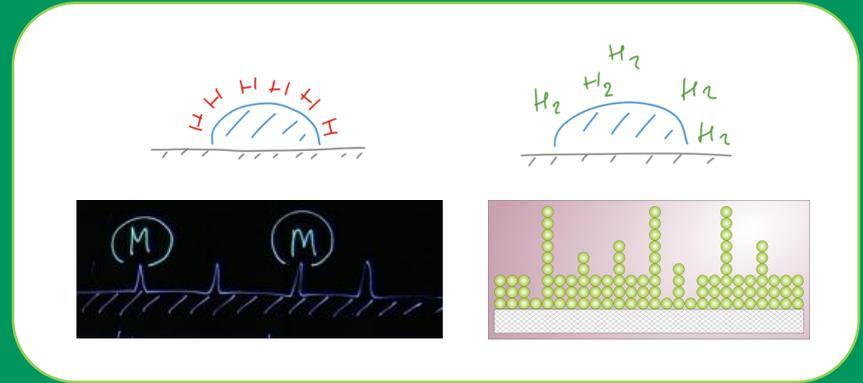


CHEM-E1130 Catalysis

Catalyst characterization 1: Adsorption methods



A''

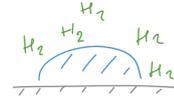
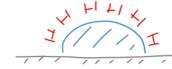
Aalto University
School of Chemical
Engineering

Prof. Riikka Puurunen

21.1.2018

Contents

- Introduction to adsorption-related concepts
 - Adsorption isotherms: experimental
 - Model adsorption isotherms
 - Physisorption isotherms: measurement and analysis
 - Chemisorption isotherms: measurement and analysis
- + Take-home message



S_{BET}
 D

+ 21.1.2019: Catalysis Glossary group works initiated

Learning outcomes (modified)

After the course the students are able to:

1. give the definition of catalysis and **describe concepts** related to heterogeneous and homogeneous catalysts
2. explain steps and methods in catalyst preparation
3. **describe** and **apply** selected **catalyst characterization methods**
4. explain why and how catalysts deactivate and how catalyst deactivation can be postponed or prevented
5. give examples of where catalysts are applied
6. recognize challenges potentially solvable by catalytic reactions

Note, Prof. Puurunen, 7.1.2019: These learning outcomes have not yet been accepted for the course. Students are welcome to comment on these proposed learning outcomes. We will in practice follow these in the course in 2018-2019

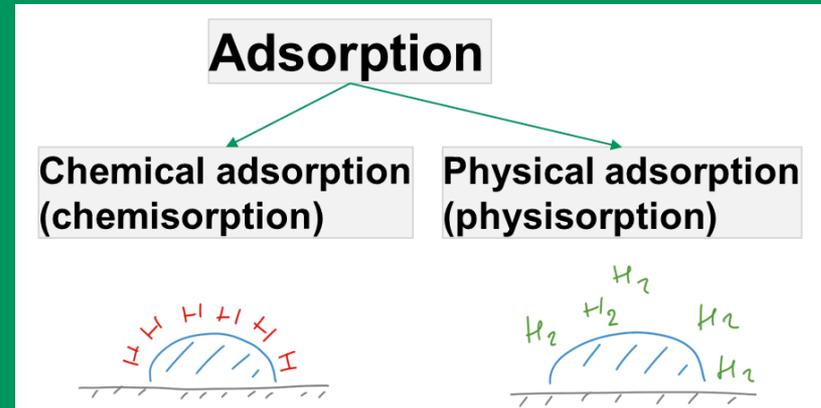
Some feedback in MyCo Quiz 1:

- “I like the way this course has been arranged! I think I will learn a lot during this course.”
- “some quite interesting points of view that I never had considered were presented during the lecture (e.g the carbon dioxide thing), these sorts of things are rarely ever brought up on courses, so thank you for that!!”
- “You can clearly see that the lecturer has invested a lot of time and effort into this course which increases my motivation towards the course. This is a nice change from many other courses ... ”
- Many positive responses on the Quizzes & lecture capture
- (One person) “I wish the quiz dead lines were put a little bit further.”

+ much more → Thank You!

Feedback will help to develop the course further

Introduction to adsorption-related concepts

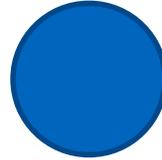


Adsorption

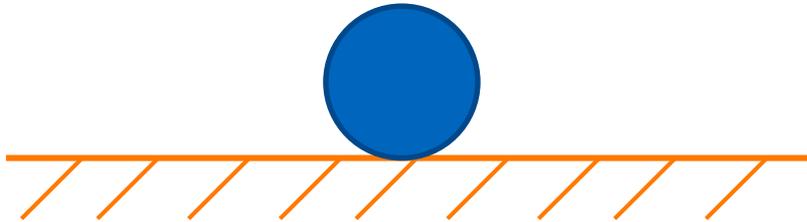
- “In general, adsorption is defined as the **enrichment of molecules, atoms or ions in the vicinity of an interface.**
- In the case of gas/solid systems, **adsorption takes place in the vicinity of the solid surface and outside the solid structure.**
- The material in the adsorbed state is known as the **adsorbate**, while the **adsorptive** is the same component in the fluid phase.
- The **adsorption space** is the space occupied by the **adsorbate.**”
- + adsorbent!

Terminology - IUPAC

Adsorbate = material in the adsorbed state



Adsorptive = same component (adsorbate) in the fluid phase as (sometimes also: **adsorbate gas**)



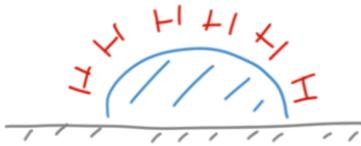
Adsorbent = solid that provides a surface for adsorption

Adsorption can be physical or chemical

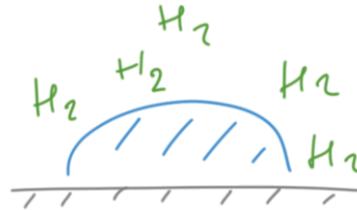
- **Physisorption** is a general phenomenon: it occurs whenever an adsorbable gas (the adsorptive) is brought into contact with the surface of a solid (the adsorbent). **The intermolecular forces involved are of the same kind as those responsible for the imperfection of real gases and the condensation of vapours. ...**
- In **chemisorption** ..., the intermolecular forces involved lead to the **formation of chemical bonds.**”

Adsorption

**Chemical adsorption
(chemisorption)**



**Physical adsorption
(physisorption)**



Absorption

- “When the molecules of the adsorptive penetrate the surface layer and enter the structure of the bulk solid, the term **absorption** is used.
- **It is sometimes difficult or impossible to distinguish between adsorption and absorption:** it is then convenient to use the wider term sorption which embraces both phenomena, and to use the derived terms **sorbent, sorbate and sorptive.**”

Sorption

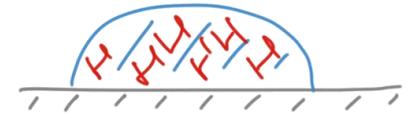
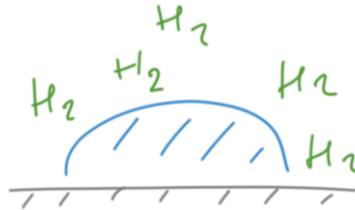
Adsorption

Absorption

**Chemical adsorption
(chemisorption)**



**Physical adsorption
(physisorption)**



Sorption

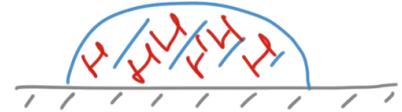
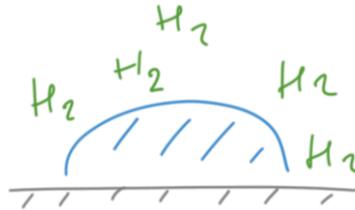
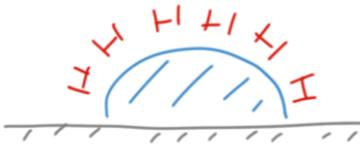
(Ion exchange)

Adsorption

Absorption

Chemical adsorption
(chemisorption)

Physical adsorption
(physisorption)



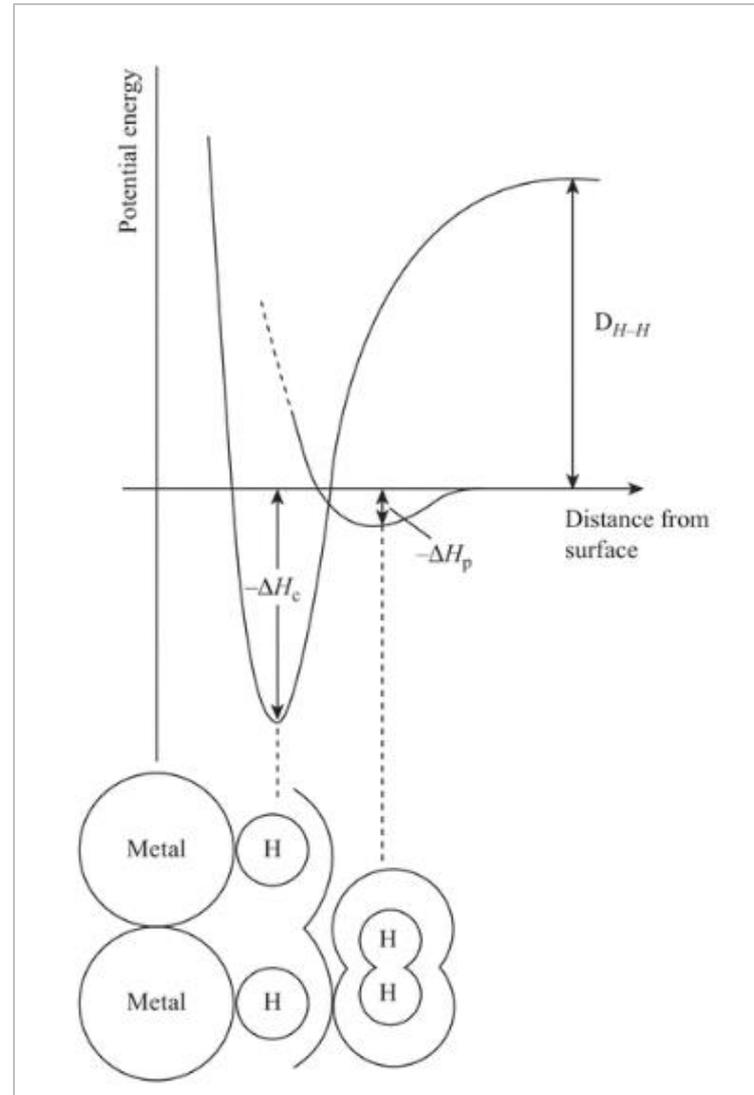
Surfaces and Adsorption

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Lennard-Jones potential energy diagram

Julian Ross: Heterogeneous Catalysis - Fundamentals and Applications, © Elsevier 2012. Chapter 2: Surfaces and Adsorption, [link](#), Figure 2.7.

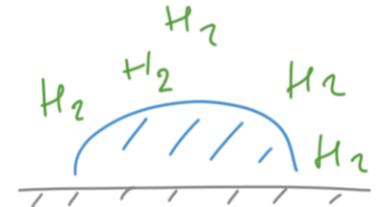
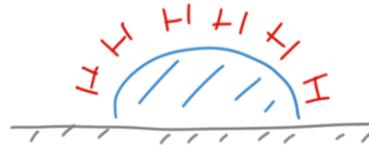


Chemisorption

- chemically specific
- changes in electronic state
- reversible/irreversible

Physisorption

- non-specific
- minimal electronic interaction
- reversible



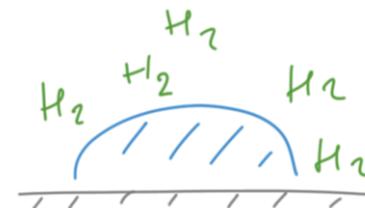
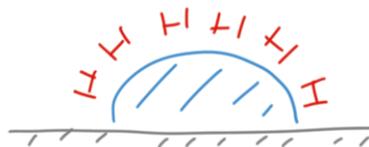
http://old.iupac.org/reports/2001/colloid_2001/manual_of_s_and_t/node16.html

Chemisorption

- chemically specific
- changes in electronic state
- reversible/irreversible
- chemisorption energy as for a chemical reaction (exothermic/endothemic)
- may involve an activation energy

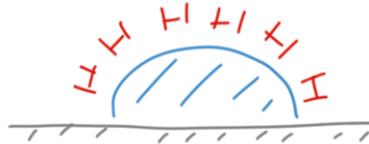
Physisorption

- non-specific
- minimal electronic interaction
- reversible
- adsorption energy exothermic and (higher or) similar to the energy of condensation
- non-activated



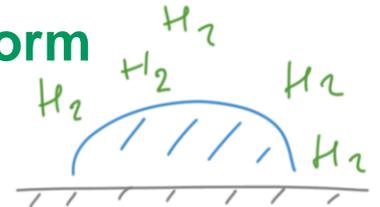
Chemisorption

- chemically specific
- changes in electronic state
- reversible/irreversible
- chemisorption energy as for a chemical reaction (exothermic/endothemic)
- may involve an activation energy
- for “large” activation energies (“activated adsorption”), true equilibrium may be achieved slowly
- **monolayer adsorption**

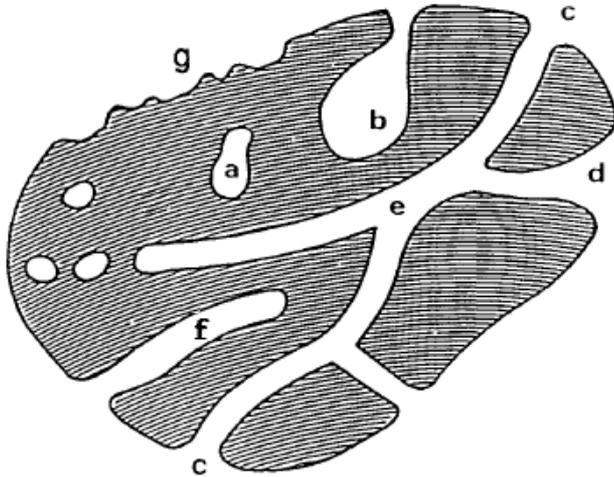


Physisorption

- non-specific
- minimal electronic interaction
- reversible
- adsorption energy exothermic and (higher or) similar to the energy of condensation
- non-activated
- equilibrium established
- chemical nature of the adsorbate & adsorbent ~not altered
- **multilayers may form**



Classification of pore sizes (IUPAC): micro-, meso-, macro-



<what is the original source for this classic figure?>

- pores with widths exceeding about 50 nm are called **macropores**;
- pores of widths between 2 nm and 50 nm are called **mesopores**;
- pores with widths not exceeding about 2 nm are called **micropores**.”

Picture:

- a = closed pores
- b,c,d,e,f = open pores (open only from one end b,f or open from both ends c,d)
- Shape of pores can vary

Adsorption isotherms: experimental

Adsorption isotherm (IUPAC)

- “The relation, at constant temperature, between the amount adsorbed ... and the equilibrium pressure of the gas is known as the adsorption isotherm.”

Experimental isotherms, examples

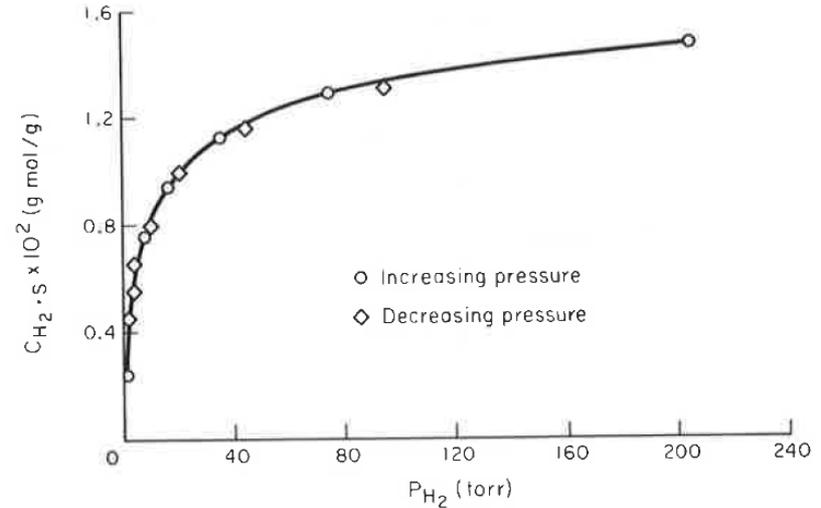
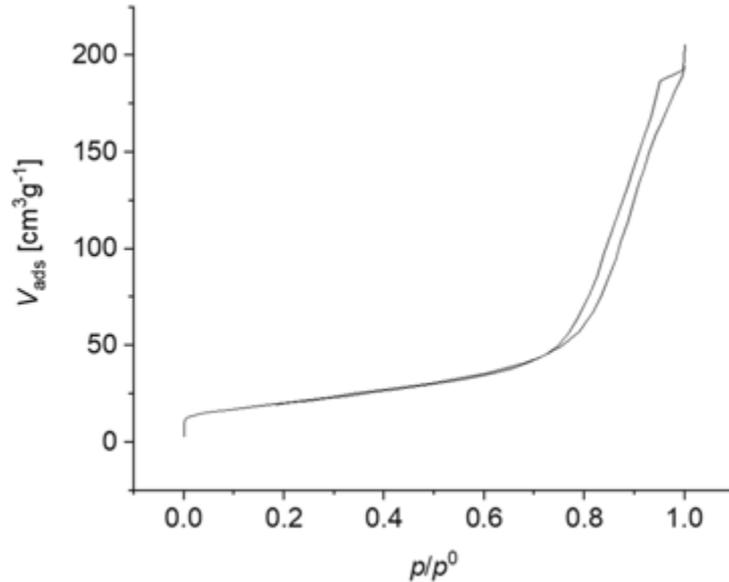


Figure 6-5 Adsorption of hydrogen on copper.

N_2 adsorption on ZrO_2 at 77 K

Voigt et al., Topics in Catalysis (2019),

<https://dx.doi.org/10.1007/s11244-019-01133-w>

H_2 adsorption on Cu at 25°C

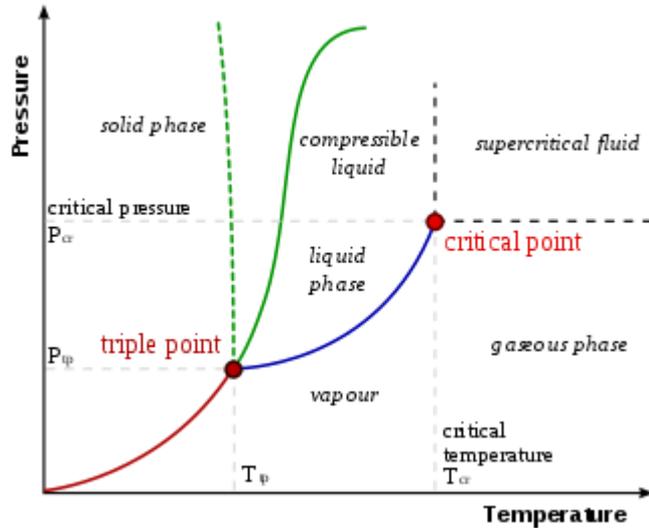
H. Scott Fogler, Elements of Chemical Reaction Engineering, 2nd Edition, Prentice Hall International Editions, 1992.

Pressure scale note, p & p/p°

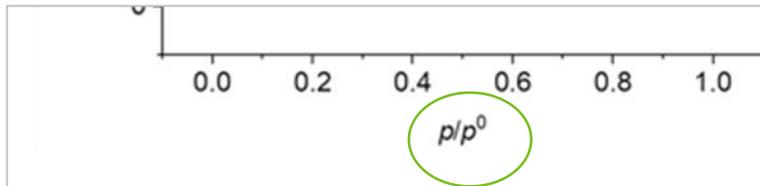
“The way the pressure is plotted depends on whether the adsorption is carried out at a temperature **under or above the critical temperature of the adsorptive**.

- At an adsorption temperature below the critical point, one usually adopts the **relative pressure p/p°** , where **p is the equilibrium pressure** and **p° the saturation vapour pressure at the adsorption temperature**.
- **At an adsorption temperature above the critical one, where there is no condensation and no p° exists, one must necessarily use the equilibrium pressure p .**”

Thommes et al., Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 2015; 87(9-10): 1051–1069, <https://doi.org/10.1515/pac-2014-1117>.



Substance ^{[14][15]} ♦	Critical temperature ♦	Critical pressure (absolute) ♦
Argon	-122.4 °C (150.8 K)	48.1 atm (4,870 kPa)
Hydrogen	-239.95 °C (33.20 K)	12.8 atm (1,300 kPa)
Krypton	-63.8 °C (209.3 K)	54.3 atm (5,500 kPa)
Methane (CH ₄)	-82.3 °C (190.8 K)	45.79 atm (4,640 kPa)
Nitrogen	-146.9 °C (126.2 K)	33.5 atm (3,390 kPa)
Oxygen	-118.6 °C (154.6 K)	49.8 atm (5,050 kPa)



N_2 adsorption on ZrO_2 at 77 K

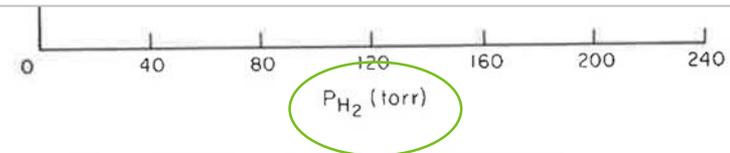


Figure 6-5 Adsorption of hydrogen on copper.

H_2 adsorption on Cu at 25°C

Liquid nitrogen boiling temperature

IUPAC classification of physisorption isotherms (refined, 2015)

Thommes et al., Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 2015; 87(9-10): 1051–1069, <https://doi.org/10.1515/pac-2014-1117>.

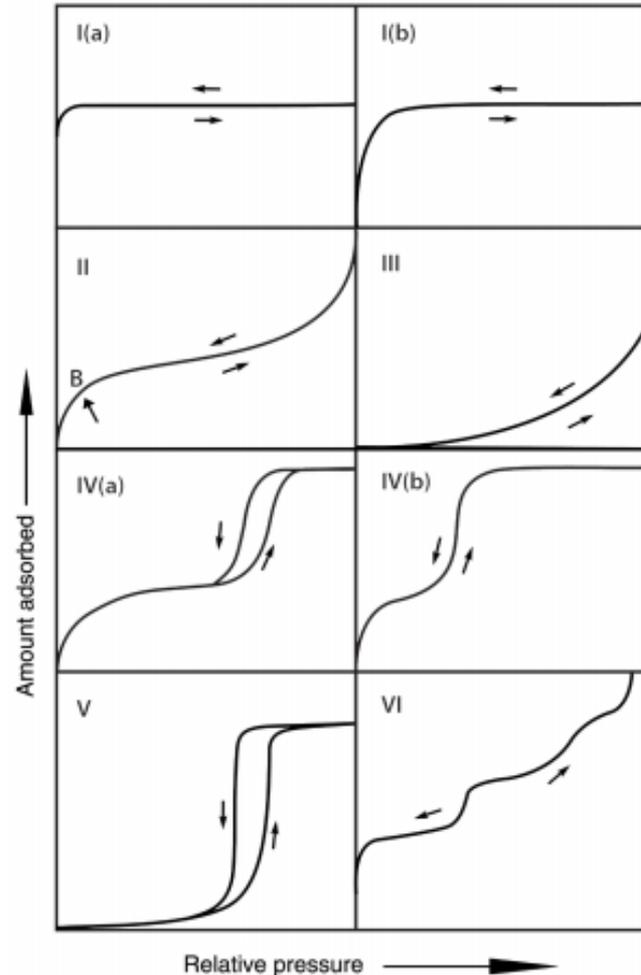
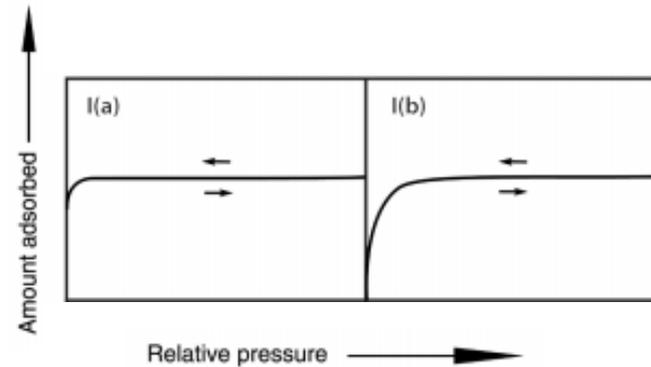


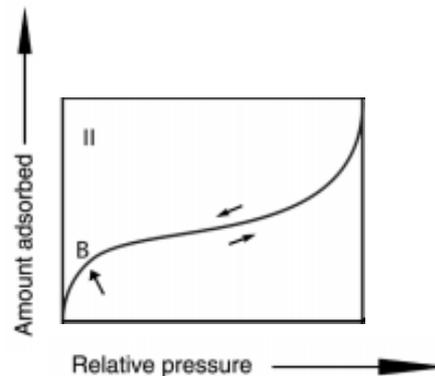
Fig. 2: Classification of physisorption isotherms.

IUPAC Type I



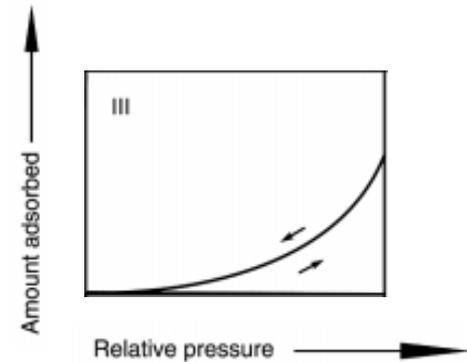
Reversible Type I isotherms are given by microporous solids having relatively small external surfaces (e.g., some activated carbons, molecular sieve zeolites and certain porous oxides). A Type I isotherm is concave to the p/p^0 axis and the amount adsorbed approaches a limiting value. This limiting uptake is governed by the accessible micropore volume rather than by the internal surface area. A steep uptake at very low p/p^0 is due to enhanced adsorbent-adsorptive interactions in narrow micropores (micropores of molecular dimensions), resulting in micropore filling at very low p/p^0 . For nitrogen and argon adsorption at 77 K and 87 K, Type I(a) isotherms are given by microporous materials having mainly narrow micropores (of width $< \sim 1$ nm); Type I(b) isotherms are found with materials having pore size distributions over a broader range including wider micropores and possibly narrow mesopores ($< \sim 2.5$ nm).

IUPAC Type II classification



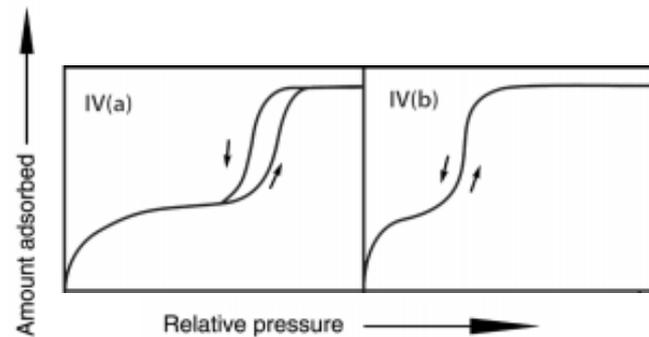
Reversible Type II isotherms are given by the physisorption of most gases on nonporous or macroporous adsorbents. The shape is the result of unrestricted monolayer-multilayer adsorption up to high p/p^0 . If the knee is sharp, Point B – the beginning of the middle almost linear section – usually corresponds 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. The thickness of the adsorbed multilayer generally appears to increase without limit when $p/p^0 = 1$.

IUPAC Type III



In the case of a Type III isotherm, there is no Point B and therefore no identifiable monolayer formation; the adsorbent-adsorbate interactions are now relatively weak and the adsorbed molecules are clustered around the most favorable 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 $p/p^0 = 1$).

IUPAC Type IV



Type IV isotherms are given by mesoporous adsorbents (e.g., many oxide gels, industrial adsorbents and mesoporous molecular sieves). The adsorption behaviour in mesopores is determined by the adsorbent-adsorptive interactions and also by the interactions between the molecules in the condensed state. In this case, the initial monolayer-multilayer adsorption on the mesopore walls, which takes the same path as the corresponding part of a Type II isotherm, is followed by pore condensation. As already mentioned in Section 2, pore condensation is the phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure p less than the saturation pressure p^0 of the bulk liquid [6, 7]. A typical feature of Type IV isotherms is a final saturation plateau, of variable length (sometimes reduced to a mere inflexion point).

In the case of a Type IVa isotherm, capillary condensation is accompanied by hysteresis. This occurs when the pore width exceeds a certain critical width, which is dependent on the adsorption system and temperature (e.g., for nitrogen and argon adsorption in cylindrical pores at 77 K and 87 K, respectively, hysteresis starts to occur for pores wider than ~ 4 nm) [4, 6, 8]. With adsorbents having mesopores of smaller width, completely reversible Type IVb isotherms are observed. In principle, Type IVb isotherms are also given by conical and cylindrical mesopores that are closed at the tapered end.

Type IV: Hysteresis comes from condensation in mesopores

Kelvin equation in the Ross book

$$\ln P_0/P' = 2\gamma V \cdot \cos\phi / rRT$$

γ is the surface tension of the liquid
(8.72 mN/m for N₂)

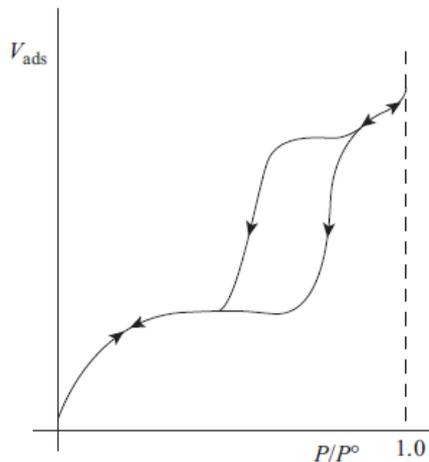


Figure 2.18:

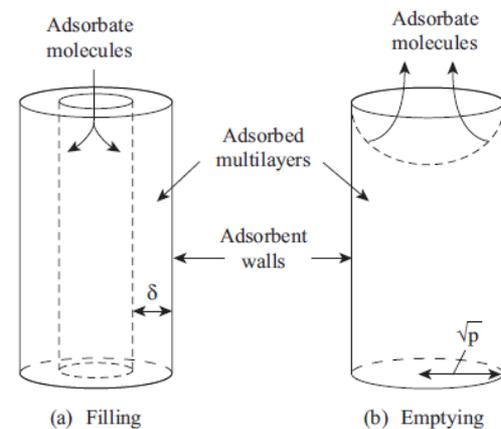
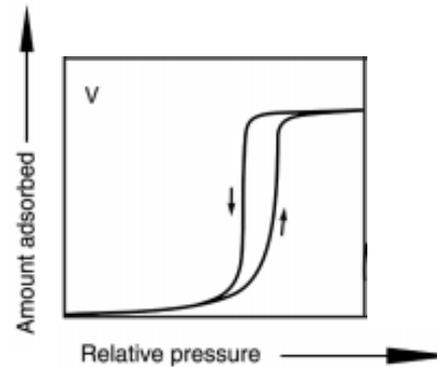


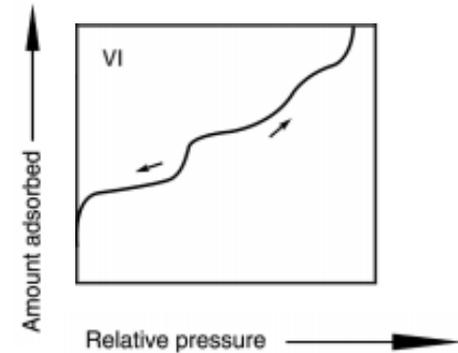
Figure 2.19:

IUPAC Type V



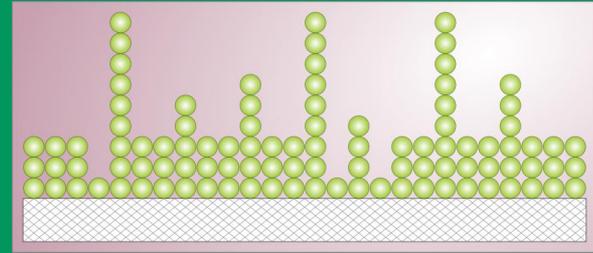
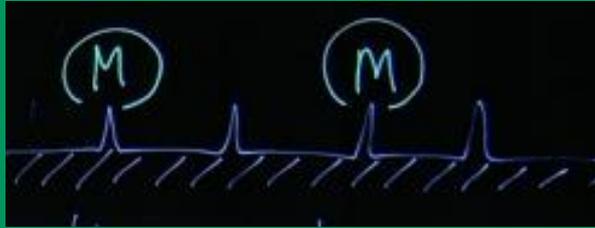
In the low p/p^0 range, the Type V isotherm shape is very similar to that of Type III and this can be attributed to relatively weak adsorbent–adsorbate interactions. At higher p/p^0 , molecular clustering is followed by pore filling. For instance, Type V isotherms are observed for water adsorption on hydrophobic microporous and mesoporous adsorbents.

IUPAC Type VI



The reversible stepwise Type VI isotherm is representative of layer-by-layer adsorption on a highly uniform nonporous surface. The step-height now represents the capacity for each adsorbed layer, while the sharpness of the step is dependent on the system and the temperature. Amongst the best examples of Type VI isotherms are those obtained with argon or krypton at low temperature on graphitised carbon blacks.

Model adsorption isotherms





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Review

Insights into the modeling of adsorption isotherm systems

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ABSTRACT

Concern about environmental protection has increased over the years from a global viewpoint. To date, the prevalence of adsorption separation in the environmental chemistry remains an aesthetic attention and consideration abroad the nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions. With the renaissance of isotherms modeling, there has been a steadily growing interest in this research field. Confirming the assertion, this paper presents a state of art review of adsorption isotherms modeling, its fundamental characteristics and mathematical derivations. Moreover, the key advance of the error functions, its utilization principles together with the comparisons of linearized and non-linearized isotherm models have been highlighted and discussed. Conclusively, the expanding of the nonlinear isotherms represents a potentially viable and powerful tool, leading to the superior improvement in the area of adsorption science.

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Model isotherms

- **Langmuir isotherm**

- Core reference isotherm
- May limiting assumptions

$$\frac{V}{V_m} = \frac{C_{m.s}}{C_t} = \frac{Kp}{1 + Kp} = \Theta$$

- **BET isotherm**

- Brunauer-Emmet-Teller
- Extension of Langmuir isotherm to multilayer adsorption

$$V_{\text{ads}} = \frac{V_m c P}{(P_0 - P) \{1 + (c - 1)P/P_0\}}$$

- Temkin, Freundlich, ...

Derivation of Langmuir adsorption isotherm for single-site adsorption

<https://aalto.cloud.panopto.eu/Panopto/Pages/Viewer.aspx?id=2d56ca40-7ab8-401e-80e9-a9d100a13c1d>

Derivation largely follows the Scott Fogler Elements of Chemical Reaction Engineering presentation

DERIVATION OF LANGMUIR ISOTHERM FOR SINGLE-SITE ADSORPTION

example isotherm

reaction equation:
 $M + S \rightleftharpoons M \cdot S$

site balance

$$C_t = C_v + C_{M \cdot S}$$

total sites vacant sites sites occupied by M

S: active site
M: unit of substance

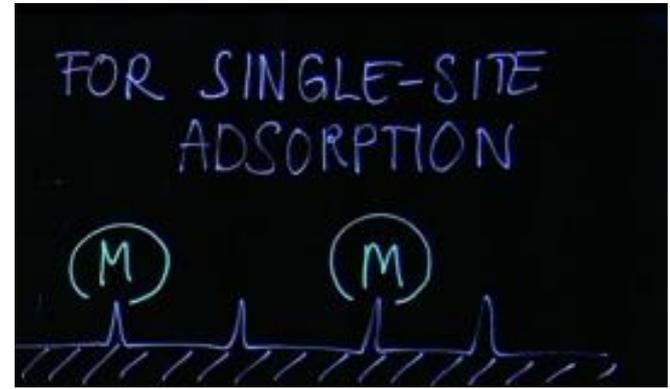
Puumanen, 10.1.2019

Langmuir isotherm: monolayer adsorption

$$\frac{V}{V_m} = \frac{C_{M.S}}{C_t} = \frac{Kp}{1 + Kp} = \Theta$$

Assumptions

- Flat surface
- Adsorption sites energetically identical
- Adsorbed species do not interact
- Monolayer adsorption



$$K = \frac{\vec{k}}{\underset{\leftarrow}{k}} \quad C_t = C_v + C_{M.S}$$

Equilibrium conditions
Constant temperature

Langmuir isotherm

Langmuir's theory offered a simple mechanism of attack of the gas molecules on the catalyst surface.

To simplify the mathematical treatment, Langmuir assumed that the metallic surface was uniform and formed by an array of sites all energetically identical and non-interacting, which would adsorb just one molecule from the gas phase. He also assumed that the adsorbed molecules did not react together and that they formed at most a single monolayer. The sites involved are normally considered active sites. The Langmuir adsorption isotherm results from this model. With these simplifications, the theory assumed a connection at constant temperature between the monolayer fraction θ of adsorbed gas molecules at pressure P , according to the famous relationship

$$\theta = \frac{\alpha \cdot P}{1 + \alpha \cdot P} \quad (2.1)$$

where α is a constant characteristic of the bond energy between the gas and the substrate, representing the ratio between the equilibrium constants of the direct (adsorption) and inverse (desorption) reactions. The first approximation α is inversely proportional to temperature. The curves of θ as a function of P are known as Langmuir's adsorption isotherms.

In different places
written with
different symbols



Limitations of Langmuir model

Langmuir was already aware that the assumption of identical and non-interacting sites was an approximation that would not hold for real surfaces, when he wrote (Langmuir, 1922):

Most finely divided catalysts must have structures of great complexity. In order to simplify our theoretical consideration of reactions at surfaces, let us confine our attention to reactions on plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies. In general, we should look upon the surface as consisting of a checkerboard.

Zecchina & Califano, The Development of Catalysis: A History of Key Processes and Personas in Catalytic Science and Technology, Wiley Online Library, <http://dx.doi.org/10.1002/9781119181286>, Copyright © 2017 by John Wiley & Sons.

Despite its obvious limitations, the Langmuir adsorption model is frequently used e.g. in the fields of

- chemical reaction engineering and
- atomic layer deposition*

LANGMUIR

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VIRTUAL ISSUE

100TH ANNIVERSARY OF THE LANGMUIR ISOTHERM: Celebrating Ongoing Discoveries at Interfaces

LANGMUIR

This virtual issue celebrates the remarkable creativity of Irving Langmuir, along with important advancements to the continuously evolving field of interface science published in our journal of the same name. Irving Langmuir's 1932 Nobel Prize in Chemistry was awarded for his discoveries and investigations in surface chemistry, however he is known for many fundamental and practical advances as developed during his 41 year research career at General Electric. Two of Irving Langmuir's papers are included in this issue: a work on monolayers at the air/water interface, and the publication, 100 years ago, in which the isotherm is reported. The journal *Langmuir*, started in 1985, continues to promote fundamental advances in interface science. In the spirit of Langmuir, a few papers representing the breadth of ideas and discoveries at the interface from monolayers to colloids have been selected. Given the > 43,300 articles published in the journal to date, it is impossible for this selection to fully represent the insight, ingenuity and inspiration reported in *Langmuir*. It is simply hoped that the reader will appreciate the variety.

Editorial

100th Anniversary of the Langmuir Isotherm: Celebrating ongoing Discoveries at Interfaces

Joseph B. Schlenoff

DOI: 10.1021/acs.langmuir.8b03558

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ACS
journal:
Langmuir

Virtual issue:

<https://pubs.acs.org/page/langd5/vi/la-Langmuir100>

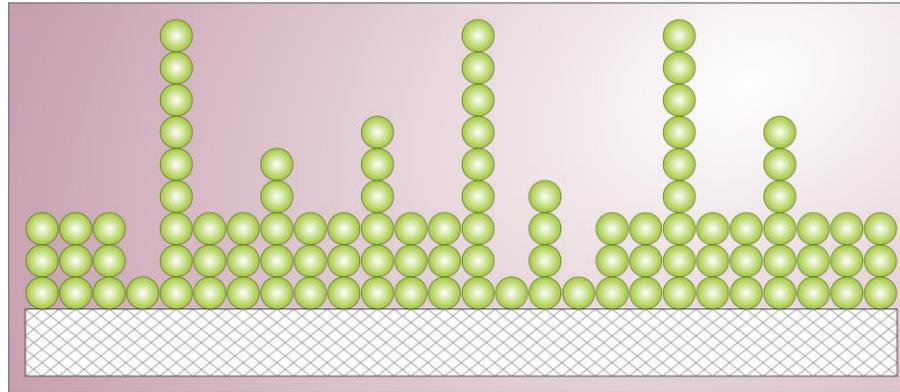
Also one article
by Puurunen in
Langmuir:

<https://dx.doi.org/10.1021/acs.langmuir.6b03007>

Extension of Langmuir isotherm to allow multilayers: BET isotherm

Additional hypotheses:

1. gas molecules physically adsorb on a solid in layers infinitely;
2. gas molecules only interact with adjacent layers; and
3. the Langmuir theory can be applied to each layer.



https://en.wikipedia.org/wiki/BET_theory, accessed 19.1.2019
https://en.wikipedia.org/wiki/BET_theory#/media/File:BET_Multilayer_Adsorption.svg

Physisorption isotherms

BET isotherm

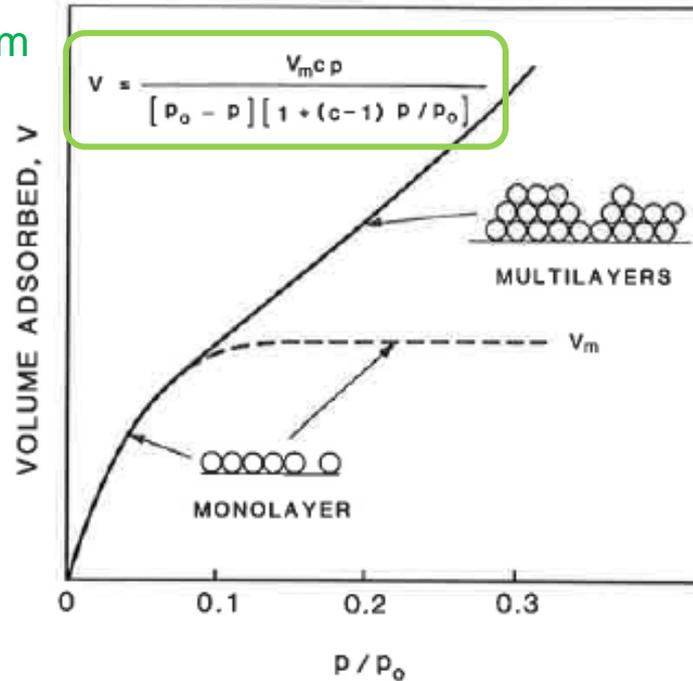


Figure 7.9. Typical isotherm for physical adsorption.

We will skip the derivation in CHEM-E1130

You can find good derivations in the literature, e.g.:

- https://nptel.ac.in/courses/103104045/pdf_version/lecture26.pdf#page9
- **Wikipedia**
- Surely many textbooks (if you find links, you can give a hint)

BET isotherm was a breakthrough

Finding V_M by fitting equation (7.4) is impractical, since it is valid in such a small region. Early workers attempted to estimate the monolayer graphically, with resulting imprecision and irreproducibility. The BET equation was a breakthrough in catalytic science by providing an accurate and reliable means of finding V_M . Rearranging variables gives

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_M c} + \frac{(c - 1)}{V_M c} (p/p_0) \quad (7.6)$$

Surface area analysis: Linearized BET equation

$$V_{\text{ads}} = \frac{V_m c P}{(P_0 - P) \{1 + (c - 1) P / P_0\}}$$



$$\frac{1}{v [(p_0/p) - 1]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c},$$

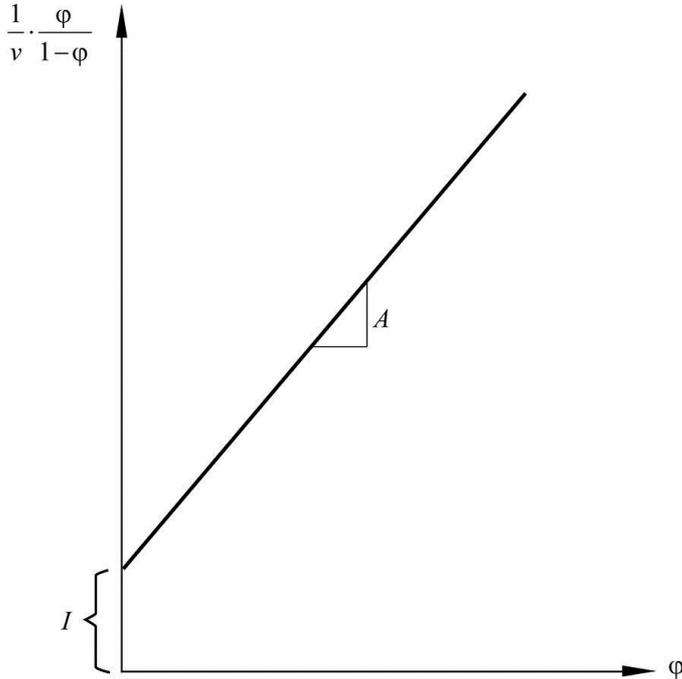
$$c = \exp\left(\frac{E_1 - E_L}{RT}\right),$$

("y = ax + b")

- p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption,
- v is the adsorbed gas quantity (for example, in volume units), v_m is the monolayer adsorbed gas quantity
- c is the BET constant
- E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction

BET plot

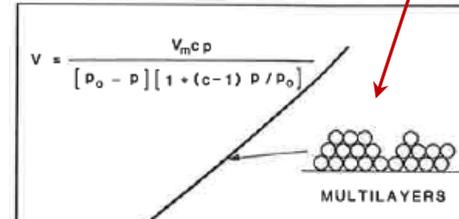
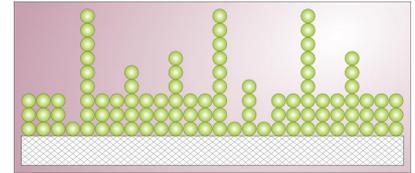
$$v_m = \frac{1}{A + I} \quad c = 1 + \frac{A}{I}$$



- Straight line with $1/v[(p_0/p)-1]$ on the y -axis and p/p_0 on the x -axis according to experimental results.
- Linear relationship only in the range of $0.05 < p/p_0 < 0.035$
- The value of the slope A and the y -intercept of the line I are used to calculate the monolayer adsorbed gas quantity v_m and the BET constant c .

There are assumptions and limitations in the BET model, too

- Same limitations as for Langmuir adsorption isotherm
- **Distinctive adsorption sites, although for physisorption**
- Not suitable for micropore surface area analysis
- **Nevertheless: standardly used for surface area analysis $\rightarrow S_{\text{BET}}$**



Physisorption isotherm measurement and analysis

→ S_{BET}

How are physisorption isotherms measured?

- Adsorption or adsorption+desorption isotherms measured at constant temperature (most typically, liquid N₂, 77 K)
- Specialized computer-controlled **high-vacuum equipment**, pre-heating is a typical step
- Measurement range (p/p^0) and no. of points recorded depends on the aimed application
- Various detection methods:
 - **Volumetric**
 - Gravimetric
 - Flow methods → 3-point BET, 1-point BET

Equipment at Aalto CHEM: 'Surfer'



- Thermo Scientific's Surfer equipment for measuring metal dispersion, surface area & pore size distribution
- Includes : byrettes, stop cocks, a vessel for liquid N₂ , a heating bag and a thermometer
- Maximum T = 450 °C, vacuum
- Connected to multiple gases (N₂, H₂, CO, He)

- Both physisorption and chemisorption measurements

Surface area: linearized BET equation

$$\frac{1}{v[(p_0/p) - 1]} = \frac{c-1}{v_m c} \left(\frac{p}{p_0} \right) + \frac{1}{v_m c},$$

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right),$$

- p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption,
- v is the adsorbed gas quantity (for example, in volume units), v_m is the monolayer adsorbed gas quantity
- c is the BET constant
- E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction

Linearized form of the BET equation

$$P/\{v(P^0 - P)\} = 1/V_{m^c} + (c - 1)P/V_{m^c} \times P^0$$

Julian Ross: Heterogeneous Catalysis - Fundamentals and Applications, © Elsevier 2012. Chapter 2: Surfaces and Adsorption, [link](#).

Slightly different order & c has been a bit lost...

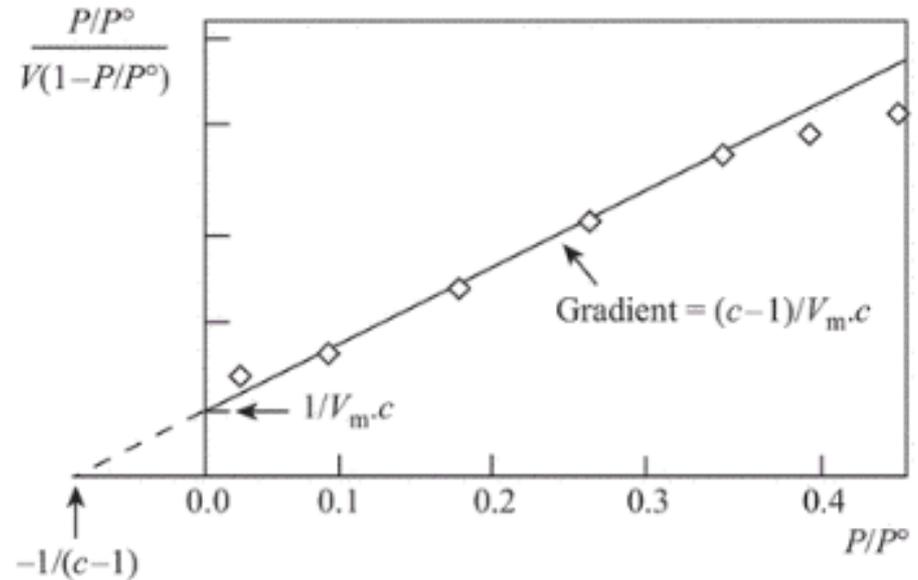
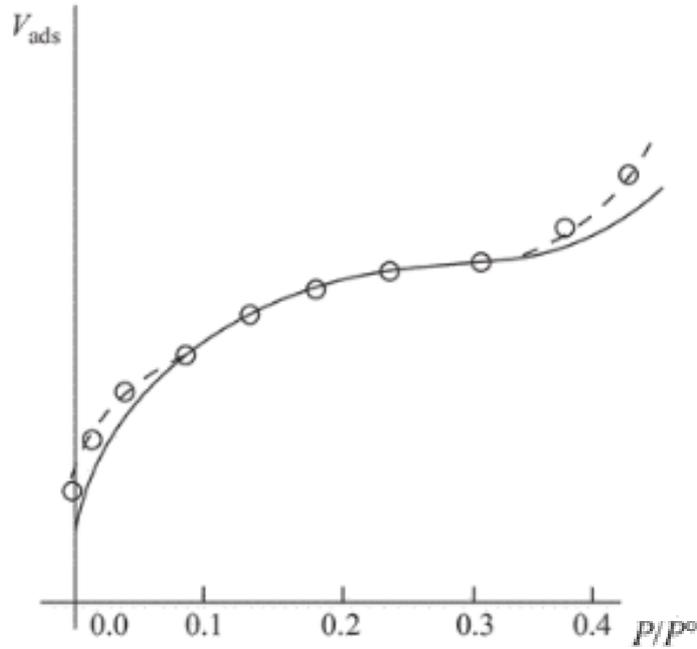
BET (mesopore) surface area calculation

$$S_{\text{total}} = \frac{(v_m N s)}{V},$$

$$S_{\text{BET}} = \frac{S_{\text{total}}}{a},$$

- The total surface area S_{total} and the specific surface area S_{BET}
- where v_m is in units of volume which are also the units of the monolayer volume of the adsorbate gas, N is Avogadro's number, s the adsorption cross section <~area> of the adsorbing species, V the molar volume of the adsorbate gas, and a the mass of the solid sample or adsorbent.

Example of isotherm & BET plot



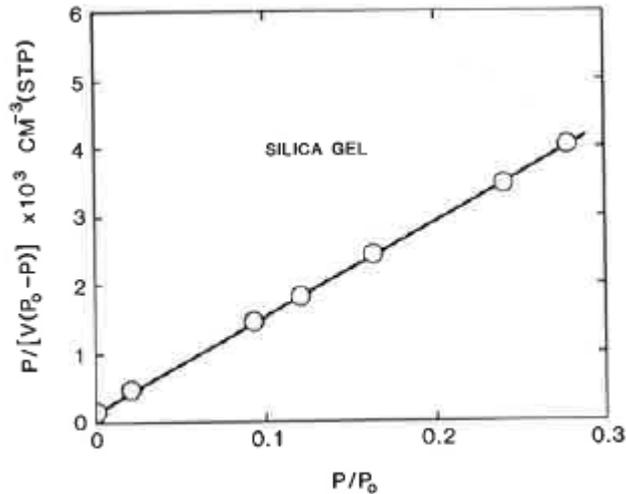


Figure 7.10. BET plot of adsorption data.

leading to BET plots shown in Fig. 7.10. Very linear results are found and the slope, S , and intercept, I , are easily measured. The example in Fig. 7.10 gives

$$S = 13.85 \times 10^{-3} \text{ cm}^{-3}$$

$$I = 0.15 \times 10^{-3} \text{ cm}^{-3} \quad (7.7)$$

$$V_M = 1/(S + I) = 71 \text{ cm}^3 \text{ (STP)}$$

and, for 0.83 g of sample,

$$S_g = \frac{(71)(6.02 \times 10^{23})(16.2 \times 10^{-20})}{(22,400)(0.83)} = 373 \text{ m}^2 \text{ g}^{-1}$$

TABLE 7.4. Typical Surface Areas for Catalysts

Catalyst	Use	S_g ($\text{m}^2 \text{g}^{-1}$)
 REHY zeolite	Cracking	1000
Activated carbon	Support	500–1000
$\text{SiO}_2\text{-Al}_2\text{O}_3$	Cracking	200–500
$\text{CoMo/Al}_2\text{O}_3$	Hydrotreating	200–300
$\text{Ni/Al}_2\text{O}_3$	Hydrogenation	250
 $\text{Fe-Al}_2\text{O}_3\text{-K}_2\text{O}$	Ammonia synthesis	10
V_2O_5	Partial oxidation	1
Pt gauze	Ammonia oxidation	0.01

Pore size distribution (PSD)

Measurement of PSD an essential feature of particle characterization

- Historically, macropores have been measured with mercury porosimetry and
- Mesopores with nitrogen adsorption-desorption isotherms
- Micropores with t-plot, density functional theory, ...

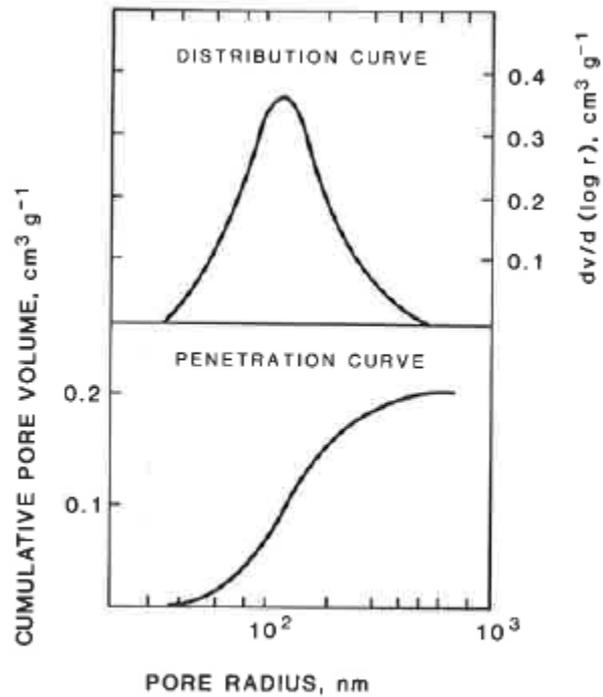


Figure 7.15. Cumulative penetration and distribution curves.

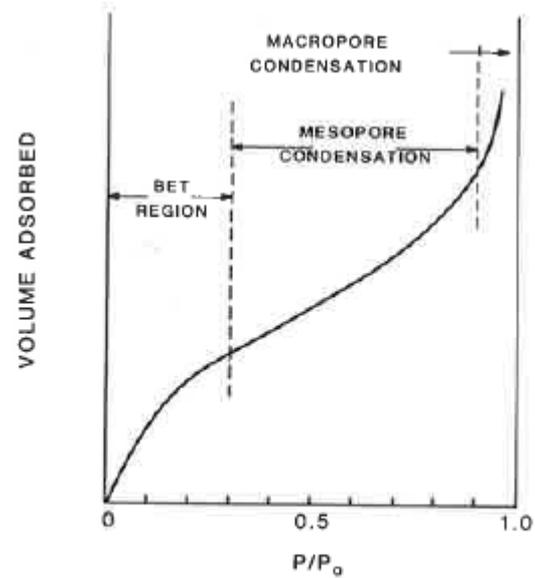


Figure 7.16. Condensation regions of adsorption isotherms.

Macropores: mercury porosimetry

7.3.5.1. Porosimetry

Some liquids wet solids very poorly. An example is mercury, which exhibits wetting angles, θ , between 112° and 142° . Such a liquid penetrates pores only when forced by a pressure

$$P = -\frac{2S \cos \theta}{r} \quad (7.10)$$

where S is the surface tension and r the pore radius.⁽²¹⁰⁾ For mercury with $S = 474 \text{ dynes cm}^{-1}$ and $\theta = 130^\circ$, the calculated values of P are shown in Table 7.5.

TABLE 7.5. Pressure Necessary to Fill Pores

Pressure (atm)	Pore radius (nm)
1	6×10^3
3.5×10^2	17.5
10^3	6
4×10^3	1.5

Mesopores: adsorption isotherms & BJH method (advanced)

- **BJH: Barrett–Joyner–Halenda**

Barrett EP, Joyner LG, Halenda PP (1951) The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J Am Chem Soc* 73:373–380.

<https://doi.org/10.1021/ja01145a126>

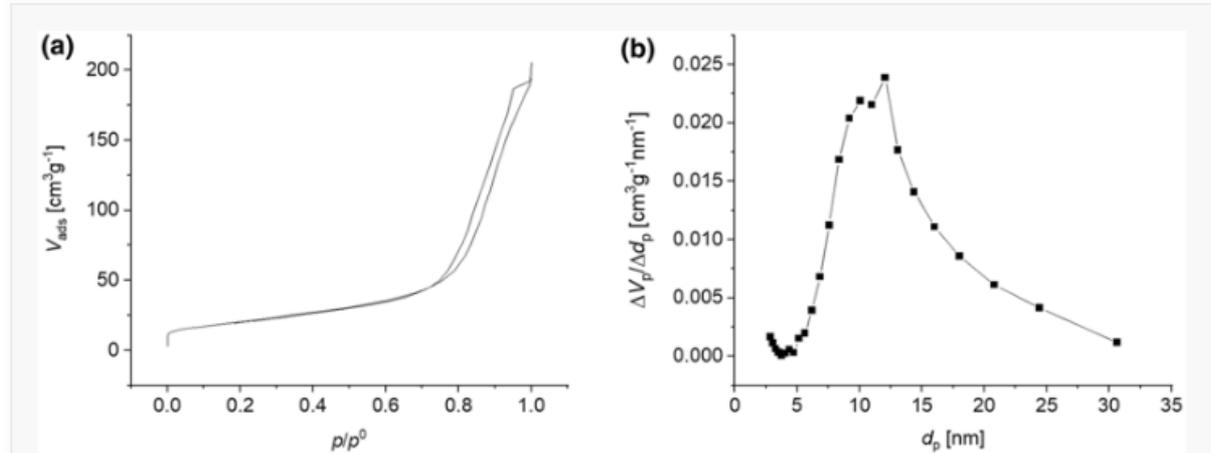


Fig. 2

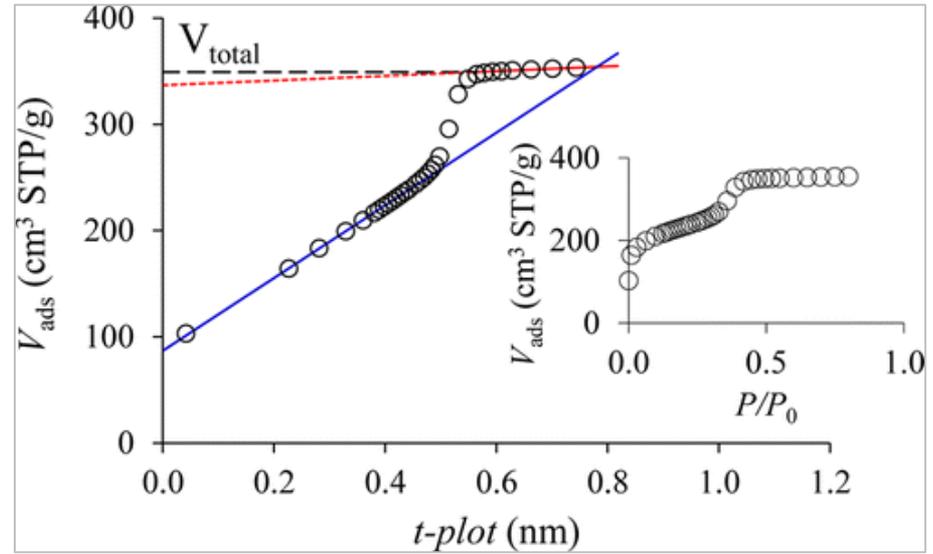
Results of nitrogen adsorption and desorption isotherms of the zirconia support: **a** volume of N_2 adsorbed V_{ads} (per gram of sample) as function of the relative pressure of nitrogen p/p^0 , and **b** pore size (d_p) distribution of the zirconia, as analysed with the BJH method

Voigt et al., *Topics in Catalysis* 2019 (in press), <https://dx.doi.org/10.1007/s11244-019-01133-w>

Micropores: t-plot, density functional theory, ... (advanced)

- Reference isotherm with similar BET c value as the material being evaluated

More, e.g.: S. Lowell, Joan E. Shields, Martin A. Thomas, Matthias Thommes. **Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density** (Chapter 9). 2004, Springer Science+Business Media, New York, <http://libproxy.aalto.fi/login?url=https://ebooks.proquest.com/lib/aalto-ebooks/detail.action?docID=3073274>



<https://dx.doi.org/10.1021/la5026679>

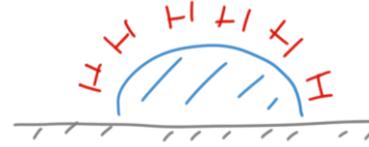
Chemisorption isotherm measurement and analysis

→ D

- **Chemisorption not only a fundamental step in catalysis by solid surfaces but...**
- **... also a powerful method of catalyst characterization**
- **Most typically, chemisorption used to probe the active surface area of metals.**
- **Many other applications also possible**

Chemisorption

- **chemically specific**
- changes in electronic state
- **reversible/irreversible**
- chemisorption energy as for a chemical reaction (exothermic/endothemic)
- may involve an activation energy
- for “large” activation energies (“activated adsorption”), true equilibrium may be achieved slowly
- **monolayer adsorption**



How are chemisorption isotherms measured?

- Total or **total + reversible isotherms** measured at constant, controlled temperature – typically room temperature or higher
 - Irreversibly adsorbed amount is the difference of these
- Specialized computer-controlled **high-vacuum equipment**, reduction at elevated temperature (e.g. 300°C) is a typical step
- Typically volumetric measurement with pressure detection

Ability of metals to chemisorb...(1)

TABLE 7.7. Metals and Gases That Form Monolayers

Metals	Gases ^a					
	N ₂	H ₂	O ₂	CO	C ₂ H ₄	C ₂ H ₂
W, Mo, Zr, Fe	+	+	+	+	+	+
Ni, Pt, Rh, Pd	-	+	+	+	+	+
Cu, Al	-	-		+	+	+
Zn, Cd, Sn	-	-	+	-	-	-
Pb, Ag, Au	-	-	-		+	+

^a +, gas forms monolayer; -, gas does not form monolayer.

Ability of metals to chemisorb...(2)

Table 2.2: A classification of metals according to their abilities in chemisorption.

Group	Metals	Gases						
		O ₂	C ₂ H ₂	C ₂ H ₄	CO	H ₂	CO ₂	N ₂
A	Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os	+	+	+	+	+	+	+
B ₁	Ni, Co	+	+	+	+	+	+	-
B ₂	Rh, Pd, Pt, Ir	+	+	+	+	+	-	-
B ₃	Mn, Cu	+	+	+	+	±	-	-
C	Al, Au	+	+	+	+	-	-	-
D	Li, Na, K	+	+	-	-	-	-	-
E	Mg, Ag, Zn, Cd, In, Sn, Ge, Sn, Pb, As, Sb, Bi	+	-	-	-	-	-	-

+ means strong chemisorption occurs; ± means it is weak; - means unobservable.

Example chemisorption isotherms

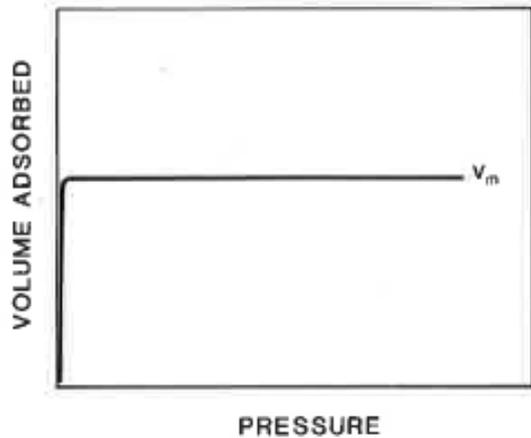


Figure 7.24. Hydrogen chemisorption on Pt/Al₂O₃.

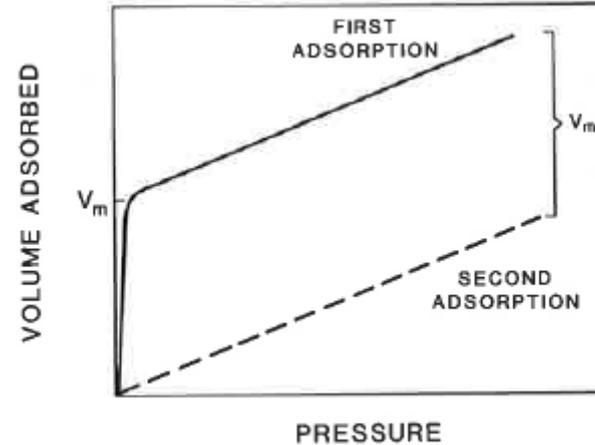


Figure 7.25. Hydrogen chemisorption on Ni/SiO₃.

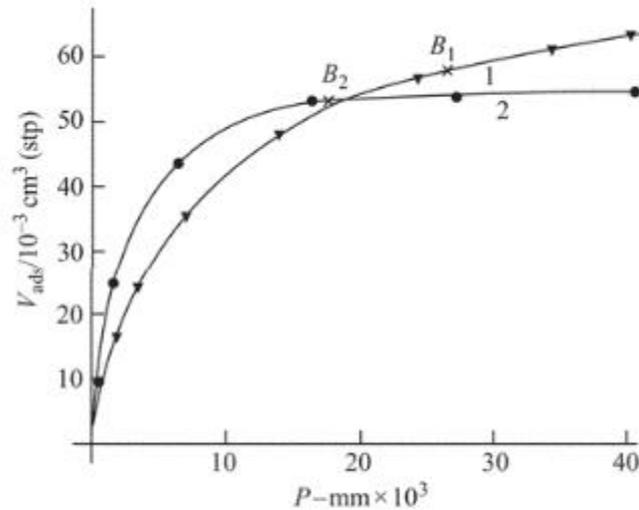
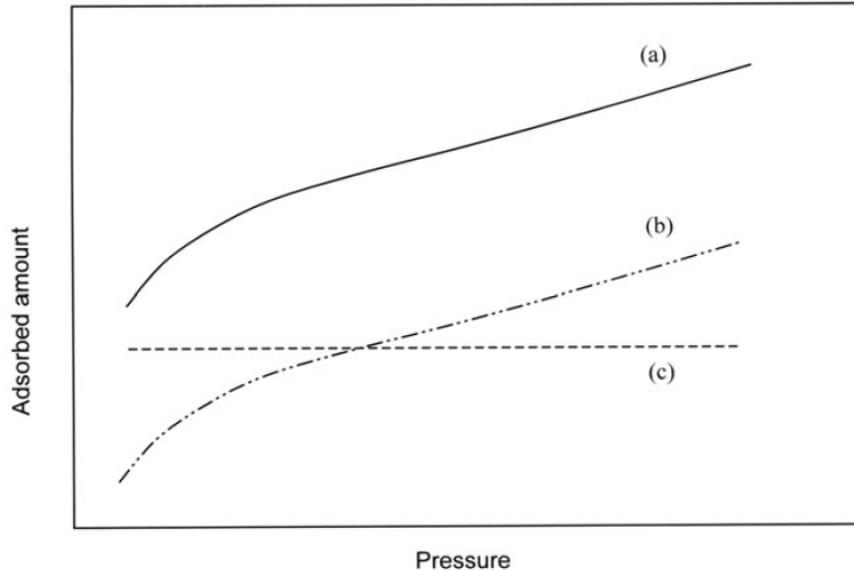


Figure 2.15:

Isotherms for Kr adsorption at 78 K for an evaporated metal film of iron (1) before and (2) after reaction with H_2S at a temperature of 306 K. Source: *J.R.H. Ross, Ph.D. thesis, QUB, 1966.*

Typical characteristics of chemisorption isotherms



The quantity of (c), i.e. of "strong adsorption" (=irreversible chemical adsorption), is calculated in the adsorption exercise.

Figure 16.2 Representation of chemisorption isotherms: (a) combined strong plus weak adsorption, (b) weak adsorption, (c) strong adsorption (by difference).

Stoichiometry of adsorption

- The adsorption stoichiometry is defined as *the average number of metal atoms with which each gas molecule reacts* ([link](#))

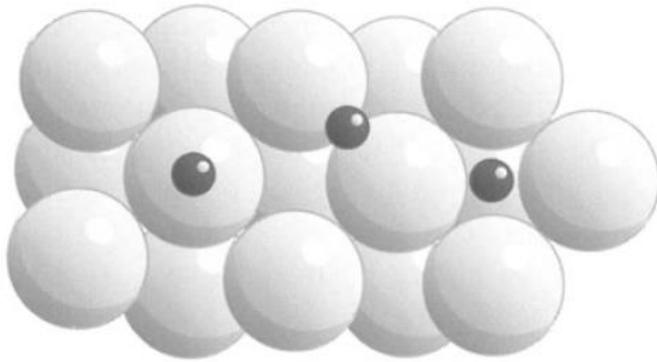


Table 16.3 Some published conditions for catalyst characterization by chemisorption isotherm(s).

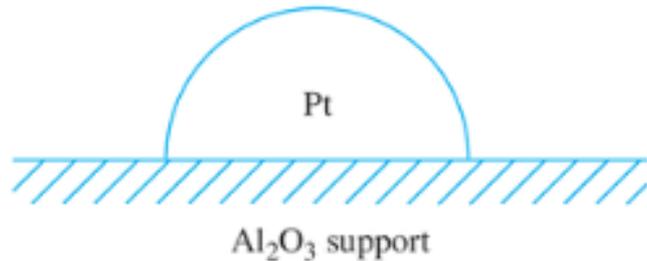
Metal	Support	Redn Temp (°C)	Redn Time (h)	Anal Temp (°C)	Gas	Stoich	Ref
Pt	C	300	2°/min	RT ¹	H ₂	2	1
Pt	Zeolite KL ²	300	2	23	H ₂	1.9+/-0.2	2
Pt	Hexagonal faujisite	300	2	23	H ₂	1.5	3
Pt	Al ₂ O ₃	300-825	1	25	H ₂	<1	6
Pt	LTL zeolite ³	400	1	RT	H ₂	2	7
Pt	SiO ₂	400	1	RT	H ₂	2	7
Pt	WOx/ZrO ₂	200, 400	1	40	H ₂	2	13
Pt	WOx/ZrO ₂	200, 400	1	40	O ₂	-	13
Pt	WOx/ZrO ₂	200, 400	1	40	CO	-	13
Pt	-	300	2	35	CO	1	14
Pd	LTL zeolite	400	1	RT	CO	1	7
Pd	SiO ₂	300	1	RT	CO	1.4	8
Ru	Al ₂ O ₃ , C, TiO ₂ , SiO ₂	300	3	-	-	-	10
Ru	C	450	2	35	H ₂	2	11
Ru	C	450	2	35	CO	uncertain	11
Ru	C	200	2	35	H ₂	2	9
Ru	Al ₂ O ₃ , C, TiO ₂ , SiO ₂	300	3	-	-	-	10
Ru/Ir	NaY	400	2	23	H ₂	~2 (Ir) ⁴ ~4 (Ru) ⁴	4
Rh	Al ₂ O ₃	320	-	25.	CO	0.5	5
Rh	Al ₂ O ₃	200-500	1	25	H ₂	1 to 1.66	6
Ir	Al ₂ O ₃	500	1	25	H ₂	<0.25	6
Ni	Al ₂ O ₃ , C, TiO ₂ , SiO ₂	500	2	?	H ₂	?	10
Fe	SiO ₂	N/a ⁵	-	-78	CO	?	12

Chemisorption standard means to access metal **dispersion**

Dispersion defined as

- $D = N_s / N_t$
- Ratio surface atoms vs total atoms

(typically used for metals)



- If the total amount of a metal is known, and
- chemisorption gives (with assumed stoichiometry!) the surface amount
- → dispersion can be calculated

Chemisorption → particle size (with further assumptions)

→ Adsorption exercise, calculation of average metal particle size

Part 2: Chemisorption

2a) Draw the total (1st) and reversible (2nd) chemisorption isotherms. 1p

2b) Calculate the irreversible adsorbed volume of your probe molecule [cm^3/g]. Specify the chosen pressure range for the calculation with reasoning. 2p

2c) Calculate the active metal surface area [m^2/g] assuming stoichiometry 2 for H_2 chemisorption and 1 for CO chemisorption. Check the surface area of your metal atom (a_m) from Table 1. 1p

2d) Calculate the metal dispersion [%] and particle size [nm] assuming spherical particles. Check the molar mass (M) and the density (ρ) of your metal from Table 1. 2p



Chemisorption at different temperatures → activation energy?

- Example: doctoral thesis of Lars-Peter Lindfors (early 1990s)
- Now: senior vice president, technology, Neste

<https://www.neste.com/corporate-info/investors/corporate-governance/ceo-and-neste-executive-board-0>



Lars Peter Lindfors

(born 1964)

Senior Vice President, Technology

Ph.D. (Tech.), MBA.

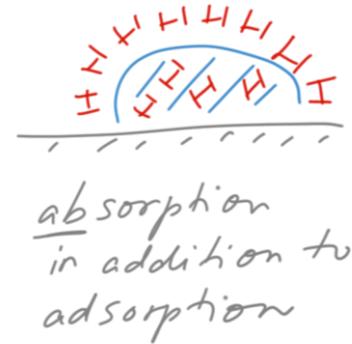
Member of the Neste Executive Board since 2009.

Joined the company in 2007. Responsible for Research & Development, Investment Management, Information Technology, Procurement, and Business Processes. Served previously as Senior Vice President, Technology and Strategy (2009–2012), Vice President for the company's Research and Technology unit (2007–2009), Executive Vice President, Renewal and Development at Perstorp Group (2004–2007), Executive Vice President, R&T&D at Perstorp Group (2001–2004), and prior to that at Neste as R&D Manager and various other positions. Member of the Board of the Fortum Foundation and Finnish Foundation for Technology Promotion.

Potential complications from **spillover** and **absorption**

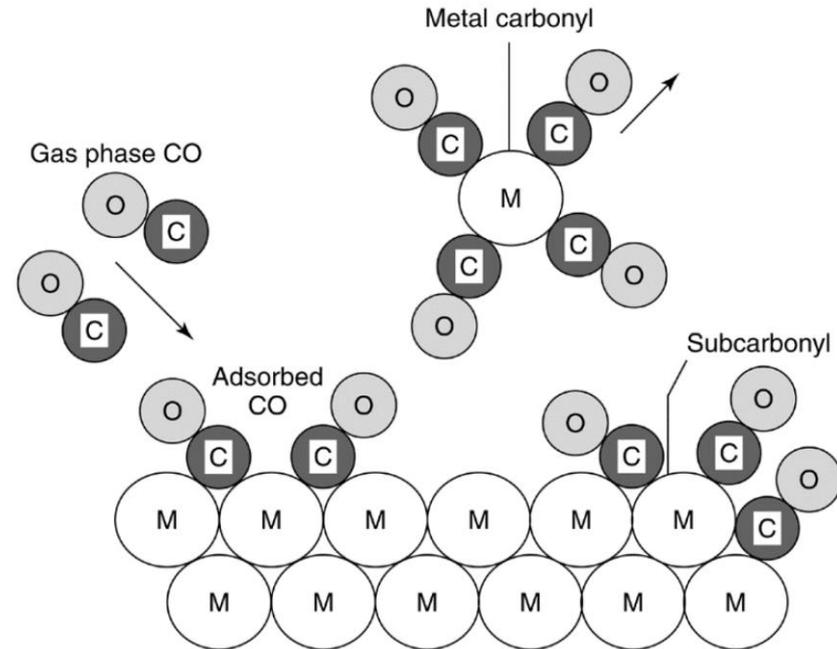
We want to measure:

We may additionally measure:



Also beware: **desorption** of **new compounds!**?!

- Many transition metals form **volatile carbonyl compounds!**



Bartholomew, C.H.; Farrauto, R.J. Fundamentals of Industrial Catalytic Processes, 2nd ed.; Wiley-Interscience: Hoboken, NJ, USA, 2006.

12 Chemisorption: Site Specific Gas Adsorption

12.1 CHEMICAL ADSORPTION

Additional material

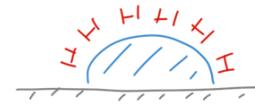
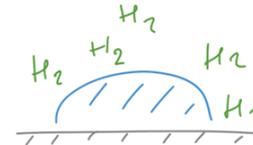
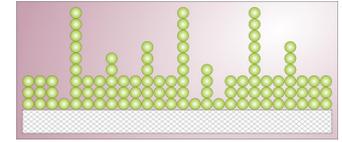
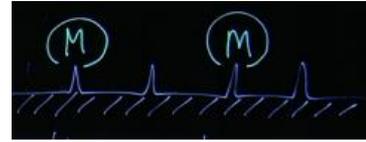
When the interaction between a surface and an adsorbate is relatively weak, only physisorption takes place via dispersion and coulombic forces (see Chapter 2). However, surface atoms often possess electrons or electron pairs that are available for chemical bond formation. Resulting chemical adsorption or chemisorption has been defined by IUPAC [1] as “adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds” and as “adsorption which results from chemical bond formation (strong interaction) between the adsorbent and the adsorbate in a monolayer on the surface” [2].

More, e.g.: S. Lowell, Joan E. Shields, Martin A. Thomas, Matthias Thommes. **Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density** (Chapter 12). 2004, Springer Science+Business Media, New York, <http://libproxy.aalto.fi/login?url=https://ebookcentral.proquest.com/lib/aalto-ebooks/detail.action?docID=3073274>

Conclusion & Take home-message

Take-home message

- **Adsorption isotherm** measurements widely used for catalyst characterization
- **Physisorption/non-specific:** surface area, pore volume, pore size distribution
- **Chemisorption/specific:** adsorbed volume, active metal area, dispersion (+ particle size)



Some words on the Group work: Catalysis Glossary (1st Ed.)

Full instructions in MyCourses

<https://mycourses.aalto.fi/course/view.php?id=20383#section-4>

Catalysis Glossary



Catalysis Glossary instructions

PDF document



Restricted Not available unless any of:

- You are a(n) **Teacher**
- You are a(n) **Student**

Materials for Catalysis Glossary Group Works



Task 0 - Group formation

Catalysis Glossary workflow



Material to Task 1
expected: 21.1.

Material to Task 2
expected: 8.2.

Material to Task 3
expected: 25.2.

Target: Catalysis
Glossary ready: 11.3.

DL Task 0: 28.1.

DL Task 1: 4.2.

DL Task 2: 20.2.

DL Task 3: 4.3.

DL 28.1.2019 - Group Task 0 - Group formation

Group Task 0.

- Find the members of your group
- Plan your schedule, discuss on the ways of working, how to share the tasks, who reports etc.
- Write a memo (a memo template available at [GoogleDrive](#)) and return it to MyCourses:
 - Are all the members present and able to participate the course?
 - Is everyone able to access [GoogleDrive](#) working environment
 - There is a folder shared with all the students (@aalto.fi – addresses) You can request access for another e-mail address, too

DL 4.2.2019 – Group task 1 - Terminology for Catalysis Glossary

Group task 1.

- **Collect the words related to catalysts and catalysis from the files appointed to your group**
 - Recommendation: At least two persons read each presentation, you do not all need to read all nine
- **Which of these words are important? Create a list of at least 15 words (max up to ~50) to be used in the Catalysis Glossary**
- **Write a memo on the group work and return in MyCo**

Reetta Kaila

Sales Manager

 Helsinki, Finland 8 years at Wärtsilä Originally from Finland AMBASSADOR185 years
185 people
185 stories
185 hearts

Enjoying the global company culture

Reetta Kaila joined Wärtsilä in 2010 as an Expert for New Technologies. Her work was about developing environmentally friendly gas-processing technologies for the offshore business, with an aim to recover flare gases from oil drilling, improving their quality and take them finally into use as fuel gas for dual-fuel engines. This development work continued for more than six years, and it took her to various roles in the team from R&D, design and sales engineering, to commissioning, project management and sales. For the last two years within that team, she worked as the Product Manager for Wärtsilä GasReformer. In 2016, she joined the Fuel Gas Supply System team and started as Sales Manager for LNG (liquefied natural gas) fuel systems in Wärtsilä Marine Business, being responsible for sales in North-Europe and Asia.

Reetta says that there is no typical workday: “You have a plan for the day and usually start with the emails. Finally you realise that you have completed the day with something completely different. Customers want LNG as fuel, so days are hectic with new requests coming in from

Introducing Dr. Reetta Kaila
<https://www.wartsila.com/about/wartsila-185/view/enjoying-the-global-company-culture>