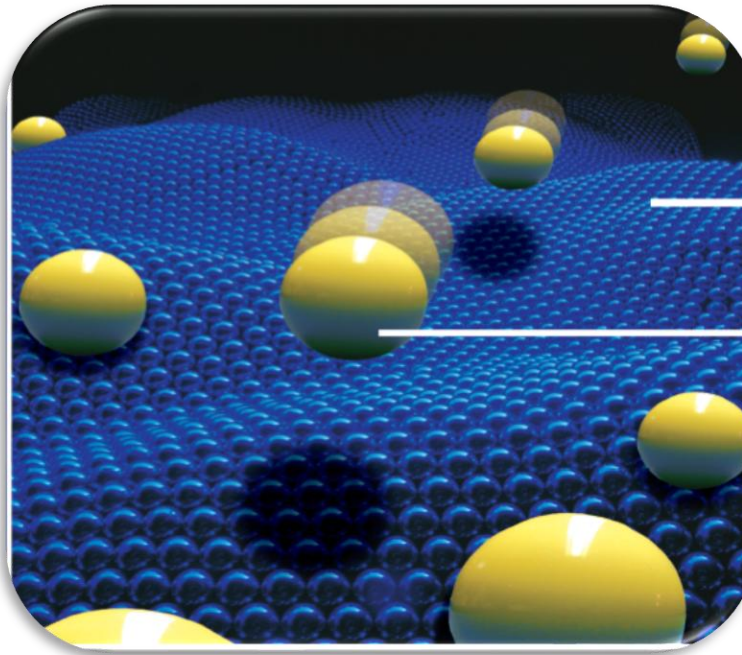


Surface phenomena at the micro and nano scale

Master's Degree in Materials Science



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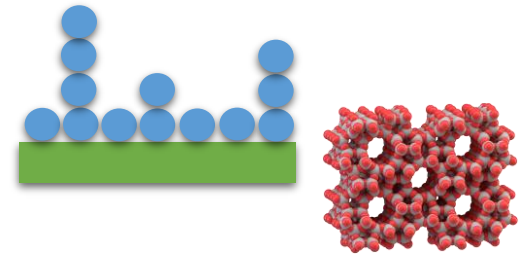
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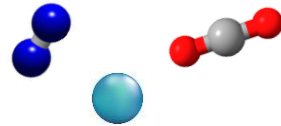
Objectives

A Practical Guide for advanced characterization of porous materials

- Understand the basics of adsorption and nanoporous materials



- Learn advanced techniques for characterizing textural properties of materials



- Bridge the gap between theoretical and practical analysis of adsorption data

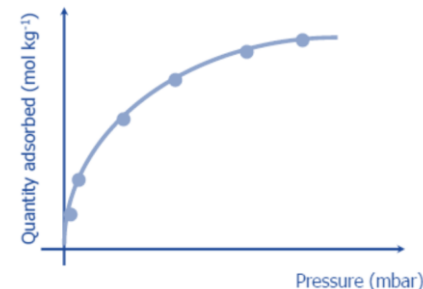


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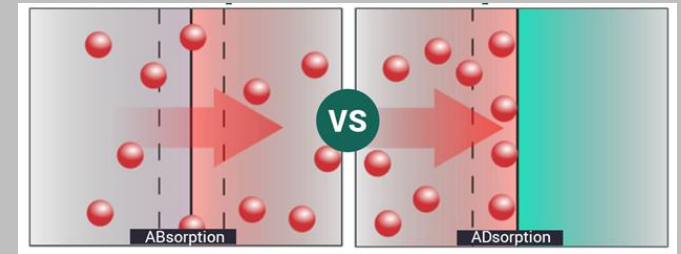
What is adsorption? (Adsorption vs Absorption)

Some historical dates

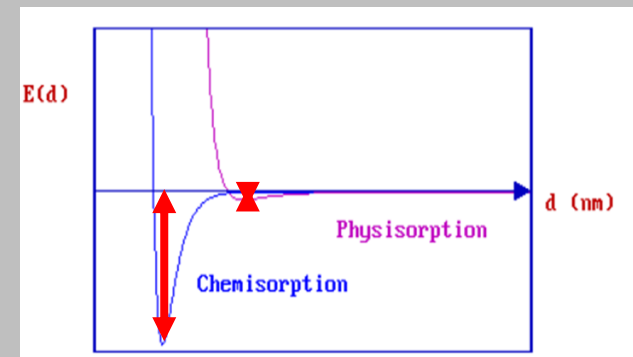
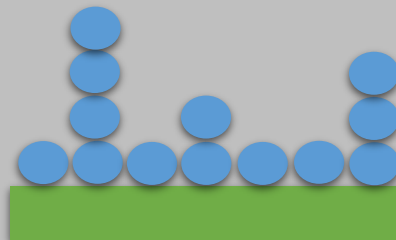
Chemisorption vs Physisorption

Enthalpy and Free Energy of Adsorption processes

Potential energy curves of Adsorption processes



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



What is an interface? And a surface?



An **interface** is the boundary between two phases.

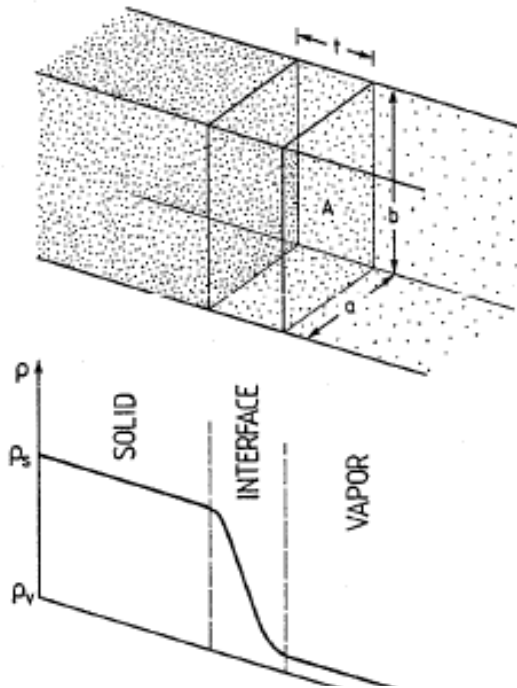
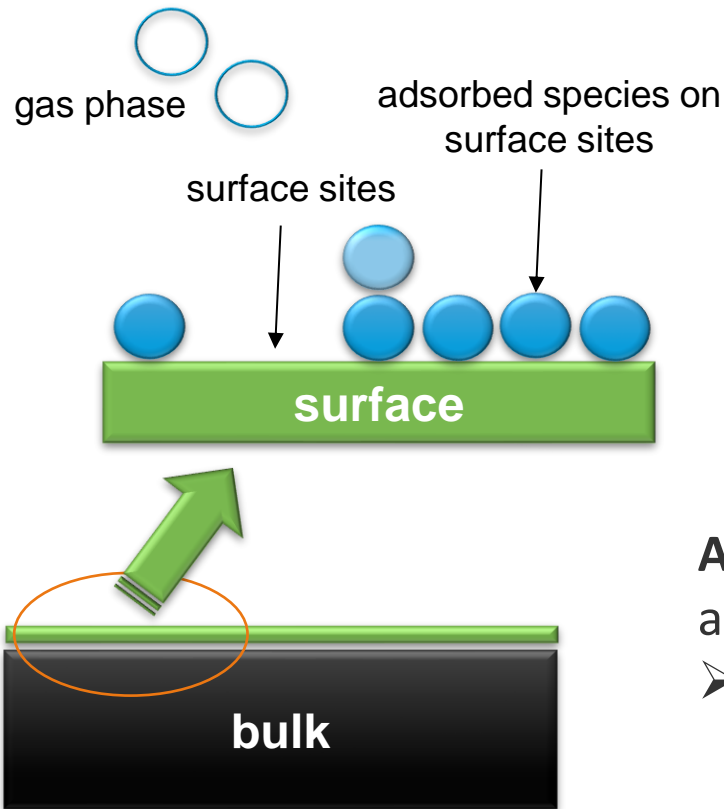


Fig.3.1. Schematic description of a solid/vapor interface (area A , thickness t). The solid is in thermodynamic equilibrium with its vapor. In the interface region the density ρ of the material changes gradually from its solid value ρ_s to its vapor value ρ_v .

At the border of a solid or liquid in contact with vapour there is usually no abrupt change in density, but more or less continuous transition from high density to low density. The interface consists either of evaporating bulk material or **condensing material from the gas phase**.

The words **interface** and **surface** are often used synonymously, although *interface* is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly, e.g. the solid/gas interface, but the surface of a solid.

Adsorption

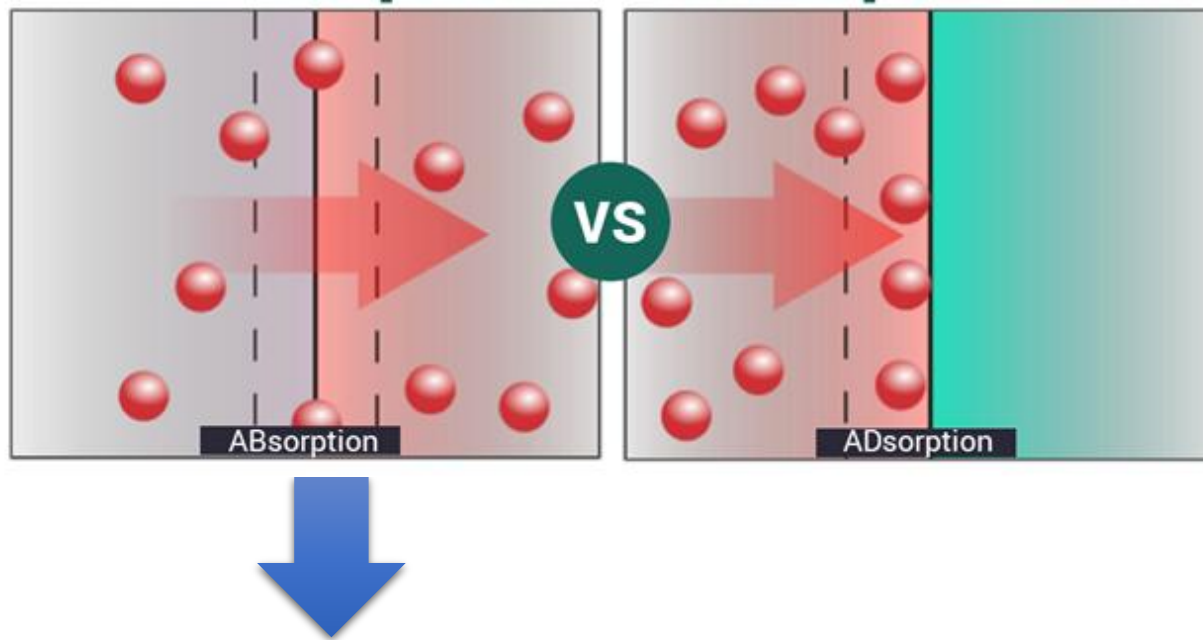


Surface phenomenon

Adsorption is the adhesion of molecules (or ions and atoms) **to the surface of a solid or liquid**.

- The molecules accumulated only at the surface and do not enter the bulk of the adsorbing material.
- The concentration of the adsorbed molecules is always greater in the immediate vicinity of the surface than in the free phase.
- Exothermic process

Absorption vs Adsorption



Absorption is a physical or chemical process in which atoms, molecules or ions enter some bulk phase solid or liquid material.

- It implies that the absorbed substance is uniformly distributed throughout the body of the solid or liquid.
- Endothermic process



Absorption

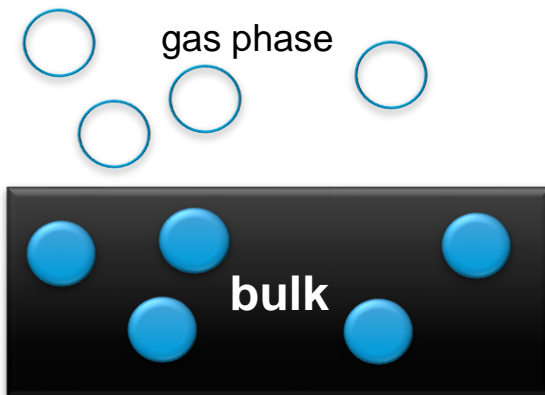
Bulk phenomenon

Absorption vs Adsorption

In general, the term «**sorption**» can be used to indicate both phenomena.
The **reverse of sorption is desorption** (used indifferently for adsorption and absorption).

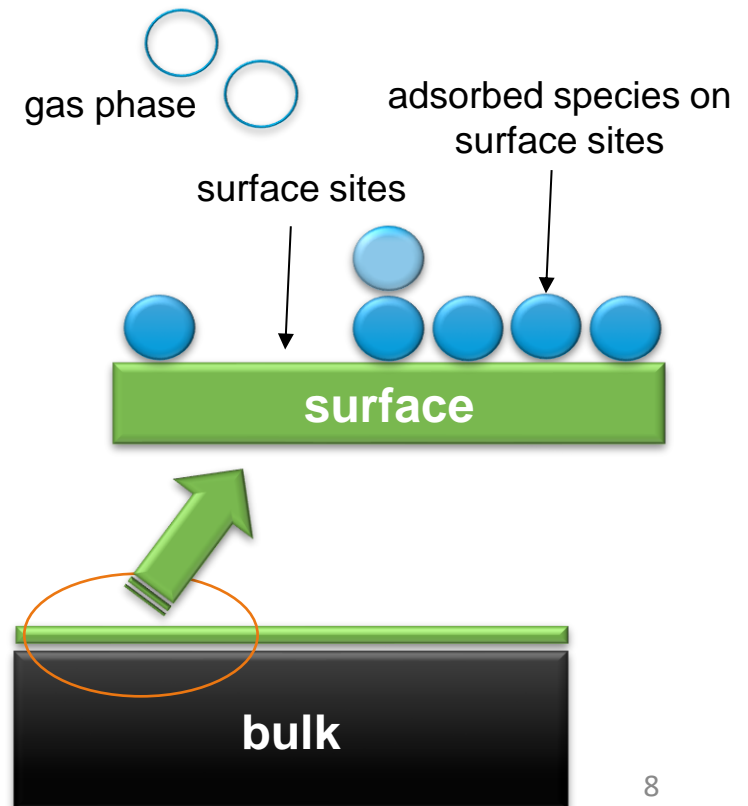
Absorption

Bulk phenomenon



Adsorption

Surface phenomenon

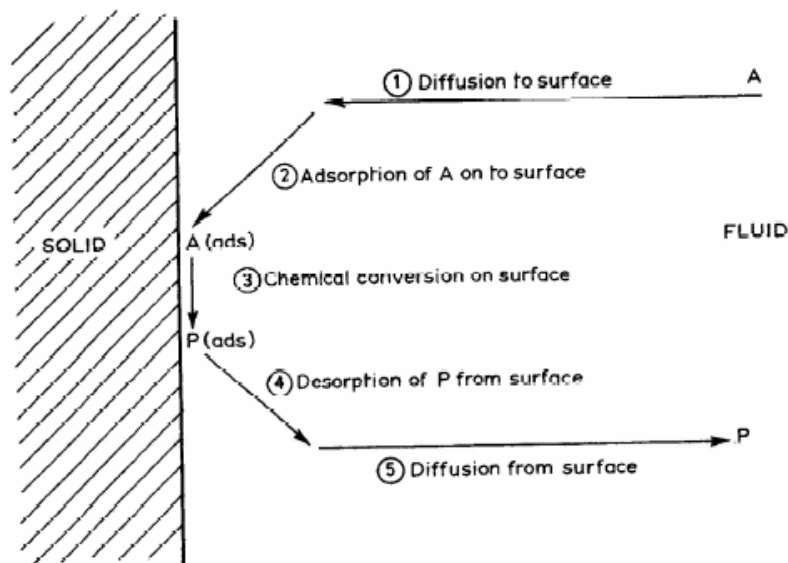


Importance of Adsorption

Solid-gas interaction is an important phenomenon in different fields:

- **Heterogeneous catalysis**, when reagents are vapours or gases
- **Separation and storage** of gases (Carbon Dioxide)

The adsorption of molecules on a surface is a prerequisite for any chemical process mediated by the surface.



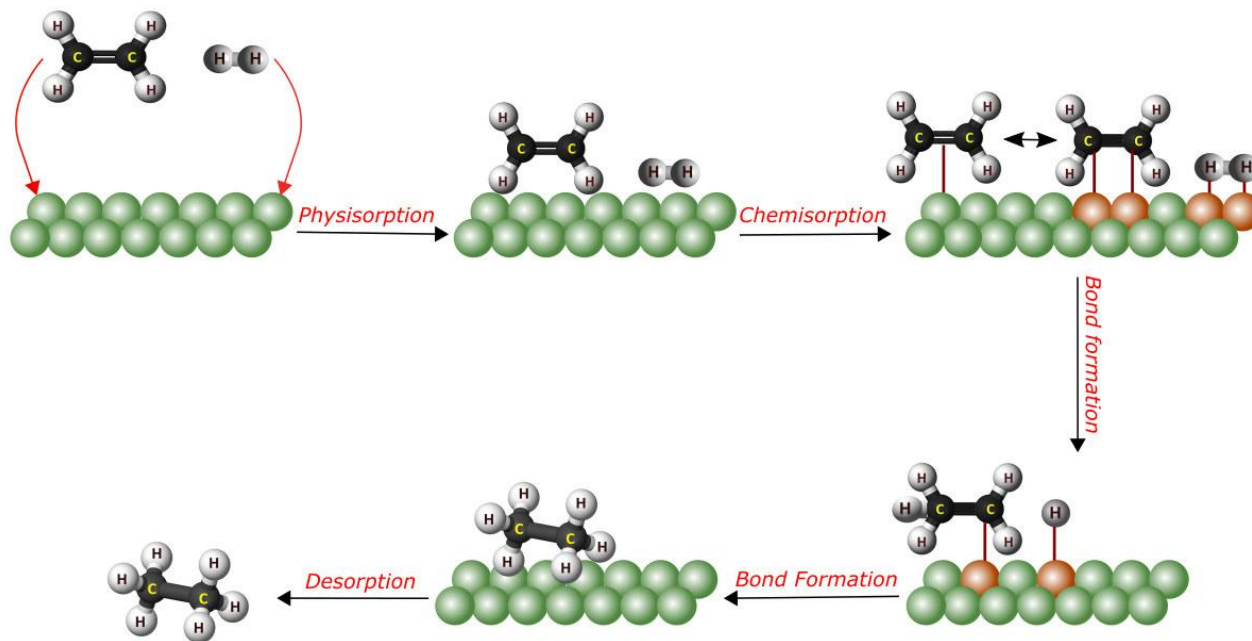
For example, in the case of a **surface catalyzed reaction**, it is possible to divide the entire process into five steps:

1. **Diffusion of reagents** to the catalyst active surface
2. **Adsorption of reagents** on the surface
3. **Surface reaction**
4. **Desorption of products** from the surface
5. **Diffusion of products** far from the catalyst surface

Importance of Adsorption

The adsorption of molecules on a surface is a prerequisite for any chemical process mediated by the surface

Catalytic hydrogenation of ethylene on metal nanoparticles



Adsorption: some historical dates

Adsorption is of great technological importance: some adsorbents are used on a large scale as desiccants, catalysts or catalyst supports; others are used for the separation or storage of gases, the purification of liquids, controlled drug delivery, pollution control or for respiratory protection. In addition, adsorption phenomena play a vital role in many solid-state reactions and biological mechanisms.



The adsorbent properties of such materials as clay, sand and wood charcoal were used by the ancient Egyptians, Greeks and Romans.



1773 The first quantitative observations of adsorption were carried out by the Swedish chemist Carl Scheele who reported some experiments of the uptake of gases by charcoal.



Carl Scheele's adsorption apparatus

“Heating the coal, the bladder, expanded...cooling down the air returned from the bladder into the coal ...the volume of air was about eight times of that of the coal...”

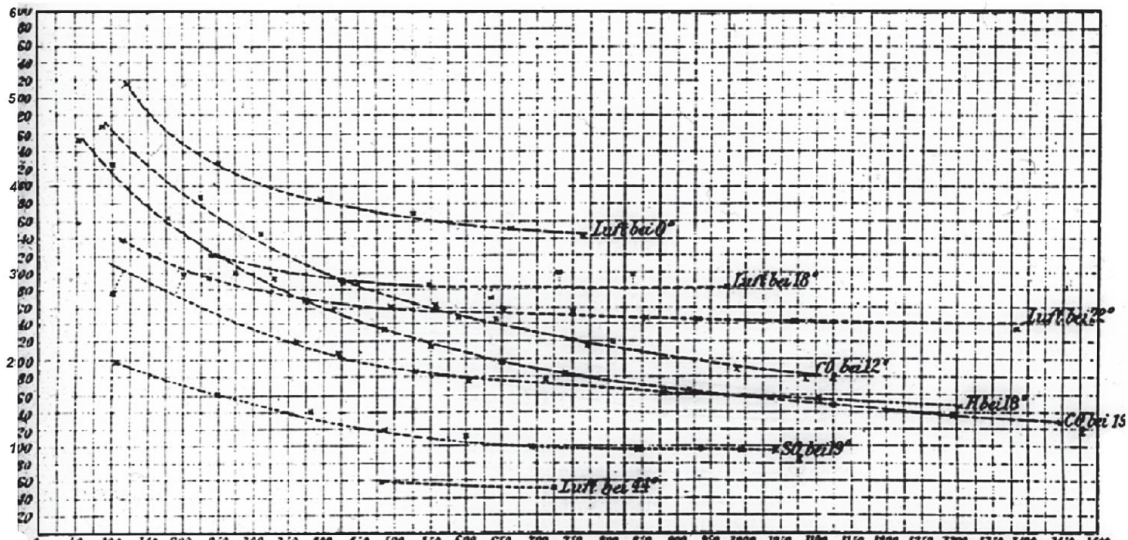
Adsorption: some historical dates

1814

Nicolas-Théodore de Saussure (a swiss chemist) concluded that all types of gases are taken up by porous substances and this process is accompanied by the evolution of heat. Thus, **he discovered the exothermic character of adsorption processes.**

1881

The term “**adsorption**” was introduced into literature by the german physicist Kayser, the first who related the amount of gas adsorbed to the pressure. He introduced the term “**isotherm**” to describe the results of adsorption measurements at a constant temperature.



The first gas adsorption isotherms recorded by Kayser.

Kayser's plots. Abscissa – equilibrium pressure; ordinate – volume adsorbed

Adsorption: some historical dates

1918

The American chemist Irving Langmuir published his monumental theory on adsorption, deriving for the first time a clear **concept of monolayer adsorption**, formed on energetically homogeneous solid surfaces.

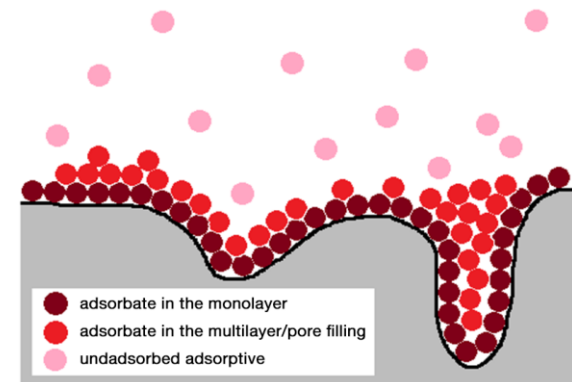


Langmuir was awarded the Nobel Prize in Chemistry in 1932 for his work in surface chemistry.



1938

Another milestone towards development of the adsorption science was the **multilayer adsorption theory** proposed by Brunauer, Emmet and Teller (BET). They proposed to determine the monolayer adsorption amount from the so-called point B of the experimental isotherm. They used, for the first time, nitrogen at low temperature to determine the surface area of an iron synthetic ammonia catalyst.

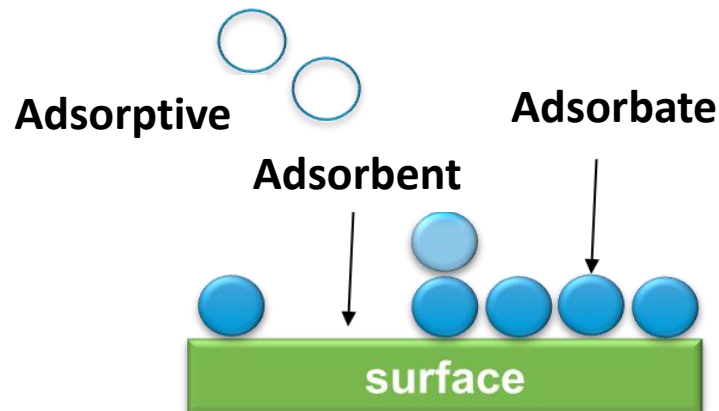


Adsorption: some definitions

The term adsorption means the enrichment of one or more components in the region between two bulk phases (i.e. the interfacial layer or the adsorption space): one of these phases is usually a solid and the other a fluid (i.e. gas or liquid).

Term	Definition
Adsorption	Enrichment of one or more components in the vicinity of an interface
Adsorbate	Substance in the adsorbed state
Adsorptive ^a	Adsorbable substance in the fluid phase
Adsorbent	Solid material on which adsorption occurs
Chemisorption	Adsorption involving chemical bonding
Physisorption	Adsorption without chemical bonding

^aTranslated into French as 'adsorbable'.



Chemisorption vs Physisorption

All adsorption processes can be divided into the two categories of **chemical** and **physical adsorption**.

Three main criteria to discriminate between Chemisorption and Physisorption

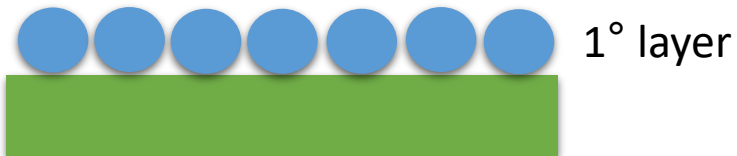
Chemisorption

- 1) Usually large
- 2) Usually irreversible
- 3) It always forms unimolecular layer

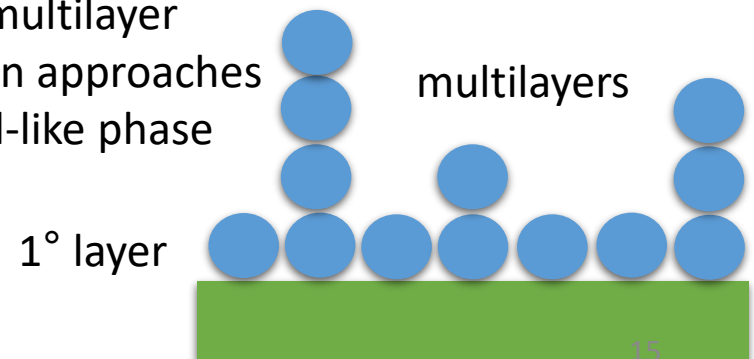
- 1) Heat of adsorption
- 2) Reversibility
- 3) Number of adsorbate layers

Physisorption

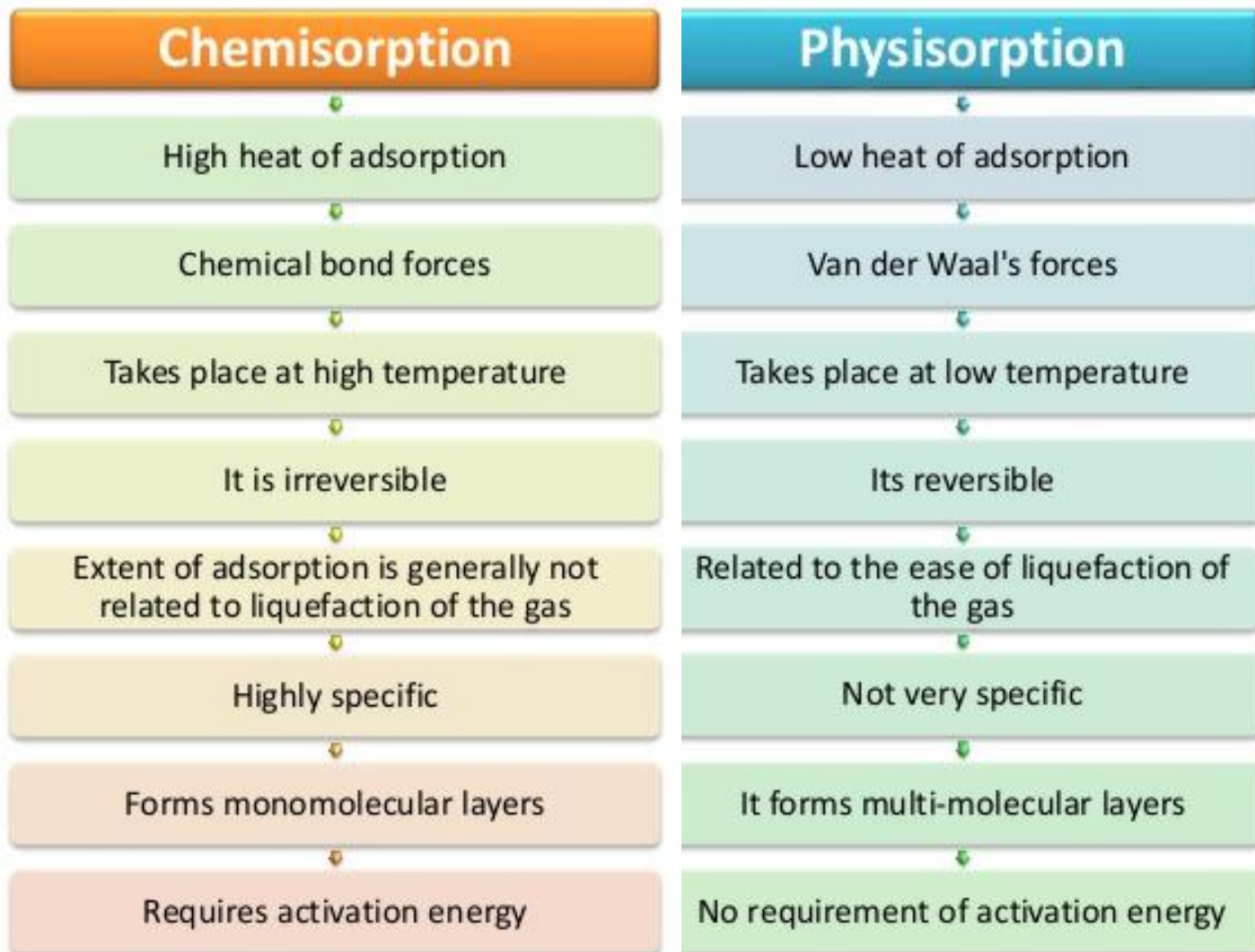
- 1) Usually small
- 2) Usually reversible
- 3) It forms multimolecular layers



The multilayer adsorption approaches a liquid-like phase



Chemisorption vs Physisorption



Chemisorption vs Physisorption

- a. Physisorption is a general phenomenon with a relatively low degree of specificity.
- b. Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to a monolayer. At high relative pressures, physisorption generally occurs as a multilayer.
- c. A physisorbed molecule keeps its identity and on desorption returns to the fluid phase in its original form. If a chemisorbed molecule undergoes reaction or dissociation, it loses its identity and cannot be recovered by desorption.
- d. The energy of chemisorption is the same order of magnitude as the energy change in a comparable chemical reaction. Physisorption is always exothermic, but the energy involved is generally not much larger than the energy of condensation of the adsorptive. However, it is appreciably enhanced when physisorption takes place in very narrow pores.
- e. An activation energy is often involved in chemisorption and at low temperature the system may not have sufficient thermal energy to attain thermodynamic equilibrium. Physisorption systems generally attain equilibrium fairly rapidly, but equilibration may be slow if the transport process is rate-determining.

- **Chemical adsorption involves true chemical bonding of the gas or vapor with the surface, indeed it is usually associated with an activation energy.**
- **Physical adsorption occurs whenever an absorbable gas (the adsorptive) is brought in contact with the surface of the solid adsorbent. It is suitable for surface area determinations**

Chemisorption vs Physisorption

Heat of adsorption

Physisorption < Chemisorption

- < 40 kJ/mol for Physisorption : similar to adsorbate heat of liquefaction
- > 80 kJ/mol for Chemisorption: approaching the value of chemical bonds

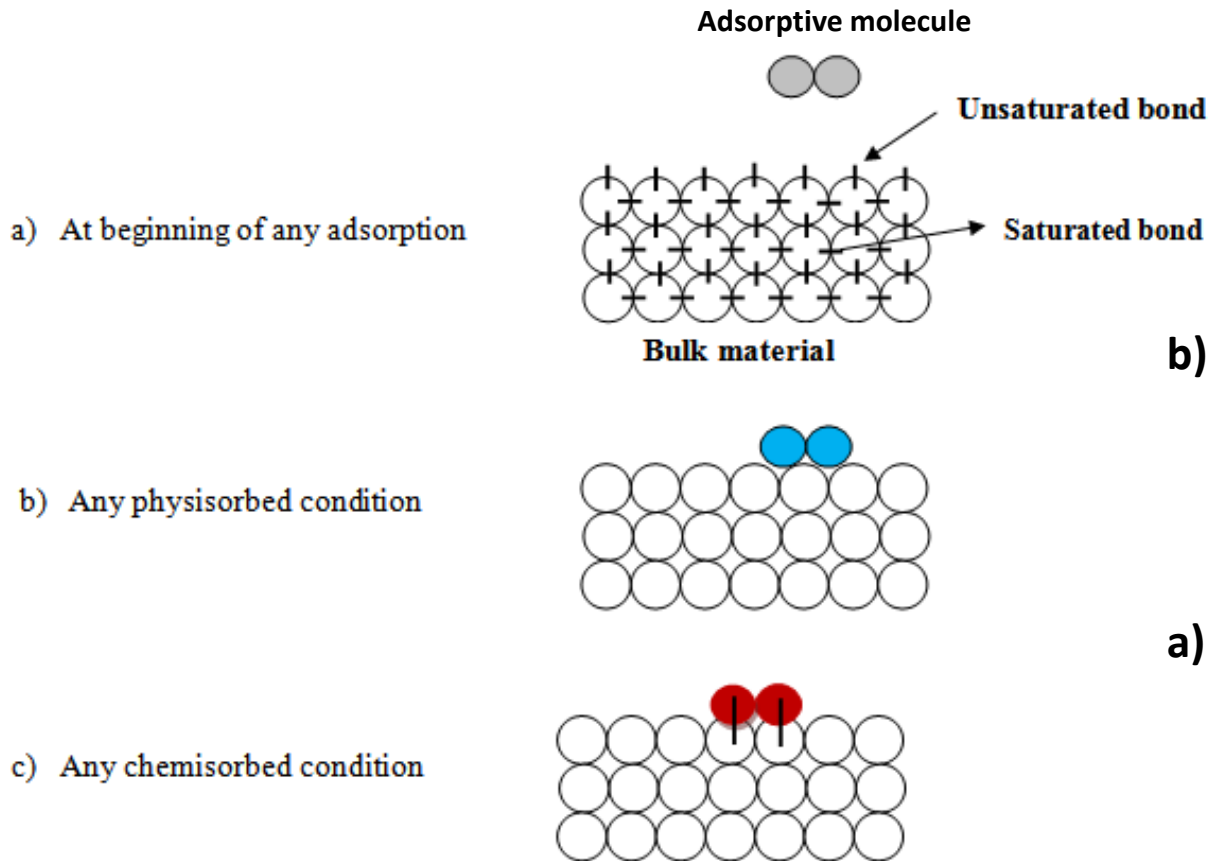
Reversibility

Physisorption > Chemisorption

- Physisorbed molecules can be desorbed by simply decreasing the p at the same T of adsorption
- Chemisorbed molecules require more drastic conditions to be desorbed (decrease the p and increase the T at the same time). The desorbed species can be different from the adsorbed ones!

Chemisorption vs Physisorption

Schematic representation of different adsorption processes



a) Adsorptive molecule approach any adsorbent surface under the influence of **attractive forces created by the unbalanced molecular forces** on adsorbent surfaces.

b) **Physisorbed molecules** on surface by van der Waals forces

a) **Weak bond formation** between adsorbate and adsorbent (**chemisorption**): adsorbate molecule are chemisorbed only on selected adsorbent surface sites.

Adsorption is a spontaneous process
($\Delta G < 0$).

Adsorption: an exothermic process

Upon adsorption:

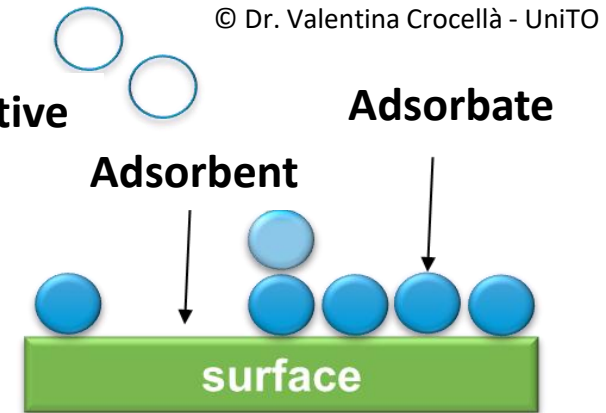
- The **entropy change of the adsorbate (ΔS_a)** is negative (the condensed state is more ordered than the gaseous state due to the loss of at least one degree of translational freedom).
- The **entropy of the adsorbent** remains essentially constant and certainly does not increase by more than the adsorbate entropy decreases.
- ΔS for the entire system is necessarily **negative**.
- The adsorption process is spontaneous: the spontaneity of the adsorption process requires that the **Gibbs free energy (ΔG)** also be a **negative quantity ($\Delta G < 0$)**.

The **enthalpy change (ΔH)** accompanying adsorption is **always negative**, indicating an **exothermic process**, as shown by:

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

However, some adsorption processes can be endothermic:

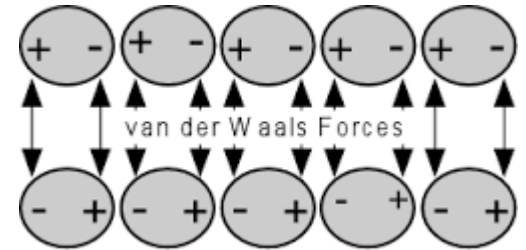
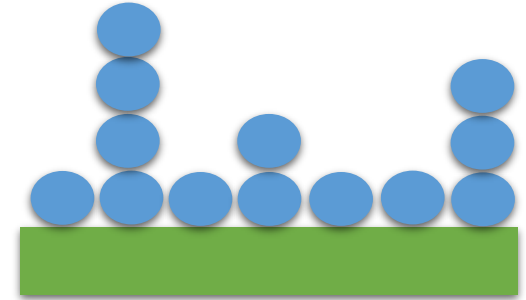
- Dissociative chemisorption
- Physisorption accompanied by swelling phenomena of the adsorbent



Physical Adsorption Forces

The **van der Waals forces** (intermolecular forces due to slight attraction between oppositely charged regions of nearby molecules) are responsible for the occurrence of **physisorption**:

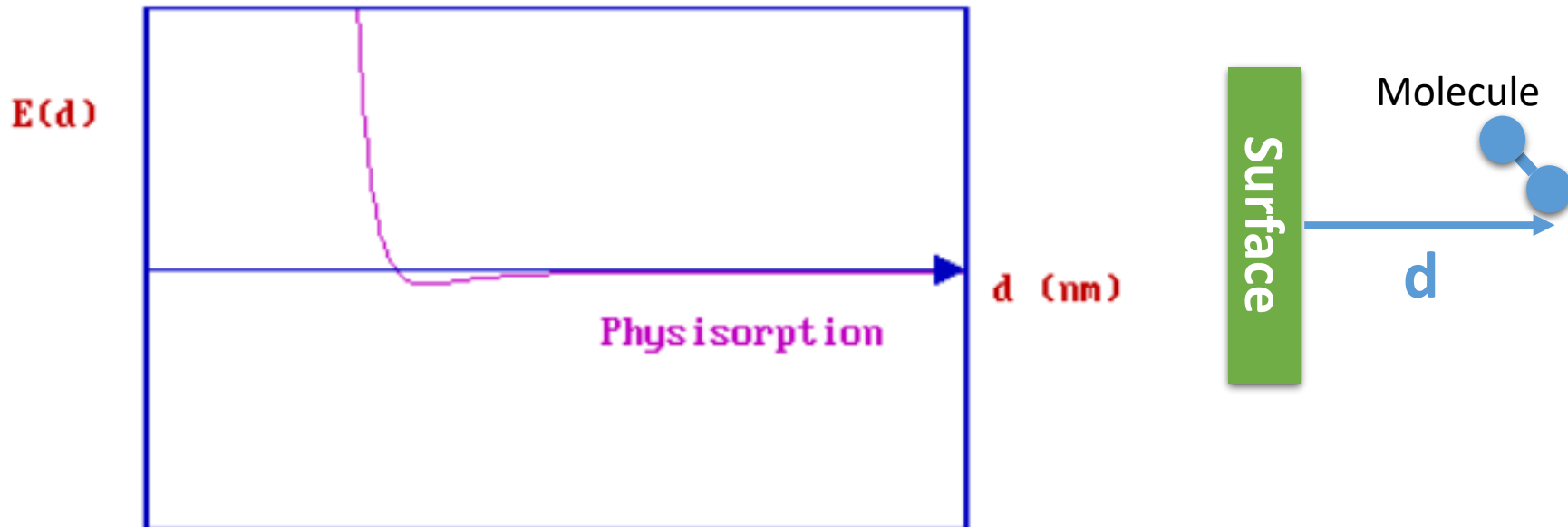
- **Dispersion forces:** these forces are present regardless of the nature of other interactions and often account for the major part of the adsorptive-adsorbent potential energy.
- **Ion-dipole:** an ionic solid and electrically neutral but polar adsorptive.
- **Ion-induced dipole:** a polar solid and polarizable adsorptive.
- **Dipole-dipole:** a polar solid and polar adsorptive.
- **Quadrupole interactions:** symmetrical molecules, such as N_2 and CO_2 , possess no dipole moment, but have a quadrupole (e.g. $^-O-C^{++}-O^-$), which can lead to interactions with polar surfaces.



HOW DO GECKOS DEFY GRAVITY?

Physical Adsorption

Potential energy profile of a physisorption process:



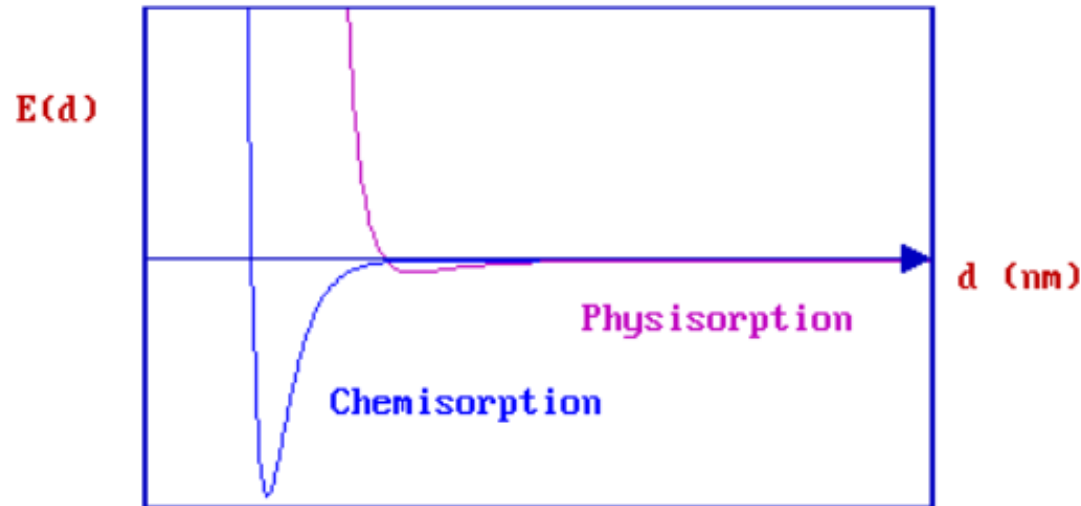
The weak van der Waals forces give rise to a **shallow minimum in the PE** curve at a relatively large distance from the surface (typically $d > 0.3\text{nm}$), before the strong repulsive forces arising from electron density overlap cause a rapid increase in the total energy.

The process is not activated and the kinetics of physisorption are fast

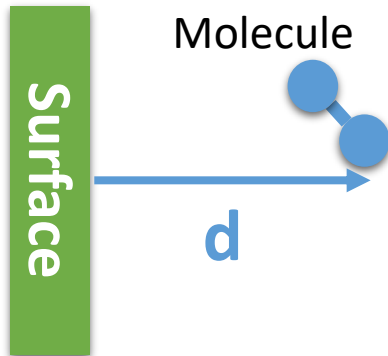
Chemical Adsorption

During chemisorption **chemical bond formation** between adsorbate and adsorbent occurs

Potential energy curve of a non activated molecular chemisorption process:



- The weak physical adsorption forces are present to varying degrees in all adsorbate/adsorbent systems.
- In case of chemisorption, the PE curve is dominated by a much deeper minimum at shorter values of d .

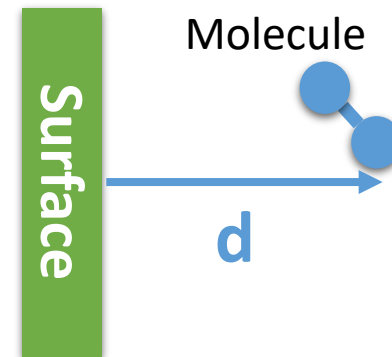
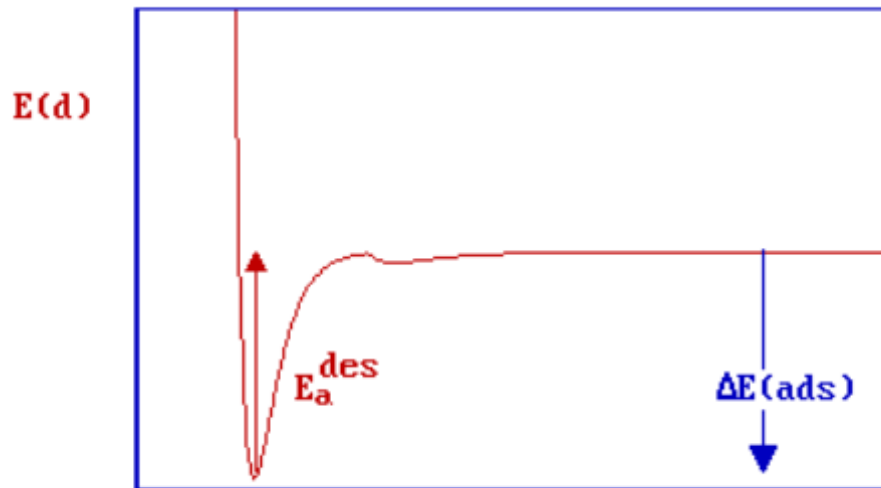


The PE curve for any real molecule capable of undergoing chemisorption is best described by **a combination of the two curves**, with a curve crossing at the point at which chemisorption forces begin to dominate over those arising from physisorption.

Chemical Adsorption

During chemisorption **chemical bond formation** between adsorbate and adsorbent occurs

Potential energy curve of a non activated molecular chemisorption process:

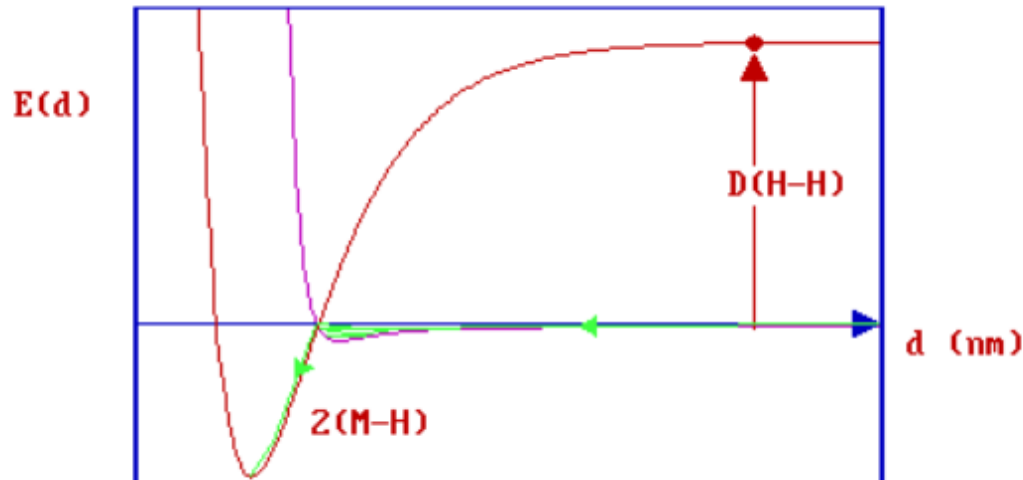


- There is no barrier to be overcome in the adsorption process and there is no activation energy of adsorption.
- There is a significant barrier to the reverse, desorption process - the red arrow in the diagram represents the activation energy for desorption.

Chemical Adsorption

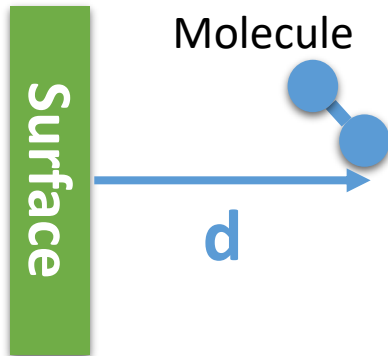
During chemisorption **chemical bond formation** between adsorbate and adsorbent occurs

Potential energy curve of an activated dissociative chemisorption process:



Example..... $H_2 + M \rightarrow 2HM$

- When the distance d is large, the H_2 molecule is completely isolated from the surface.
- A substantial amount of energy is necessary to cause its dissociation: the energy downpayment associated with breaking the H-H bond is too high.

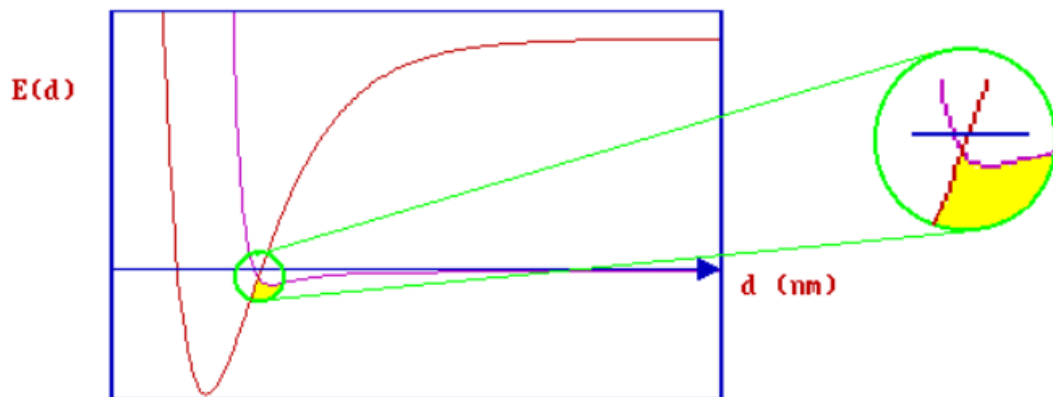


The H_2 molecule may first undergoes transient physisorption (a hydrogen molecule will initially approach the surface along the physisorption curve), a state from which it can then either desorb back as a molecule into the gas phase or cross over the barrier into the dissociated state for chemisorption.

The process is activated

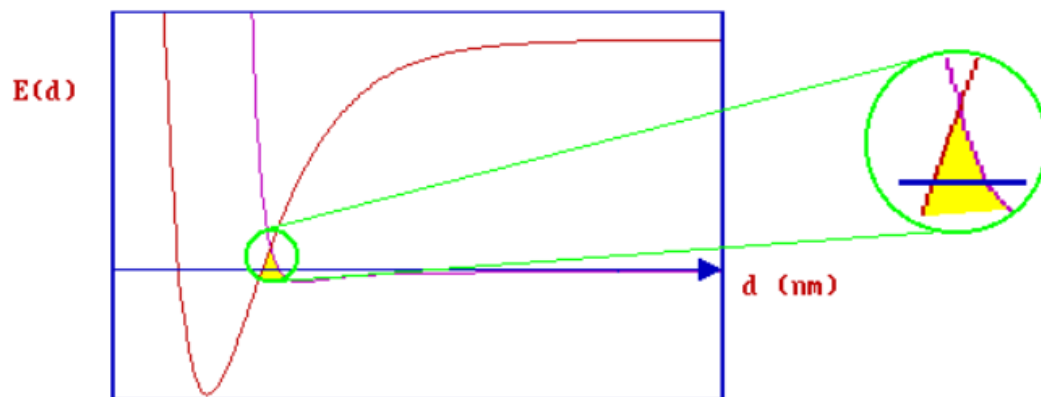
Chemical Adsorption

This dissociative adsorption process is strongly influenced by the position of the **crossing point of the two curves** (molecular physisorption vs dissociative chemisorption): small shifts in the position of the two curves can significantly alter the barrier to chemisorption.



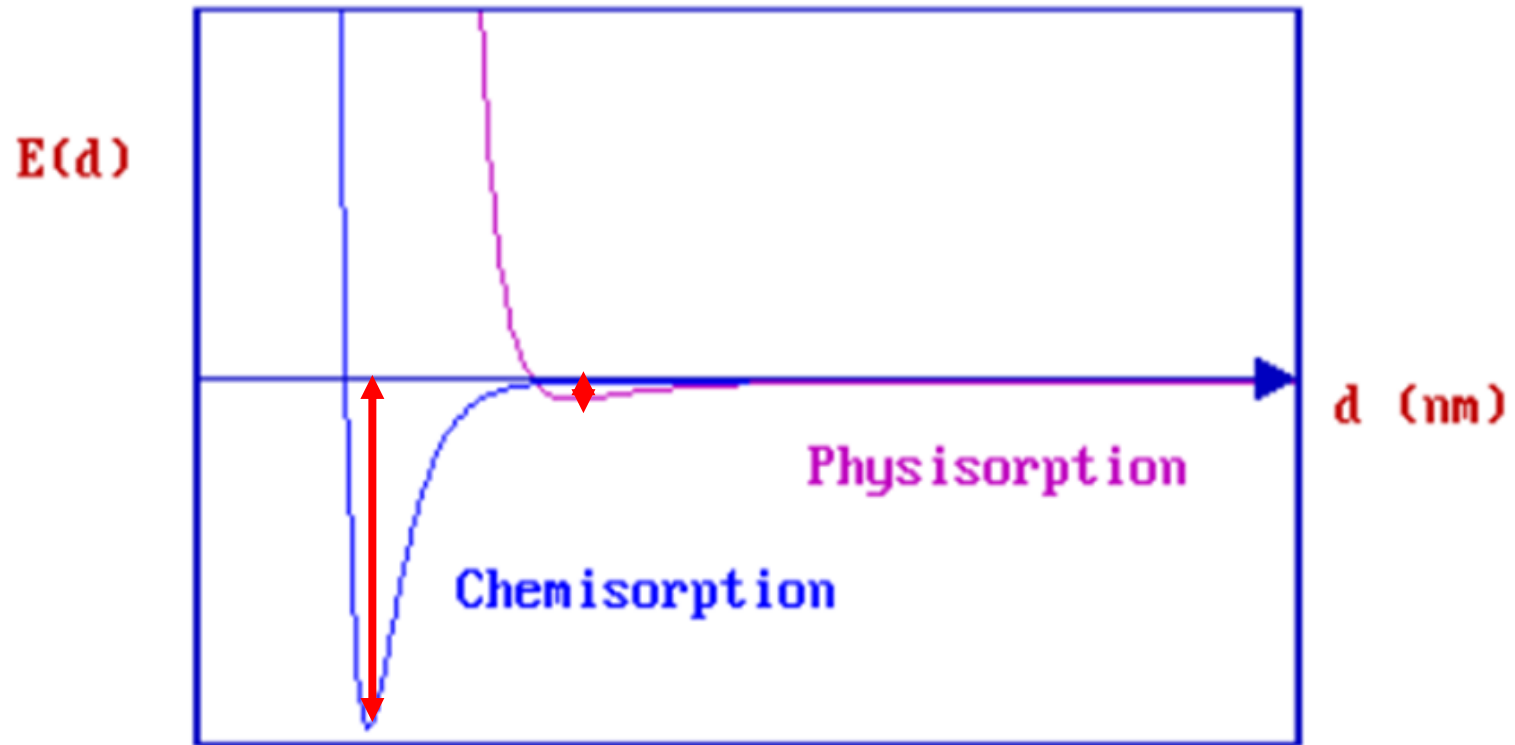
No direct activation barrier to dissociative adsorption - the curve crossing is below the initial "zero energy" of the system.

The curve crossing is above the initial "zero energy" of the system: **substantial barrier to chemisorption**. Such a barrier has a major influence on the kinetics of adsorption.



The process is activated

Chemisorption vs Physisorption



Physisorption:

- Well depth: few meV. The **weak van der Waals attractions** give rise to **shallow potential wells** with energy of few meV (10-100).
- Well position: 0.3 - 1 nm

Chemisorption:

- Well depth: several eV. The **chemical bond formation** between adsorbate and adsorbent gives rise to **deep chemisorption potential well**.
- Well position: 0.1 -0.3 nm