## Modern Methods in Heterogeneous Catalysis Research

# Surface area and pore size determination

30. October 2015

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## Further reading

S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publisher, Dordrecht, 2004, Springer 2006.

R. Brdička, Grundlagen der physikalischen Chemie, Deutscher Verlag der Wissenschaften, Berlin 1982.
P.W. Atkins, J. de Paula, Physikalische Chemie, Wiley-VCH, Weinheim 2013.
G. Wedler, H.-J. Freund, Lehrbuch der Pysikalischen Chemie, Wiley-VCH, 2012.

F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), Handbook of Porous Solids, Vol. 1, Wiley-VCH, Weinheim 2002.

G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997.

# Outline

1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

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# *Heterogeneous catalysis* 1

- Heterogeneous catalysis happens at the interface between phases
- The number of active sites depends on the surface area

- Surface area is related to
  - Particle size
  - Particle morphology
  - Surface texturing
  - Porosity

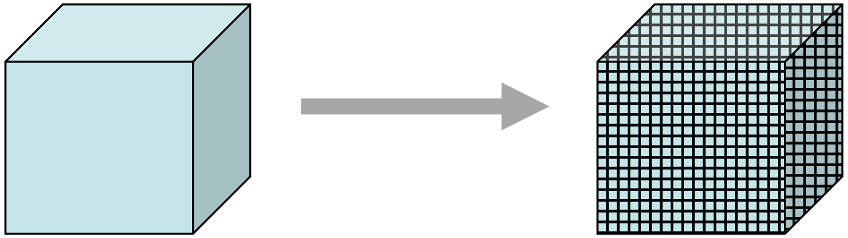
- The accessibility of active sites requires pores that allow molecular transport
- Porosity: fraction of the total void volume with respect to the volume of the catalyst
- Texture:
  - pore size
  - pore size distribution
  - pore shape

# *Factors affecting surface area*

*1*

1 particle of edge
lenght = 1 m

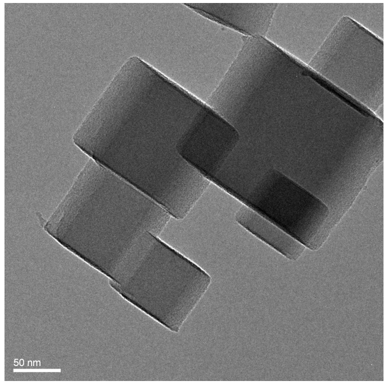
$10^{18}$ particles of edge
lenght = $10^{-6}$ m

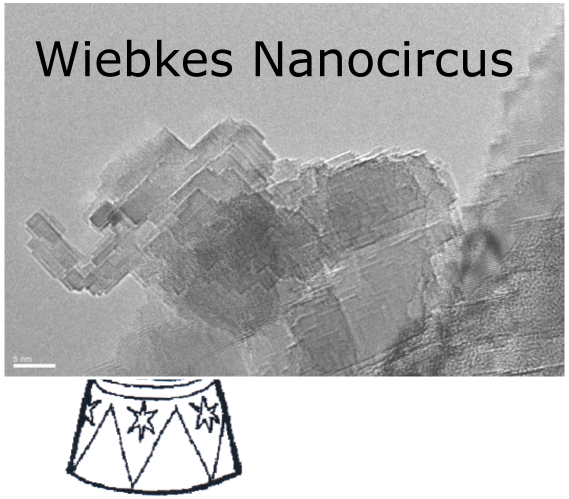


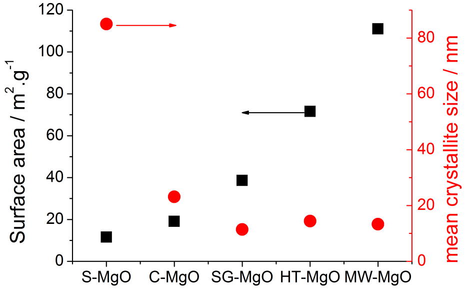
$S=6\ m^2$

$S_i=6\times10^{-12}\ m^2$
$S_{total}=6\times10^6\ m^2$

size



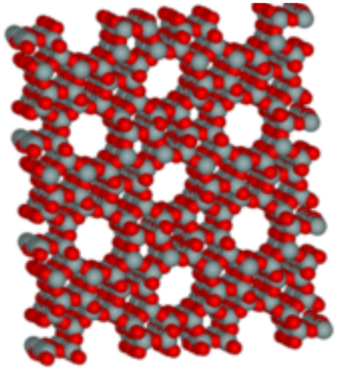




shape

$S=10\ m^2$ **MgO** $S=100\ m^2$

Numbers = orders of magnitude



porosity

$S=400\ m^2$ **Zeolite ZSM-5**

# Surface area measurements

1

- Surface area from particle size distribution

  *Dynamic light scattering*
  Measures Brownian motion and relates this to the size of the particles by using a correlation function and the Stokes-Einstein equation

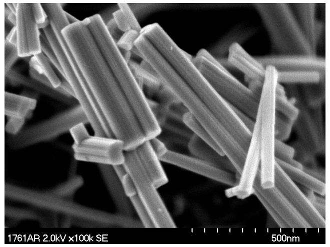
  Non-spherical particles will be measured as equivalent spheres

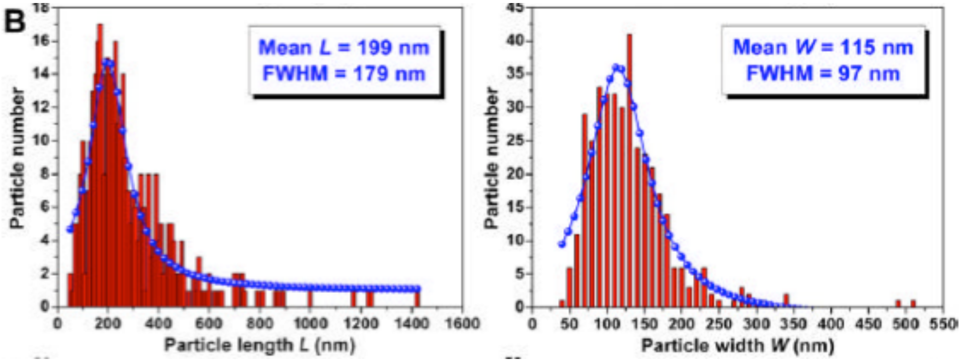
$$D_0 = \frac{kT}{6\pi\eta R}$$

D= Diffusion coefficient
k= Boltzmann constant
T= absolute temperature
η= dynamic viscosity of the solvent
R= radius of the particle

- Microscopy

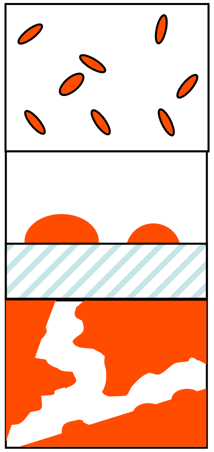
  Shape analysis





- Small angle X-ray scattering

  Scattering of X-rays by small domains of uniform matter (crystalline or amorphous), for which the electron density $\rho^e$ is different from the continuous medium
  The central peak of scattered intensity gets broader as the domain size (particles, voids) decreases
  SAXS parameters (mean size / size distribution / specific surface area) are derived from analysis of the profile of the SAXS curve



- Mercury porosimetry

  Intrusion of a non-wetting liquid (often Hg) at high pressure, measurement based on the external pressure needed to force the liquid into a pore against the opposing force of the liquid's surface tension, Inner surface of porous materials, pore width > 2nm

# *Surface area measurements*

- Gas adsorption
  - Surface area
  - Pore volume
  - Texture
    - Pore size distribution
    - Pore geometry
    - Connectivity

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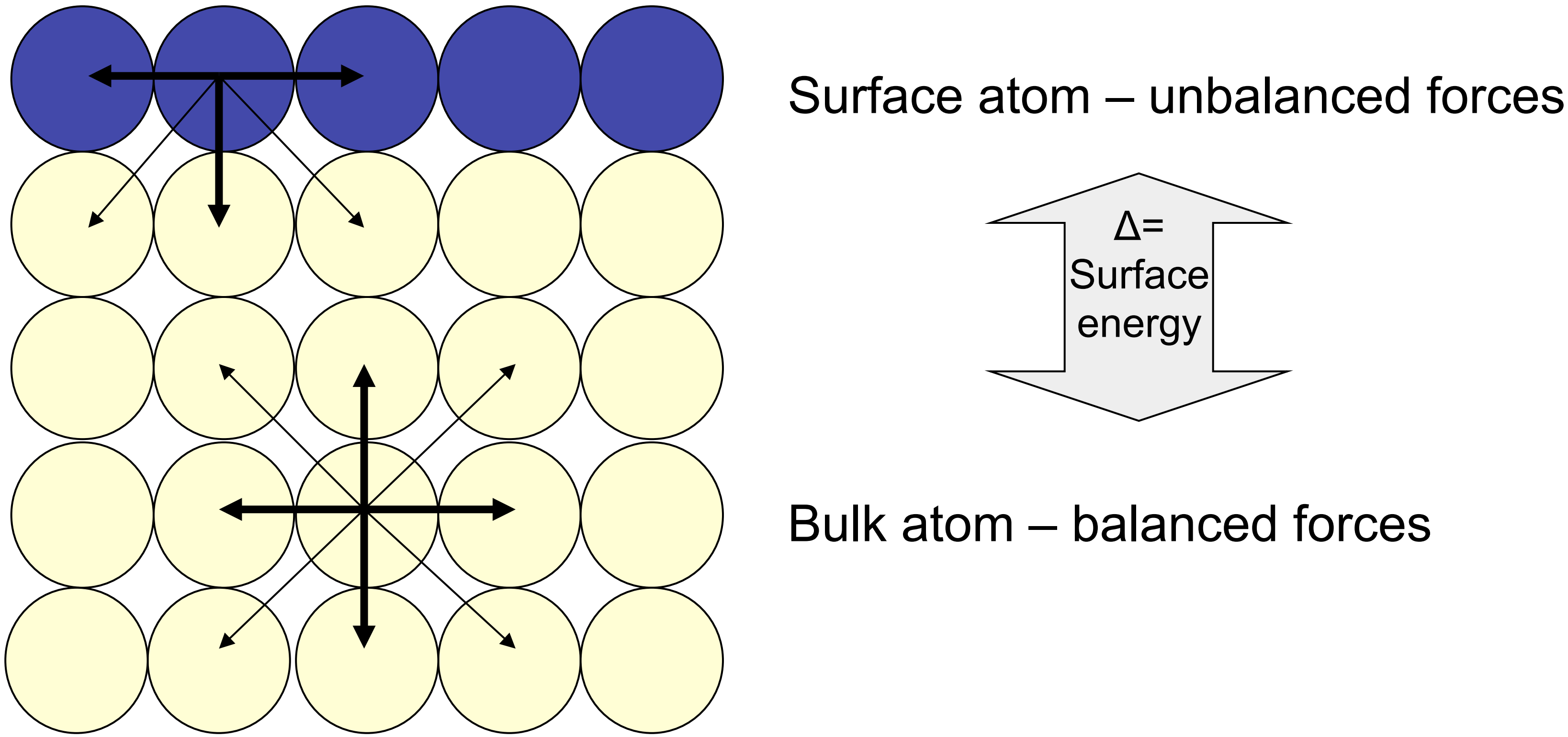
# Driving force of adsorption

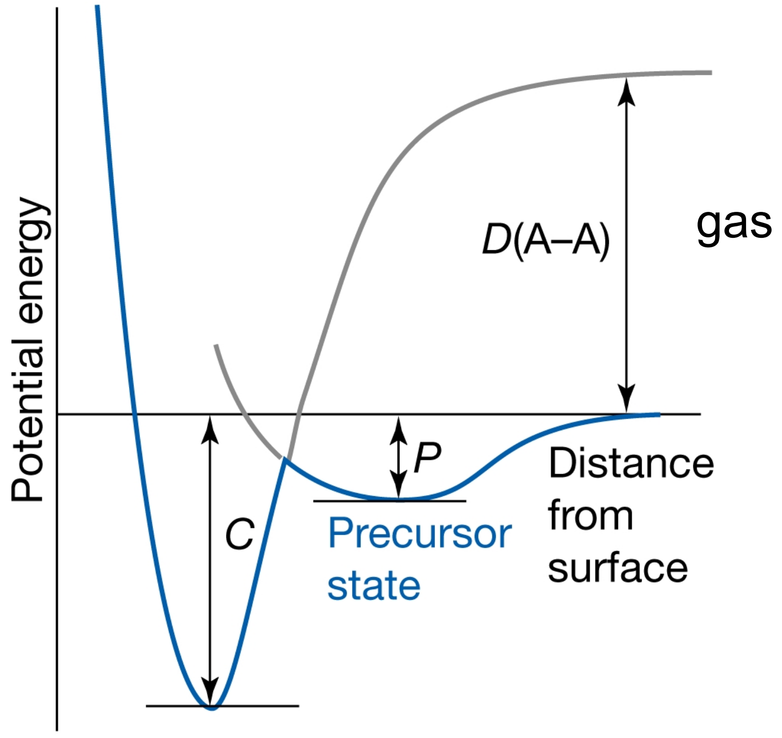


Surface atom – unbalanced forces

Δ=
Surface
energy

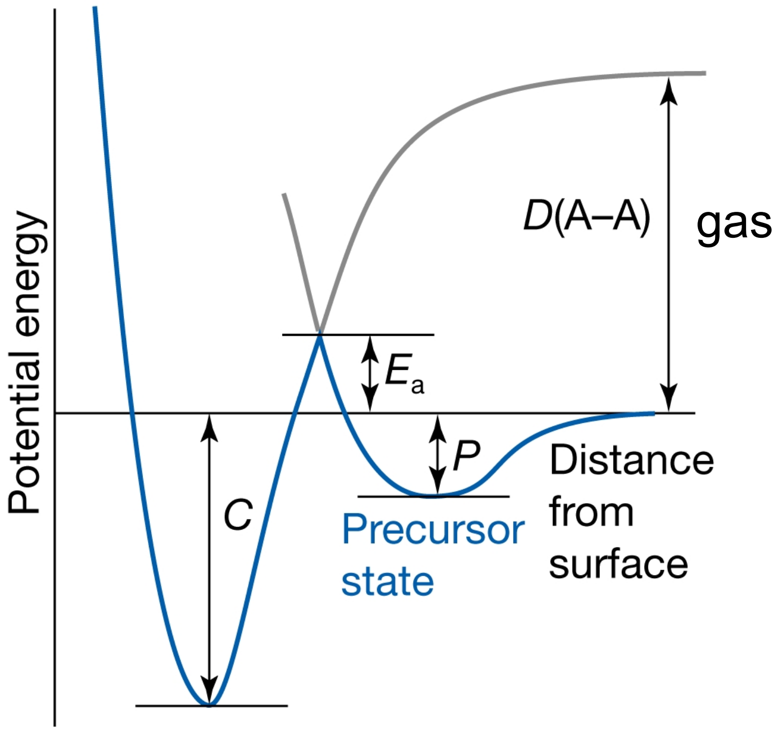
Bulk atom – balanced forces

# *Adsorption*



chemisorption physisorption

activated chemisorption



chemisorption physisorption

Heterogeneous catalysis

Surface area/pore size determination

# Physisorption forces

***Van der Waal´s forces***

1. Dispersion forces* (major part of the interaction potential)
   The electron motion in an atom or molecule leads to a rapidly oscillating dipole moment
   coupling of two neighboring moments into phase leads to a net attractive potential
2. Ion-dipole (ionic solid/polar gas molecule)
3. Ion-induced dipole (polar solid/polarizable gas molecule)
4. Dipole-dipole (polar solid/polar gas molecule)
5. Quadrupole interactions (symmetrical molecules e.g. $^{-}O\text{-}C^{++}\text{-}O^{-}$)

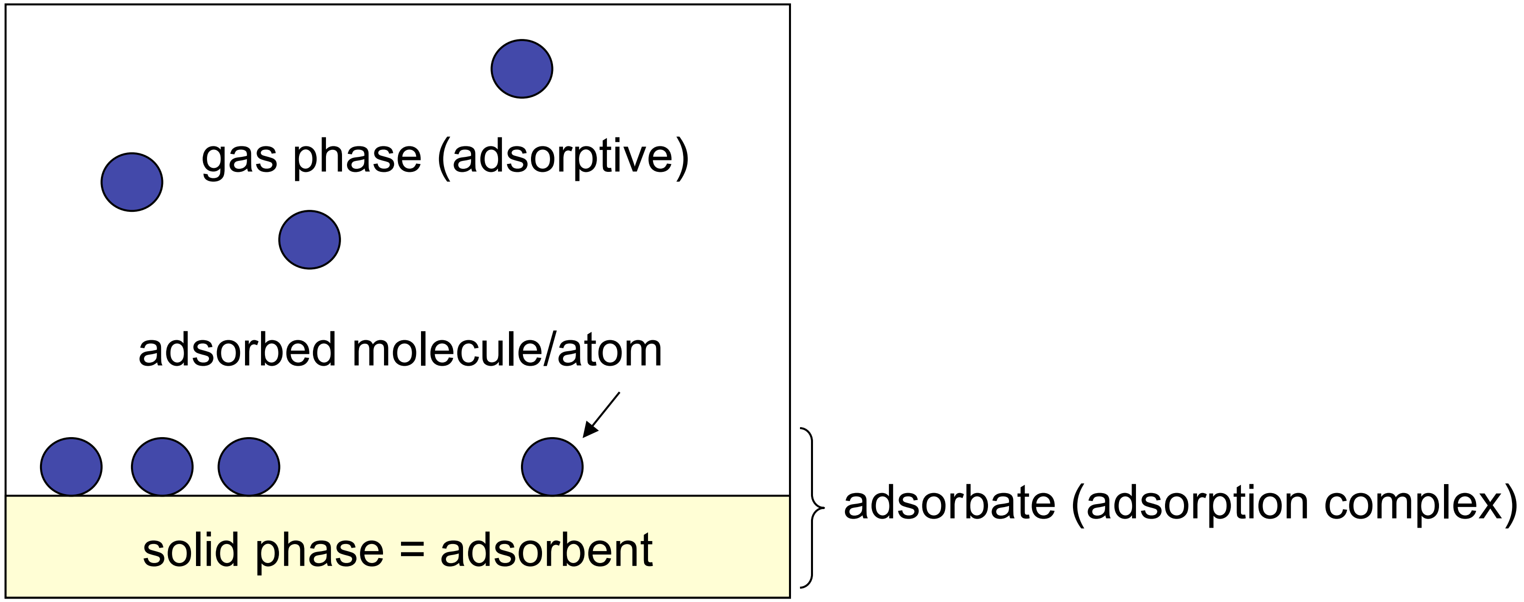
* F. London, Z. Phys. 63 (1930) 245.

Similar to forces that lead to liquifidation of vapors

## Adsorption

| | Physisorption | Chemisorption |
|---|---|---|
| Heat of adsorption | < 50 kJ $mol^{-1}$ | > 50 kJ $mol^{-1}$ |
| Coverage | Multilayer →<br>Measurement of surface area | Monolayer or less, site restriction →<br>Titration of active sites |
| Interaction | No structural changes, reversible | Disruption of chemical bonds may happen |
| Kinetics | Fast | Activation required |
| Pores | Pores may be filled →<br>Pore volume measurements | - |

# Adsorption


gas phase (adsorptive)
adsorbed molecule/atom
solid phase = adsorbent
adsorbate (adsorption complex)

# Description of adsorption

*Relation between T, p, adsorbed amount (surface concentration)*

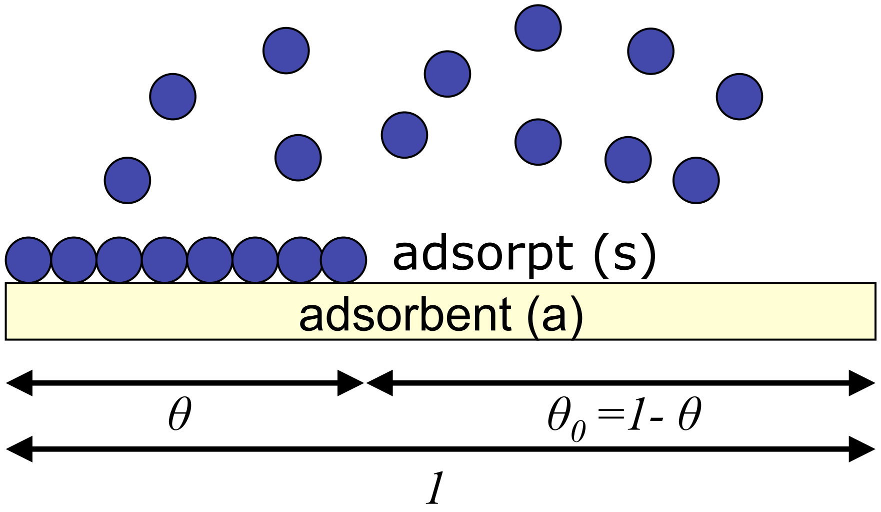
$\Gamma = n_s/s_a$

$\gamma = n_s/m_a$

$\Gamma = \gamma/S_{a,sp.}$

$W_s$

$V_s$



*Fraction of occupied surface (coverage)*

$\theta = \Gamma/\Gamma_m = \gamma/\gamma_m = N/N_m = W/W_m$

$\Gamma = f(p)$ $<eq., T = \text{const.}>$ adsorption isotherm

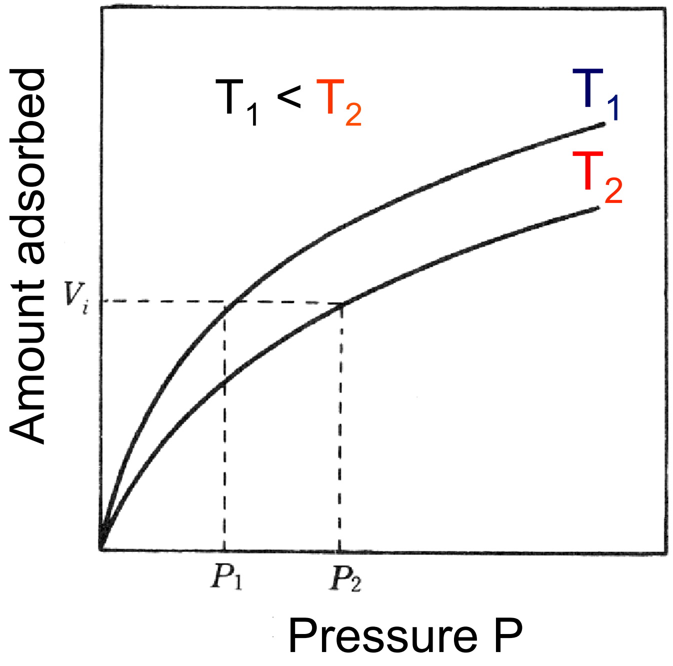
$\Gamma = f(T)$ $<eq., p = \text{const.}>$ adsorption isobar

$p = f(T)$ $<eq., \Gamma = \text{const.}>$ adsorption isostere

# Adsorption isotherm

$$\Gamma = f\,(p)_T$$

Adsorption is favored at lower temperatures



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

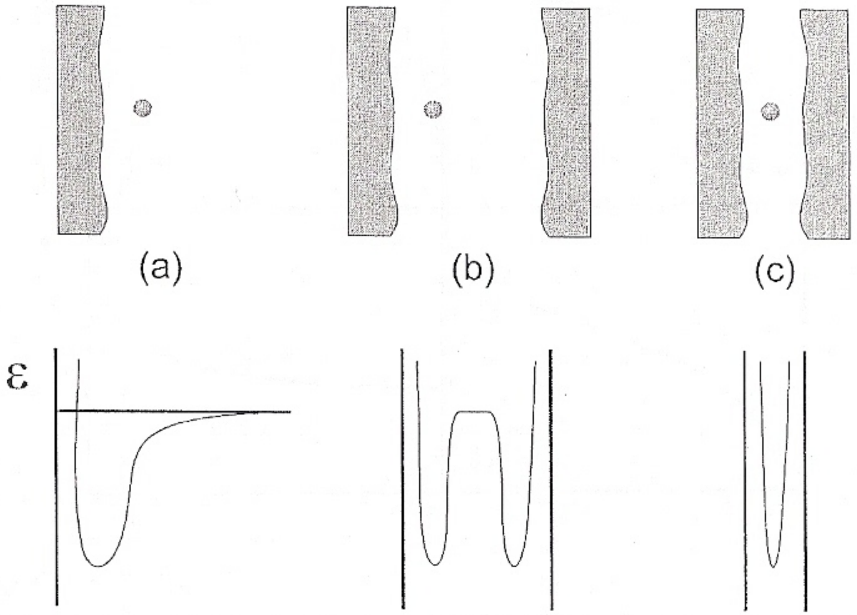
Decrease in translation freedom by adsorption: $\Delta S<0$
Adsorption is a spontaneous process: $\Delta G<0$

↓

$\Delta H<0$ Exothermic process

# Adsorption isotherm

Planar, nonporous, macropores    mesoporous    microporous



Schematic illustration of adsorption potential

# Adsorption isotherm

$\Gamma = f\,(p)_T$

The shape of the isotherm of pure fluids depends on

- Interplay between the strength of fluid-wall and fluid-fluid interaction
- Pore space

Classification by the International Union of Pure and Applied Chemistry*

| | Width* [nm] |
|---|---|
| Micropores | < 2 |
| Mesopores | 2 ~ 50 |
| Macropores | > 50 |

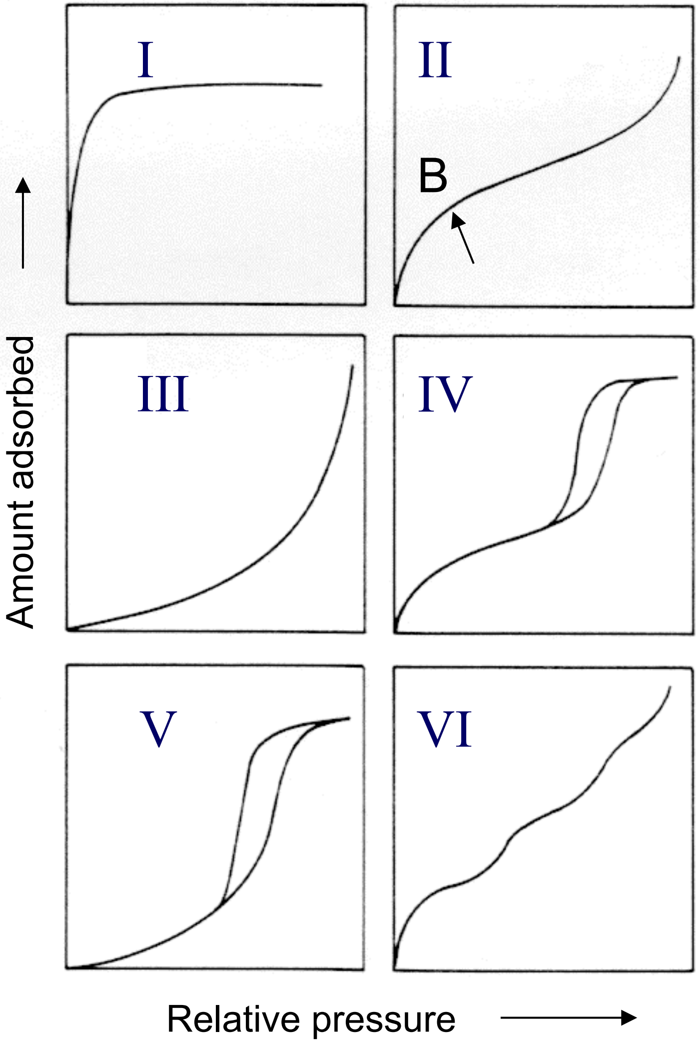
- Ultramicropores below 0.7nm
- Supramicropores 0.7~2nm

Width*

- Diameter of a cylindrical pore
- Distance between opposite walls in case of slit pores

* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

# *IUPAC classification of adsorption isotherms**



Adorption in micropores

Adsorption limited to a few molecular layers

true chemisorption

Zeolites, active carbon

Unrestricted monolayer-multilayer adsorption

Nonporous or macroporous adsorbent

B monolayer coverage complete

Weak adsorbtive-adsorbent interactions

Nitrogen on polyethylene

Monolayer-multilayer adsorption and capillary condensation

Complete pore filling

Weak interactions and capillary condensation

Stepwise multilayer adsorption on a nonporous non-uniform surface

Ar or Kr on graphitized carbon

* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

# *Adsorption isotherm*

- Mathematical description of the adsorption isotherms allows to determine surface area and pore data
- The models used for mathematical description are often empirical models that fit more or less to experimental data
- The results are useful and required to interpret catalytic data
- Please consider in the discussion of your results that the surface area or the pore volume determined by using the various empirical models are approximated values

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# Surface area measurements

$$\boxed{S = A_x N_m}$$

| | | |
|---|---|---|
| $A_x$ | cross-sectional area of the adsorbed molecule | |
| | • Nitrogen | 0.162 nm$^2$ |
| | • Argon | 0.166 nm$^2$ |
| | • Krypton | 0.210 nm$^2$ |

$N_m$ number of adsorbate molecules required to cover the solid with a single monolayer

Theories that give access to the monolayer capacity using the isotherm

- Langmuir
- BET

# Langmuir isotherm*

Description of Type I Isotherm

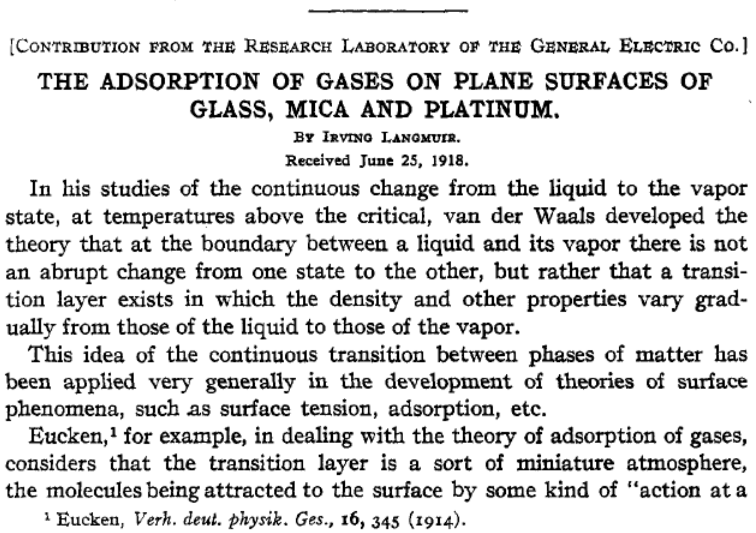
Assumptions

- Monolayer adsorption
- Energetically uniform surface
- No interactions between adsorbed species (heat of adsorption independent of coverage)

kinetic expression of the adsorption equilibrium

$$\mathbf{r_{ads} = r_{des}}$$

$$\mathrm{d}N_{\mathrm{ads}} = \mathrm{d}N_{\mathrm{des}}$$



[Contribution from the Research Laboratory of the General Electric Co.]

THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM.

By Irving Langmuir.

Received June 25, 1918.

In his studies of the continuous change from the liquid to the vapor state, at temperatures above the critical, van der Waals developed the theory that at the boundary between a liquid and its vapor there is not an abrupt change from one state to the other, but rather that a transition layer exists in which the density and other properties vary gradually from those of the liquid to those of the vapor.

This idea of the continuous transition between phases of matter has been applied very generally in the development of theories of surface phenomena, such as surface tension, adsorption, etc.

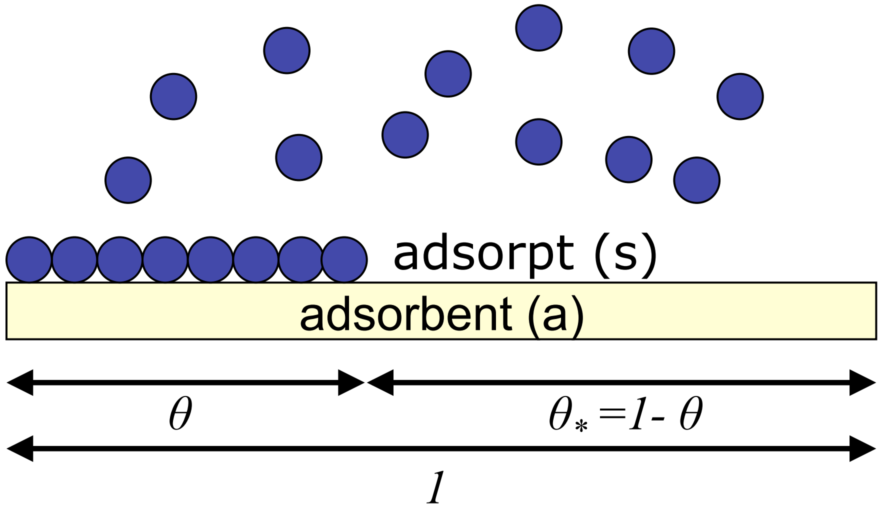
Eucken,[1] for example, in dealing with the theory of adsorption of gases, considers that the transition layer is a sort of miniature atmosphere, the molecules being attracted to the surface by some kind of "action at a

[1] Eucken, *Verh. deut. physik. Ges.*, **16**, 345 (1914).

* I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361.

# Langmuir isotherm

$$\mathrm{A} + * \underset{k_A^-}{\overset{k_A^+}{\rightleftarrows}} \mathrm{A}^*$$



$$\frac{d\theta_A}{dt} = p_A k_A^+ (1 - \theta_A) - k_A^- \theta_A$$

$$K_A = \frac{k_A^+}{k_A^-}$$

$$in\ equilibrium:$$

$$p_A k_A^+ (1 - \theta_A) = k_A^- \theta_A$$

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A}$$

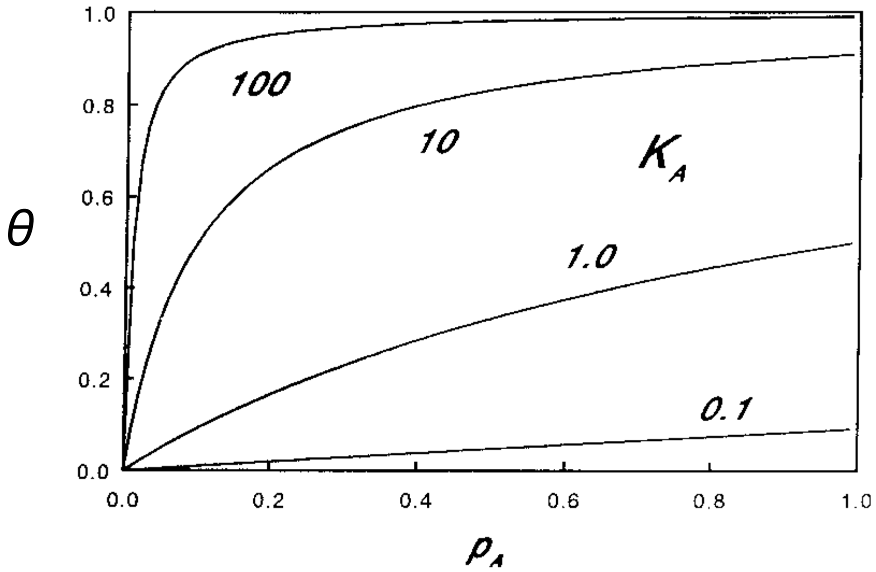
$$\theta_* = (1 - \theta_A) = \frac{1}{1 + K_A p_A} \Rightarrow \theta_A = K_A p_A \theta_*$$

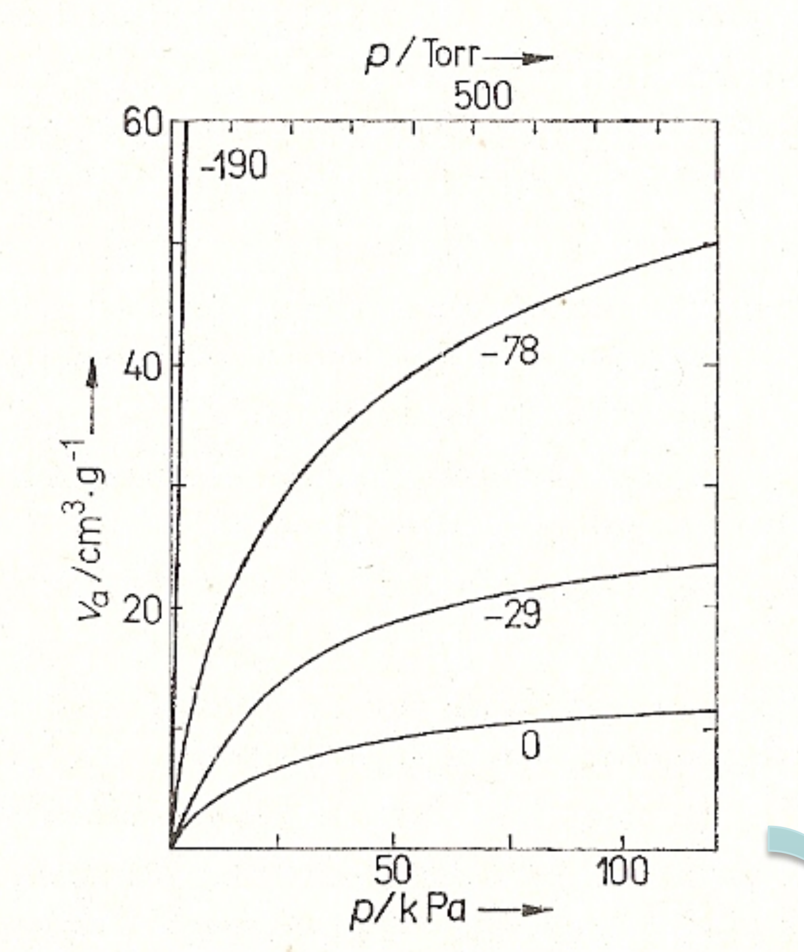
Irving Langmuir
Nobel Prize in Chemistry in 1932

# Langmuir isotherm

$$\boxed{\theta = \frac{N}{N_m} = \frac{K\,p}{1+K\,p}}$$

$$K = \frac{k_{ads}}{k_{des}}$$





Adsorption of nitrogen on charcoal at different T

$$\left(\frac{\partial \ln K}{\partial T}\right)_{\Theta} = \frac{\Delta_{ads}H}{RT^2}$$

# Langmuir isotherm

3

$$\boxed{\theta = \frac{N}{N_m} = \frac{K\ p}{1 + K\ p}} \xrightarrow{\text{Linear plot}} \boxed{\frac{p}{N} = \frac{1}{KN_m} + \frac{p}{N_m}}$$

$$n = \frac{N}{N_A} = \frac{m_m}{M_{asdorptive}}$$

$$S = N_m A_x = \frac{m_m N_A A_x}{M_{asdorptive}}$$

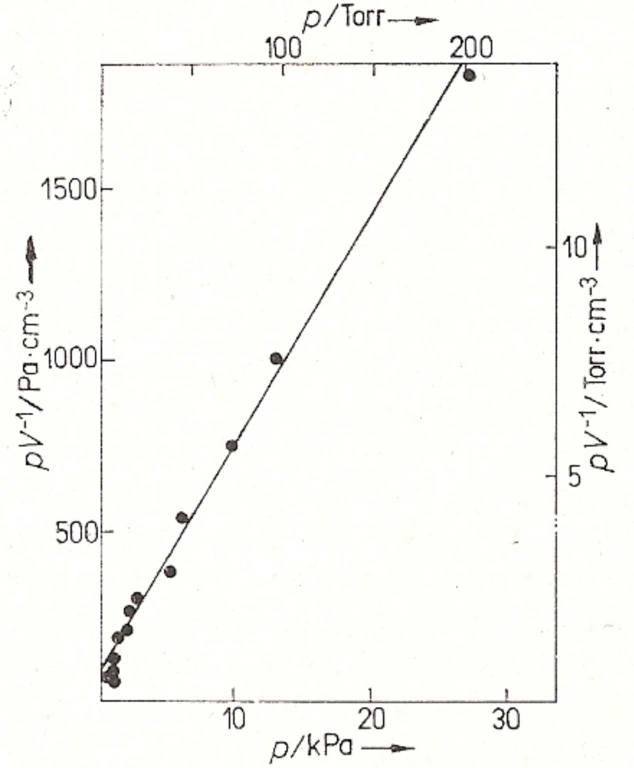
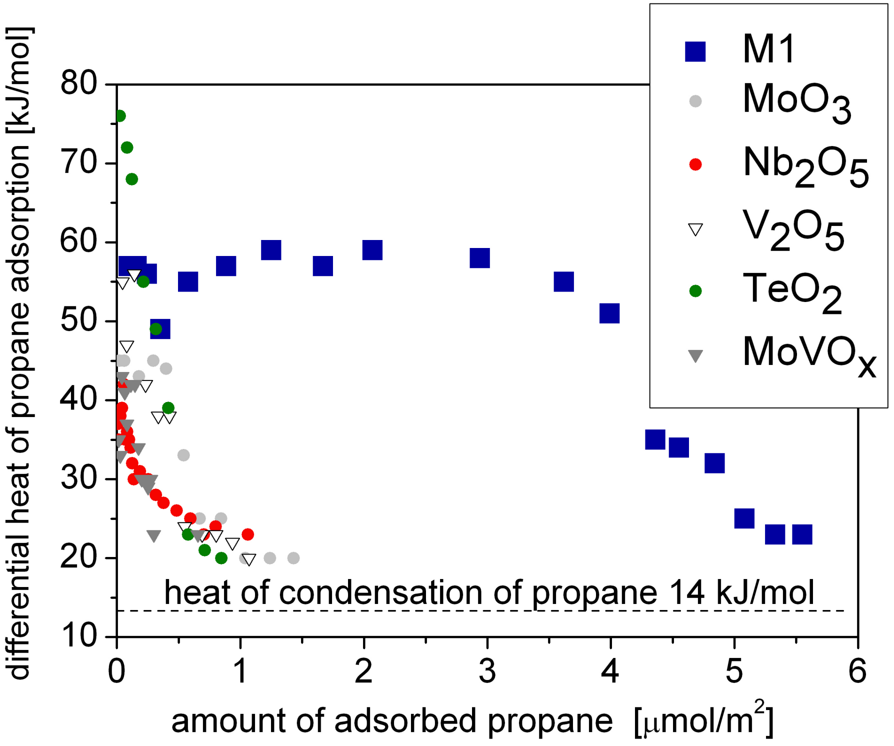


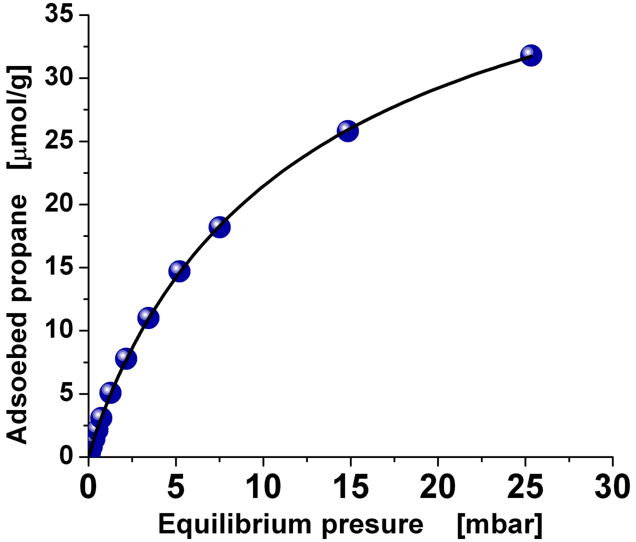
Abb. 6.47
Linearisierte Langmuirsche Adsorptionsisotherme für die Adsorption von Wasserstoff an Kupferpulver bei 25 °C

# Langmuir isotherm – adsorption of propane on oxides

M. Hävecker *et al.*, Journal of Catalysis 285 (2012) 48–60.



## Adsoption isotherm of propane over M1 at T=313 K



Cross-sectional area of propane: 36 Å²

$K = 0.111(6)\ hPa^{-1}$

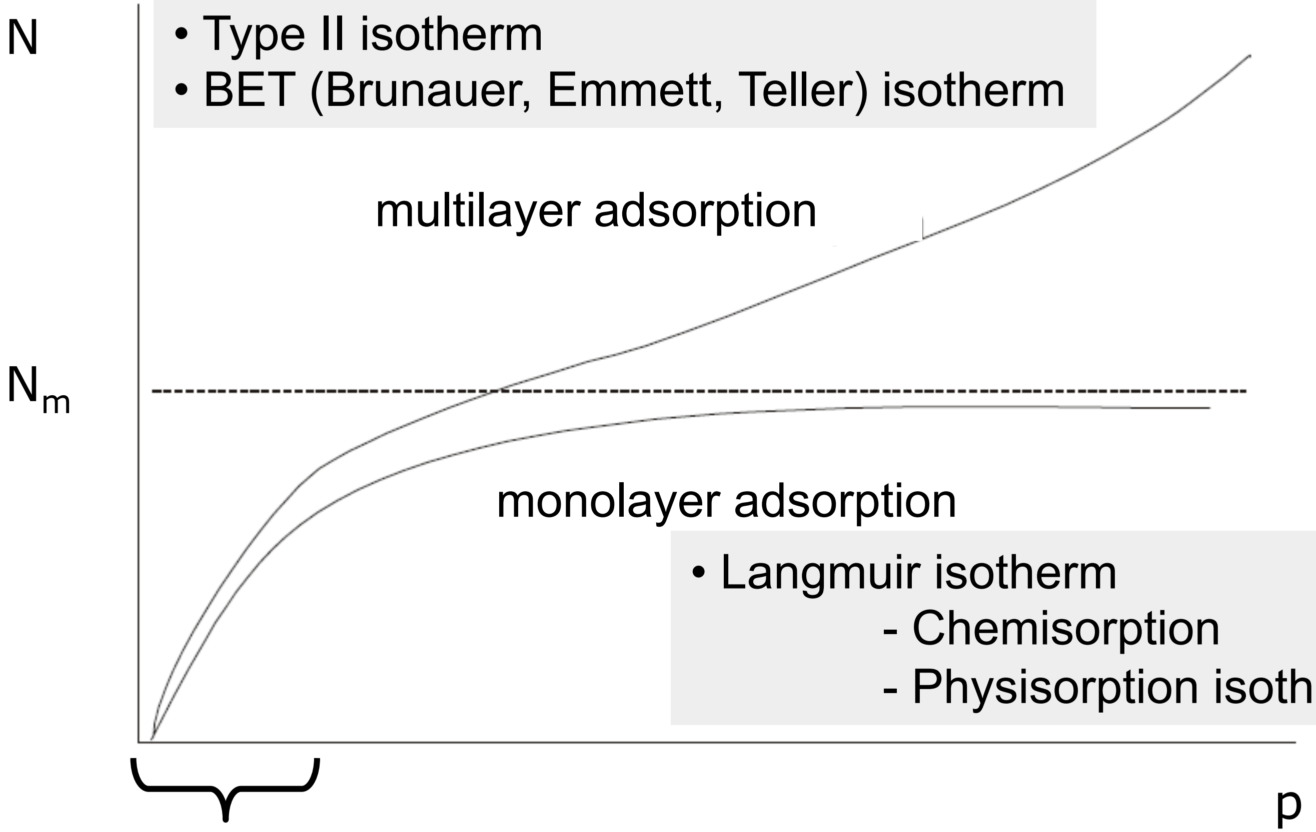
$N_m = 43\ \mu mol\ g^{-1}$

$S_{Langmuir} = 9.2\ m^2\ g^{-1}$

$S_{BET} = 8.8\ m^2\ g^{-1}$

A.L. McClellan, H.F. Harnsberger, J. Colloid Interface Sci. 23 (1967) 577.
S.J. Gregg, R. Stock, Trans. Faraday Soc. 53 (1957) 1355.

# Other isotherms



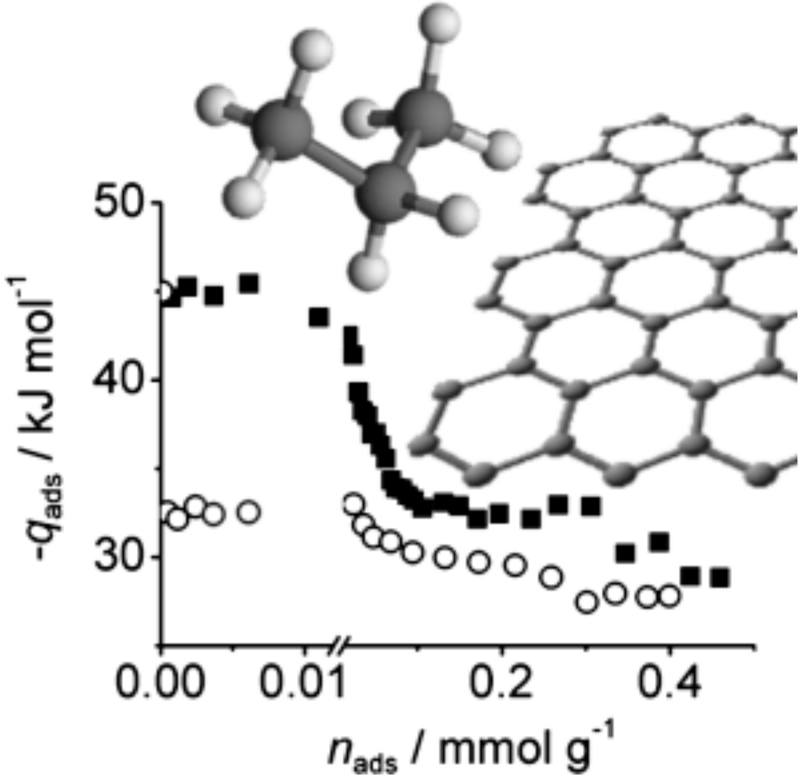
- Type II isotherm
- BET (Brunauer, Emmett, Teller) isotherm

- Langmuir isotherm
  - Chemisorption
  - Physisorption isotherms of type I

- Freundlich isotherm
  (interaction of adsorbed molecules)
  $$\theta = c_1 p^{1/c2}$$
- Temkin isotherm
  (adsorption enthalpy is a function of the pressure)
  $$\theta = c_1 ln(c_2 p)$$

# Other isotherms – $C_3H_8$ adsorption on CNTs - Temkin

B. Frank *et al.*, ChemPhysChem 12 (2011) 2709 – 2713.



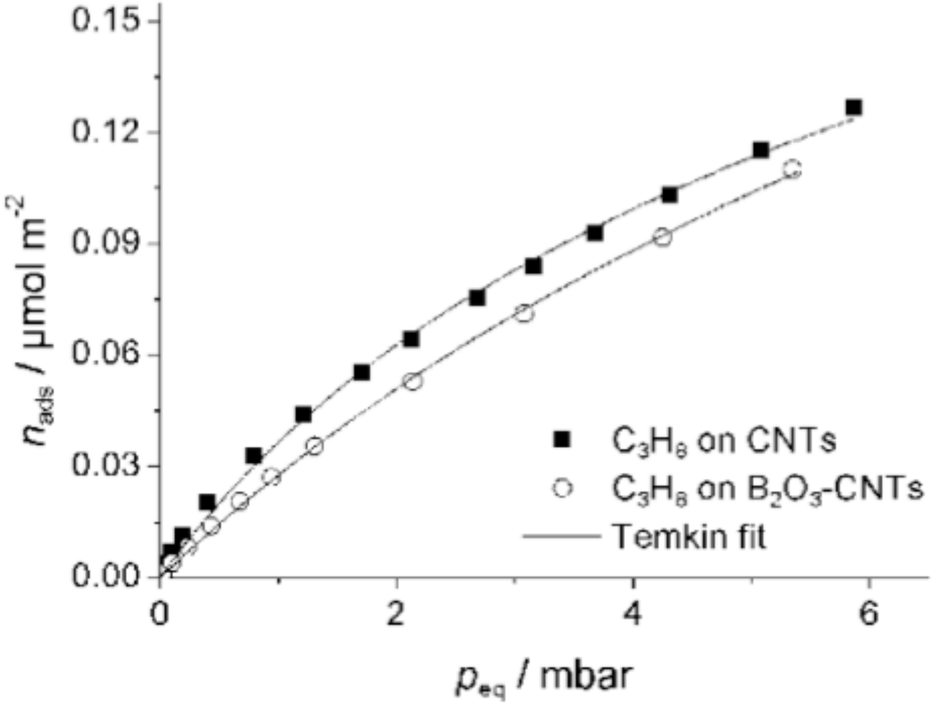
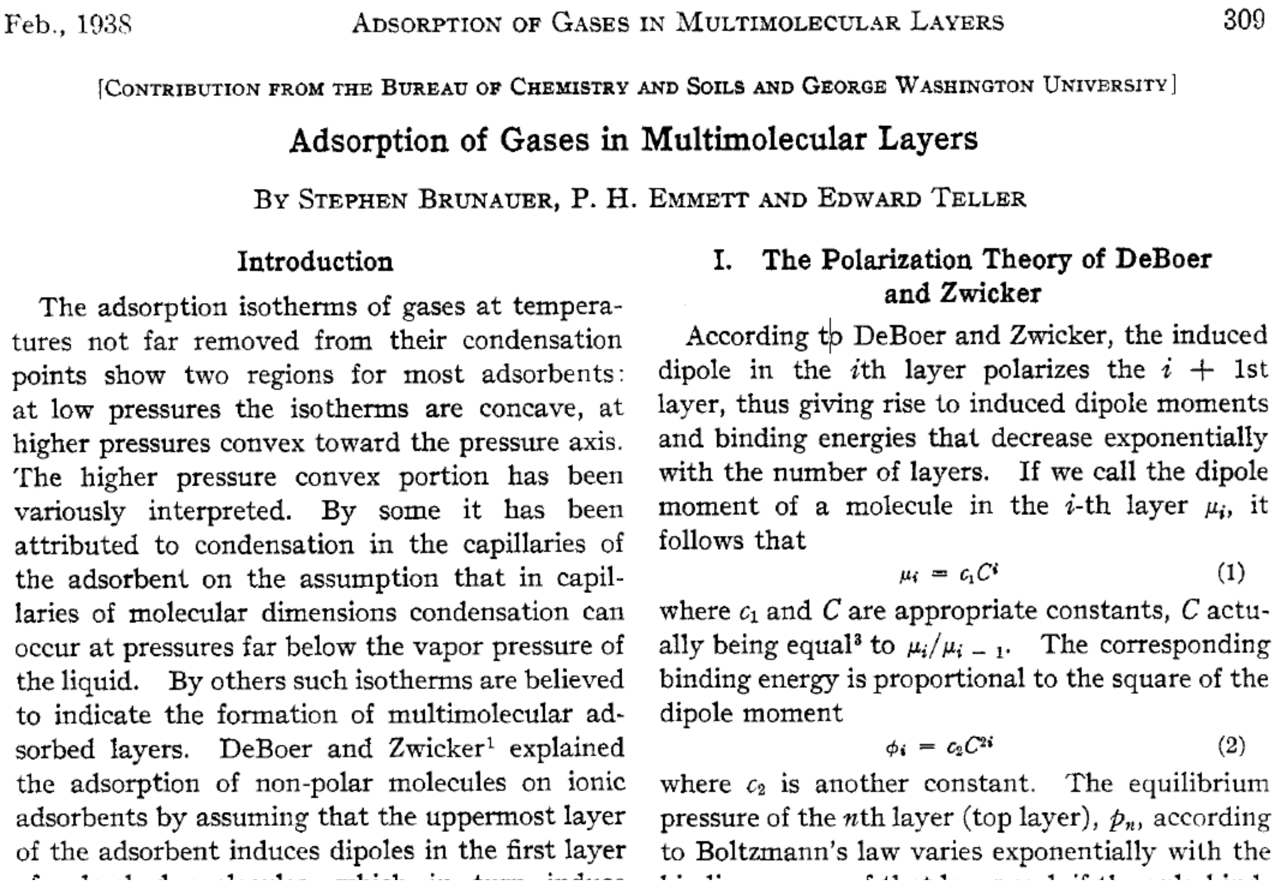


**Figure 3.** Isotherms of propane adsorption (313 K) on the oxygen surface groups of CNT and $B_2O_3$–CNT catalysts used in ODH of propane.

M. I. Temkin, Zhur. Fiz. Khim. 15 (1941) 296.

# BET isotherm (Brunauer, Emmett, Teller)*

3



Feb., 1938 ADSORPTION OF GASES IN MULTIMOLECULAR LAYERS 309

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS AND GEORGE WASHINGTON UNIVERSITY]

## Adsorption of Gases in Multimolecular Layers

BY STEPHEN BRUNAUER, P. H. EMMETT AND EDWARD TELLER

### Introduction

The adsorption isotherms of gases at temperatures not far removed from their condensation points show two regions for most adsorbents: at low pressures the isotherms are concave, at higher pressures convex toward the pressure axis. The higher pressure convex portion has been variously interpreted. By some it has been attributed to condensation in the capillaries of the adsorbent on the assumption that in capillaries of molecular dimensions condensation can occur at pressures far below the vapor pressure of the liquid. By others such isotherms are believed to indicate the formation of multimolecular adsorbed layers. DeBoer and Zwicker[1] explained the adsorption of non-polar molecules on ionic adsorbents by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer

### I. The Polarization Theory of DeBoer and Zwicker

According to DeBoer and Zwicker, the induced dipole in the $i$th layer polarizes the $i + 1$st layer, thus giving rise to induced dipole moments and binding energies that decrease exponentially with the number of layers. If we call the dipole moment of a molecule in the $i$-th layer $\mu_i$, it follows that

$$\mu_i = c_1 C^i \qquad (1)$$

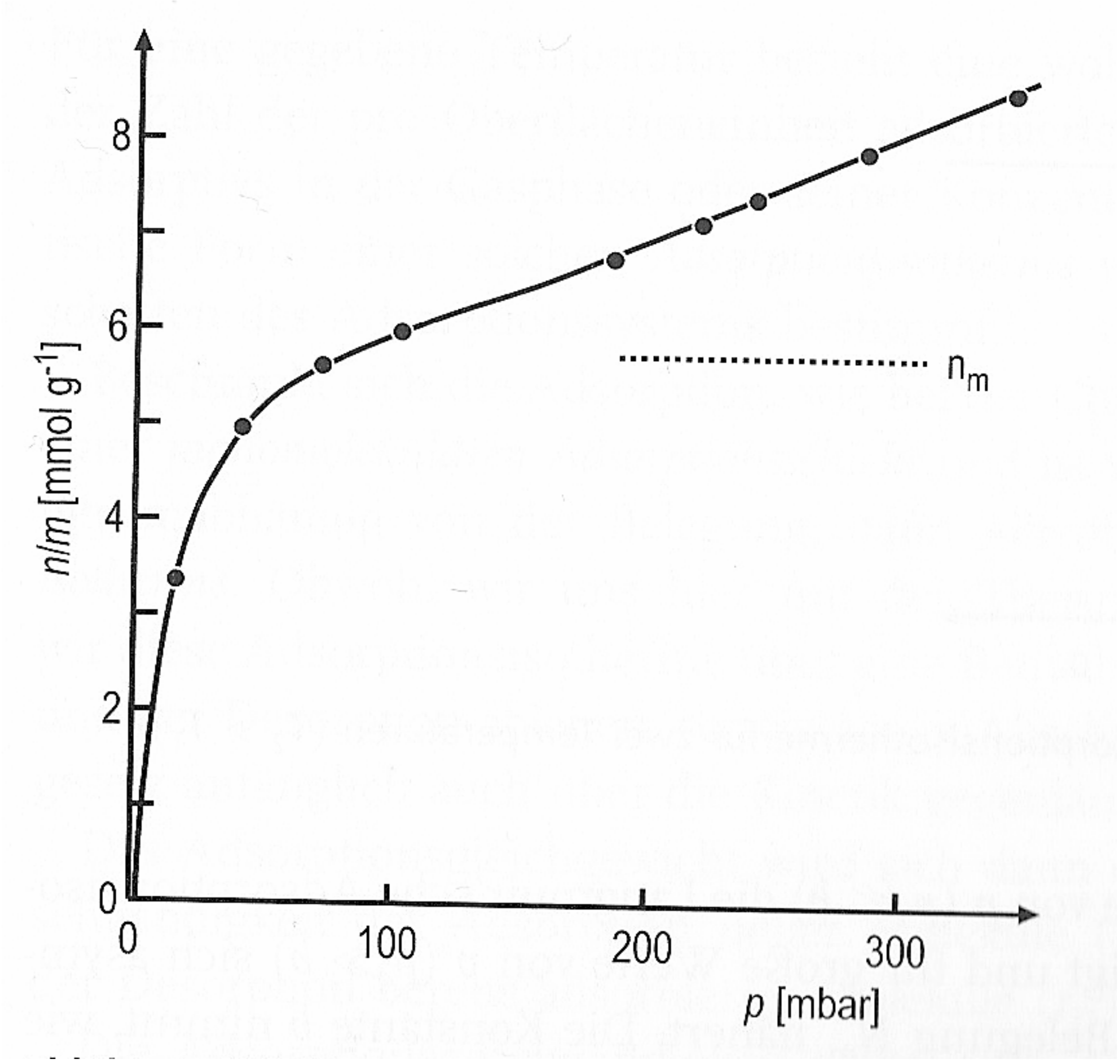
where $c_1$ and $C$ are appropriate constants, $C$ actually being equal[3] to $\mu_i/\mu_{i-1}$. The corresponding binding energy is proportional to the square of the dipole moment

$$\phi_i = c_2 C^{2i} \qquad (2)$$

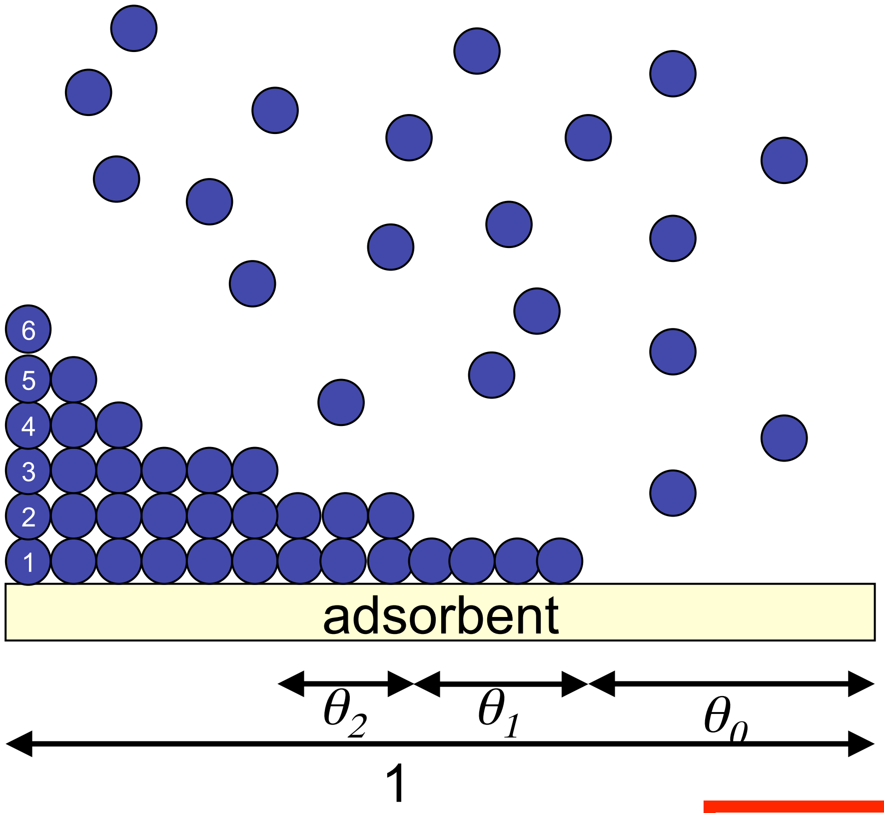
where $c_2$ is another constant. The equilibrium pressure of the $n$th layer (top layer), $p_n$, according to Boltzmann's law varies exponentially with the

* S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

# Nitrogen adsorption on silica at 77 K



# BET isotherm (Brunauer, Emmett, Teller)*



Description of all isotherm types

Assumptions

- Multilayer adsorption
- First layer: Langmuir adsorption
- Second and further layers: condensation of gas onto liquid
- Heat of adsorption:

  First layer > second layer = … = …= heat of condensation

$$\boxed{\theta = \frac{N}{N_m} = \frac{C \cdot (p/p_0)}{(1 - p/p_0) \cdot [1 - p/p_0 + C(p/p_0)]}}$$

$p_0$ ...vapor pressure of liquid $N_2$

* S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

# BET plot

$$\boxed{\frac{1}{W\left[p/p_0 - 1\right]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{p}{p_0}\right)}$$

*W* … mass of adsorbed $N_2$

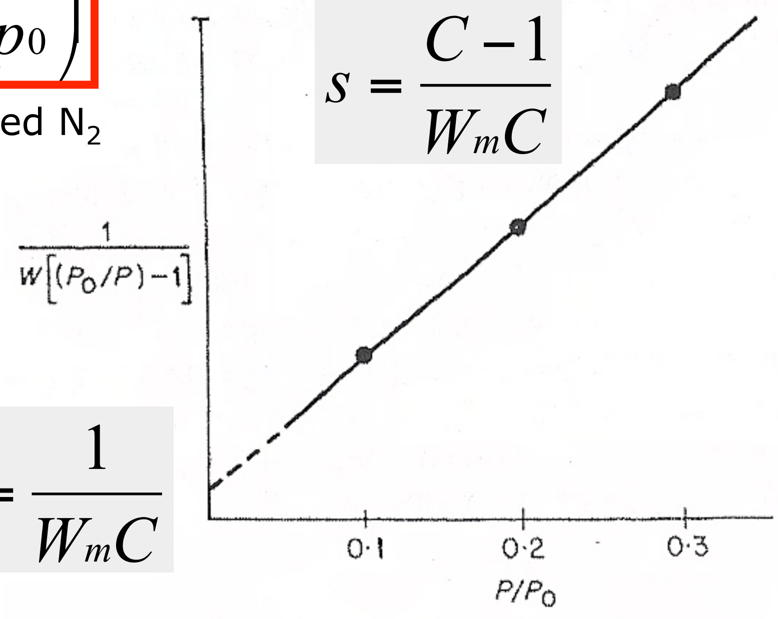
$$W_m = \frac{1}{s+i}$$

$$C = \frac{s}{i} + 1$$

$$\boxed{S = \frac{W_m N_A A_x}{M_{adsorptive}}}$$

$$\boxed{S_{sp.} = \frac{S}{m}}$$

Relative pressures near completed monolayers
$0.05 < p/p_0 < 0.3$



$$s = \frac{C-1}{W_m C}$$

$$i = \frac{1}{W_m C}$$

Single point BET
Assumption: For high values of C the intercept may be taken as zero

$$\boxed{W_m = W\left(1 - \frac{p}{p_0}\right)}$$

$$\boxed{S = W\left(1 - \frac{p}{p_0}\right)\frac{N_A}{M_{adsorptive}} A_x}$$

# Applicability of the BET theory

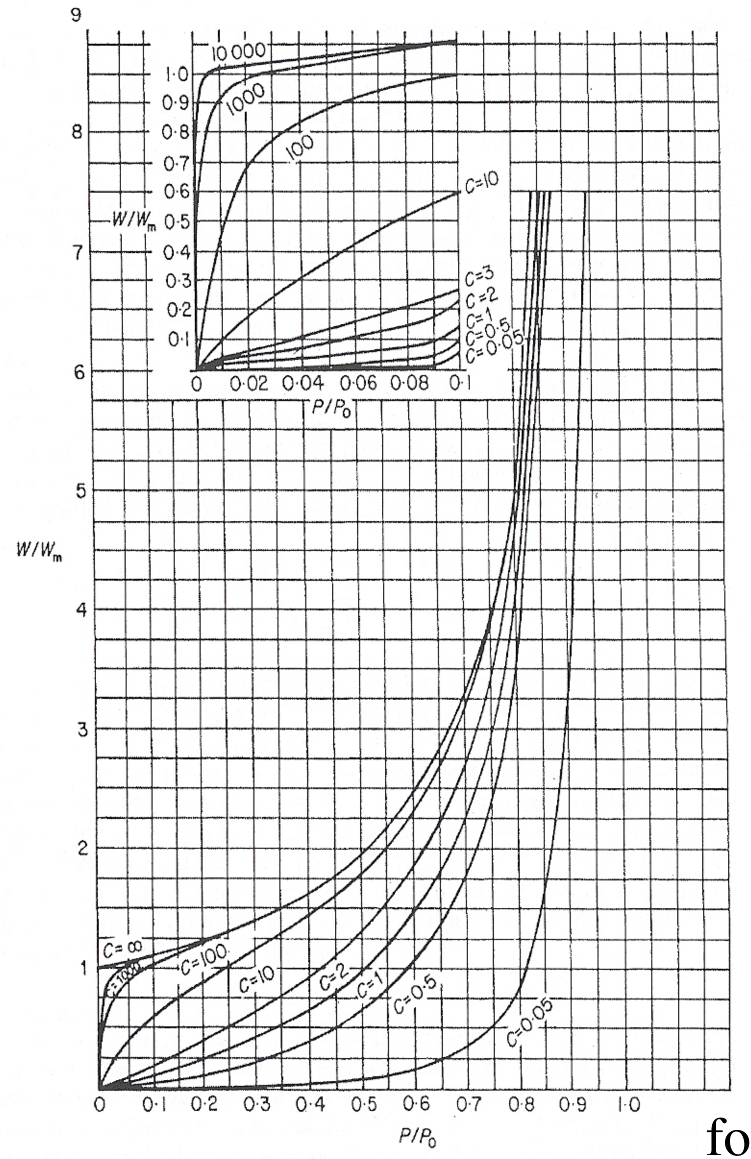
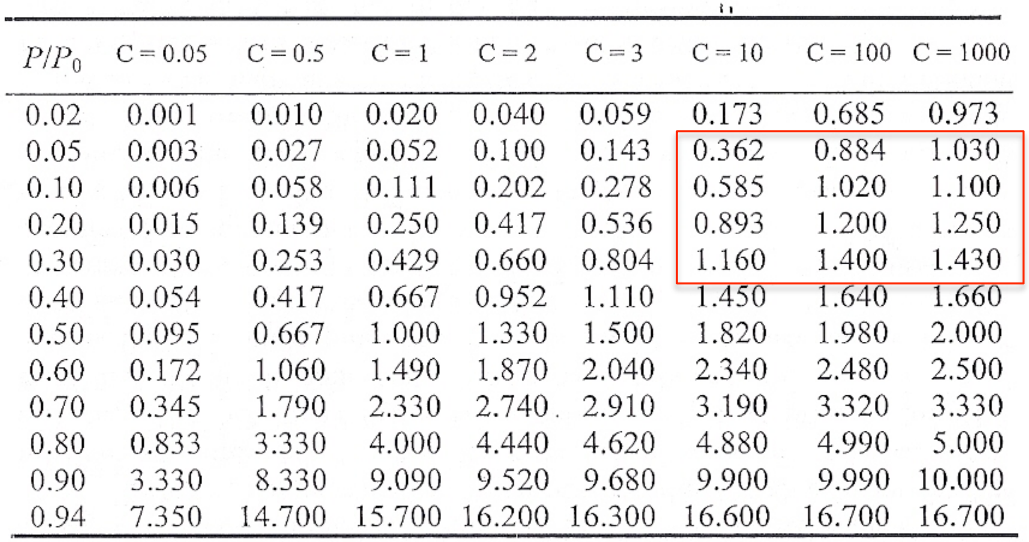


*Figure 5.3* Isotherm shapes as a function of BET C values.

In the region of relative pressures near completed monolayers (0.05<$p/p_0$<0.3) experiment and theory agree well → powerful method of surface area determination

$$C = e^{(\Delta_{des}H - \Delta_{evac}H/RT)}$$

*Table 5.3* Values of $W/W_m$ and relative pressures for various values of $C$.



| $P/P_0$ | C = 0.05 | C = 0.5 | C = 1 | C = 2 | C = 3 | C = 10 | C = 100 | C = 1000 |
|---|---|---|---|---|---|---|---|---|
| 0.02 | 0.001 | 0.010 | 0.020 | 0.040 | 0.059 | 0.173 | 0.685 | 0.973 |
| 0.05 | 0.003 | 0.027 | 0.052 | 0.100 | 0.143 | 0.362 | 0.884 | 1.030 |
| 0.10 | 0.006 | 0.058 | 0.111 | 0.202 | 0.278 | 0.585 | 1.020 | 1.100 |
| 0.20 | 0.015 | 0.139 | 0.250 | 0.417 | 0.536 | 0.893 | 1.200 | 1.250 |
| 0.30 | 0.030 | 0.253 | 0.429 | 0.660 | 0.804 | 1.160 | 1.400 | 1.430 |
| 0.40 | 0.054 | 0.417 | 0.667 | 0.952 | 1.110 | 1.450 | 1.640 | 1.660 |
| 0.50 | 0.095 | 0.667 | 1.000 | 1.330 | 1.500 | 1.820 | 1.980 | 2.000 |
| 0.60 | 0.172 | 1.060 | 1.490 | 1.870 | 2.040 | 2.340 | 2.480 | 2.500 |
| 0.70 | 0.345 | 1.790 | 2.330 | 2.740 | 2.910 | 3.190 | 3.320 | 3.330 |
| 0.80 | 0.833 | 3.330 | 4.000 | 4.440 | 4.620 | 4.880 | 4.990 | 5.000 |
| 0.90 | 3.330 | 8.330 | 9.090 | 9.520 | 9.680 | 9.900 | 9.990 | 10.000 |
| 0.94 | 7.350 | 14.700 | 15.700 | 16.200 | 16.300 | 16.600 | 16.700 | 16.700 |

for most of the adsorbents observed: $50 \le C \le 300$

# Cross-sectional area

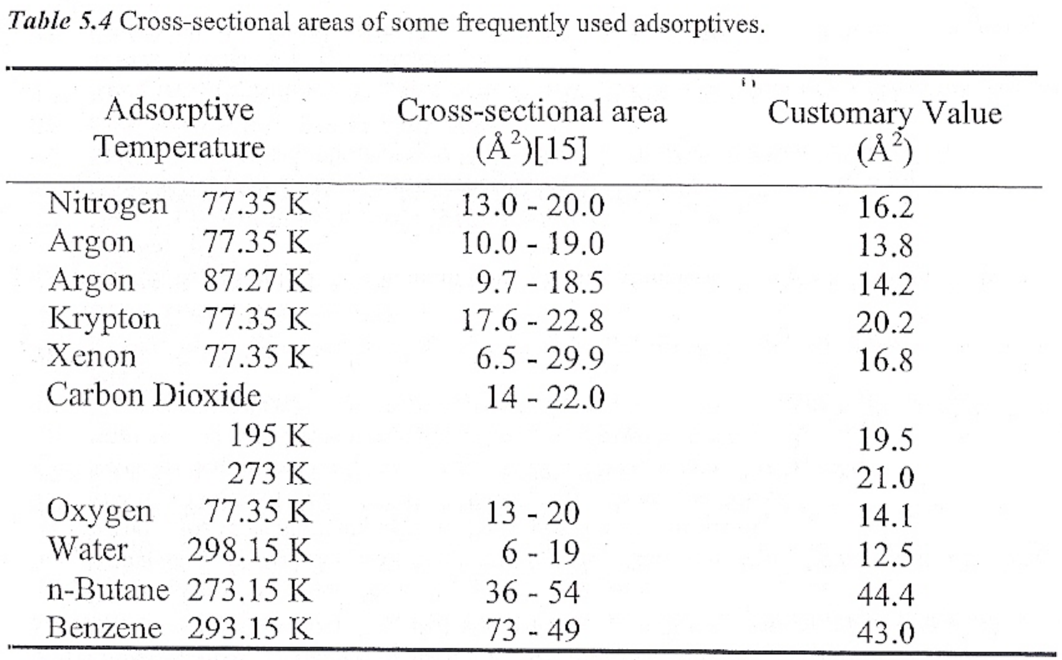


*Table 5.4* Cross-sectional areas of some frequently used adsorptives.

| Adsorptive | Temperature | Cross-sectional area ($Å^2$)[15] | Customary Value ($Å^2$) |
|---|---|---|---|
| Nitrogen | 77.35 K | 13.0 - 20.0 | 16.2 |
| Argon | 77.35 K | 10.0 - 19.0 | 13.8 |
| Argon | 87.27 K | 9.7 - 18.5 | 14.2 |
| Krypton | 77.35 K | 17.6 - 22.8 | 20.2 |
| Xenon | 77.35 K | 6.5 - 29.9 | 16.8 |
| Carbon Dioxide | | 14 - 22.0 | |
| | 195 K | | 19.5 |
| | 273 K | | 21.0 |
| Oxygen | 77.35 K | 13 - 20 | 14.1 |
| Water | 298.15 K | 6 - 19 | 12.5 |
| n-Butane | 273.15 K | 36 - 54 | 44.4 |
| Benzene | 293.15 K | 73 - 49 | 43.0 |

Krypton established for low surface area measurements (0.5-0.05 $m^2$) due to its low saturation pressure at 77K

***Nitrogen as the standard adsorptive***

- For most of the adsorbents the C constant lies in the range from about 50 to 300 (no very weak interaction, no chemisorption)
- Its permanent quadrupole moment is responsible for the formation of well-defined monolayers on most of the surfaces
- Overestimation of surface areas of hydroxylated silica surfaces by 20% due to specific interactions with the polar surface groups (use 13.5 $Å^2$)

* Literatur IUPAC.

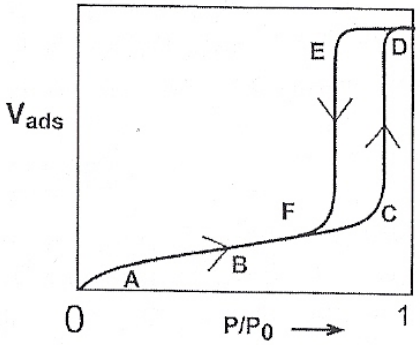
# Outline

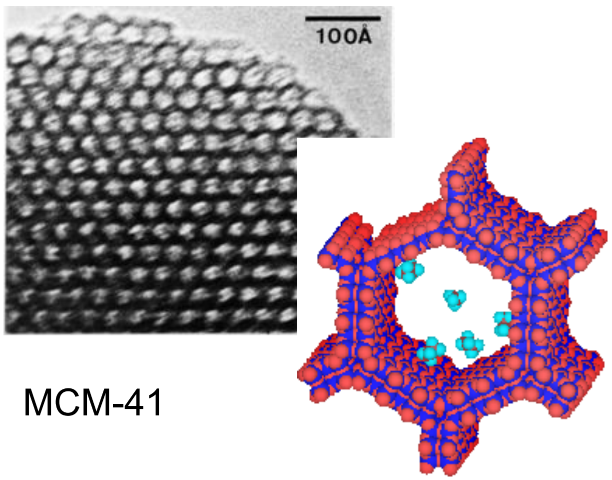
1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

# Capillary condensation in mesopores (2 – 50 nm)

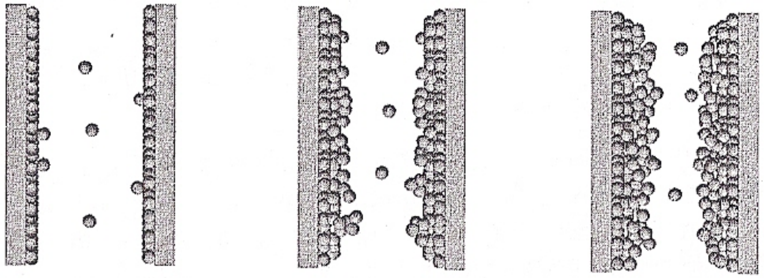
Capillary condensation

Phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure *p* less than saturation pressure $p_0$ of the bulk liquid





MCM-41



A Monolayer formation

B Multilayer adsorption

C Critical film thickness reached

D Capillary condensation

E Pore evaporation

F multilayer film

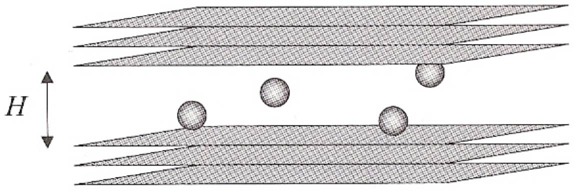


**Fig. 3.** The slit pore model. Each layer represents a graphene layer.

# Classification* of the hysteresis loops

The wider the pore size distribution the less sharper is the pore condensation step

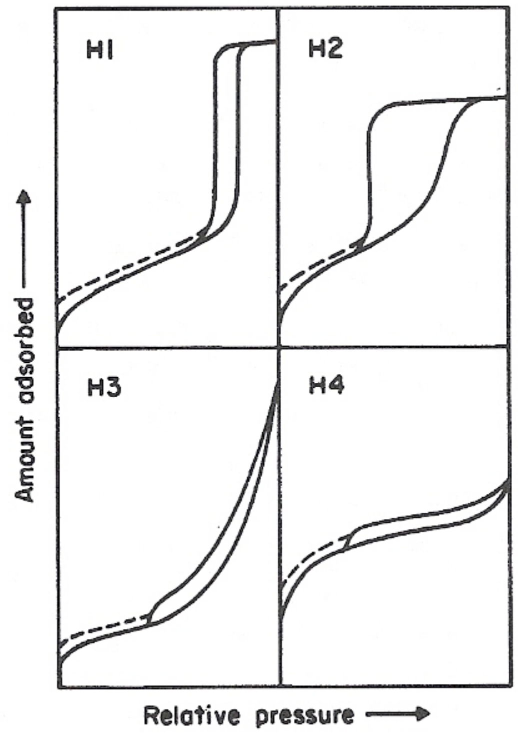


Fig. 3. Types of hysteresis loops

H1 well defined cylyndrical pore channels

H2 disordered pores
(pore blocking, percolation phenomena)

H3 non-rigid aggregates of plate-like particles
(slit-shaped pores)

H4 narrow slit pores including pores in the
micropore region

***Low pressure hysteresis***
***no accurate pore size analysis possible!***
- Changes in the volume of the adsorbent
  - Swelling of non-rigid pores
- Irreversible uptake of molecules in the pores
- Chemisorption

* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

# Kelvin equation

The relative pressure where the pore condensation occurs depends on the pore radius

The Kelvin equation provides a correlation between pore diameter and pore condesation pressure

Assumptions

•Pores of cylindrical shape
•No fluid-wall interactions

$$\boxed{\ln \frac{p}{p_0} = \frac{-2\gamma V_l}{r_p RT}}$$

$\gamma$ surface tension of liquid nitrogen
$V_l$ liquid molar volume
$r_p$ pore radius
$r_k$ critical radius
$R$ universal gas constant
$t$ statistical thickness

$$r_k = \frac{4.15}{\log(p_0/p)}\,\text{Å}$$

($N_2$, 77 K)

$$r_p = r_k + t$$

$$t = 3.54\left[\frac{5}{\ln(p/p_0)}\right]\text{Å}$$

- The depth of the adsorbed multilayer film present prior to condensation is expressed in form of the statistical thickness *t* (number of layers times thickness of one layer)
- The thickness of one closed-packed hexagonal $N_2$ layer is 3.54 A
- *t* is a function of the relative pressure
- The empirical equation depends on the adsorbent

## Pore size distribution

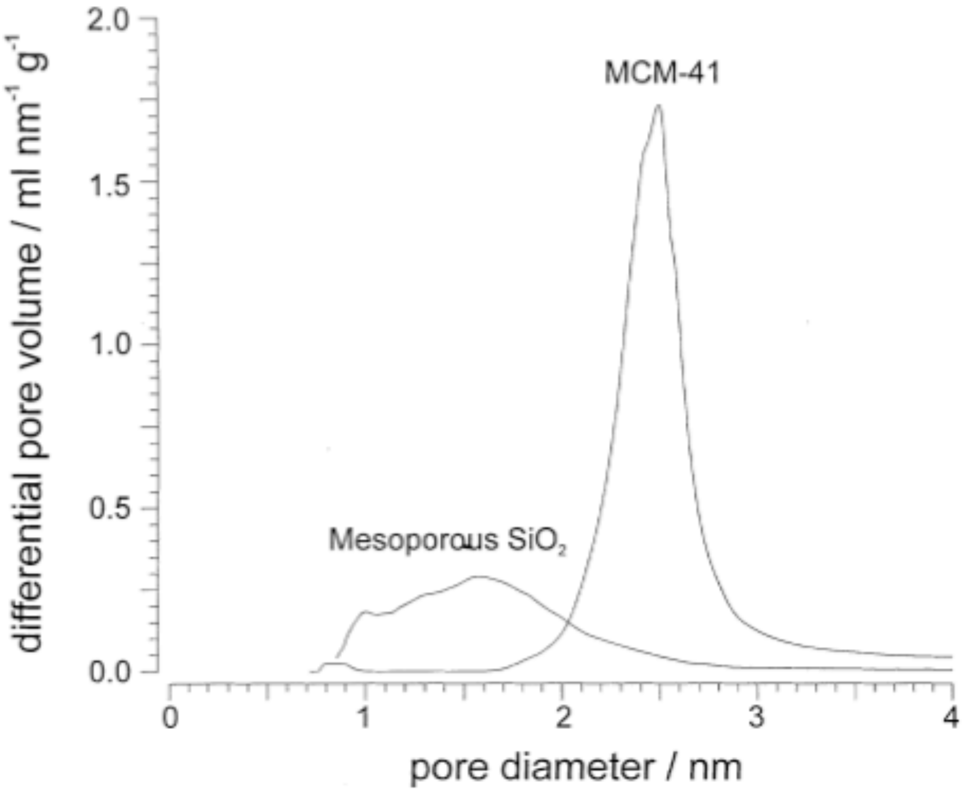


Fig. 3. Pore-size distribution according to the BJH method.

*S. Storck et al. / Applied Catalysis A: General 174 (1998) 137-146.*

# *Why hysteresis? Which branch to use?*

The shape of the isotherm does not depend only on the texture of the porous material, but also on the differences of the thermodynamic states between the confined fluid and the bulk fluid

### *H1 - independent cylindrical pores (MCM-41, SBA-15)*

„Independent pore model“

- Pore condensation is associated with metastable states of the pore fluid in ordered materials
- The **desorption branch** of the hysteresis loop reflects the equilibrium phase transition
- Methods, which describe the equilibrium phase transition (**BJH**) have to be applied to the desorption branch
- Applicable also to three-dimensional network of pores

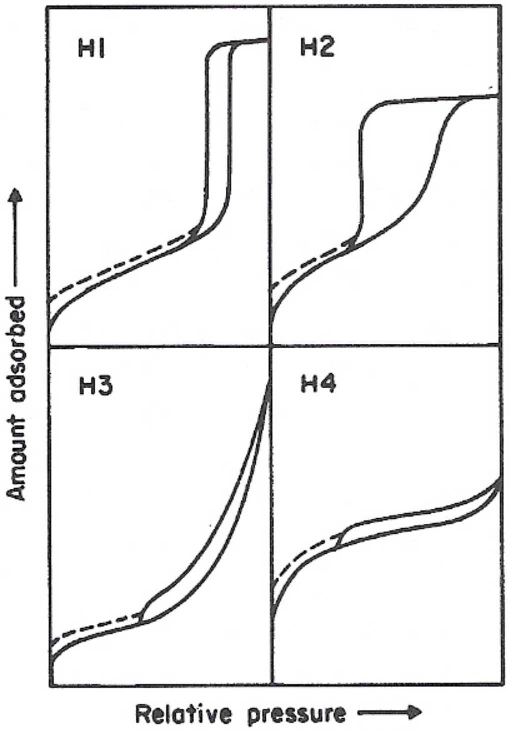


Fig. 3. Types of hysteresis loops

### *H2, H3 – disordered, connected pores*

- Origin of hysteresis not yet completely understood
- Pore blocking (inkbottle pores) associated with the desorption process
- Analysis of the **adsorption branch** (**NLDFT**-spinodal condensation method, Kelvin equation based approach calibrated for the adsorption branch)

# *Why hysteresis? Which branch to use?*

**4**

## Tensile Strength Effect (TSE)

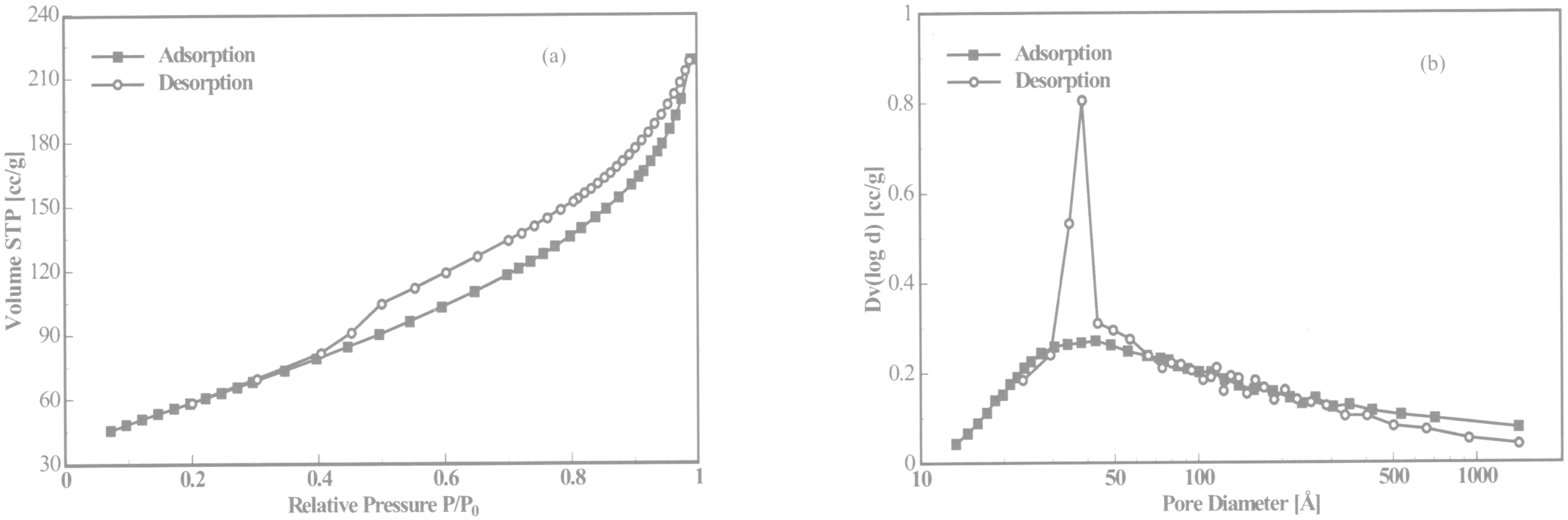


*Figure 8.7* (a) Nitrogen adsorption/desorption at ~77 K on a disordered alumina catalyst; (b) BJH pore size distribution curves from adsorption and desorption branches.

S. Lowell, p. 122.

# Outline

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# Adsorption in Micropores

| Micropores | Width* [nm] | Pore filling governed by |
|---|---|---|
| Supermicropores | 0.7 ~ 2 | Gas-solid interactions<br>Cooperative mechanism |
| Ultramicropores | < 0.7 | Bilayer thickness of the $N_2$ molecule!<br>Gas-solid interaction |

Micropore filling is a continuous process and different from pore condensation in mesopores, filling of micropores is completed at $p/p_0$ <0.01

***Adsorption potential theories (0.4 nm ~ )***

Classical methods based on macroscopic, thermodynamic assumptions
- Polanyi
- Dubinin (DR method)
- Stoeckli
- Horvath-Kawazoe

Density Functional Theory

Monto Carlo simulations

***Empirical methods (0.7~2nm)***

t-method

MP-method

$\alpha_s$-method

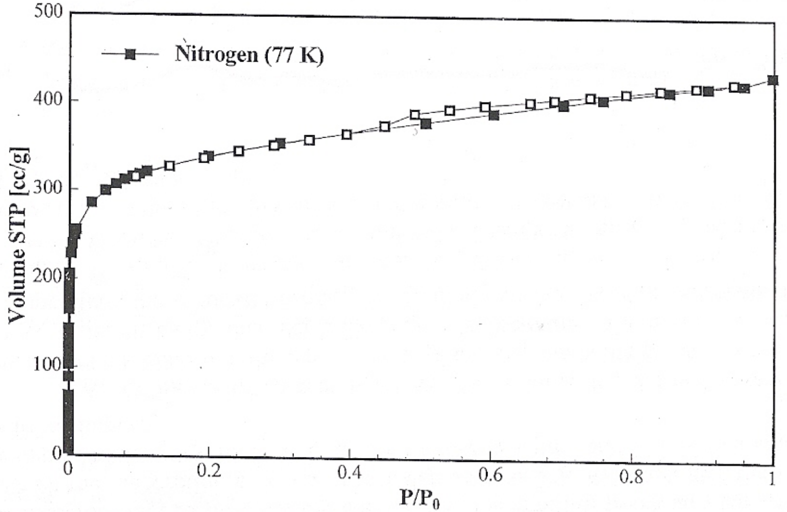

*Figure 4.2* Nitrogen adsorption at 77.35 K on an active carbon sample, which contains, in addition to its microporosity, some mesoporosity indicated by the occurrence of hysteresis and the fact that the adsorption isotherm does not reveal a truly horizontal plateau at relative pressures > 0.1; the observed slope being associated with the filling of mesopores.

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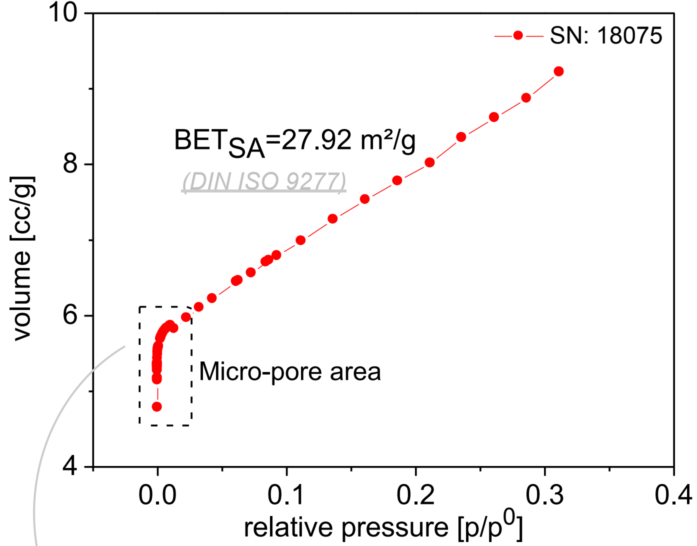
* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

# *Adsorption in Micropores*

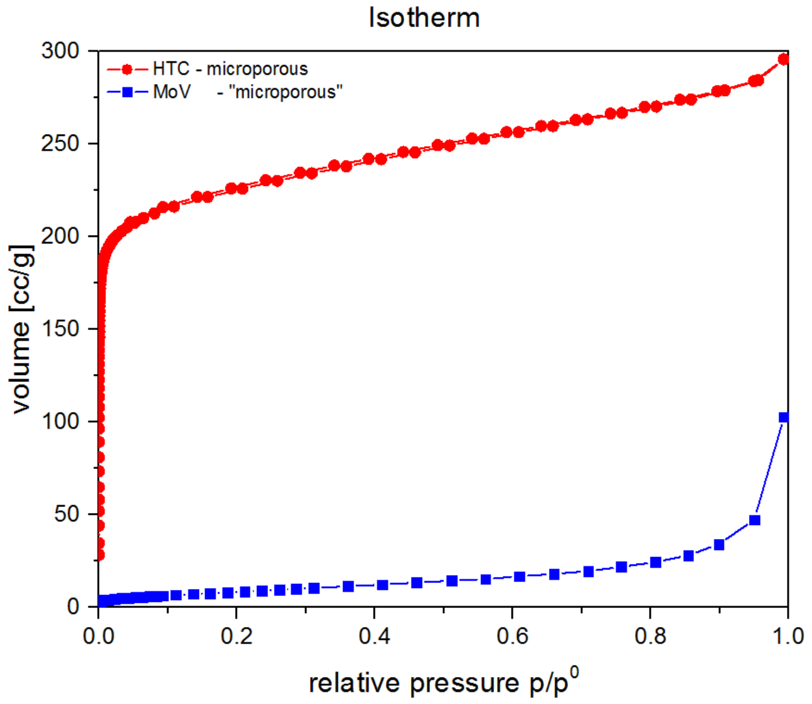
**Multipoint BET with micropore analysis**

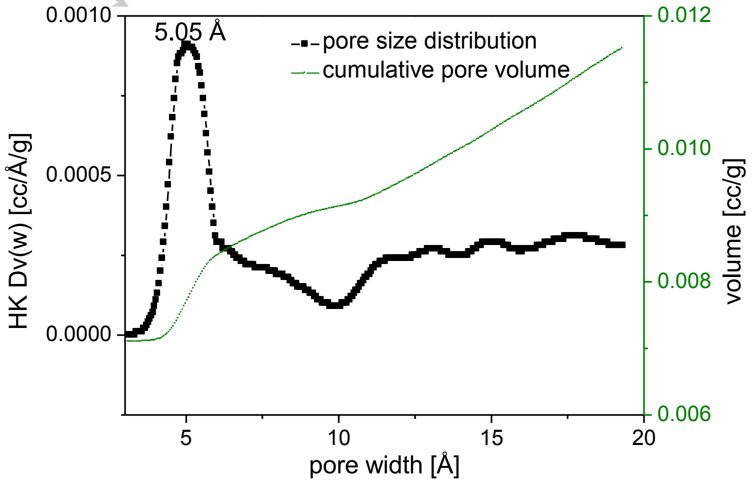


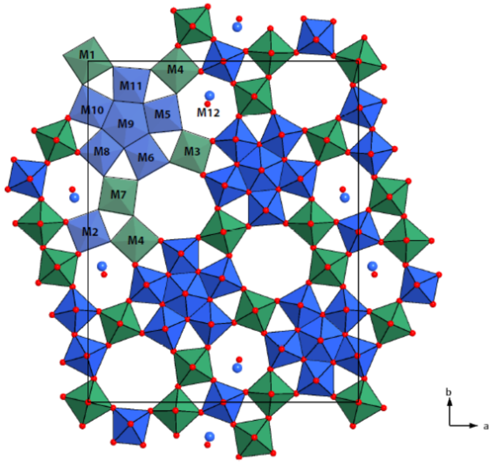
t-Method de Boer (DIN 66135)

External Surface Area = **9.84** m²/g

Micro-pore area = 18.08 m²/g







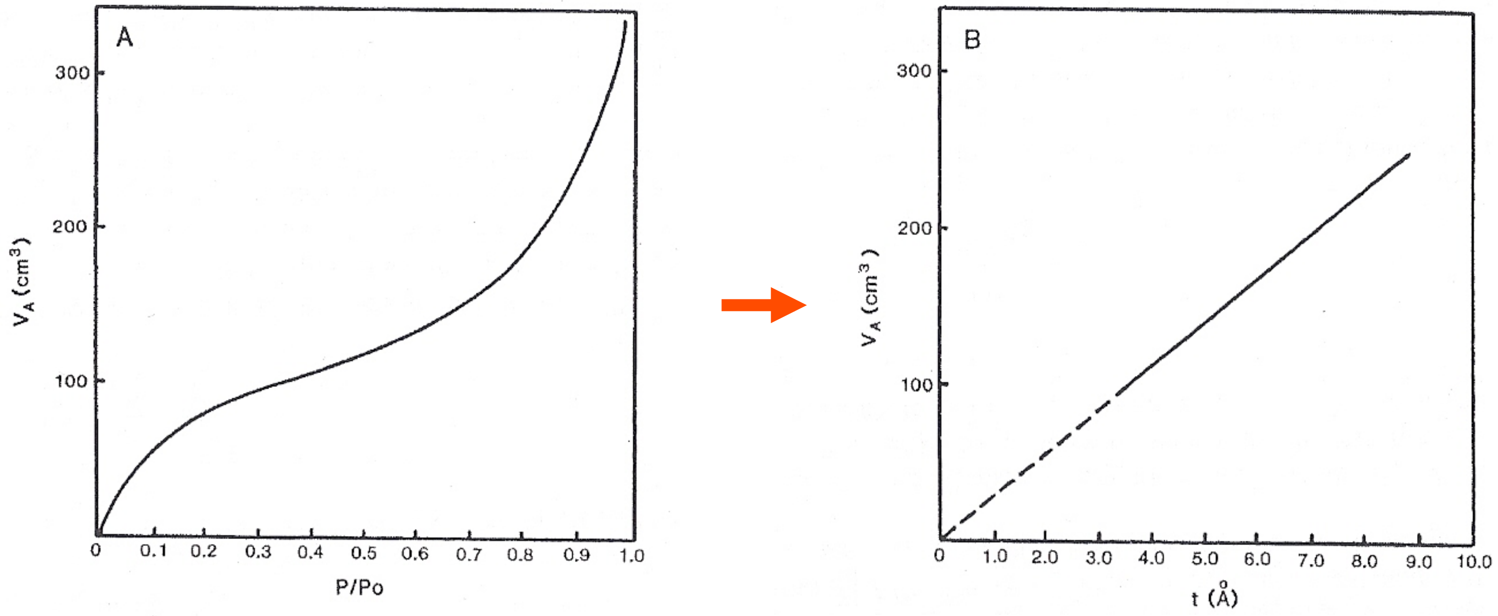
Crystal structure:
Channels between
5 and 7 Angström

# Concept of V-t curves

Assumption

- The thickness of the absorbed film on pore walls is uniform → statistical thickness *t*
- It has been shown for type II isotherms that a plot of the volume adsorbed versus t gives a staight line through the origin

V-t curve



In absence of micropores surface areas calculated from the slope comparable to BET values

# The t-method

- The t values are in practice calculated with the help of thickness equations that describe the particular standard reference curve

Siliceous materials

$$t = \left[ \frac{13.99}{\log(p/p_0) + 0.034} \right]^{\frac{1}{2}} \text{Å}$$

J.H.De Boer *et al.,* J. Colloid Interface Sci. 21 (1966) 405.

C-like materials

$$t = 0.88(p/p_0)^2 + 6.45(p/p_0) + 2.98 \text{ Å}$$

ASTM standard D-6556-01

# The t-method

Intercept: Volume of micropores

$V_{micro} = i \times 0.001547\ \mathrm{cm}^3$

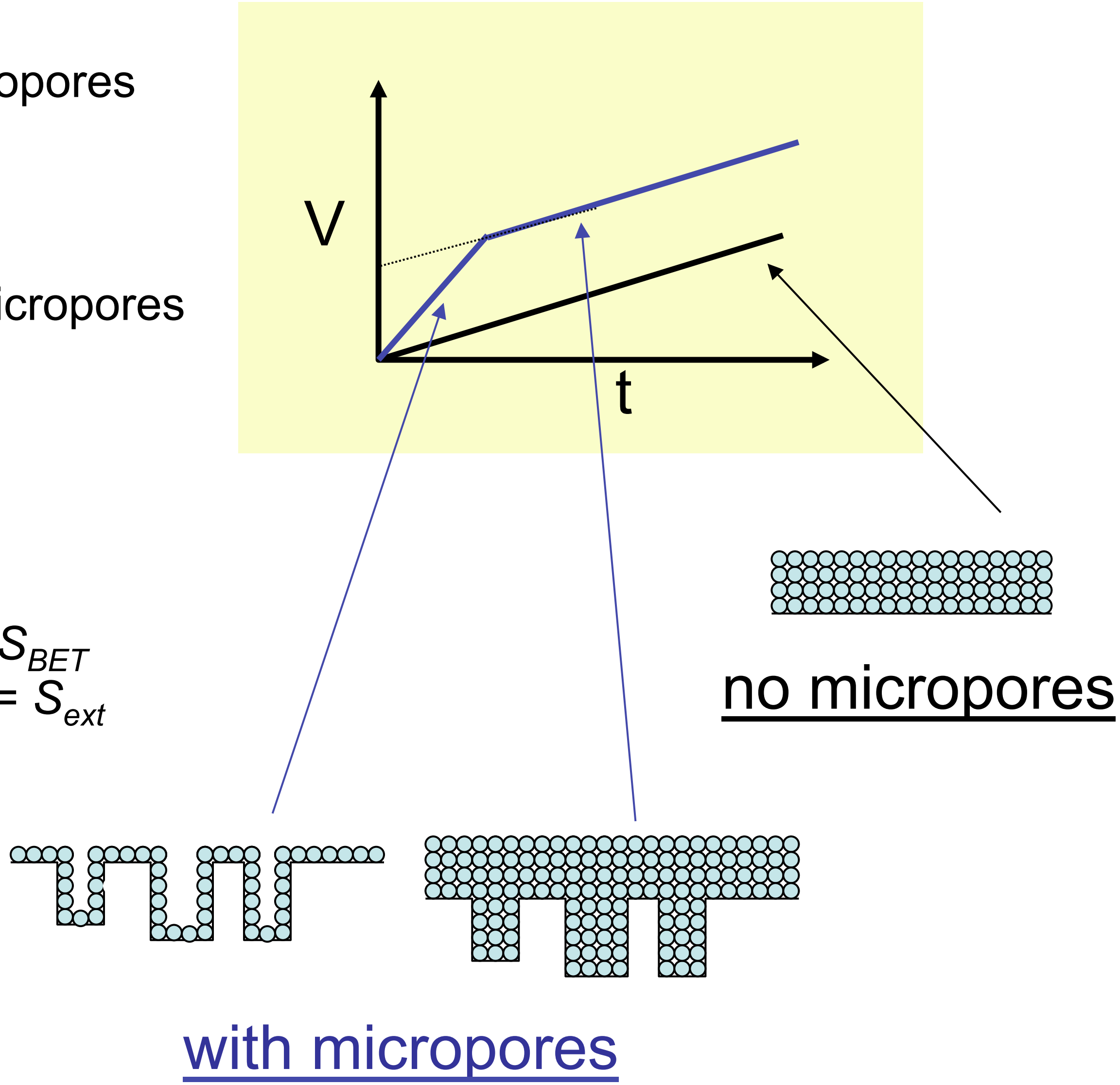
Slope: Surface area of micropores

$$t = \frac{V_{liq}}{S} \times 10^4\ \text{Å}$$

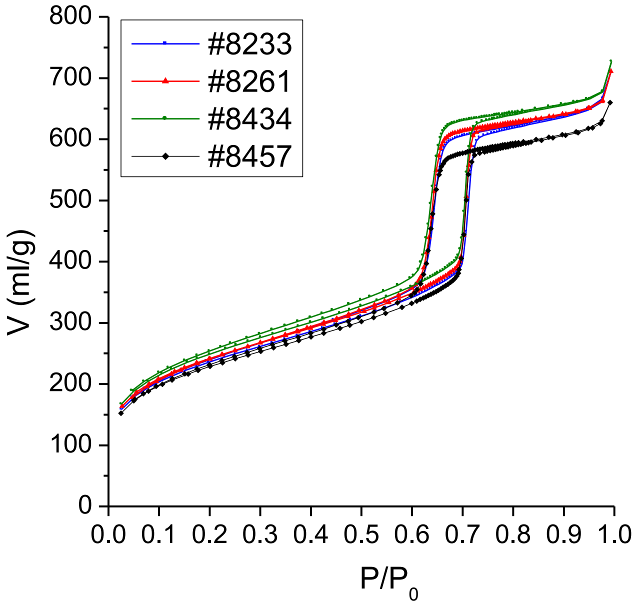
$S_t = s \times 15.47\ \mathrm{m}^2/\mathrm{g}$

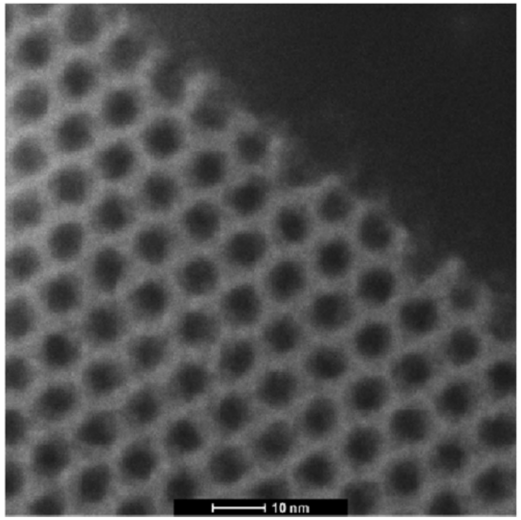
nonporous material: $S_t = S_{BET}$
microporous material: $S_t = S_{ext}$

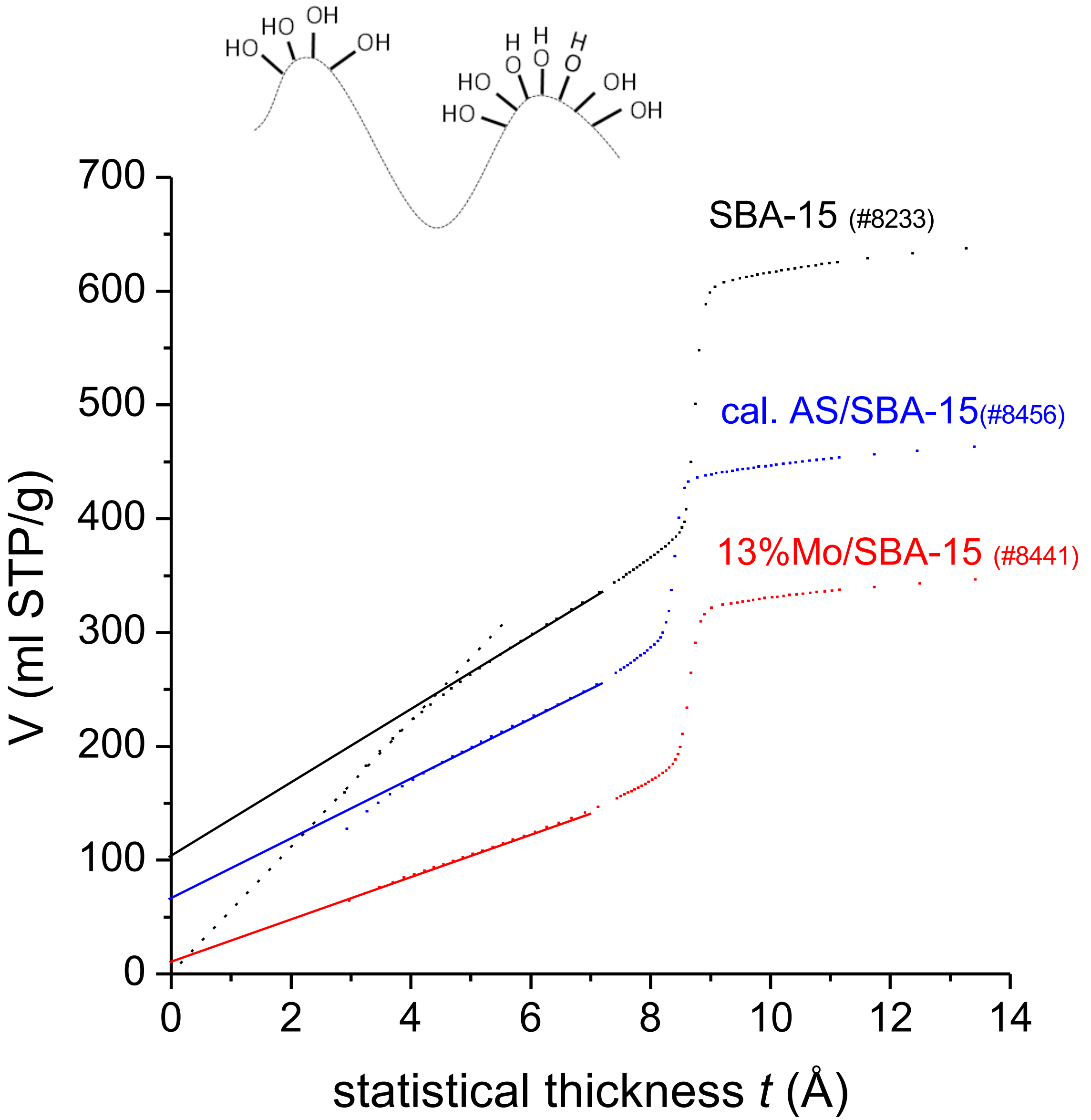
$S_{micro} = S_{BET} - S_{ext}$



# SBA-15: micropores and mesopores







# Surface area and textural properties of modified SBA-15

Properties of $MoO_x$/SBA-15

| Mo loading [a] | Surface Mo density (nm$^{-2}$) | | $A_s$ | $A_\mu$ [e] | | $V_p$ [g] | $d_p$ [h] |
|---|---|---|---|---|---|---|---|
| (wt%) | Mo [b] (nm$^{-2}$) | Isolated SiOH [c, d] (nm$^{-2}$) | (m$^2$/g) | (m$^2$/g) | (%) [f] | (ml/g) | (nm) |
| 0 | 0 | 1.6 [c] | 859 | 261 | 36 | 1 | 7.5 |
| 2.1 | 0.21 | 1.1 [d] | 637 | 164 | 31 | 0.79 | 7.1 |
| 5.1 | 0.58 | 0.88 [d] | 554 | 127 | 28 | 0.71 | 7.1 |
| 6.6 | 0.85 | 0.68 [d] | 490 | 135 | 28 | 0.61 | 7.1 |
| 9.7 | 1.09 | 0.39 [d] | 556 | 96 | 21 | 0.78 | 7.2 |
| 13.3 | 2.51 | 0.07 [d] | 332 | 36 | 13 | 0.55 | 7.4 |

[a] by XRF, [b] Mo loading (at%) divided by $A_s$, [c] by TG, [d] by IR at the dehydrated state using relative heights of the silanol peak at 3745cm$^{-1}$, [e] micropore (< ~0.9 nm of width) surface estimated by *t*-plot method, [f] $A_\mu$ divided by $A_S$, [g] at $P/P_0 = 0.95$, [g] at the dehydrated state; [h] estimated by NLDFT approach.

# *Acknowledgements*

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for measurements and discussion

Thank you for your attention