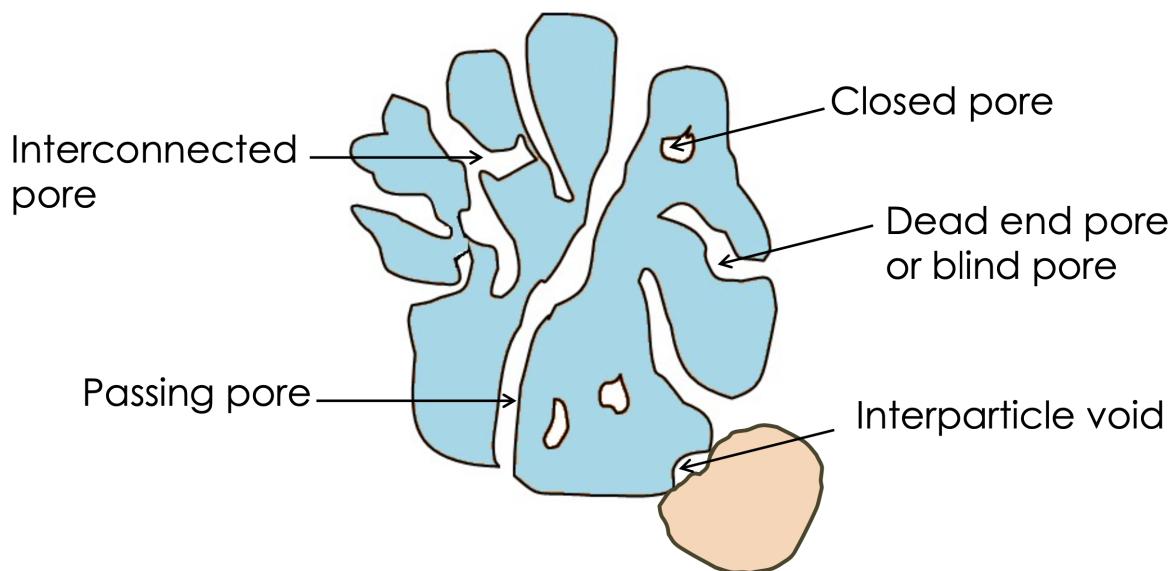


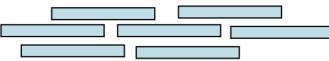
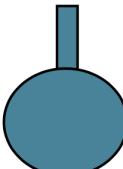
## 4. Porosity Analysis

### Introduction to Porosity

Porosity refers to the presence of void spaces or pores within a material. Porous materials are substances that possess these void spaces or pores. These void spaces can exist at various scales, ranging from microscopic to macroscopic, and can be interconnected (open) or isolated (closed), passing or blind:



The pores can also be classified according to the pore shapes:

Cylindrical	Slit
 e.g. catalytic converter support	 e.g. graphite
<b>Cylindrical</b>	<b>Slit</b>
 e.g. highly ordered alumina membrane	

and pore size:

<b>Micropores</b>	<b>Mesopores</b>	<b>Macropores</b>
< 2 nm	2-50 nm	> 50 nm
Activated carbon	Activated carbon	Sintered metals
Zeolite	Zeolite	Ion-exchange resin
Metal-Organic Framework	Silica	Catalytic converter
		Ceramic

## Surface Area

Porosity and surface area are closely linked and interdependent properties of porous materials. The surface area of a solid material is of great importance as it represents the primary means through which the material interacts with its surroundings. A larger surface area provides more opportunities for these interactions:

- ▶ In solid-solid interactions, the surface area affects adhesion, which is the ability of two solid materials to stick or bond to each other. When the surface area is larger, there is more contact between the materials, allowing for stronger adhesion. This is important in applications such as joining materials, coatings, and bonding in construction or manufacturing processes.
- ▶ In solid-liquid interactions, for example, in wetting, a liquid spreads over a solid surface. A larger surface area provides more contact points for the liquid to spread, leading to enhanced wetting. On the other hand, in non-wetting situations, the liquid tends to bead up and not spread over the surface, which can be influenced by the surface area as well. Moreover, surface area plays a vital role in processes like adsorption, where a liquid is adsorbed onto the solid surface, such as in water treatment or purification applications.
- ▶ In solid-gas interactions, such as adsorption and catalysis. A larger surface area provides more sites for gas molecules to adhere to, resulting in higher adsorption capacity. This is valuable in applications such as air purification, gas storage, and separation processes. In catalysis, the surface area of the catalyst material influences the number of active sites available for chemical reactions, thereby affecting the efficiency of the catalytic process.

The surface area of a material is influenced by several factors:

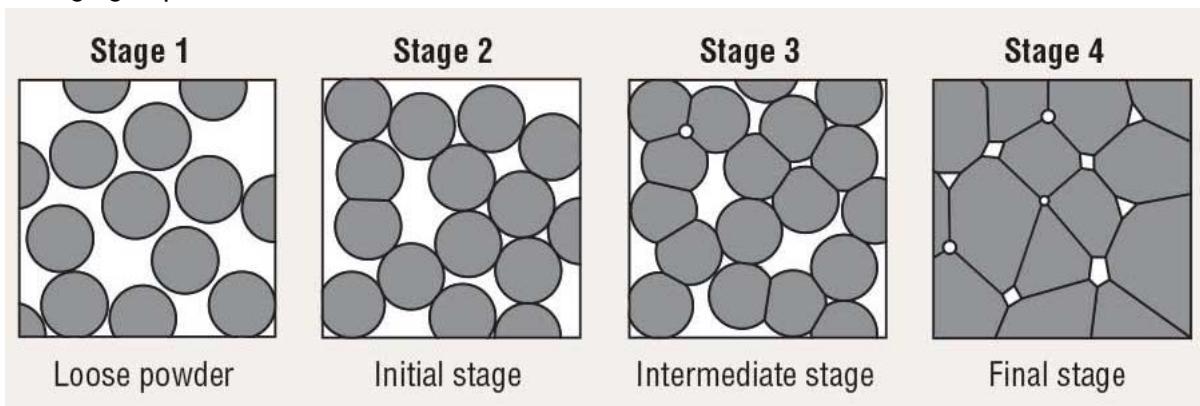
- ▶ Particle size: smaller particle size generally leads to a larger surface area, as smaller particles have a higher surface area-to-volume ratio.
- ▶ Morphology: the shape and structure of particles.
- ▶ Texture: irregular or rough surfaces tend to have a higher surface area compared to smooth or spherical particles of the same size. This is because irregular surfaces create more edges, corners, and surface features.
- ▶ Porosity: the internal pore structures contribute significantly to the total surface area. The higher the porosity, the larger the surface area.

Based on these, the surface area of a material can be enhanced in various ways:

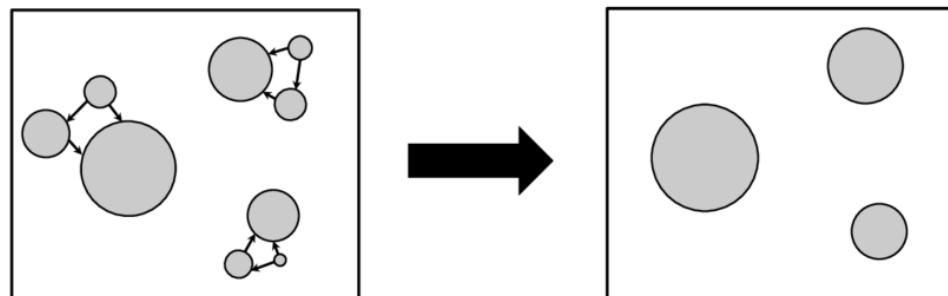
- ▶ Grinding, milling: particle size reduction by mechanical forces.
- ▶ Synthesis process: during the synthesis of materials, factors such as temperature, pressure, and chemical environment can influence the particle morphology and texture. By modifying these synthesis conditions, it is possible to change the shape, structure, and surface features of the particles. For example, a synthesis process may be designed to produce particles with a high degree of surface roughness or a more porous structure, both of which contribute to a larger surface area.
- ▶ Activation, partial decomposition, lyophilisation, etc., to create or enhance the presence of pores within a material: activation refers to the deliberate modification of a material to increase its porosity, which can involve chemical or thermal treatment to induce structural changes and create pores. Partial decomposition or pyrolysis of certain materials generates pores. Lyophilisation, or freeze-drying, is a technique that involves freezing a material and then removing the ice by sublimation to create pores.

The surface area can also be decreased by:

- ▶ Melting: when a solid material melts, the individual particles lose their distinct boundaries and merge together to form a liquid. The liquid phase tends to have a lower surface area compared to the solid phase, as the particles become more closely packed and lose the exposed surfaces that were present in the solid state. As a result, the surface area of the material decreases significantly.
- ▶ Sintering: this involves heating a compacted mass of particles to a temperature below their melting point but high enough to cause bonding and structural changes. During the process, particles begin to fuse together, resulting in a reduction in the number of individual particles and the overall surface area. As the temperature increases, the particles diffuse and rearrange, leading to neck formation and grain growth. The merging of particles reduces the total surface area available.



- ▶ Ostwald ripening: this is a process that occurs in multi-component systems where there is a difference in solubility between small and large particles. It involves the gradual dissolution of smaller particles and the subsequent redeposition of the dissolved material onto larger particles. This preferential dissolution and redeposition lead to the growth of larger particles at the expense of smaller ones. As a result, the overall surface area decreases as the smaller particles diminish, and the larger particles continue to grow.



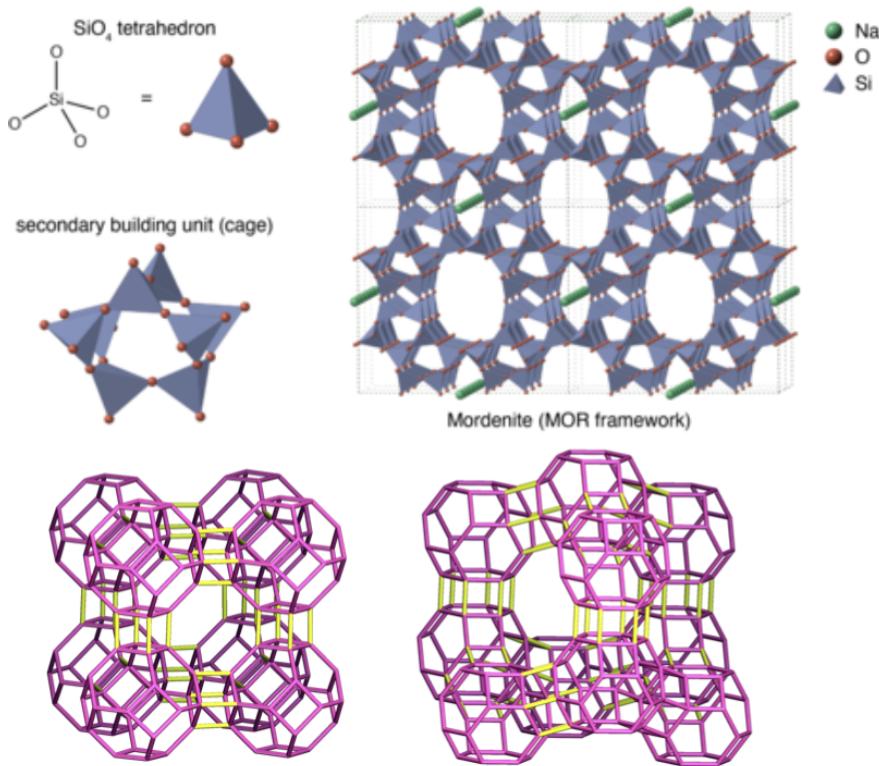
## Industrial Relevance

Porosity and surface area play a crucial role in various industrial sectors:

### 1. Petrochemical Sector:

- ▶ Catalytic cracking: zeolite-based catalysts are used in catalytic cracking processes to convert larger hydrocarbon molecules into smaller ones. The porosity and surface area of the catalysts are essential for providing a large active surface for the desired reactions to occur efficiently.
- ▶ Separation of chemicals: zeolites are used for the separation of branched and linear alkanes. The porous structure of zeolites enables selective adsorption and separation of different molecules based on their size, shape, and polarity.

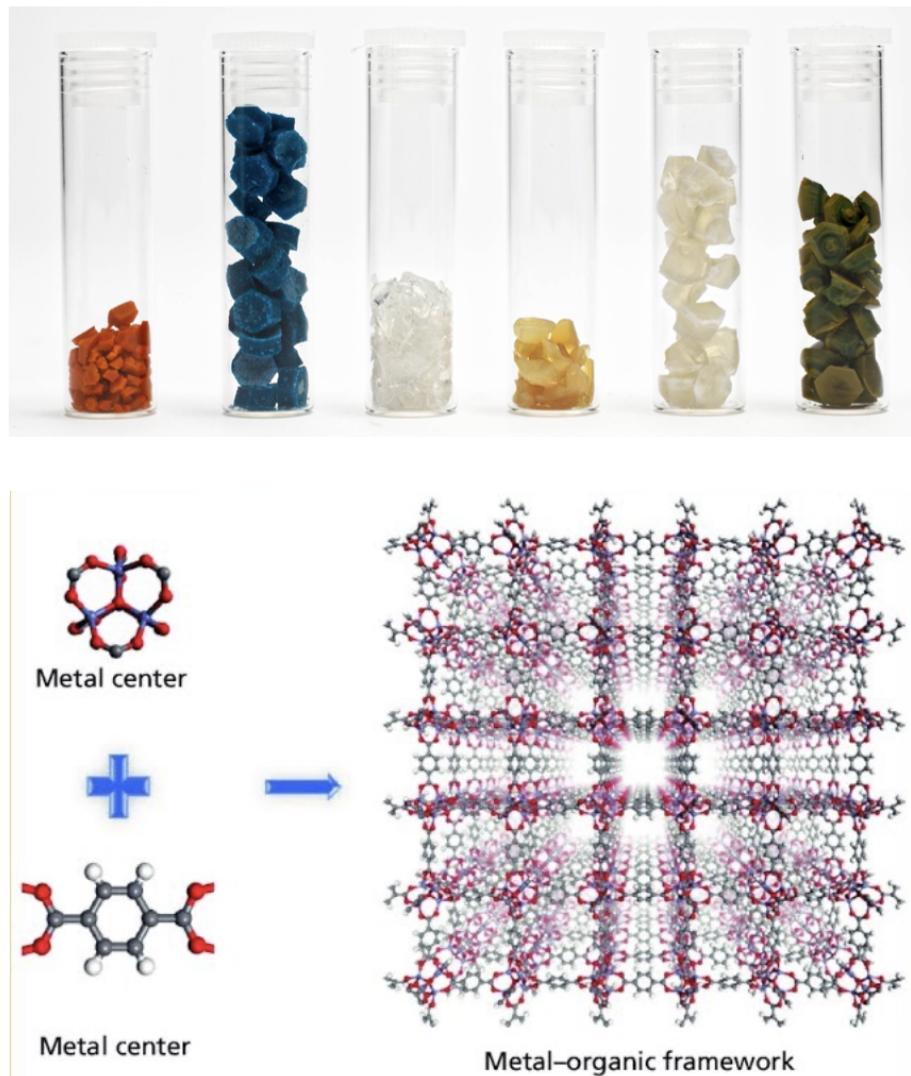
## Zeolite



### 2. Energy Sector:

- Gas storage: metal-organic frameworks (MOFs) are employed for gas storage applications, such as the storage of methane or hydrogen. The high porosity and large surface area of MOFs allow for high-capacity adsorption of gases, enabling their storage and release as needed. (Notice that in the graph below, the second "metal centre" should be "organic ligands")

## Metal organic frameworks



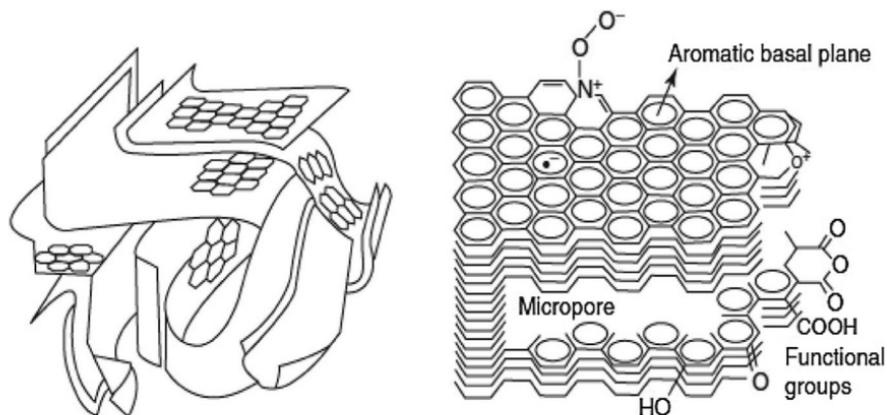
### 3. Automotive Sector:

- Catalyst support: porous materials are used as catalyst supports in automotive applications, such as catalytic converters. These materials, often based on ceramics or metals with high surface area and porosity, provide a large contact surface for catalytic reactions to occur, aiding in the conversion of harmful emissions into less toxic compounds.

### 4. Environmental Sector:

- Contaminant removal from water: activated carbon are widely used in water treatment processes for the removal of contaminants. The high porosity and surface area of activated carbon enable efficient adsorption of impurities, pollutants, and organic compounds, improving water quality.

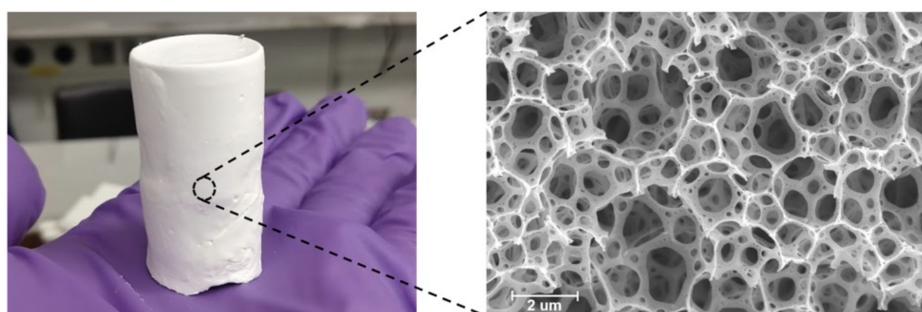
# Activated carbon



## 5. Pharmaceutical Sector:

- ▶ Pharmaceutical dissolution: pharmaceutical excipients with controlled porosity and surface area are used to enhance drug dissolution rates. The porosity allows for increased contact between the drug and the surrounding medium, facilitating faster dissolution and absorption.
- ▶ Drug delivery: mesoporous silica nanoparticles or polymer-based matrices, are utilised in drug delivery systems. The porosity and surface area of these materials enable efficient loading and controlled release of drugs, improving therapeutic efficacy.

# Porous polymers



Therefore, determining the surface area and characterising the porosity of materials is of paramount importance, as the data can provide insights into material properties, structure-property relationships, and guide the design of novel materials with tailored characteristics.

We have seen the steps and techniques for determining the surface area in the case of non-porous samples:

1. Determine the particle size/particle size distribution. Techniques such as Dynamic Light Scattering (DLS), Small-Angle X-ray Scattering (SAXS), or Scanning Electron Microscopy (SEM)/Transmission Electron Microscopy (TEM) can be used to measure or observe the particle size and distribution.
2. Calculate the external surface area using particle shape. Once the particle size is determined, the external surface area of the non-porous sample can be calculated by considering the shape of the particles. The surface area calculation takes into account the geometry of the particles, such as their shape and dimensions.

In the case of porous materials, two characterisation methods will be presented:

- ▶ Gas adsorption, for micropores and mesopores below 50 nm.
- ▶ Mercury porosimetry, for mesopores and macropores above 3.5 nm.

## Basic Definitions

Before proceeding to introducing the determination techniques for porosity, a few important definitions are herein outlined:

- ▶ Specific surface area: the surface area of a material per unit mass.

$$\text{Specific surface area } (\text{m}^2/\text{g}) = \frac{S (\text{m}^2)}{m_{\text{adsorbent}} (\text{g})}$$

- ▶ Specific pore volume: the volume of pores in a material per unit mass.

$$\text{Specific pore volume } (\text{cm}^3/\text{g}) = \frac{V (\text{cm}^3)}{m_{\text{adsorbent}} (\text{g})}$$

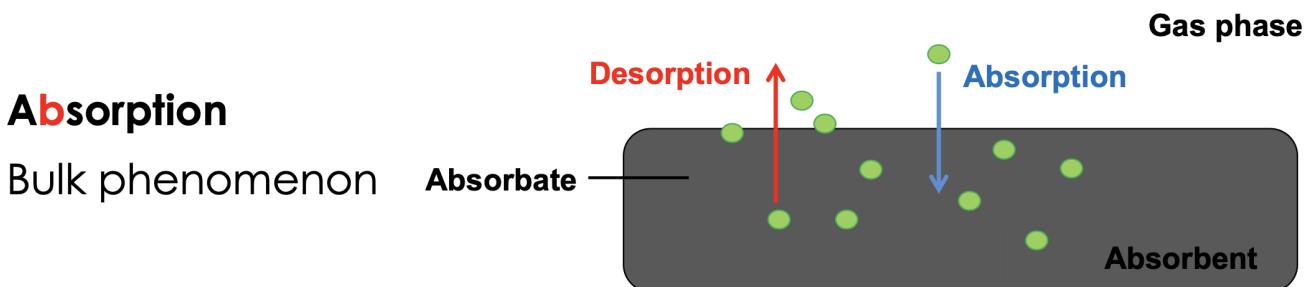
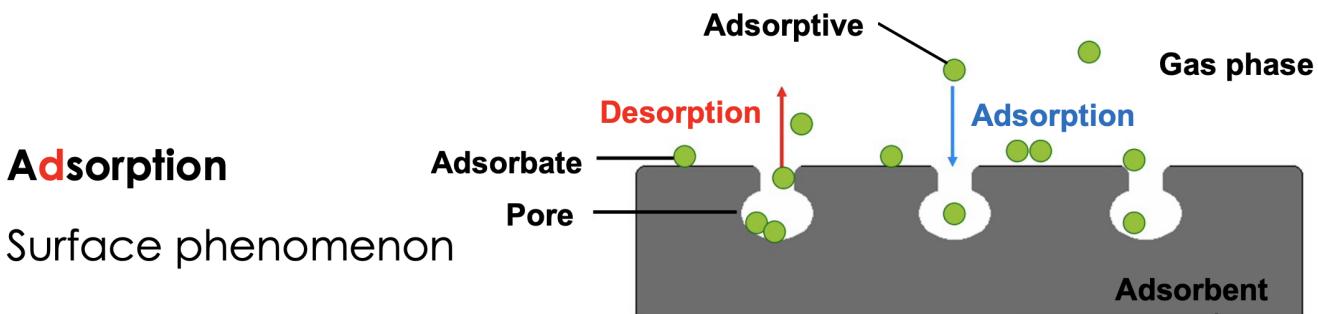
- ▶ Porosity: the ratio of the volume of void spaces to the total volume of the material, typically expressed as a percentage.

$$\text{Porosity } (\%) = \frac{V (\text{cm}^3)}{V_{\text{solid}} (\text{cm}^3)} \times 100$$

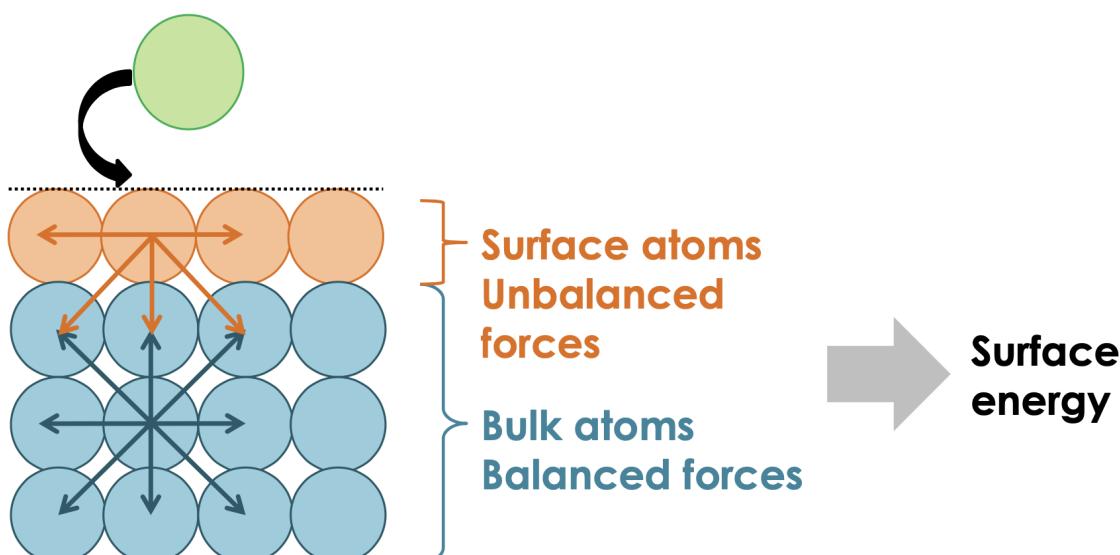
- ▶ Pore size distribution: the range or distribution of pore sizes present in a material. It represents the variation in pore sizes and the relative abundance of pores within different size ranges. Pore size distribution is typically characterised using techniques such as gas adsorption or mercury intrusion porosimetry.

# Gas Adsorption

Adsorption refers to the adhesion or attachment of gas molecules of a liquid or gas to a surface, which is a surface phenomenon as it occurs at the interface or boundary between the gas phase and the solid surface. This is to be distinguished with absorption, which refers to the bulk phenomenon where molecules permeate or dissolve into the bulk of a material. In absorption, the molecules are distributed throughout the material rather than being confined to the surface:



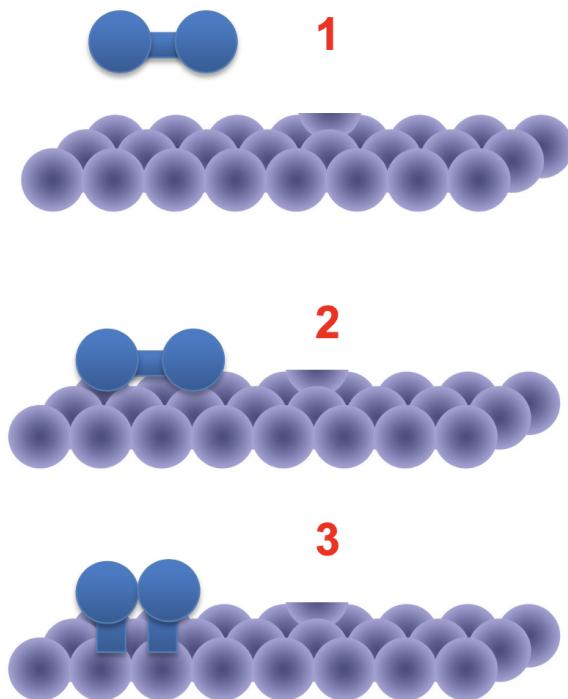
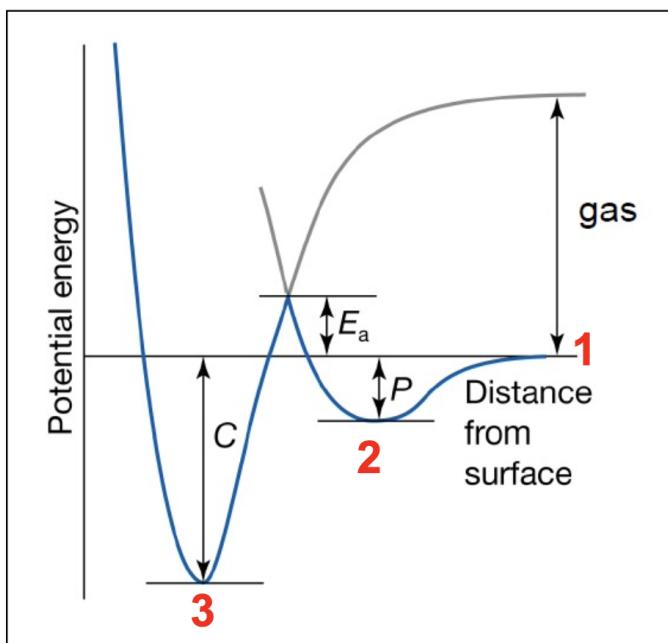
Adsorption occurs due to the presence of surface energy, which is a property associated with the surface of a solid material, and it arises from the imbalance of intermolecular forces between the surface molecules and the molecules within the bulk of the material. Because the surface molecules have fewer neighbouring molecules to interact with compared to the molecules within the bulk of the material, they have a higher energy state. To minimise this energy and achieve a more stable state, gas molecules are attracted to the surface.



The gas molecules experience a lower energy state by interacting with the surface, as they can occupy sites and participate in intermolecular forces with the surface molecules. As a result, the overall energy of the system is reduced, which suggests that adsorption is a spontaneous process, meaning it occurs naturally without the need for external energy or intervention. The Lennard-Jones potential

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

can be a useful mathematical model to explain the adsorption process, where  $V_{LJ}$  represents the interaction potential energy between two molecules at a distance  $r$ ,  $\epsilon$  is the depth of the potential energy well, and  $\sigma$  is the distance at which the potential energy between the molecules is zero.



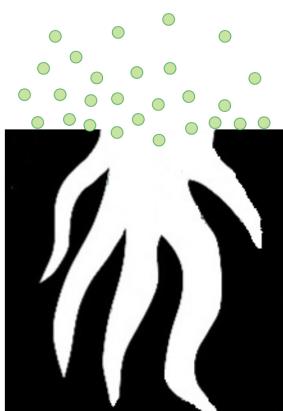
The attractive part of the potential, represented by the first term  $(\sigma/r)^{12}$ , accounts for the attraction between the gas molecules and the surface molecules, promoting adsorption. As the distance between the gas and surface molecules ( $r$ ) decreases, the attractive potential energy becomes more negative, leading to a stronger attractive force. The repulsive part of the potential, represented by the second term  $(\sigma/r)^6$ , describes the short-range repulsion between the molecules. It arises from the overlap of electron clouds or steric hindrance. This term prevents the gas molecules from getting too close to the surface. The balance between the attractive and repulsive forces yield the equilibrium distance, state 2, which is referred to as physisorption. This interaction is relatively weak as it originates from the balance between weak intermolecular forces and electrostatic repulsion. If the gas molecules were to approach more closely, an activation energy  $E_a$  must be provided. Some particles may possess sufficient energy to overcome the potential energy barrier and enter the primary energy minimum (state 1), which is referred to as chemisorption. This is much stronger and involves the formation of chemical bonds between the gas molecules and the adsorbent surface. The Lennard-Jones potential alone is not sufficient to describe chemisorption since it primarily accounts for non-covalent interactions. (cf. the DLVO curve mentioned in rheology). The process also highlights that chemisorption cannot occur without physisorption. The table below presents a comprehensive comparison between physisorption and chemisorption:

PHYSISORPTION	CHEMISORPTION
WEAK, LONG RANGE BONDING Van der Waals interactions	STRONG, SHORT RANGE BONDING Chemical bonding
NOT SURFACE SPECIFIC Physisorption takes place between all molecules on any surface (if temperature low enough)	SURFACE SPECIFIC A species can chemisorbed on a material but not another depending on the chemistry
$\Delta H_{ads} = 5 \dots 50 \text{ kJ mol}^{-1}$	$\Delta H_{ads} = 50 \dots 500 \text{ kJ mol}^{-1}$
NON ACTIVATED Equilibrium reached relatively quickly. Increasing temperature always reduces surface coverage.	ACTIVATION ENERGY (OFTEN) Equilibrium can be slow and increasing temperature <i>can</i> favour adsorption.
NO REACTION	SURFACE REACTION
MULTILAYER ADSORPTION	MONOLAYER ADSORPTION

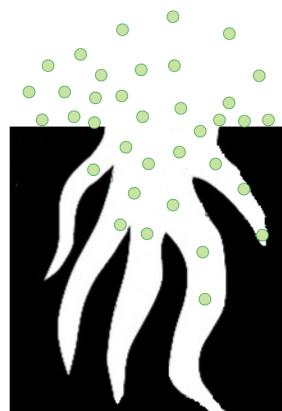
Note that the heat of adsorption  $\Delta H$  represents the depth of potential well.

Based on the underlying principles discussions, the process gas adsorption can be summarised as:

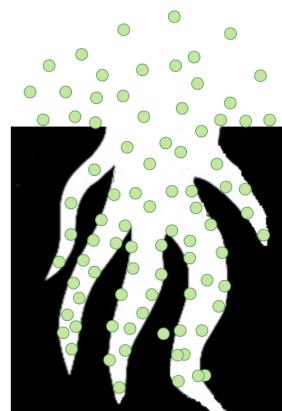
1. Diffusion to the adsorbent surface: through diffusion, the gas molecules move from the bulk gas phase toward the surface of the adsorbent material.
2. Migration to the adsorption sites: once the gas molecules reach the adsorbent surface, they need to migrate or move from the surface to the specific adsorption sites. Adsorption sites are locations on the surface that have the necessary characteristics, such as suitable surface chemistry or specific intermolecular forces, to attract and retain the gas molecules. The gas molecules move along the surface, driven by attractive forces, until they reach these favourable adsorption sites.
3. Monolayer formation: at the adsorption sites, the gas molecules adhere to the surface of the adsorbent material. Initially, a monolayer of gas molecules forms, where the surface sites become occupied by a single layer of gas molecules. This monolayer can cover the entire available surface area. If the gas concentration or pressure is high enough, additional gas molecules can adsorb onto the surface, forming multiple layers above the initial monolayer - multilayer adsorption.



**1. Diffusion to the adsorbent's surface**



**2. Migration to the pores**



**3. Monolayer (and then multilayer) formation**

## Gas Adsorption Isotherm

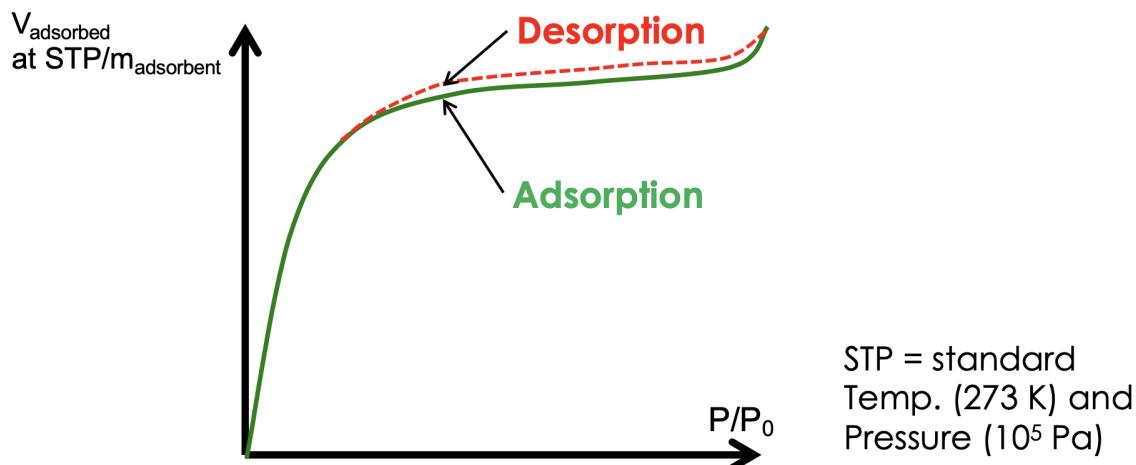
The ability of an adsorbent to retain adsorbates is limited, and the amount of gas adsorbed (volume or moles) per mass of adsorbent is called adsorption capacity. It can depend on a range of factors, including temperature, pressure, and interactions. When the temperature and interactions are held constant, the adsorption capacity becomes primarily dependent on the pressure of the gas:

$$\left( \frac{V_{\text{adsorbed}}}{m_{\text{adsorbent}}} \right)_T = f\left( \frac{P}{P_0} \right)_T \quad \text{or} \quad \left( \frac{n_{\text{adsorbed}}}{m_{\text{adsorbent}}} \right)_T = f\left( \frac{P}{P_0} \right)_T$$

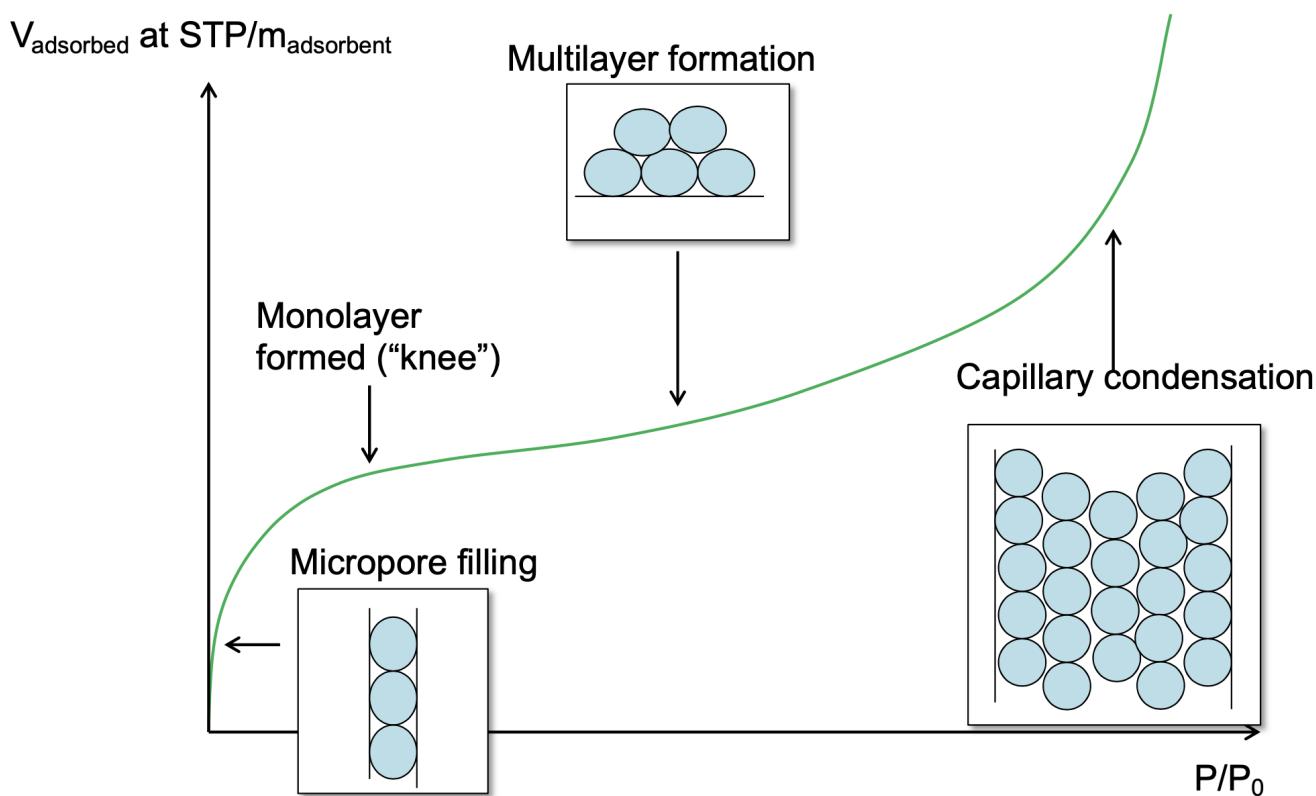
where  $n_{\text{adsorbed}}$  is the amount of gas adsorbed (mol),  $V_{\text{adsorbed}}$  is the volume of gas adsorbed at STP ( $\text{cm}^3$ ),  $m_{\text{adsorbent}}$  is the mass of adsorbent (g),  $P$  is the pressure and  $P_0$  is the saturation pressure of the adsorptive at temperature  $T$ . This relationship between the amount of gas adsorbed on a solid surface and the pressure at a constant temperature is known as a gas adsorption isotherm, which describes the equilibrium state between the adsorbed gas and the gas phase. It is usually represented graphically:

Gas	Temperature	Cross sectional area ( $\text{nm}^2$ )	Comments
$\text{N}_2$	-195.8 °C (liquid $\text{N}_2$ )	0.162	readily available, but at low pressure, rates of diffusion very slow, micro, meso, macro
Ar	-183 °C (liquid Ar) -195.8 °C (liquid $\text{N}_2$ )	0.138	micro, meso, macro
$\text{CO}_2$	-78 °C, -25 °C, 0 °C	0.210	good for very small pores, some specific interactions can take place, pore size analysis
Kr	-195.8 °C (liquid $\text{N}_2$ )	0.202	pore size analysis

Note that the terms adsorbate and adsorptive can be used interchangeably. Some common adsorptives include:



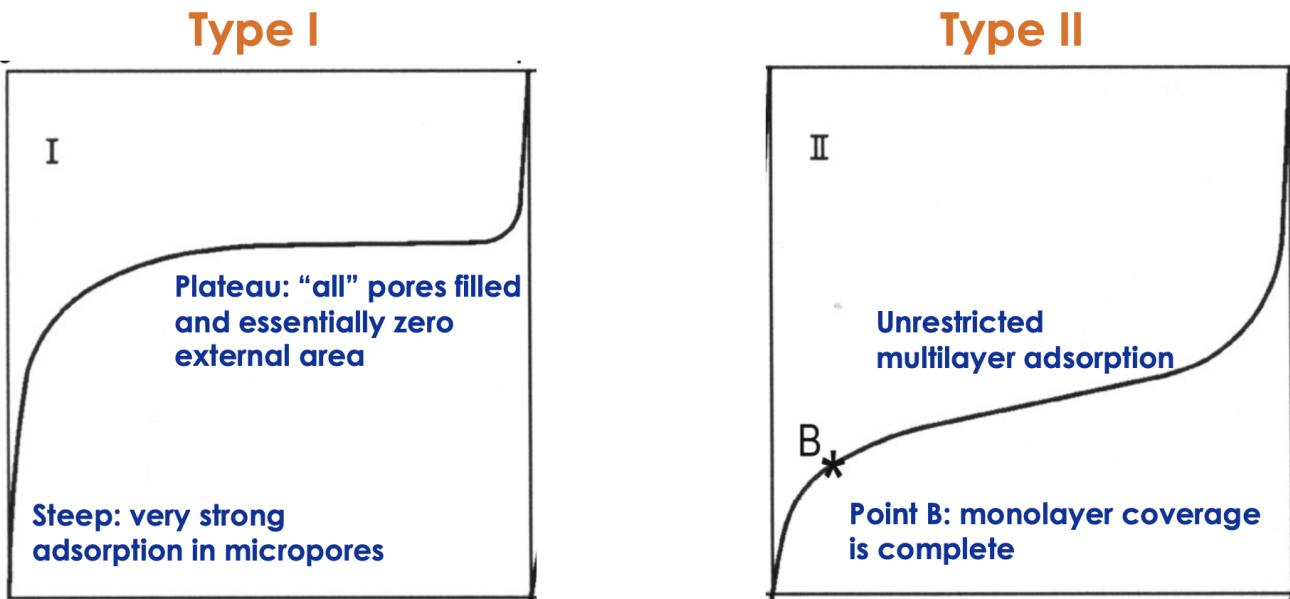
Generally, when an adsorbate gas exposed to an adsorbent with micropores, the adsorption initially occurs in these micropores. The adsorption isotherm graph shows a gradual increase in adsorption with increasing pressure, as the adsorbate molecules enter and occupy the micropores. This initial region of the isotherm is often referred to as micropore filling. A knee on the isotherm graph occurs when a significant number of micropores are filled with adsorbate molecules, causing a change in the adsorption behavior. At this point, the adsorption rate begins to slow down, and the graph exhibits a less steep slope compared to the initial adsorption region. As the pressure of the adsorbate continues to increase, the adsorbate molecules may form additional layers on top of the initially adsorbed monolayer. This is known as multilayer adsorption. When the pressure of the adsorbate continues increasing and reaches a critical point, the isotherm graph shows a sudden increase in adsorption, known as the capillary condensation region. This abrupt rise in adsorption is due to the condensation of the adsorbate into liquid-like films within the larger pores and capillary-like structures. The adsorbate molecules undergo a phase transition from a gas phase to a condensed liquid-like phase as the pressure increases. The capillary condensation region can be observed as a distinct plateau in the isotherm graph.



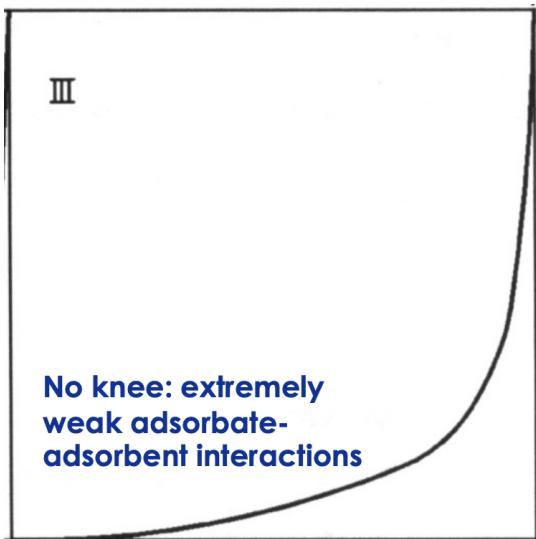
The shape of the adsorption isotherm graph depend on the specific nature of the adsorbent material. The various characteristics can be classified into six types, based on the [IUPAC classification system](#) :

- Type I isotherm (Langmuir) is characterised by a steep initial increase in adsorption followed by a plateau at higher pressures. It indicates monolayer adsorption on a homogeneous adsorbent surface. The adsorption capacity reaches a maximum at the plateau, representing the saturation point where the adsorbent surface is fully covered by a single layer of adsorbate molecules. The curve is concave because the rate of adsorption decreases as the pressure increases. The curvature represents the diminishing adsorption rate as the adsorbate molecules become more crowded on the surface and the available adsorption sites become limited.

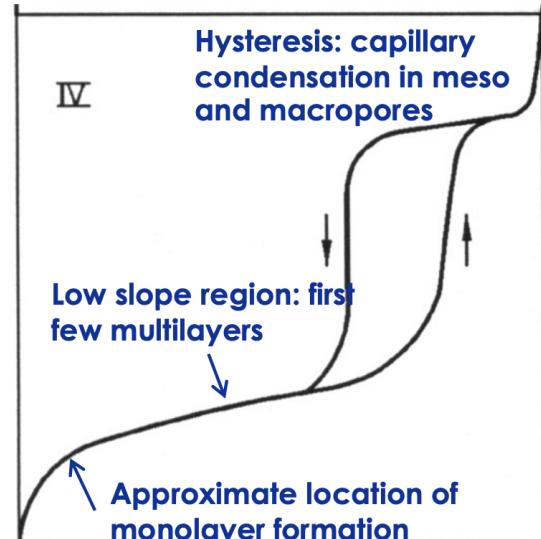
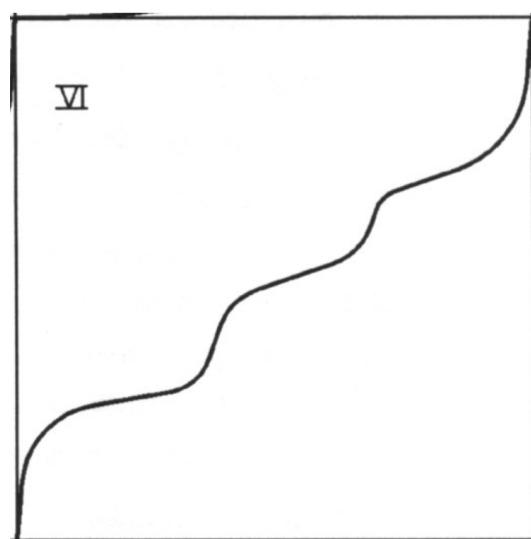
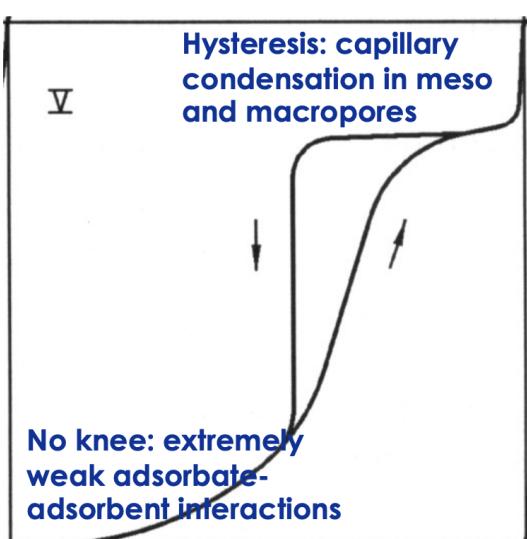
- Type II isotherm is typically observed for non-porous or macroporous materials. The shape is the result of unrestricted monolayer-multilayer adsorption up to high  $p/p_0$ . If the knee is sharp, Point B, the beginning of the middle almost linear section, usually corresponds to the completion of monolayer coverage. A more gradual curvature (i.e., a less distinctive Point B) is an indication of a significant amount of overlap of monolayer coverage and the onset of multilayer adsorption. There is no distinct plateau, and the thickness of the adsorbed multilayer generally appears to increase without limit when  $p/p_0 = 1$ .



- Type III isotherm is typically observed for non-porous or macroporous materials. There is no Point B, the knee, and therefore no identifiable monolayer formation; the adsorbent-adsorbate interactions are now relatively weak and the adsorbed molecules are clustered around the most favourable sites on the surface of a nonporous or macroporous solid. In contrast to a Type II isotherm, the amount adsorbed remains finite at the saturation pressure (i.e., at  $p/p_0 = 1$ ). In addition, the curve is convex. This type of isotherm is rare.
- Type IV isotherm is commonly observed for mesoporous materials. It exhibits a similar continuous increase in adsorption as the Type II isotherm. However, it is characterised by a hysteresis loop, indicating a difference in the adsorption and desorption curves. This hysteresis suggests the presence of capillary condensation or irreversible adsorption-desorption processes within the material's pore structure. Another typical feature of Type IV isotherms is a final saturation plateau.

**Type III**

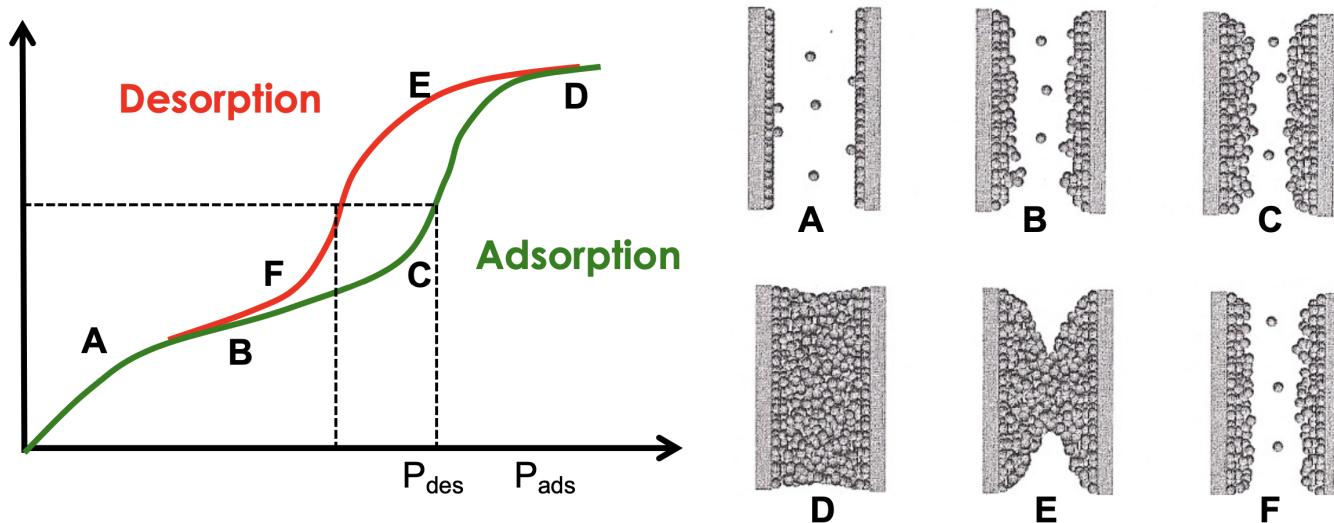
**No knee: extremely weak adsorbate-adsorbent interactions**

**Type IV****Type VI****Type V**

**No knee: extremely weak adsorbate-adsorbent interactions**

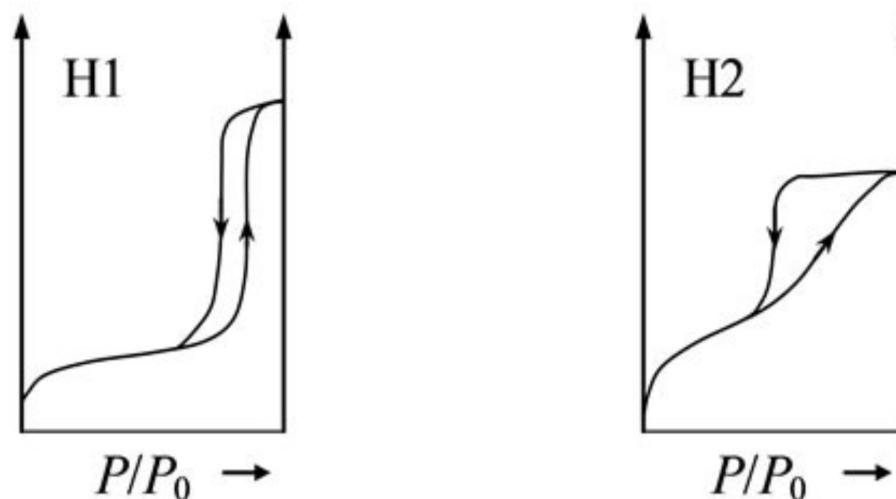
Hysteresis refers to the phenomenon where the adsorption and desorption curves of an adsorbate do not follow the same path during a cycle of increasing and decreasing pressure. This means that the amount of adsorbate adsorbed during the desorption process is different from the amount desorbed during the adsorption process at the same pressure. The occurrence of hysteresis is usually associated with the presence of mesopores or macropores in the adsorbent material and the capillary condensation phenomenon. During the adsorption process, the adsorbate molecules enter and fill the larger pores, resulting in increased adsorption. However, during the subsequent desorption process, the adsorbate molecules may remain trapped

or partially retained in the pores due to capillary forces or other interactions, leading to a slower desorption rate and a higher amount of adsorbate remaining.

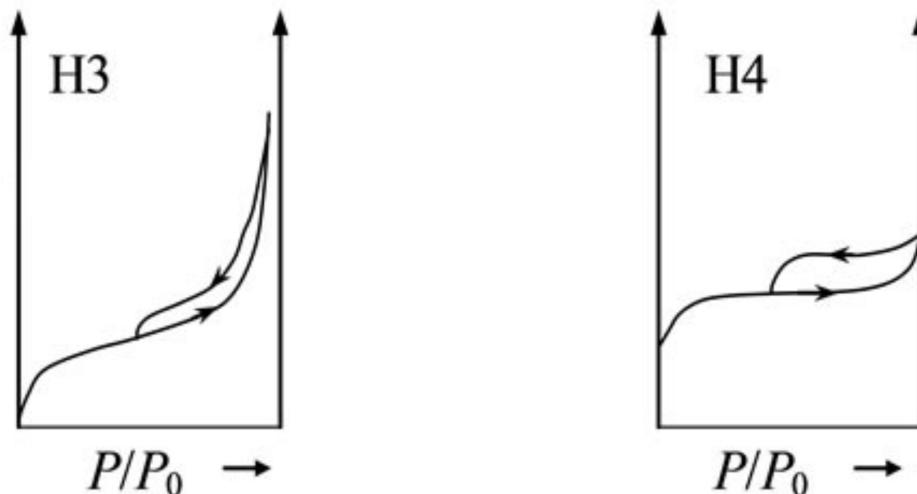


Analogously, there are four commonly observed types of hysteresis loops:

- ▶ Type I hysteresis is characterised by a narrow and nearly symmetric loop. The adsorption and desorption curves closely follow each other. This type of hysteresis is typically observed in a narrow range of uniform mesopores. Usually, network effects (the phenomenon where the presence of adsorbed molecules can create a connected network or structure within the adsorbent material) are minimal and the steep, narrow loop is a clear sign of delayed condensation on the adsorption branch.
- ▶ Type II hysteresis is given by more complex pore structures in which network effects are important. The adsorption isotherm exhibits a steep desorption branch. This steep desorption branch can be attributed to two factors: pore blocking or percolation in a narrow range of pore necks, where the adsorbate molecules may encounter difficulty in accessing certain pores and this may result in slower adsorption; or cavitation-induced evaporation, where the presence of interconnected pores can facilitate the formation of vapor-filled regions, and during desorption, when the pressure decreases, these vapor-filled regions can act as nucleation sites for evaporation, causing a sudden release of adsorbate molecules and leading to a steep desorption branch.



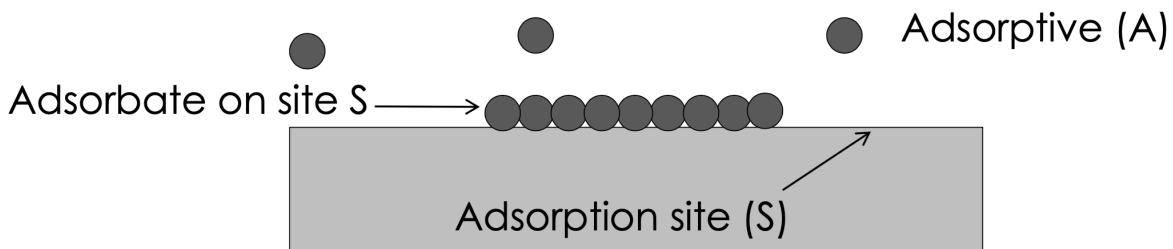
- ▶ Type III hysteresis exhibits two distinctive features: (i) the adsorption branch resembles a Type II isotherm; (ii) the lower limit of the desorption branch is normally located at the cavitation-induced  $p/p_0$ . Loops of this type are given by non-rigid aggregates of plate-like particles (e.g., certain clays) but also if the pore network consists of macropores which are not completely filled with pore condensate.
- ▶ Type IV hysteresis is somewhat similar to Type III, but the adsorption branch is now a composite of Types I and II, the more pronounced uptake at low  $p/p_0$  being associated with the filling of micropores. These loops are often found with narrow slit pores including pores in the micropore region, such as aggregated crystals of zeolites, some mesoporous zeolites, and micro-mesoporous carbons. When the entrance to the pore is smaller than the pore itself, the adsorbate is retained within the pores due to capillary forces even at lower pressures, resulting in a higher desorption pressure compared to the initial adsorption.



## Modelling of Adsorption Isotherms

### Langmuir

According to the Langmuir model, adsorption occurs on a homogeneous surface with a finite number of identical adsorption sites, where only monolayer adsorption occurs. Each adsorption site can only accommodate one molecule, and interactions between neighbouring adsorbates are negligible.



The model also assumes that adsorption takes place through a reversible process:



Thus, the rates of adsorption and desorption are:

$$r_{ads} = k_{ads} P_A [S]$$

$$r_{des} = k_{des} [AS]$$

At equilibrium,

$$r_{ads} = r_{des}$$

$$k_{ads} P_A [S] = k_{des} [AS]$$

$$\frac{[AS]}{P_A[S]} = \frac{k_{ads}}{k_{des}} = K$$

where  $K$  is the Langmuir constant, which is related to the strength of adsorption and the number of available adsorption sites. Furthermore, the adsorption sites are either free or bounded to an adsorbate,

$$[S]_0 = [S] + [AS]$$

Therefore, the surface coverage in the Langmuir model is

$$\theta = \frac{[AS]}{[S]_0} = \frac{KP_A}{1 + KP_A}$$

At low pressures, the denominator is dominated by 1, and thus

$$\theta = KP_A$$

which is the Henry equation.

Moreover, by rearranging the surface coverage equation in the Langmuir model:

$$\theta = \frac{V_A}{V_m} = \frac{KP_A}{1 + KP_A}$$

$$\frac{P_A}{V_A} = \left( \frac{1}{V_m K} \right) + \left( \frac{1}{V_m} \right) \cdot P_A$$

where  $V_A$  is the volume of adsorbed gas per kg adsorbent and  $V_m$  is the adsorption volume per kg adsorbent corresponding to complete monolayer coverage. Therefore, by plotting  $P_A/V_A$  as a linear function of  $P_A$ , the slope  $1/V_m$  can be readily determined, which can be injected into

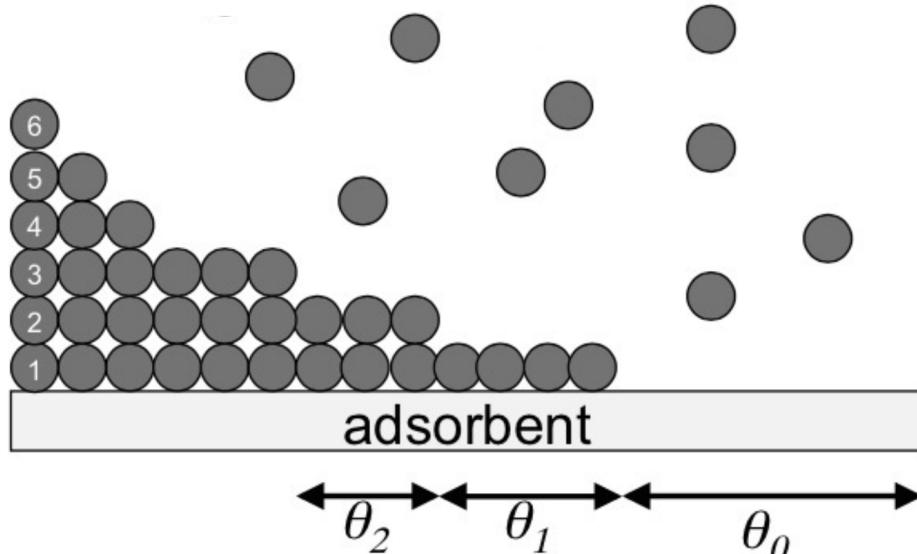
$$S_m = \frac{V_m S_{\text{adsorptive}} N_{\text{avogadro}}}{V_M}$$

to determine the surface area of the adsorbate  $S_m$  ( $\text{m}^2/\text{g}$ ), where  $S_{\text{adsorptive}}$  is the cross sectional area of the adsorptive,  $N_{\text{avogadro}}$  is the Avogadro's constant ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ) and  $V_M$  is the molar volume of the adsorptive at STP ( $22414 \text{ cm}^3/\text{mol}$ ).

## Brunauer Emmet Teller (BET)

The BET is also based on several assumptions:

- ▶ Adsorption takes place in sequential layers on the solid surface. The first layer is a monolayer, where gas molecules adsorb individually onto available sites on the surface. Subsequent layers involve the condensation of gas molecules onto the already formed monolayer.
- ▶ The heat of adsorption for the first layer is higher than that of the subsequent layers. This is because the first layer experiences direct interactions with the solid surface, resulting in stronger binding forces. The heat of adsorption for the subsequent layers is assumed to be equal to the heat of condensation between neighboring adsorbates, as the gas molecules transition from the gas phase to the condensed phase.
- ▶ All adsorption sites on the surface are energetically equivalent.
- ▶ Negligible interactions between neighboring adsorbates.



The BET model is expressed as

$$\frac{V}{V_m} = \frac{CP/P_0}{(1 - P/P_0)(1 - P/P_0 + CP/P_0)}$$

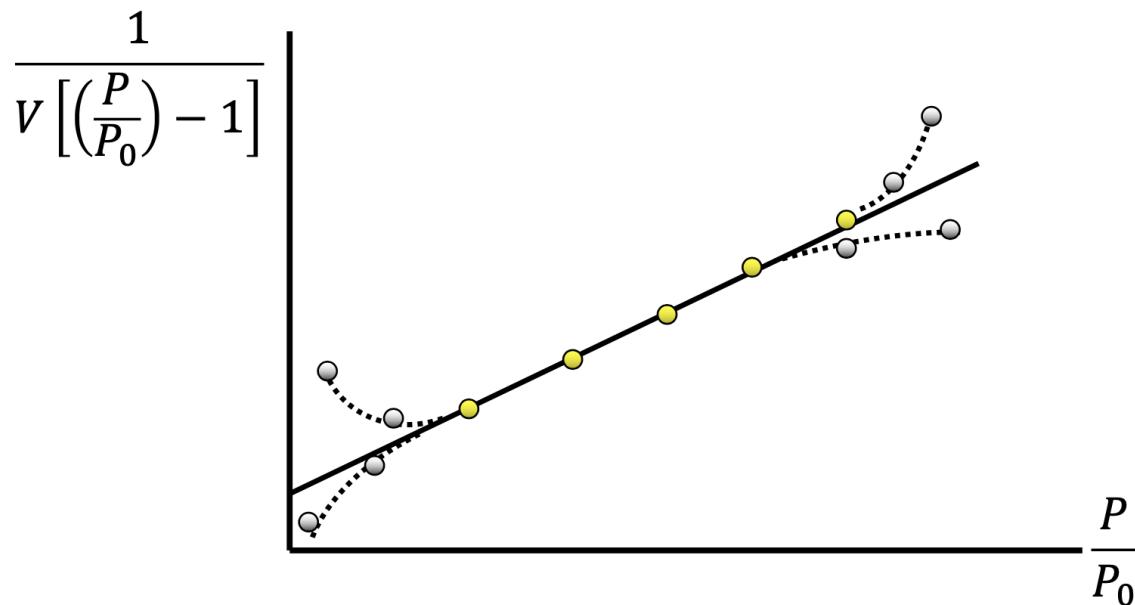
where  $V$  is the volume of gas adsorbed,  $V_m$  is the volume corresponding to the monolayer coverage,  $P$  is the pressure of gas at equilibrium,  $P_0$  is the saturation pressure and  $C$  is a constant associated with adsorption heat of the first layer  $E_1$  and condensation heat of the adsorptive  $E_L$

$$C = \alpha \exp\left(\frac{E_1 - E_L}{RT}\right)$$

where  $\alpha$  is a constant,  $R$  is the gas constant and  $T$  is the temperature. Again, the BET model can be linearised:

$$\frac{P/P_0}{V(1 - P/P_0)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C}(P/P_0)$$

By plotting a linear function,  $V_m$  and  $C$  can be determined, and  $V_m$  can be used to determine the surface area of the adsorbate.



## Freundlich

The Freundlich model assumes an energetically heterogeneous adsorbent surface and an exponential decrease in enthalpy of adsorption with surface coverage.

$$q = KP^{1/n}$$

where  $q$  is the amount of solute adsorbed per unit mass of adsorbent,  $K$  is the Freundlich constant related to the adsorption capacity of the adsorbent and  $n$  is the Freundlich exponent, which characterises the intensity of adsorption. The exponent  $1/n$  accounts for the nonlinearity of the relationship between adsorption and concentration. If  $n > 1$ , the adsorption process is favourable and exhibits cooperative behaviour. If  $n = 1$ , the adsorption is linear, and if  $n < 1$ , it indicates a less favourable adsorption process.

## Toth

The Toth model considers a wider range of adsorption phenomena and can account for both favourable and unfavourable adsorptions, as well as cooperative and competitive adsorption processes.

$$\frac{q}{q_m} = \frac{P}{(b + P^m)^{1/m}}$$

where  $q_m$  is the maximum adsorption capacity (corresponding to complete surface coverage),  $b$  is the Toth constant related to the adsorption capacity of the adsorbent, and  $m$  is a constant.

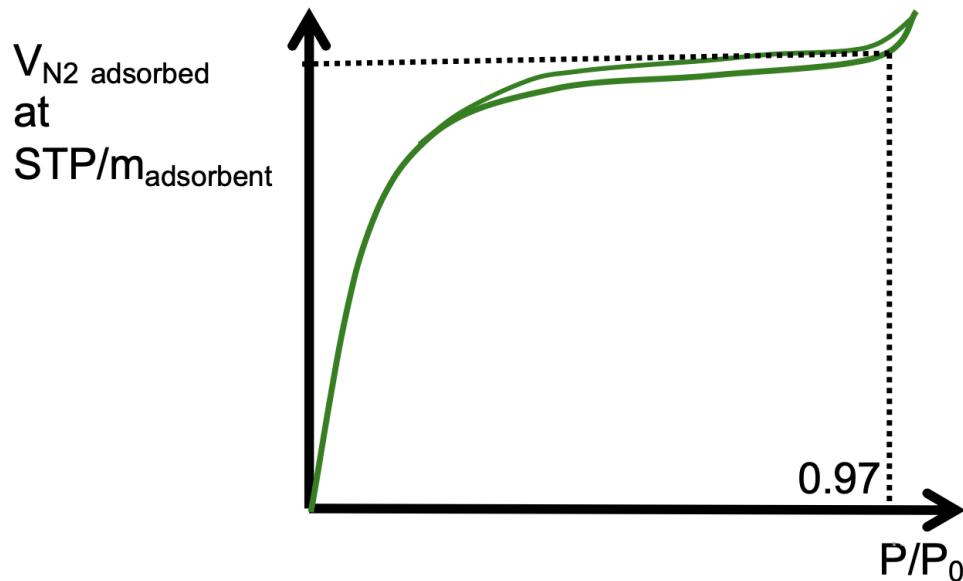
## Pore Size, Volume and Size Distribution

Adsorption is often used to measure various properties of a porous material, where the adsorbate gas is commonly nitrogen.

### Total Pore Volume

At cryogenic temperatures (77 K, the boiling point of liquid nitrogen), nitrogen can be condensed into the pores of the material being analysed. As the relative pressure of nitrogen increases, more and more nitrogen molecules are adsorbed onto the pore surfaces. The adsorption process continues until the pores become saturated or filled with the adsorbate. At the highest relative pressure reached during the measurement, the pores are assumed to be completely filled with liquid nitrogen. By measuring the volume of liquid nitrogen adsorbed at this point, the total pore volume of the material can be calculated. This is because the volume of liquid nitrogen corresponds to the volume of the pores that were accessible to the nitrogen gas during the measurement.

Let  $V_{\text{tot}}$  denote the liquid nitrogen volume (77 K) corresponding to the volume of nitrogen gas occupied at STP and measured at  $P/P_0 = 0.97$ ,



then the amount of liquid nitrogen is:

$$n_{\text{ads}} = \frac{V_{\text{tot}}}{V_M}$$

where  $V_M$  is the molar volume of liquid nitrogen at 77K,  $34.65 \text{ cm}^3/\text{mol}$ . The amount of liquid nitrogen is equal to the amount of gaseous adsorptive:

$$n_{\text{ads}} = \frac{P_{\text{standard}} V_{\text{adsorbed}}}{R T_{\text{standard}}}$$

where  $P_{\text{standard}}$  is the standard pressure ( $10^5$  Pa),  $V_{\text{adsorbed}}$  is the volume of nitrogen adsorbed at  $P/P_0 = 0.97$ ,  $R$  is the gas constant and  $T$  is the temperature. Combining the equations:

$$V_{\text{tot}} = \frac{P_{\text{standard}} V_{\text{adsorbed}} V_M}{R T_{\text{standard}}}$$

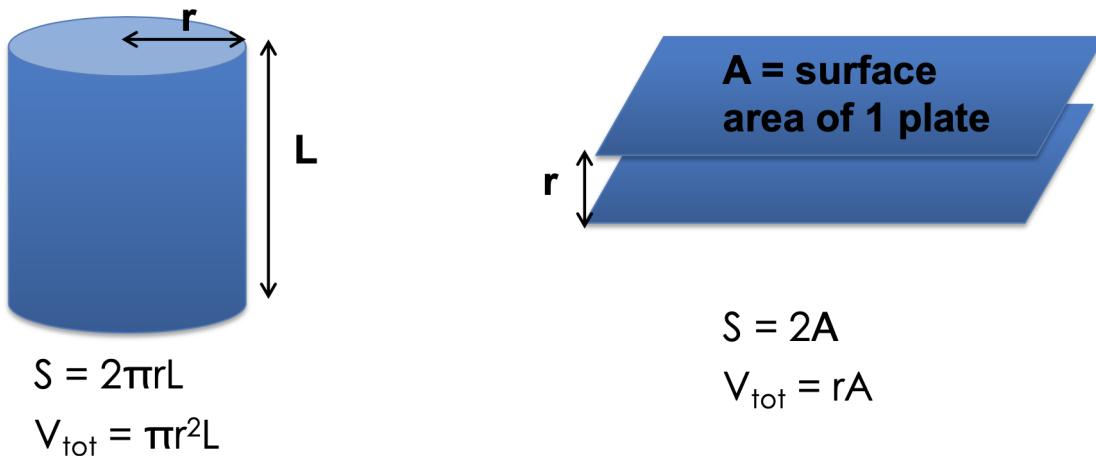
which gives the volume of liquid nitrogen, hence the total pore volume.

## Pore Size

Moreover, together with the surface area off the adsorbate as previously obtained, the average pore size  $r$  can be determined:

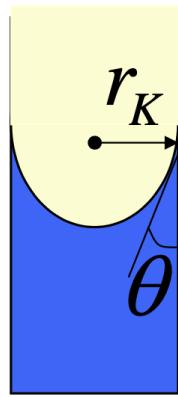
$$r = \frac{2V_{\text{tot}}}{S_m}$$

This is applicable to solid products with uniform pore size.



For mesoporous solids, as capillary condensation occurs, the Kelvin equation can be used to describe the equilibrium vapor pressure at which this condensation occurs.

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\gamma V_M}{r_k RT}$$

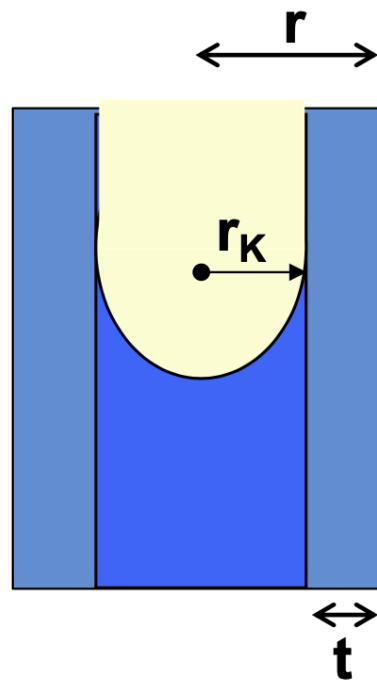


where  $V_M$  is the molar volume of the liquid adsorbate,  $P$  is the pressure (where capillary condensation occurs),  $P_0$  is the saturation pressure,  $R$  is the gas constant,  $T$  is the temperature and  $\gamma$  is the surface tension. In the case of nitrogen adsorption at 77 K,

$$r_k = -\frac{0.415}{\log\left(\frac{P}{P_0}\right)}$$

as measured in nm. This, however, does not exactly represent the pore radius, as the thickness of the adsorbed layer needs to be accounted for:

$$r = r_k + t$$



where  $t$  is the thickness of the adsorbed layer and  $r_K$  is the Kelvin radius of the pore.

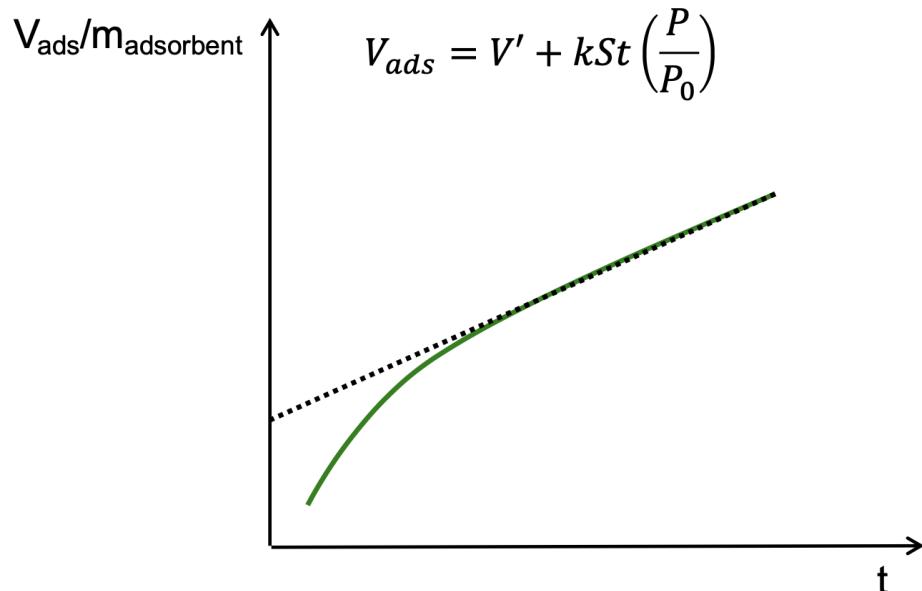
## Micropore Volume

The t-plot method is a technique to determine the micropore volume of a porous material. It is based on the concept of the t-curve, which represents the relationship between the volume of adsorbed gas at a given relative pressure and the thickness of the adsorbed film on the pore walls. The method assumes:

- ▶ No presence of ultramicropores.
- ▶ Micropores already filled-up.
- ▶ Adsorption in larger pores occurs (below condensation) according to:

$$V_{ads} \left( \frac{P}{P_0} \right) = V' + kSt \left( \frac{P}{P_0} \right)$$

where  $V_{ads} \left( \frac{P}{P_0} \right)$  is the volume adsorbed at  $P$ ,  $V'$  is the volume adsorbed in the saturated micropores at STP,  $k$  is a coefficient,  $S$  is the surface area from pores larger than micropores at STP,  $t \left( \frac{P}{P_0} \right)$  is the statistical thickness of adsorbed layer in pores > micropores, which can be given by selected model equations (e.g. Harkins-Jura and Halsey/Frenkel-Halsey-Hill). By constructing a linear plot,



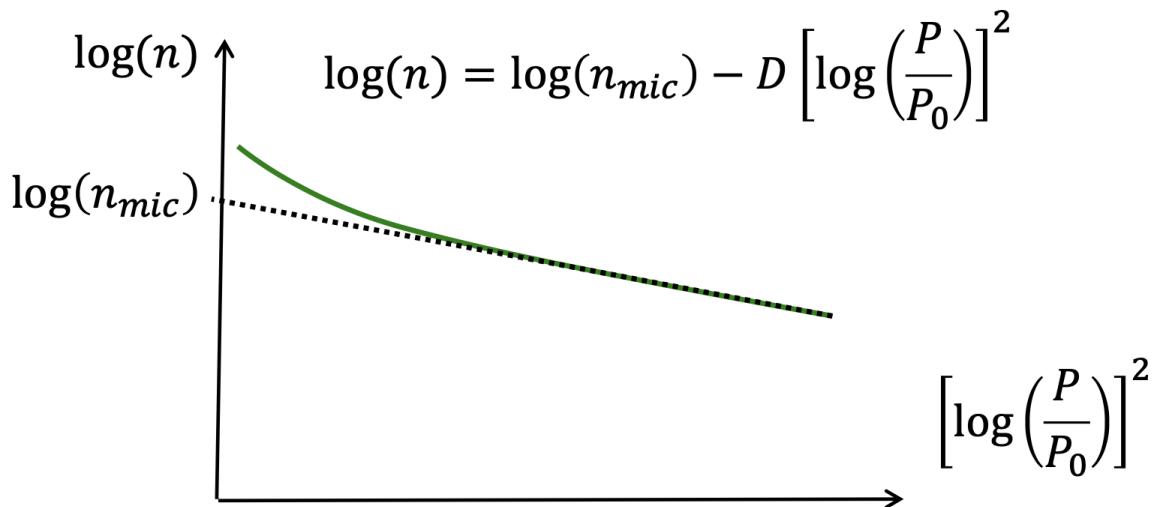
the  $y$ -intercept,  $V'$ , can be determined and used to calculate the micropore volume

$$V_{mic} = V' \frac{1.25}{0.808}$$

Another technique is the Dubinin-Radushkevich (DR) equation, which is based on the assumption that adsorption occurs in a system of uniform micropores with a certain adsorption potential:

$$\log(n) = \log(n_{mic}) - D \left[ \log \left( \frac{P}{P_0} \right) \right]^2$$

where  $n$  is the adsorption capacity at  $P$ ,  $n_{\text{mic}}$  is the adsorption capacity from the micropores,  $D$  is an empirical constant,  $P$  is the equilibrium pressure and  $P_0$  is the saturation pressure. Again, by plotting a linear graph,



$n_{\text{mic}}$  can be determined from the  $y$ -intercept, and

$$V_{\text{mic}} = \frac{n_{\text{mic}} M}{\rho}$$

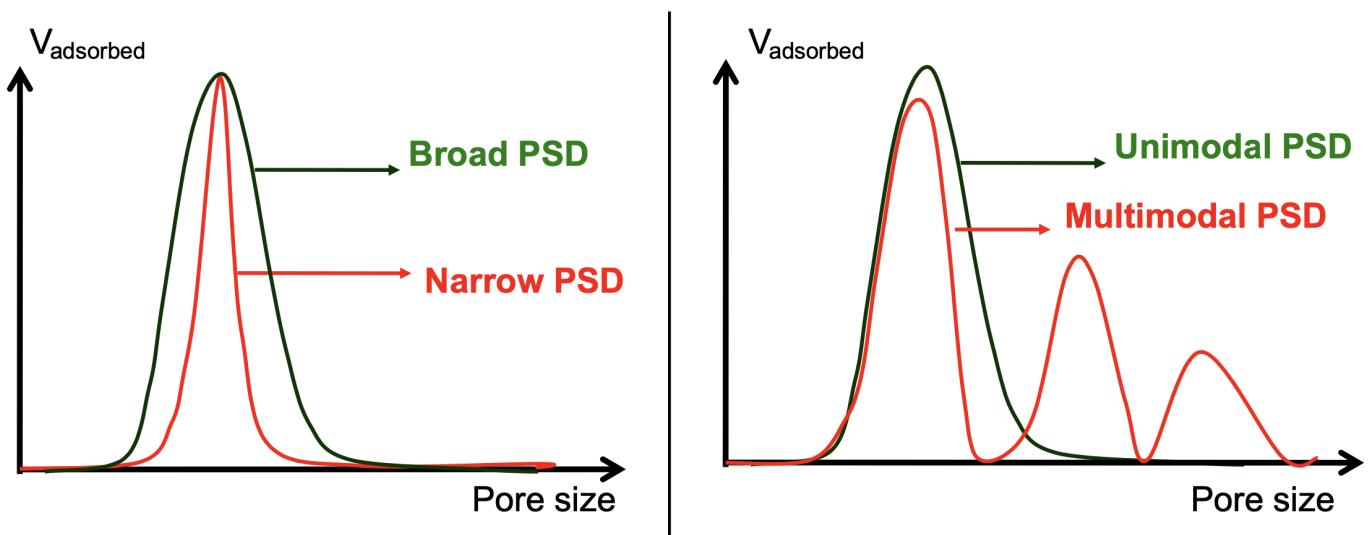
where  $\rho$  is the adsorbate density and  $M$  is the adsorbate molar mass.

## Pore Size Distribution

The distribution of pore volume with respect to pore size is called pore size distribution (PSD). Different models have been developed to determine PSD. The most common models are:

- ▶ For mesoporous: BJH (Barrett, Joyner and Halenda)
- ▶ For microporous: DA (Dubinin-Astakhov) method and HK (Horvath-Kawazoe)
- ▶ For micro/mesoporous: NLDFT(Non Local Density Functional Theory) or Monte Carlo

The PSDs can have various characteristics:



1. A narrow PSD indicates that the pores in the material are concentrated around a specific size range. This can have several implications:

- ▶ Selectivity: narrow PSDs can provide materials with high selectivity for specific molecules or gases. Materials with well-defined pore sizes can preferentially adsorb certain molecules while excluding others based on size. This selectivity can be advantageous in applications such as gas separation or purification processes.
- ▶ Limited adsorption capacity: while PSDs can exhibit high selectivity, they may have a limited overall adsorption capacity. The small range of pore sizes restricts the total volume available for adsorption, potentially reducing the material's adsorption capacity.
- ▶ Limited diffusion: materials with narrow PSDs may also exhibit limited diffusion of molecules within the pores. The restricted pore size range can hinder the movement of molecules, resulting in slower adsorption and desorption kinetics.

2. A wide PSD indicates that the pores in the material span a broad range of sizes. As opposed to a narrow PSD, this can lead to broad selectivity, higher adsorption capacity, and enhanced diffusion.

3. A unimodal PSD indicates that the pores in the material are predominantly concentrated around a single size range. This can have the following implications:

- ▶ Targeted applications: unimodal pore size distributions can be advantageous for applications that require specific pore sizes. They provide materials with a well-defined and targeted pore structure, enabling tailored performance for specific applications.
- ▶ Enhanced selectivity: materials with an unimodal pore size distribution can exhibit higher selectivity for specific molecules compared to materials with broader distributions. The uniform pore sizes allow for preferential adsorption of molecules that can fit within the available pore size range.

4. A multimodal pore size distribution indicates the presence of multiple distinct pore size ranges within the material. This can lead to versatile applications and tunable properties.

## Porosity Analyser

A porosity analyser is a device used to measure the porosity of a material, by determining the relationship between the amount of gas adsorbed by a material at different pressures and temperatures.

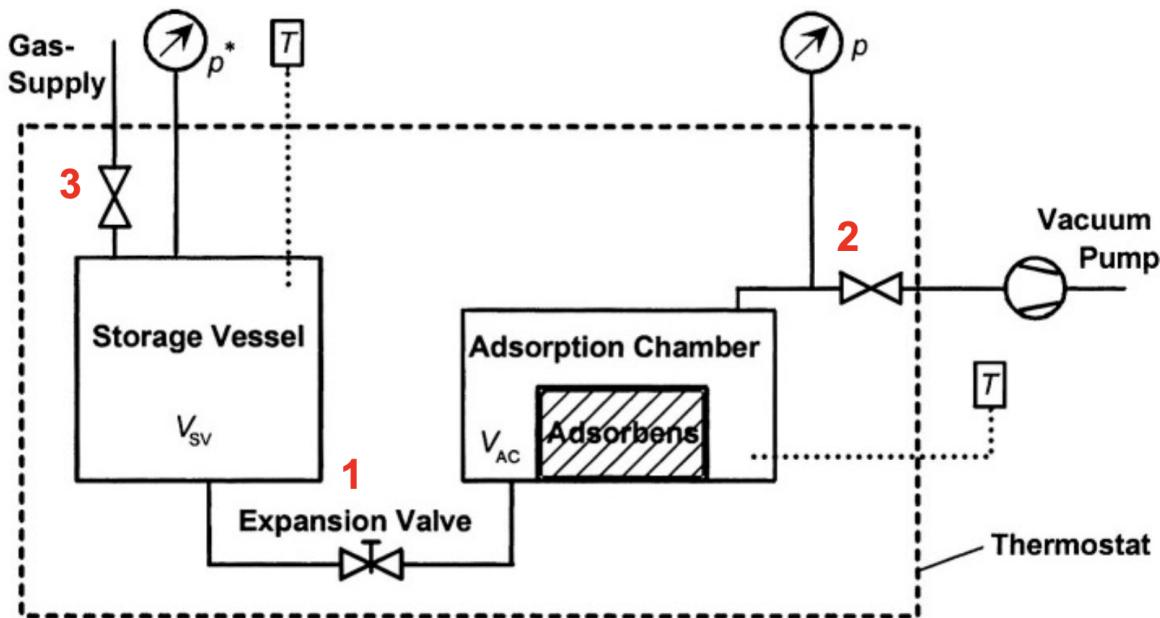
It is crucial to follow a rigorous sample preparation process to obtain rigorous measurements. Before the measurement, the sample must undergo a degassing step, which is the process of removing any molecules that may be adsorbed on the surface or within the pores of the material. This is important because these adsorbed molecules can interfere with the measurement and affect the accuracy of the results. The degassing step involves drying the sample under vacuum conditions, which helps in removing any volatile components or adsorbed gases by applying a low-pressure environment. The IUPAC recommends a minimum degas step of 16 hours.



The overall procedure for the measurement involves:

1. A given amount of adsorptive gas is expanded into a vessel containing the adsorbent sample.
2. When the adsorptive gas comes into contact with the adsorbent sample, part of the gas is adsorbed on the surface of the adsorbent, and another portion of the gas remains in the gas phase within the vessel.
3. At equilibrium, a mass balance can be applied: the mass of adsorptive gas adsorbed on the surface of the adsorbent and the mass of gas remaining in the gas phase should be equal to the initial mass of adsorptive gas added to the vessel.

When conducted in practice,



1. (1) and (3) closed, (2) open: evacuation
2. (1) and (2) closed, (3) open then closed: storage vessel filling
3. (1) open and then closed,(2) and (3) closed: gasadsorbs

Thus,

$$n^{\text{tot}} = \frac{P_{\text{SV}} V_{\text{SV}}}{R T_{\text{SV}}}$$

$$n^{\text{not adsorbed}} = \frac{P_{\text{AC}} (V_{\text{SV}} + V_{\text{AC}} - V_{\text{adsorbent}})}{R T_{\text{AC}}}$$

$$n^{\text{adsorbed}} = n^{\text{tot}} - n^{\text{not adsorbed}}$$

## Mercury Porosimetry

Mercury porosimetry, also known as mercury intrusion, is a technique used to determine the porosity of solid materials, specifically meso/macroporous solids with pore sizes ranging from 3.5 nm to 500 µm. Instead of a gas, mercury porosimetry relies on the principle that mercury can be used as a non-reactive fluid to measure the volume of pores within a solid material. Prior to the measurement, the sample is usually evacuated to remove any residual gases. Then, mercury is introduced into the sample, and its intrusion into the pores is measured.

However, one limitation of mercury porosimetry is that it measures the largest entrance to a pore, rather than the actual inner size of the pore. This means that if a pore has a non-uniform shape or a constriction within it, the technique will only provide information about the largest dimension of the pore entrance. It does not provide detailed information about the internal structure or shape of the pore. Another limitation of mercury porosimetry is that it assumes a cylindrical pore geometry when calculating pore size distribution. This assumption may not accurately represent the actual pore shape of the material being analysed. If the pores have irregular or non-cylindrical shapes, the results may not fully capture their complexity. Finally, mercury porosimetry is destructive, as the process of mercury intrusion can potentially cause damage to the material being analysed, especially if the material is not able to withstand the applied pressures. Therefore, it is typically used on samples that are either expendable or can tolerate the invasive nature of the technique.

By the Washburn equation, the pore radius is:

$$P = \frac{2\gamma \cos \theta}{r_{\text{pore}}}$$

where  $P$  is the pressure,  $\gamma$  is the surface tension of mercury,  $\theta$  is the contact angle between the liquid and the solid material, and  $r_{\text{pore}}$  is the pore radius. The total volume of pores can be approximated as the total intruded volume at the highest pressure. Thus, the surface area is

$$A = -\frac{1}{\gamma_{\text{Hg}} \cos \theta} \int_0^V P dV$$

where  $V$  is the volume adsorbed.