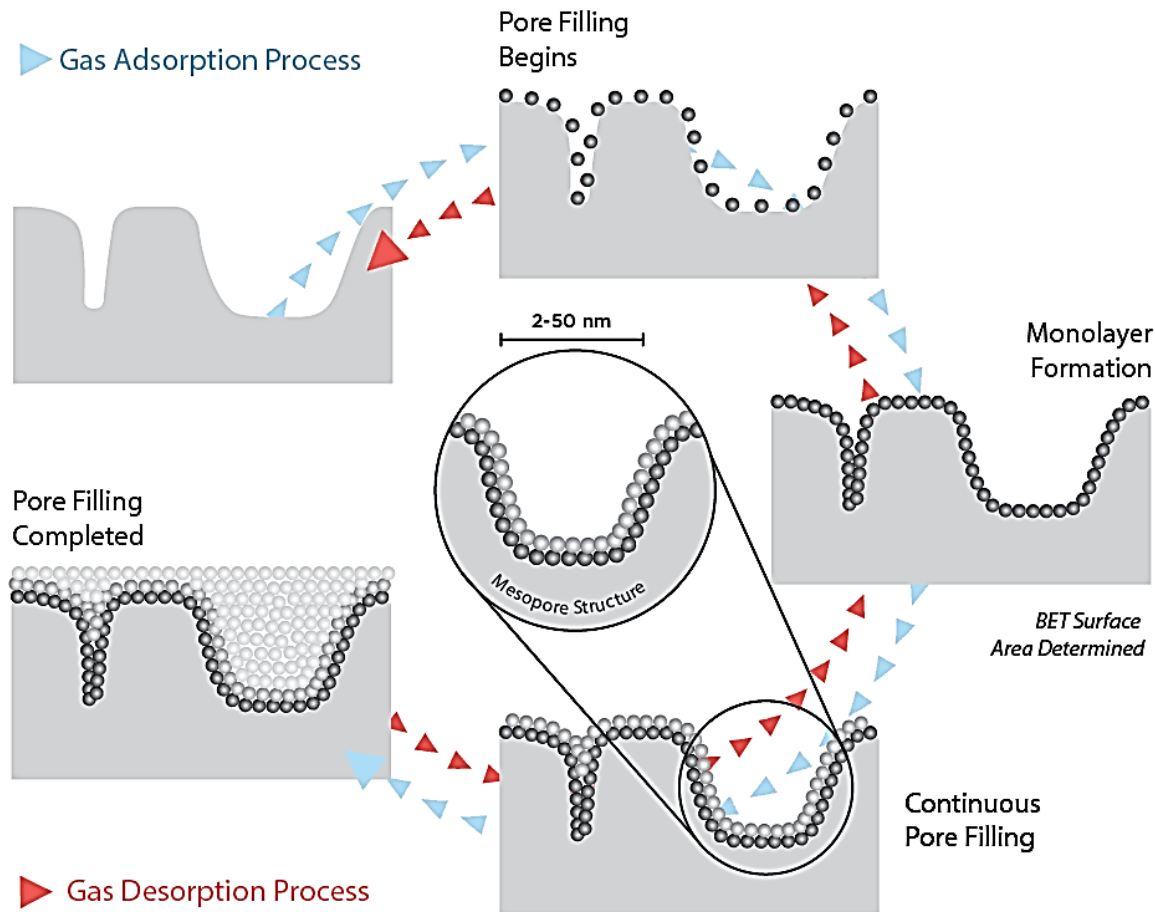
Physical adsorption models

Multilayer adsorption processes are simulated using theoretical physical adsorption isotherm models. The main driving factor of physical adsorption is the van der Waals force.

Brunauer-Emmett-Teller (BET)

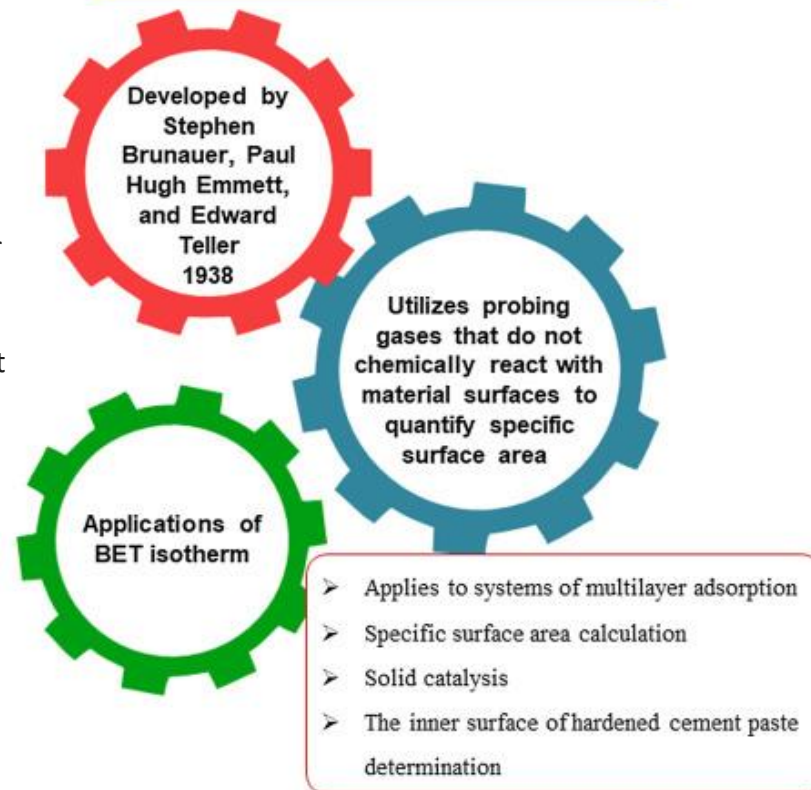
Aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

- Gas adsorption or Nitrogen adsorption
- Stephen **Brunauer**, Paul Hugh **Emmett**, and Edward **Teller**
- Directly measures **surface area** and **pore size distribution**
- BET theory deviates from ideal to actual analysis



The following are the assumptions of the isotherm of BET:

- BET theory assumes physisorption to result in the formation of multilayer adsorption. Thus, claiming that adsorption is a multilayer homogeneous process.
- The theory assumes that the solid surface has uniform sites of adsorption, and adsorption at one site does not affect adsorption at neighboring sites.
- The adsorption energy in the first layer differs from other layers.
- The adsorption rate equals the desorption rate for each layer.
- After the formation of the monolayer, the adsorption process can continue with the formation of multilayers involving the second layer, third, and so on.



Drawbacks of BET adsorption theory

Surface is assumed to be homogenous.

Interaction between the adsorbed molecules in neglected.

Heat of Adsorption from the second layer onward is considered equal to the subsequent layers, which is not usually true.

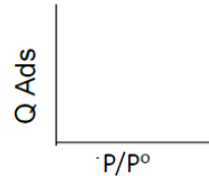
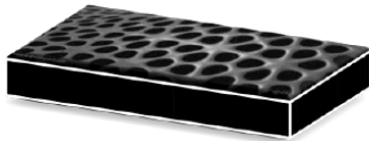
- Nitrogen is the most commonly used gaseous adsorbate used for surface probing.
- BET analysis conducted at boiling temperature of N₂ (77 K).
- Other probing adsorbents: Argon, carbon dioxide and water.
- The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses.
- Gas molecules physically adsorb on a solid in layers infinitely.
- Gas molecules only interact with adjacent layers.
- Langmuir theory can be applied to each layer.

Basic principle

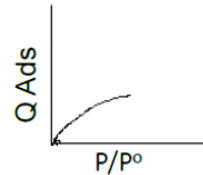
Ideal

$$PV = nRT$$

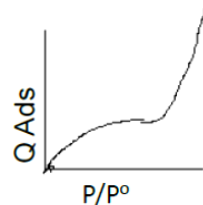
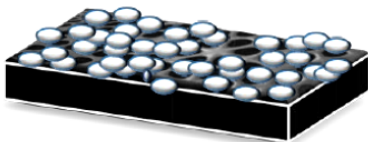
No gas molecules



Nitrogen gas molecules



Saturated Nitrogen gas molecules



Actual

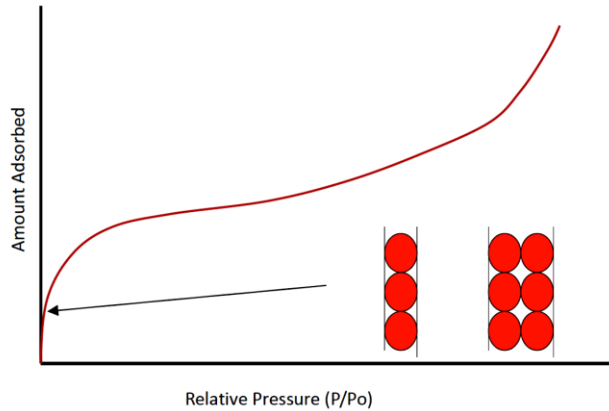
➤ Never start from no gas molecules

➤ Monolayer: Gas molecules clump together

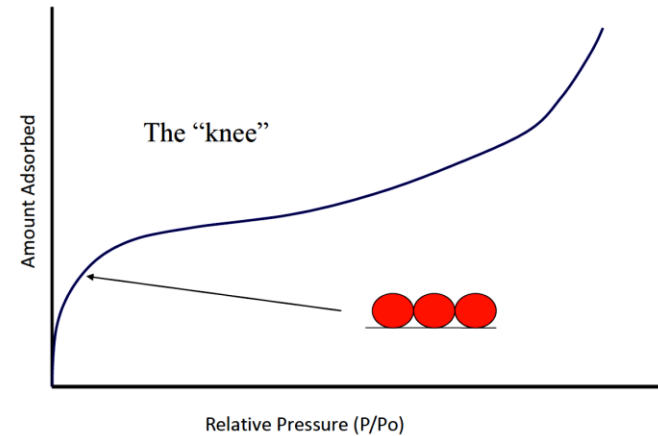
➤ Multilayer: Gas molecules clump together

➤ Some pores are not filled

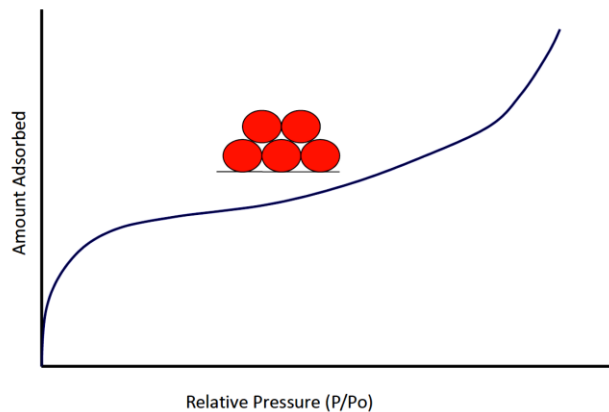
Very Low Pressure Behavior (micropore filling)



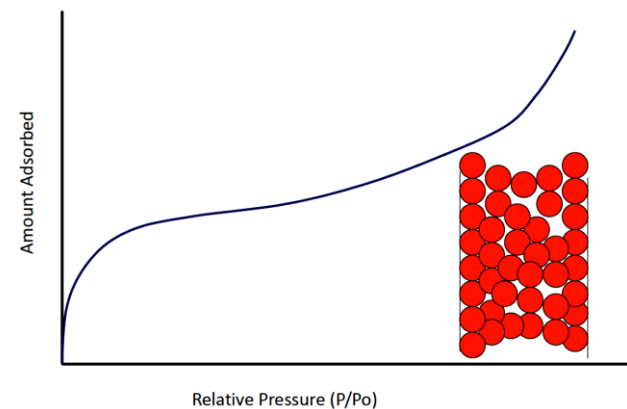
Low Pressure Behavior (monolayer)



Medium Pressure Behavior (multilayer)



High Pressure Behavior (capillary condensation)



The Aranovich isotherm is a theoretically corrected polymolecular adsorption isotherm with two parameters. It is applied to represent adsorption over a larger range of adsorbate concentration. This method can be used to properly compute the surface areas of porous adsorbents.

The following are the assumptions of the model:

Only the “nearest neighbors” interact on the adsorbents' surfaces, which are flat and uniform.

The desorption energy is proportional to the number of layers.

The model can handle the problem of lateral interactions not being taken into consideration, as well as the prohibition of voids in the adsorbate.





One-parameter isotherm

This is the simplest adsorption isotherm where the amount of surface adsorbate is proportional to the partial pressure of the adsorptive gas or concentration of adsorbate in liquid solution. The most commonly used isotherm in this class is:

- Henry's Isotherm

Two-parameter isotherm

There are several isotherm models under this category. Examples include the following:

- Hill-Deboer Model
- Fowler–Guggenheim Model
- Langmuir Isotherm
- Freundlich Isotherm
- Dubinin–Radushkevich Isotherm
- Temkin Isotherm
- Flory–Huggins Isotherm
- Hill Isotherm
- Halsey Isotherm
- Harkin–Jura Isotherm
- Jovanovic Isotherm
- Elovich Isotherm
- Kiselev Isotherm



Three-parameter isotherms

There are several isotherm models under this category. Examples include the following:

- Redlich–Peterson Isotherm
- Sips Isotherm
- Toth Isotherm
- Koble–Carrigan Isotherm
- Kahn Isotherm
- Radke-Prausniiz Isotherm
- Langmuir–Freundlich Isotherm
- Jossens Isotherm

Four-parameter isotherms

There are several isotherm models under this category. Examples include the following:

- Fritz–Schlunder Isotherm
- Baudu Isotherm
- Weber–van Vliet Isotherm
- Marczewski–Jaroniec Isotherm

Five-parameter isotherms

Fritz and Schlunder derived an empirical equation that can fit a wide range of experimental results due to the large number of coefficients in the isotherm. The model is called:

- Fritz and Schlunder five-parameter empirical isotherm model

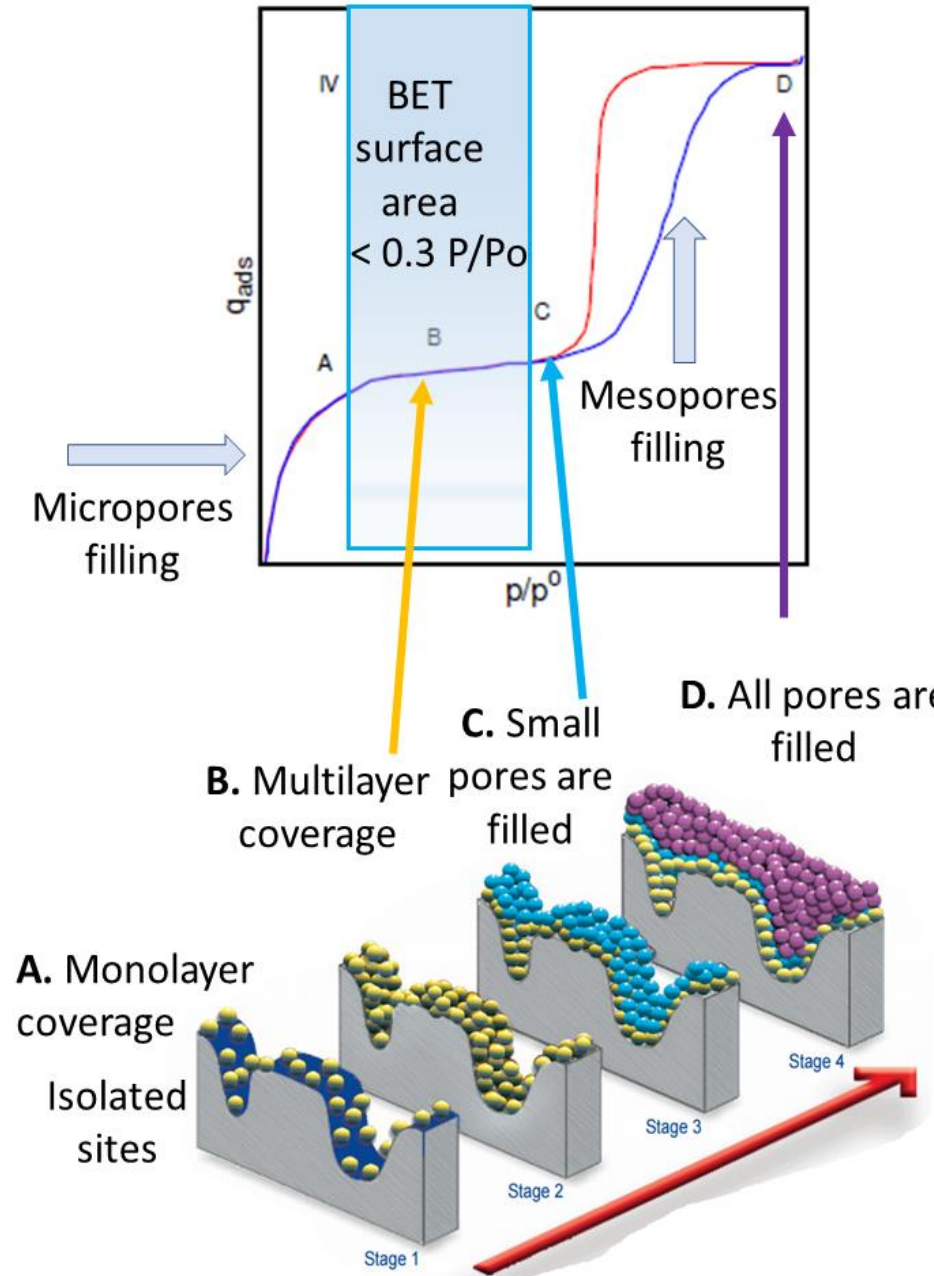


- To compute the capacity and percentage removal of adsorbates from a certain media or environment.
- To acquire the greatest adsorbent absorption and affinity between adsorbent and adsorbate, Langmuir parameters can be applied.
- Freundlich parameters can be used to obtain adsorption capacity of adsorbents.
- To calculate the adsorption capacity of adsorbents using Freundlich parameters.
- To calculate the specific surface area and pore size distribution from BET isotherms using BET curves.
- D–R parameters are used for adsorption mechanism.
- Temkin parameters can be used for understanding adsorbent–adsorbate interactions.
- To understand the spontaneity of a system.
- To have more information on the exothermicity of a system.





- Surface area is related to;
 - Particle size
 - Particle morphology
 - Surface texturing
 - Porosity
- The accessibility of active sites requires pores that allow molecular transport.
- Porosity: fraction of the total void volume with respect to the volume of the catalyst.
- Texture:
 - pore size
 - pore size distribution
 - pore shape





Porosity

There are three parameters used to measure porosity; specific surface area, specific pore volume or porosity, and pore size and its distribution.

Pore size



$$\text{Specific Surface Area, m}^2/\text{g} = \frac{\text{Total surface area, m}^2}{\text{Mass of the solid, g}}$$

$$\text{Porosity, \%} = \frac{\text{Volume of pores}}{\text{Volume of solid (including pores)}} \times 100$$

$$\text{Specific Pore volume, cm}^3/\text{g} = \frac{\text{Total pore volume, cm}^3}{\text{Mass of the solid, g}}$$

Pore size and its distribution





Non-porous solid

Low specific surface area
Low specific pore volume



Porous solid

High specific surface area
High specific pore volume

Porous materials have highly developed internal surface area that can be used to perform a specific function.
Almost all solids have some amount of porosity.

Particles:
Size and surface area



Active sites:
Porosity and
concentration of active
Sites.

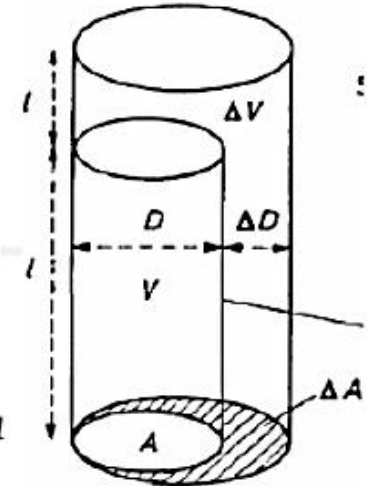


Swelling

For circular fibers is $S_R = 2 * S_D + S_D^2$

Dimensional changes due to water sorption

Radial swelling S_D , area swelling S_R , axial swelling S_A volume swelling S_V). $S_V = S_R + S_A + S_A * S_R$



Fibre	Transverse swelling		Longitudinal swelling (%)	Volume swelling (%)
	Diameter (%)	Area (%)		
Cotton	20, 23, 7	40, 42, 21		42, 44
Mercerised cotton	17	46, 24	0.1	
Viscose	25, 35, 52	50, 65, 67, 66, 113, 114	3.7, 4.8	109, 117, 115, 119, 123, 126, 74, 122, 127
Acetate	9, 11, 14, 0.6	6, 8	0.1, 0.3	
Wool	14.8–17	25, 26		36, 37, 41
Silk	16.5, 16.3–18.7	19	1.3, 1.6	30, 32
Nylon	1.9–2.6	1.6, 3.2	2.7–6.9	8.1–11.0



- Radial swelling arises due to creation of hydrogen bonds in the fibers amorphous regions mainly. Longitudinal swelling is noticeable lower, i.e. swelling anisotropy occurs

Fiber	Radial swelling S_R [%]	Axial swelling S_A [%]
cotton	40	< 1
viscose	60–130	~ 4
wool	25	~1
PA 6.6	2–3	~ 6



Fiber	v_p [%]	Regain at 65%, 20 °C
cotton	8,5	7,6–8,6
flax	12	10,2–10,7, 15
hemp	12	10, 15
jute	13,75	9,6–9,8, 17
wool	15–18,25	10–12 (16–18)
silk	11	12
viscose	13	12–14
PA 6	6,25 staple, 5,75 filament	3,2–3,5 (4–4,5)
PES	1,5 staple, 3,04 filament	0,4–0,5
PAN	2	1–2