Modern Methods in Heterogeneous Catalysis Research

Surface area and pore size determination

19/10/2007

A. Trunschke

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.

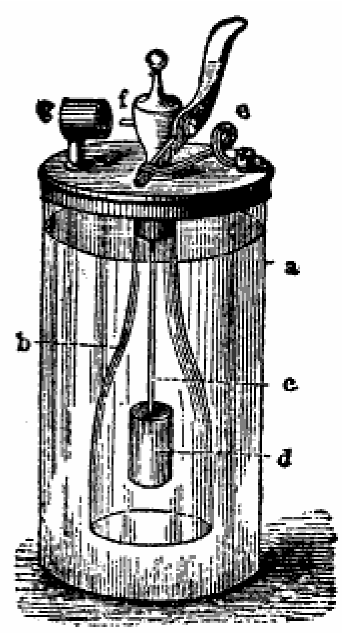
R. Brdička, Grundlagen der physikalischen Chemie, Deutscher Verlag der Wissenschaften, Berlin 1982.

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
4. Adsorption in micropores
5. Capillary condensation in mesopores
6. Experimental



$(NH_4)_2[PtCl_6] \xrightarrow{600\text{-}800°C}$ Pt with high surface area

$\downarrow$

$2 H_2 + O_2 \rightarrow 2 H_2O$

Johann Wolfgang Döbereiner‘s lighter (1823)

Some catalysts and support materials in heterogeneous catalysis

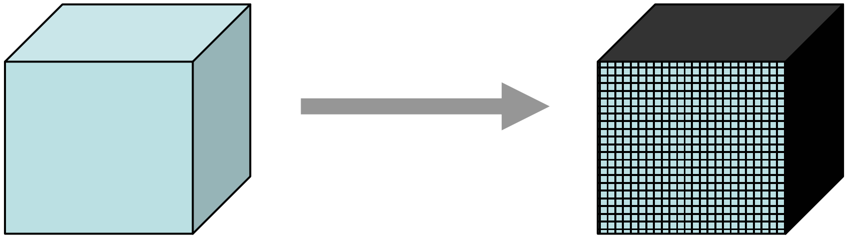
adsorbent	surface area [m^2/g]
charcoal	300 - 2500
silica gel	300 -350
γ-alumina	200 - 500
zeolites	500 - 1100

Factors affecting surface area

1

1 particle of edge
lenght = 1 m

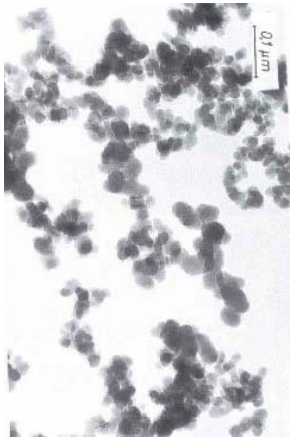
10^{18} particles of edge
lenght = 10^{-6} m



$S=6\ m^2$

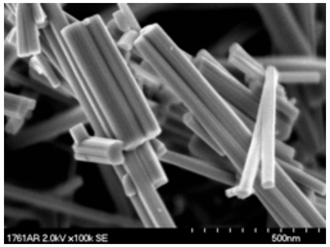
$S_i=6\times10^{-12}\ m^2$
$S_{total}=6\times10^{6}\ m^2$

size



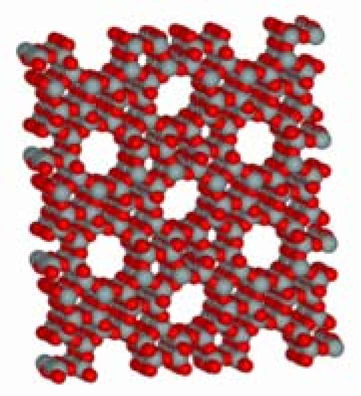
Aerosil 300
$S = 300\ m^2/g$

www.aerosil com



$MoVTeNbO_x$

shape



Structure of ZSM-5

porosity

Surface area measurements

- 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

$$g_1(Q,t) = e^{-DQ^2 t} = e^{-\frac{t}{\tau}}$$

Q= scattering vector

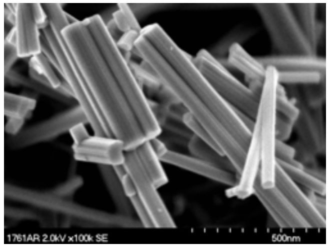
$$Q = \frac{4\pi n_M}{\lambda} * \sin(\theta)$$

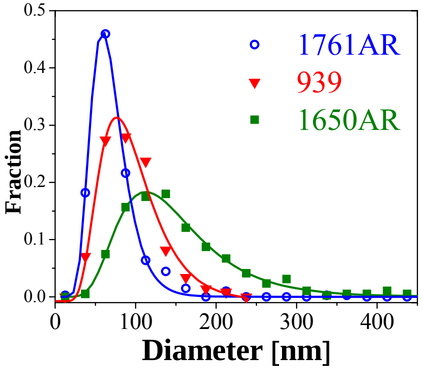
$$D_0 = \frac{kT}{6\pi\eta R}$$

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

- Microscopy

  Shape analysis





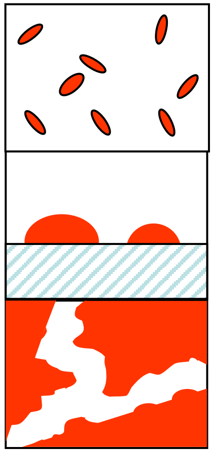
- Small angle X-ray scattering

  Scattering of X-rays by small domains of uniform matter (crystalline or amorphous), for which the electron density ρ^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



Surface area measurements

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

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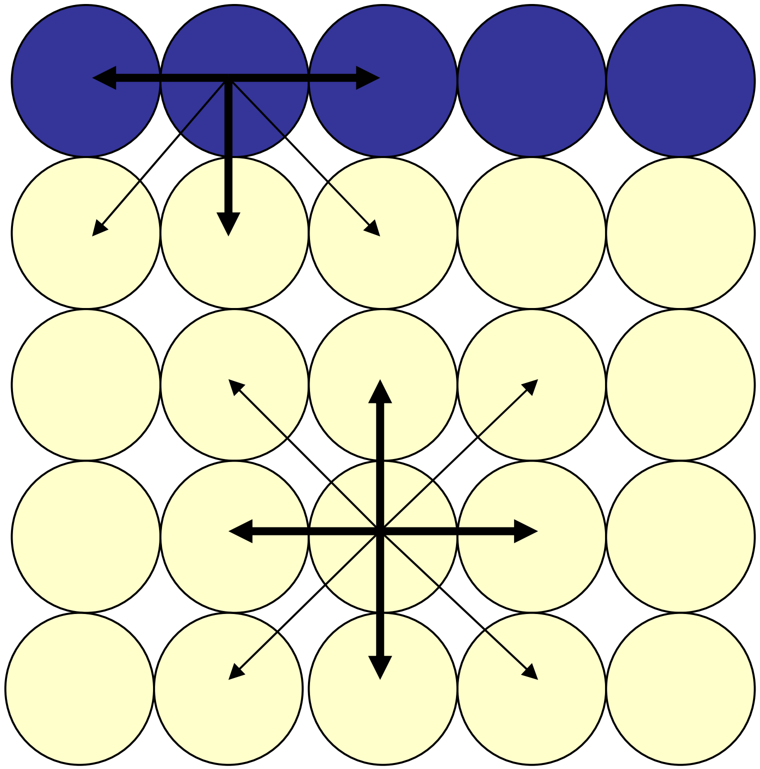
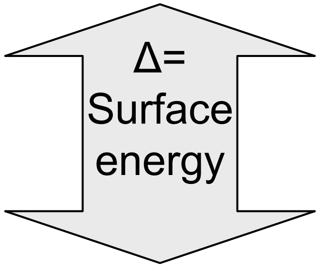
Driving force of adsorption



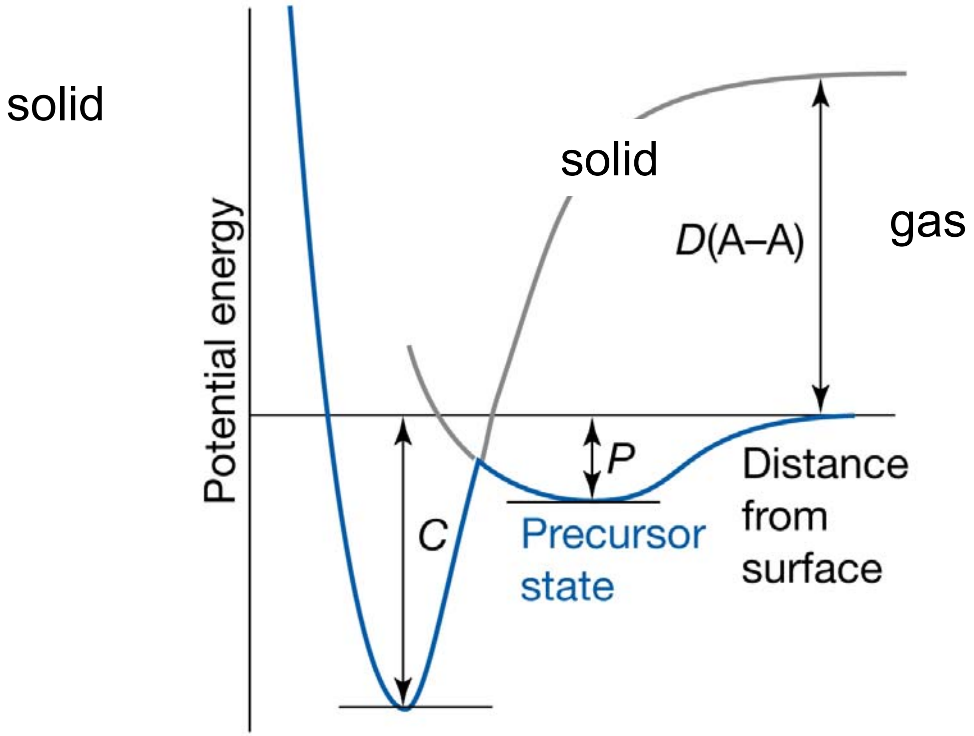
Surface atom – unbalanced forces



Δ=
Surface
energy

Bulk atom – balanced forces

Adsorption

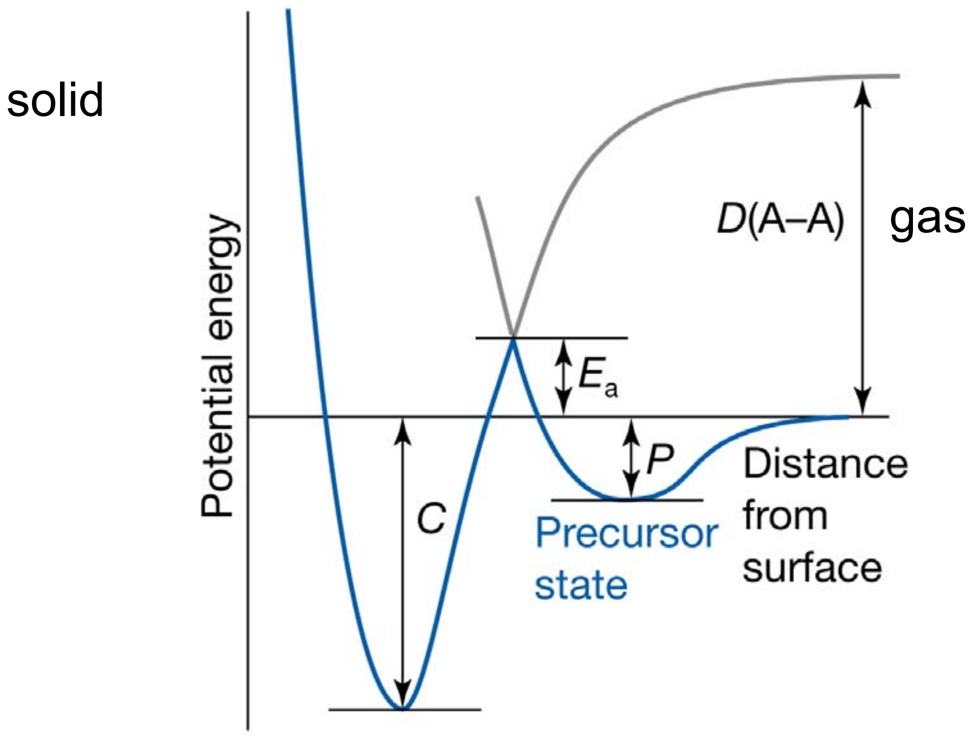


chemisorption physisorption

Adsorption

2

activated chemisorption



chemisorption → Heterogeneous catalysis

physisorption → 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 (e.g. $^{-}\mathrm{O\text{-}C}^{++}\mathrm{\text{-}O}^{-}$)

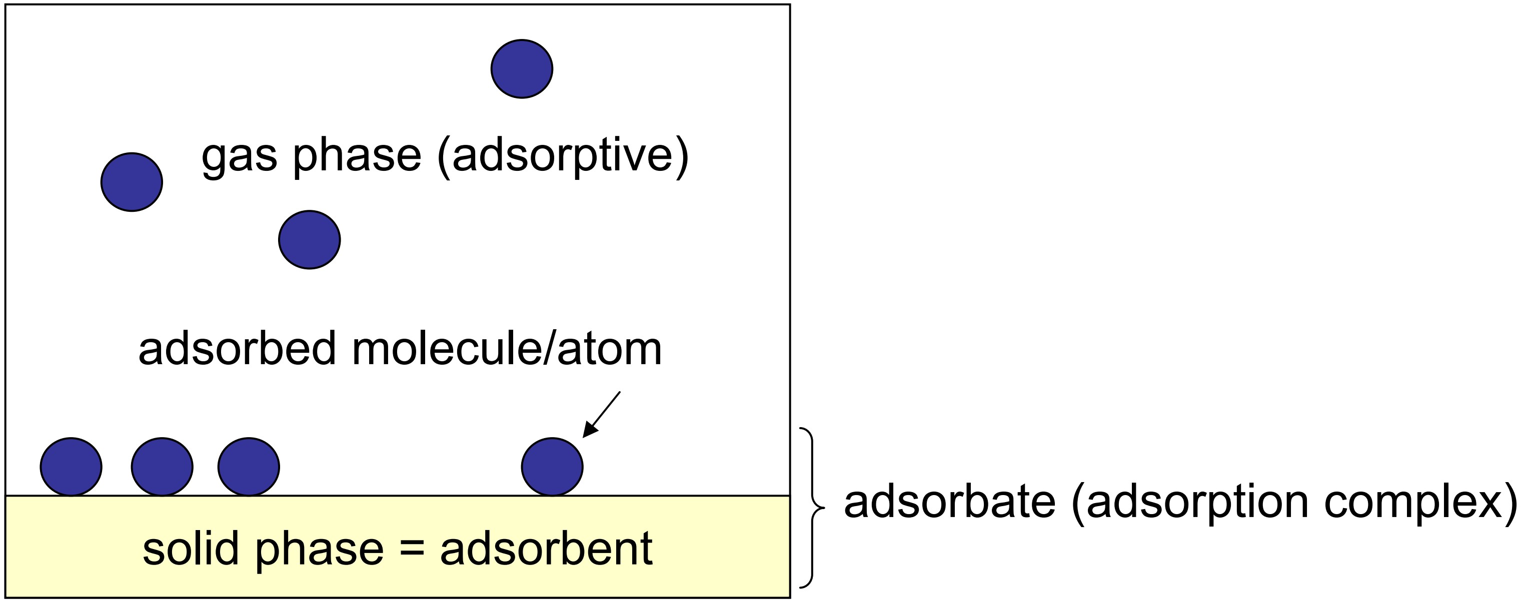
* F. London, Z. Phys. 63 (1930) 245.

Similar to forces that lead to liquifidation of vapors

Adsorption

	Physisorption	Chemisorption
$\Delta_a H$	< 50 kJ mol^{-1}	> 500 kJ mol^{-1}
Coverage	Multilayer → Measurement of surface area	Monolayer or less, site restriction → Titration of active sites
Interaction	No structural changes, reversible	Disruption of chemical bonds may happen
Kinetics	Fast	Activation required
Pores	Pores may be filled → 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)

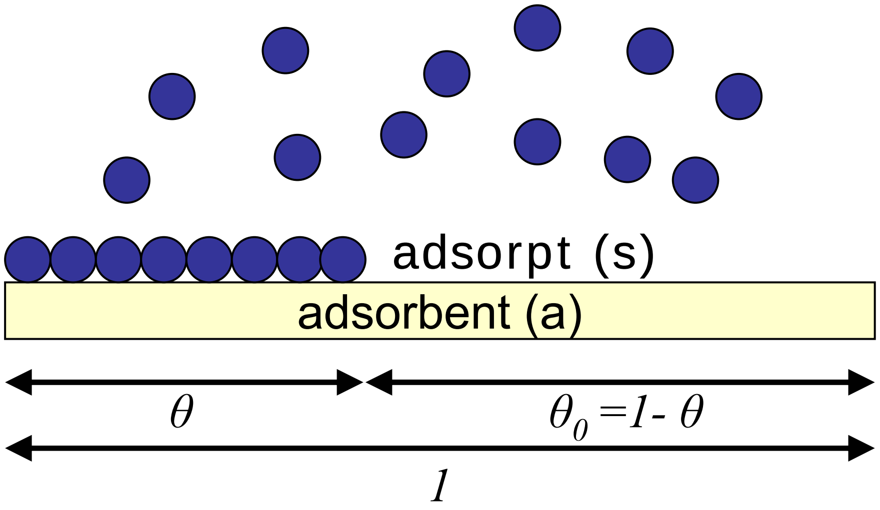
$\Gamma = n_s/s_a$

$\gamma = n_s/m_a$

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

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

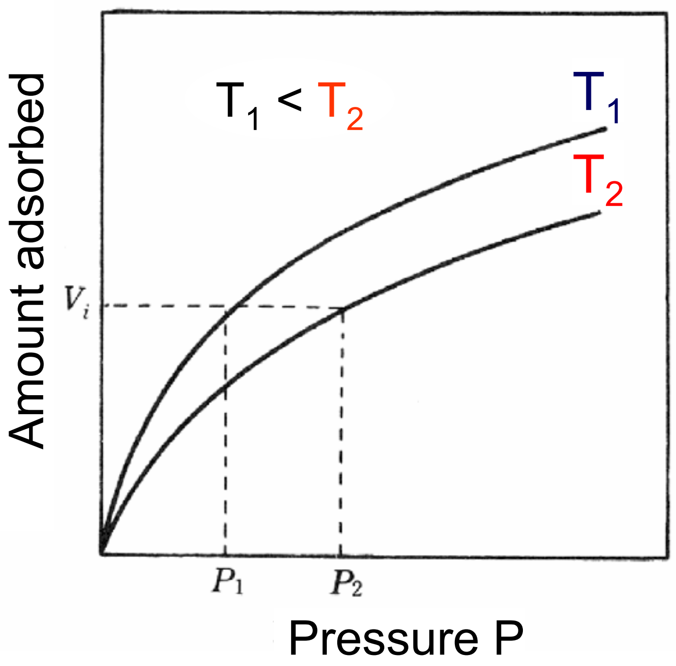
$\Gamma = f(T)$ $<eq., p = \text{const.}>$ adsorption isobar

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

$\Gamma = f(p)_T$

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

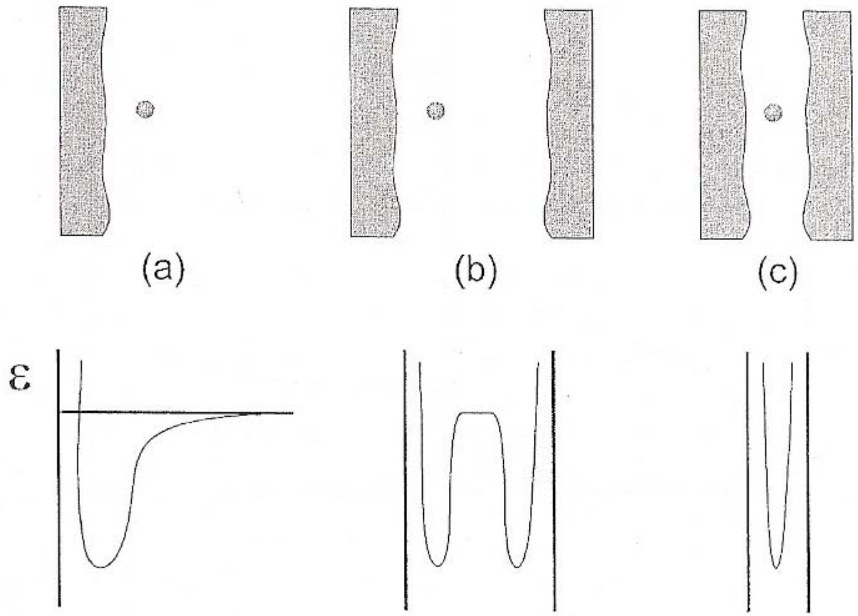
- Ultramicropores below 0.7nm
- Supramicropores 0.7~2nm

Width*

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

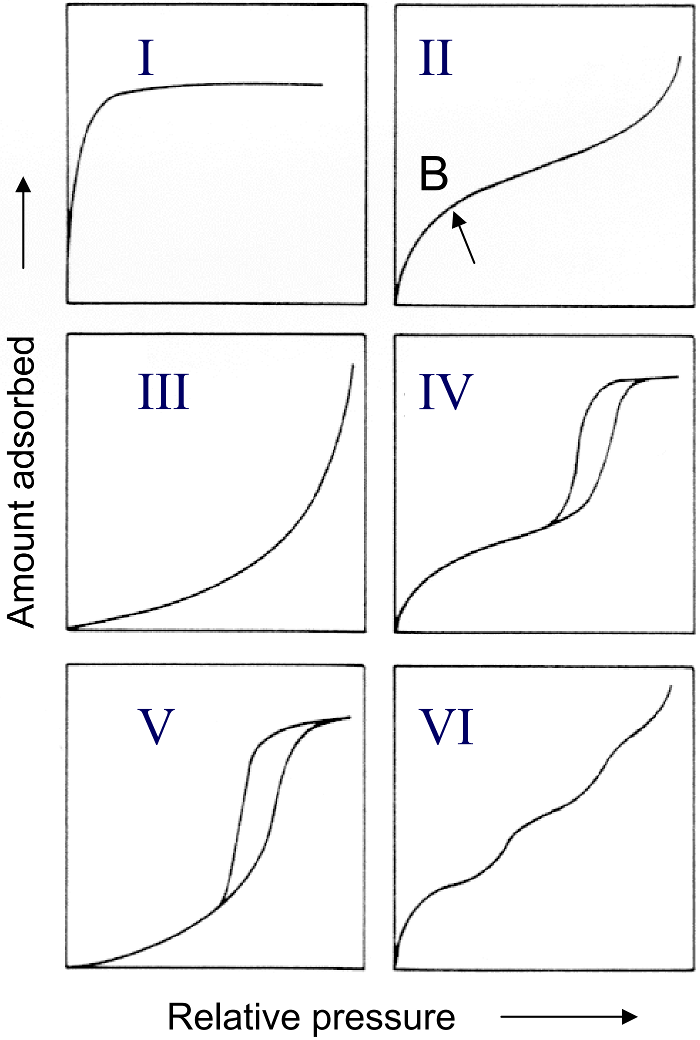
* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

Planar, nonporous, macropores   mesoporous   microporous



Schematic illustration of adsorption potential

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.

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Surface area measurements 3

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

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*

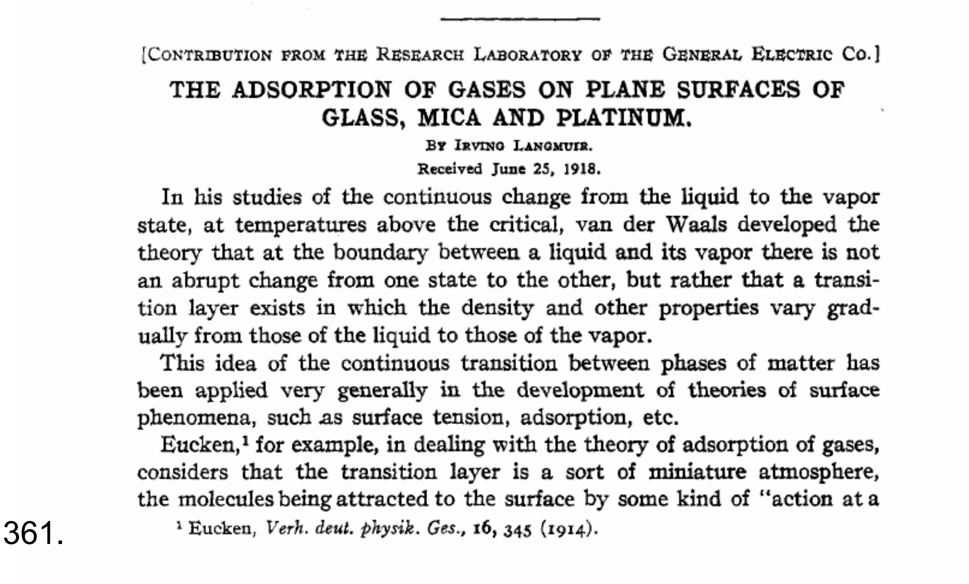
Description of Type I Isotherm

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

$$dN/dt = k\,p\,\theta_0$$

Kinetic gas theory:

$$k = N_A / (2\pi\, M\, R\, T)^{1/2}$$

$$N_{ads} = k\,p\,\theta_0\,A$$

$$N_{des} = N_m\,\theta\,v_1 e^{-E/RT}$$

$$k\,p\,\theta_0\,A = N_m\,\theta\;\;v\,e^{-E/RT}$$

$$N_m\,\theta\,v\,e^{-E/RT} = k\,p\,A - \theta\,k\,p\,A \qquad \theta_0 = 1 - \theta$$

$$\theta = Kp/(1 + Kp) = N/N_{\mathrm{m}} = W/W_{\mathrm{m}} \qquad K = k\,A/(N_m v\,e^{-E/RT})$$

N	number of collisions with the surface
θ_0	fraction of surface unoccupied
θ	fraction of surface occupied
A	condensation coefficient (probability of a molecule of being adsorbed upon collision)
N_m	number of molecules in a complete monolayer
v	vibr. frequency of adsorbate normal to the surface
N_A	$= 6{,}022\ 141\ 79\ (30) \times 10^{23}\ \mathrm{mol}^{-1}$

$$\theta = \frac{W}{W_m} = \frac{K\ p}{1 + K\ p}$$

Langmuir isotherm

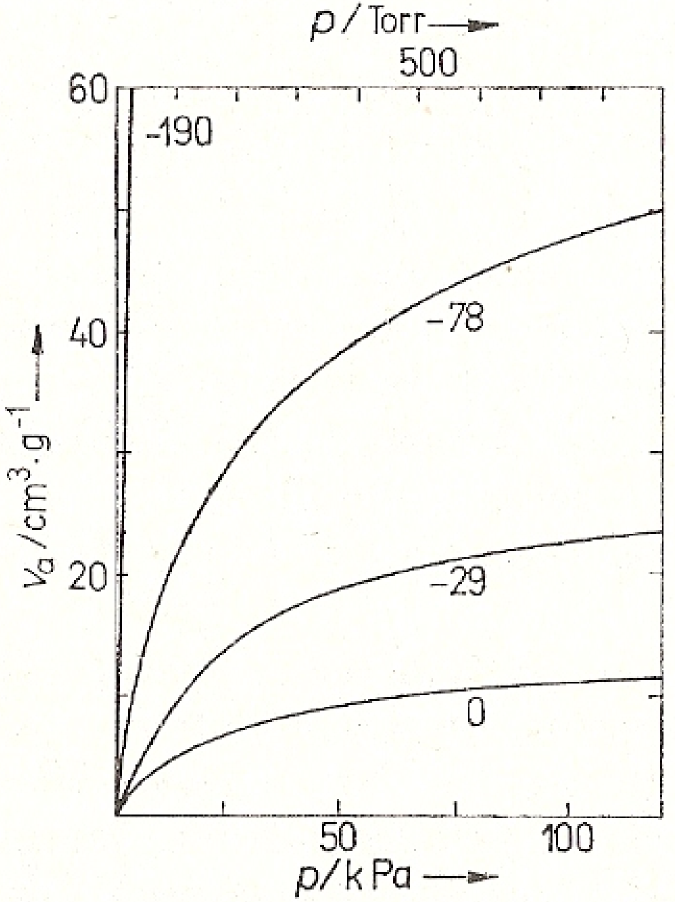
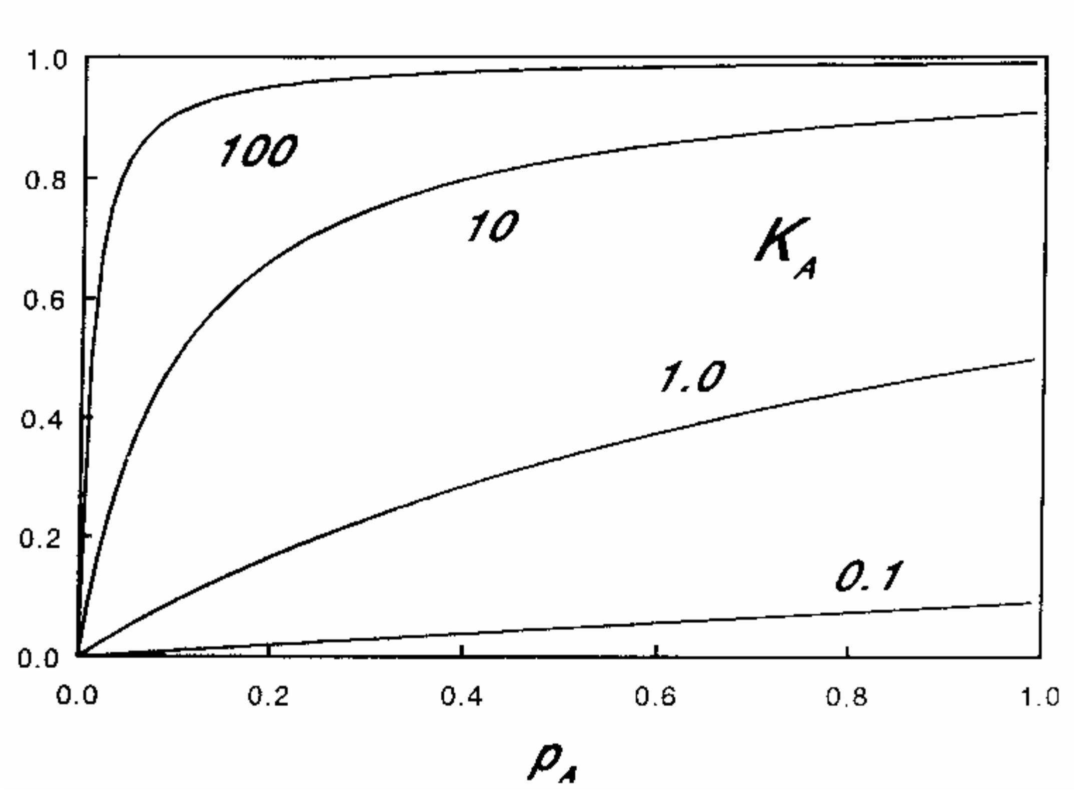


Abb. 6.45
Adsorptionsisotherme des Stickstoffs an Aktivkohle bei verschiedenen Temperaturen
(in °C bei den Kurven angegeben)

$$\theta = \frac{W}{W_m} = \frac{K\ p}{1 + K\ p}$$

Langmuir isotherm

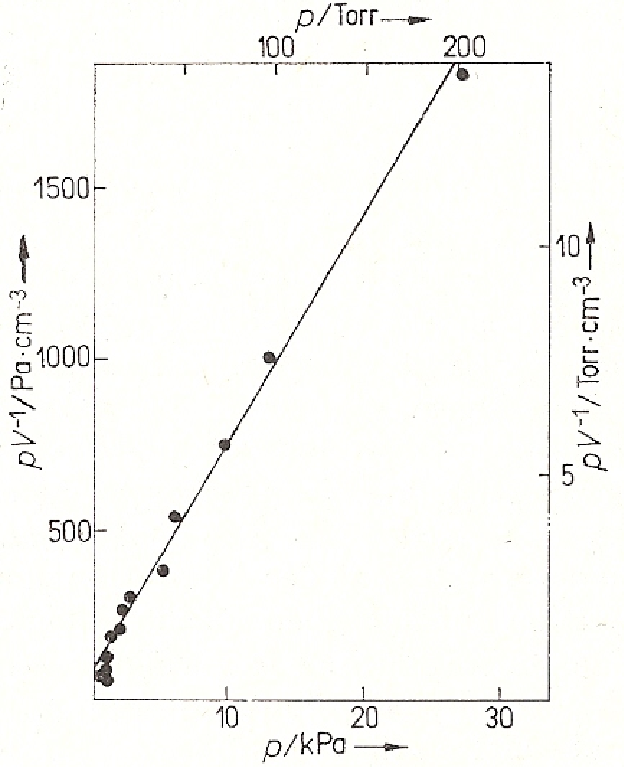


$$\theta = \frac{W}{W_m} = \frac{K\ p}{1 + K\ p}$$

Langmuir isotherm

Linear plot

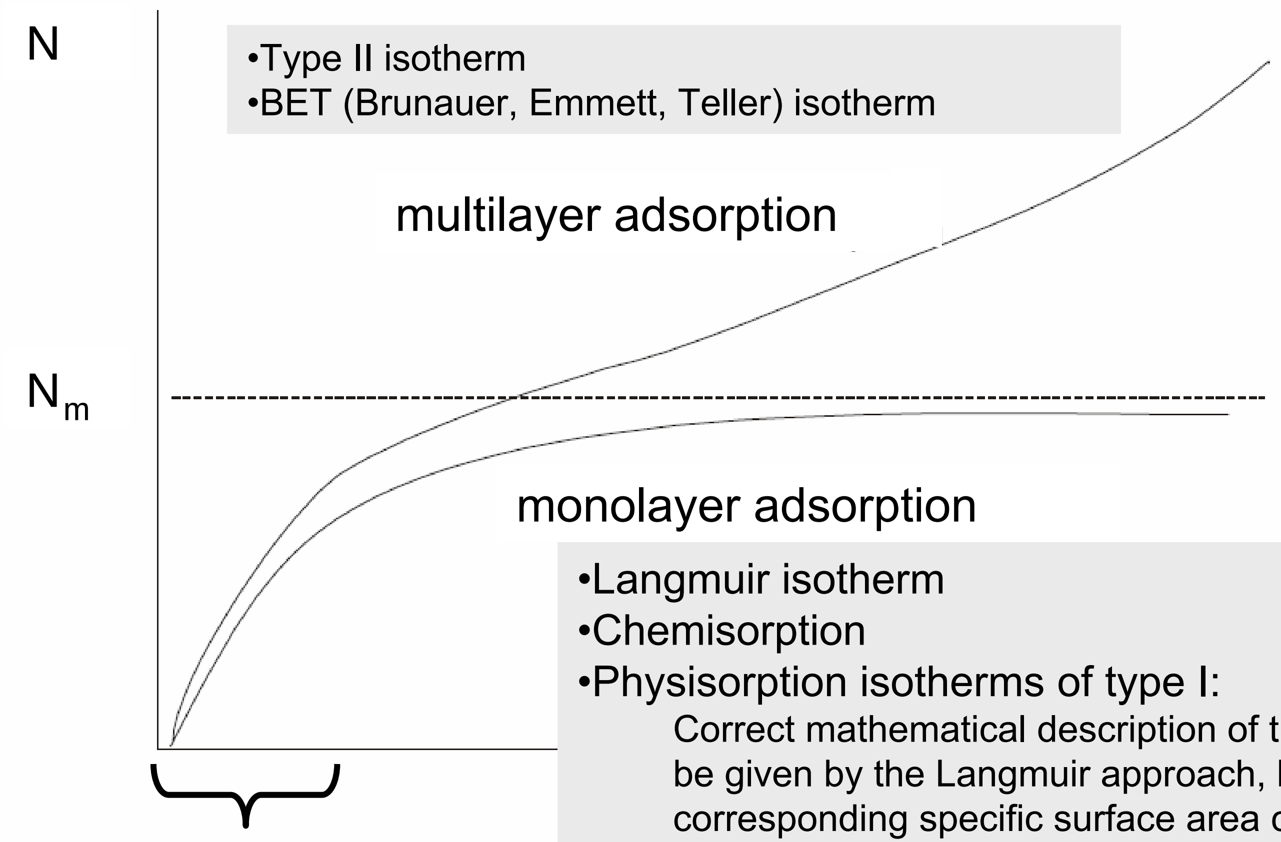
$$\frac{p}{W} = \frac{1}{KW_m} + \frac{p}{W_m}$$



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

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

Other isotherms



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

- Langmuir isotherm
- Chemisorption
- Physisorption isotherms of type I:

  Correct mathematical description of the type I isotherm may be given by the Langmuir approach, however, the corresponding specific surface area calculated using the monolayer capacity **does not reflect a true surface area!**

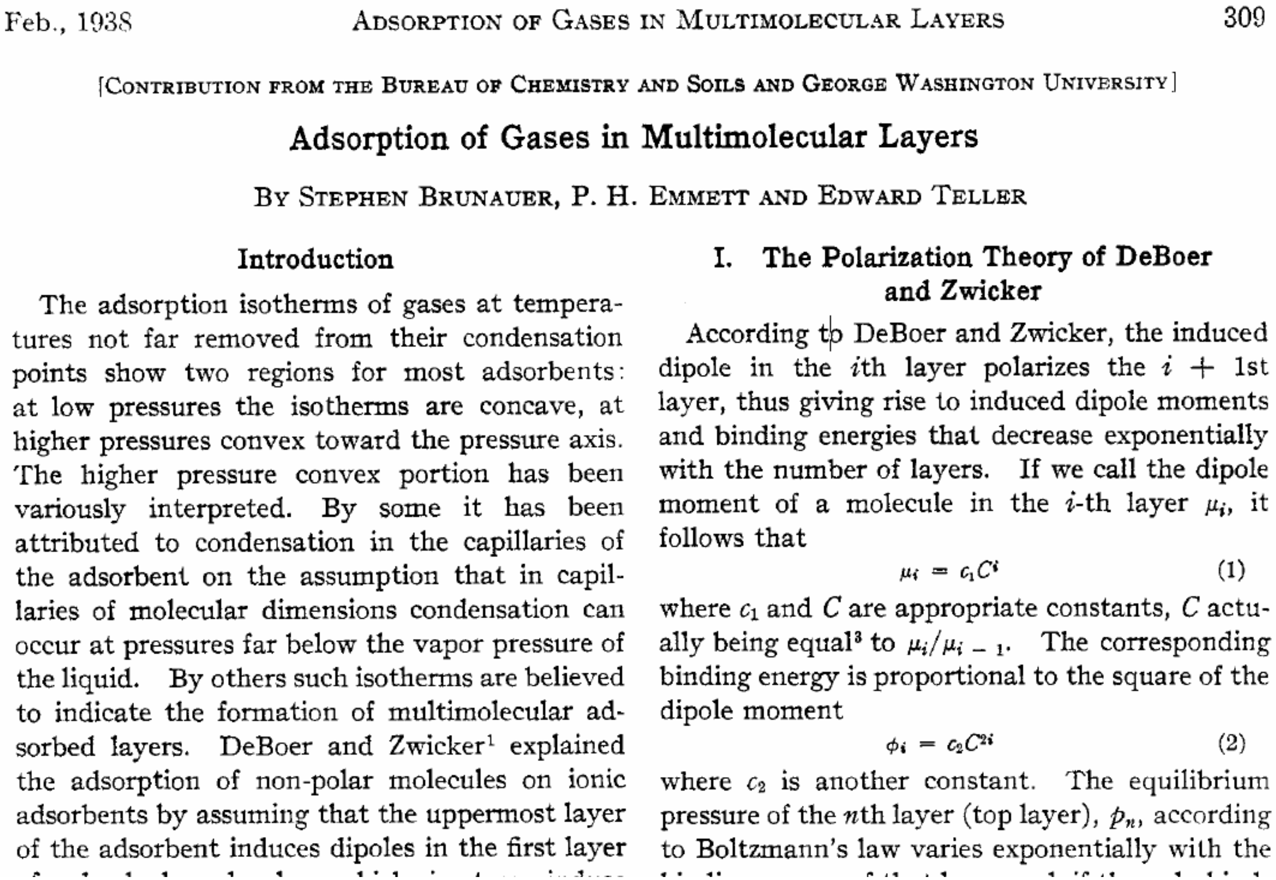
- Freundlich isotherm

Empiric relation between adsorbed amount and pressure

$n_a = kp^n$

$0<n<1$

BET isotherm (Brunauer, Emmett, Teller)*



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 ith 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 μ_i, it follows that

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

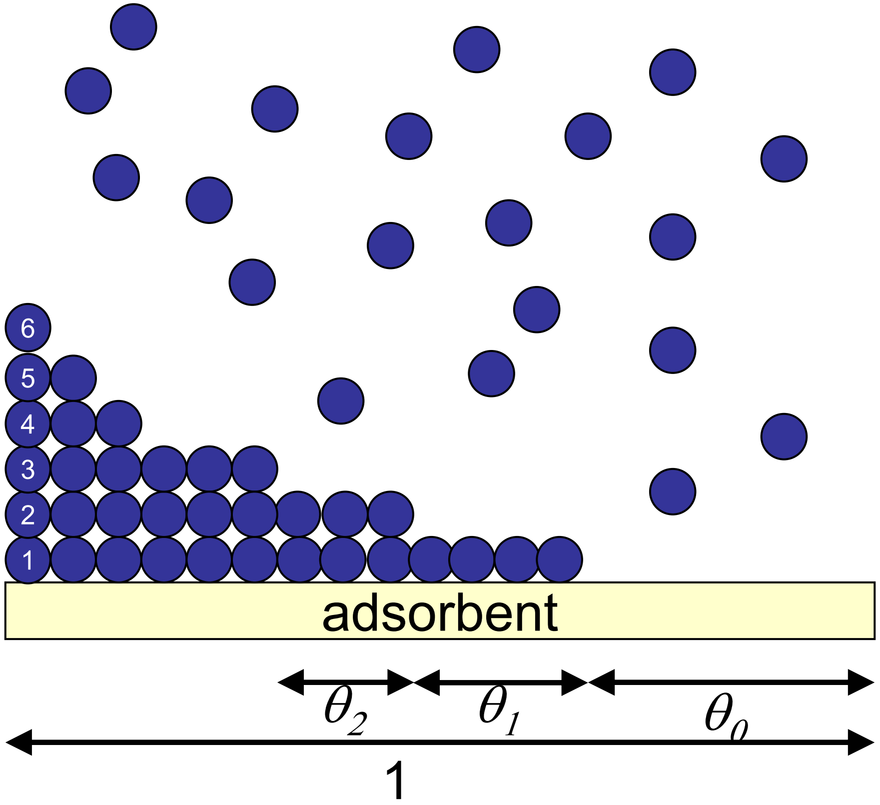
where c_1 and C are appropriate constants, C actually being equal[3] to μ_i/μ_{i-1}. The corresponding binding energy is proportional to the square of the dipole moment

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

where c_2 is another constant. The equilibrium pressure of the nth 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.

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

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

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

BET plot

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

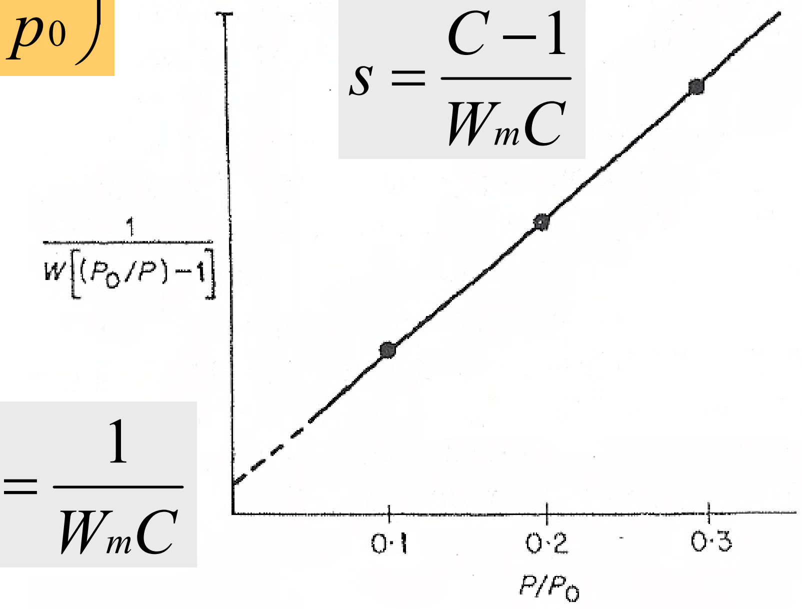
$$W_m=\frac{1}{s+i}$$

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

$$S=\frac{W_mN_AA_x}{M_{adsorptive}}$$

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

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



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

$$i=\frac{1}{W_mC}$$

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

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

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

BET isotherm (Brunauer, Emmett, Teller)

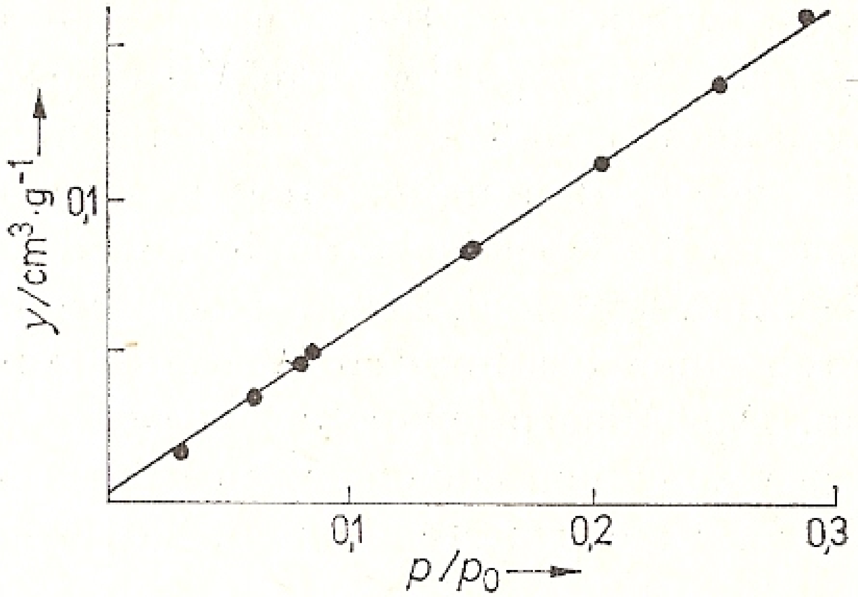
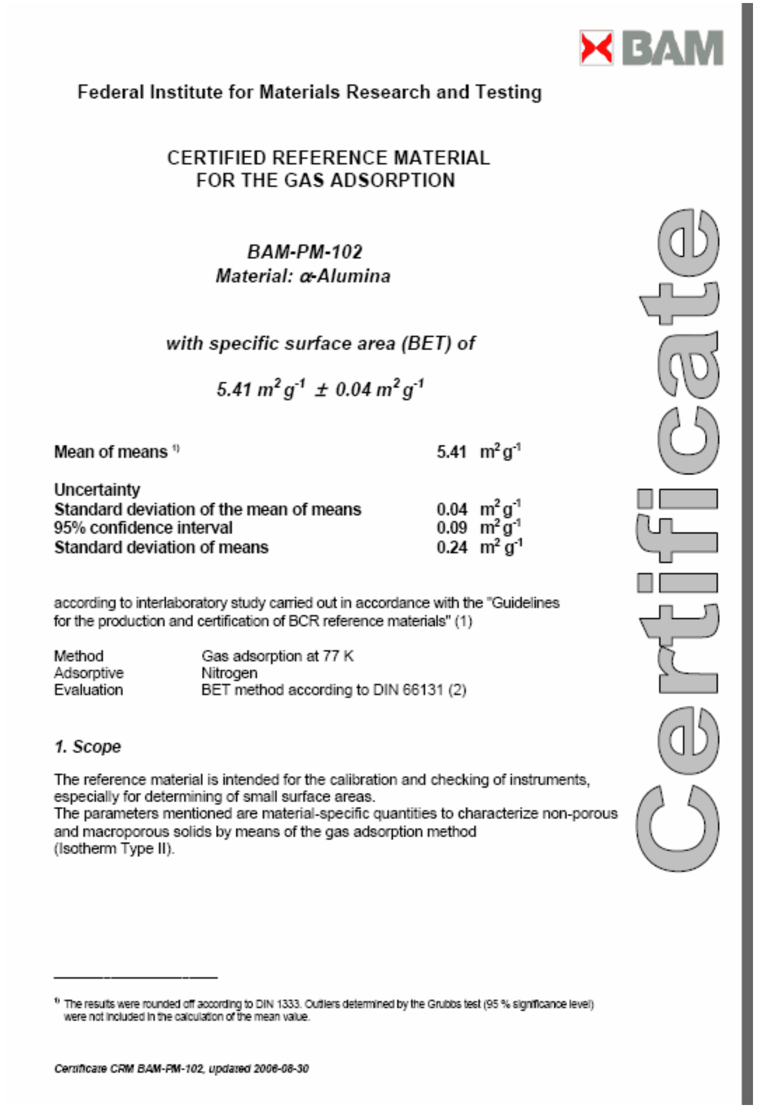


Abb. 6.48
Linearisierte BET-Isotherme für die Adsorption von N_2 an TiO_2 bei 78 K; $y = p/(p_0 - p)\,v$, wobei v das an 1 g TiO_2 adsorbierte N_2-Volumen (cm^3) ist

$S = 8\ m^2/g$

Available in our laboratory: BAM-PM-102 *(α-Al_3O_3)*



BAM

Federal Institute for Materials Research and Testing

CERTIFIED REFERENCE MATERIAL
FOR THE GAS ADSORPTION

BAM-PM-102
Material: α-Alumina

with specific surface area (BET) of

5.41 $m^2 g^{-1}$ ± 0.04 $m^2 g^{-1}$

Certificate

Mean of means [1]	5.41 $m^2 g^{-1}$
Uncertainty	
Standard deviation of the mean of means	0.04 $m^2 g^{-1}$
95% confidence interval	0.09 $m^2 g^{-1}$
Standard deviation of means	0.24 $m^2 g^{-1}$

according to interlaboratory study carried out in accordance with the "Guidelines for the production and certification of BCR reference materials" (1)

Method	Gas adsorption at 77 K
Adsorptive	Nitrogen
Evaluation	BET method according to DIN 66131 (2)

1. Scope

The reference material is intended for the calibration and checking of instruments, especially for determining of small surface areas.
The parameters mentioned are material-specific quantities to characterize non-porous and macroporous solids by means of the gas adsorption method (Isotherm Type II).

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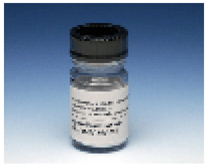
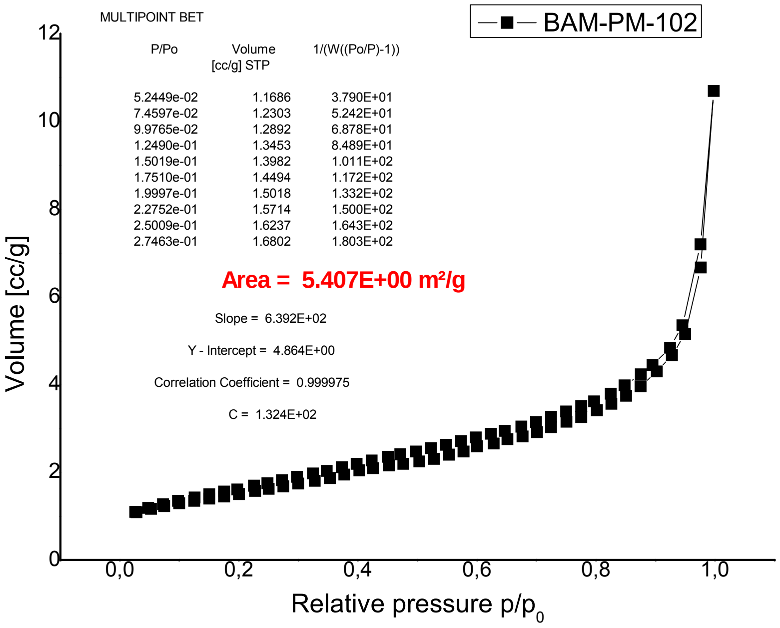
[1] The results were rounded off according to DIN 1333. Outliers determined by the Grubbs test (95 % significance level) were not included in the calculation of the mean value.

Certificate CRM BAM-PM-102, updated 2006-08-30

Alumina powder with small specific surface area. Method: Multipoint N_2-BET at 77 K. Certified property: BET surface area





MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
5.2449e-02	1.1686	3.790E+01
7.4597e-02	1.2303	5.242E+01
9.9765e-02	1.2892	6.878E+01
1.2490e-01	1.3453	8.489E+01
1.5019e-01	1.3982	1.011E+02
1.7510e-01	1.4494	1.172E+02
1.9997e-01	1.5018	1.332E+02
2.2752e-01	1.5714	1.500E+02
2.5009e-01	1.6237	1.643E+02
2.7463e-01	1.6802	1.803E+02

Area = 5.407E+00 m²/g

Slope = 6.392E+02

Y - Intercept = 4.864E+00

Correlation Coefficient = 0.999975

C = 1.324E+02

Applicability of the BET theory

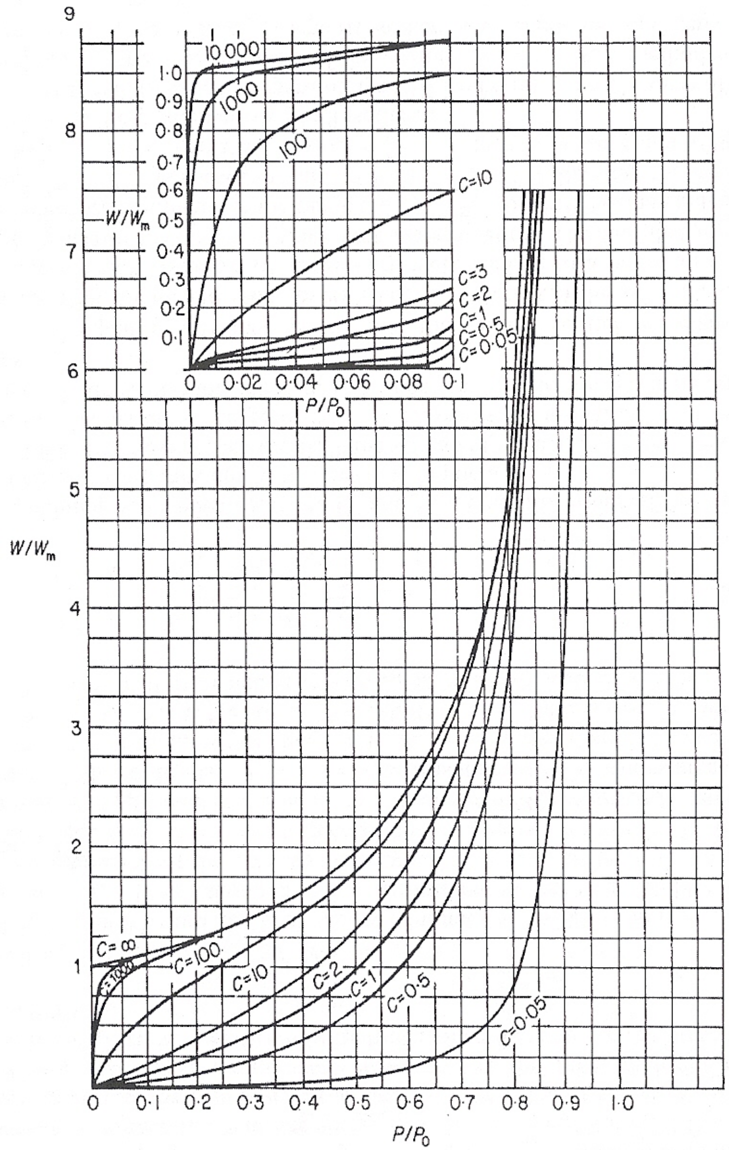


Figure 5.3 Isotherm shapes as a function of BET C values.

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

$$C = \frac{A_1 v_1}{A_2 v_2} e^{(E-L)/RT}$$

A condensation coefficient (probability of a molecule of being adsorbed upon collision)

v vibrational frequency of adsorbate normal to the surface

E heat of adsorption

L heat of liquefaction

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

Applicability of the BET theory

Limitations

- BET theory ignores inhomogeneities of the surface and lateral adsorbate-adsorbate interactions

  High energy sites will be occupied at lower relative pressures

  Reason for the nonlinearity of BET plots at $p/p_0 < 0.05$

- Polarization forces would induce a higher heat of adsorption in the second layer than in the third and so forth

  Reason for the failure of the BET equation at $p/p_0 > 0.3$

- The BET equation is applicable for surface area analysis of nonporous materials

  Difficulties to separate mono-multilayer adsorption from pore filling

  Filling of ***micropores*** *is completed at* $p/p_0 < 0.1$*, however, linear BET plot are found at even lower relative pressures*

  → measured surface area reflects not a real internal surface, but a „characteristic“ BET surface area

  For ***mesoporous materials*** *exhibiting pore diameters between* ***2 and 4 nm (MCM-41, MCM-48)*** *pore filling is observed at pressures close to mono-multilayer formation*

  → overestimation of monolayer capacity

Cross-sectional area

$$S = \frac{W_m N_A A_x}{M_{adsorptive}} \times 10^{-20}\,\mathrm{m}^2$$

A_x cross sectional area in $Å^2$
W_m monolayer weight in g
$N_A = 6{,}022\ \ 141\ \ 79\ (30) \times 10^{23}\ \mathrm{mol}^{-1}$
V_l liquid molar volume

Assumptions
Adorbate molecules are spherical and form a close packed hexagonal arrangement
Bulk liquid properties are used

$$A_x = 1.091\left(\frac{V_l}{N_A}\right)^{\frac{2}{3}} \times 10^{-16}\,Å^2$$

Relationship between BET C constant and cross-sectional area

Effective cross-sectional area depends on

- Temperature
- Nature of adsorbate-adsorbate interaction
- Nature of adsorbent-adsorptive interaction
- Texture of the adsorbent surface

Cross-sectional area

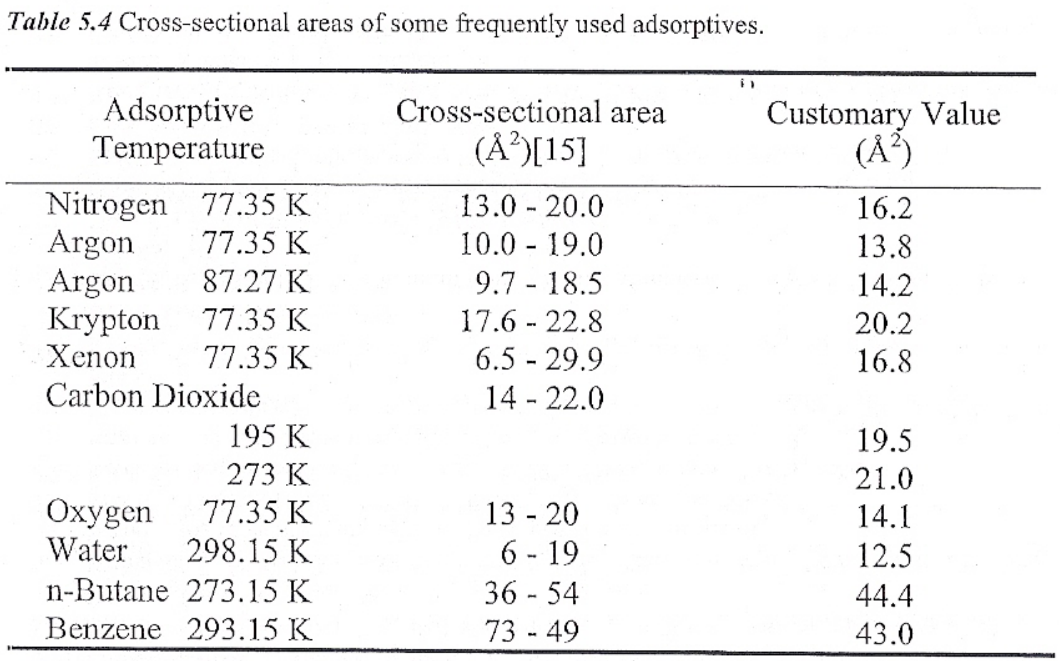


Table 5.4 Cross-sectional areas of some frequently used adsorptives.

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 ist 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 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

* Literatur IUPAC.

Outline

1. Introduction
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Adsorption in Micropores

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

Adsorption potential theories (0.4 nm ~)

Classical methods based on macroscopic, thermodynamic assumptions
- Polanyi
- Dubinin
- Stoeckli
- Horvath-Kawazoe

Density Functional Theory

Monto Carlo simulations

Empirical methods (0.7~2nm)

t-method

MP-method

α_s-method

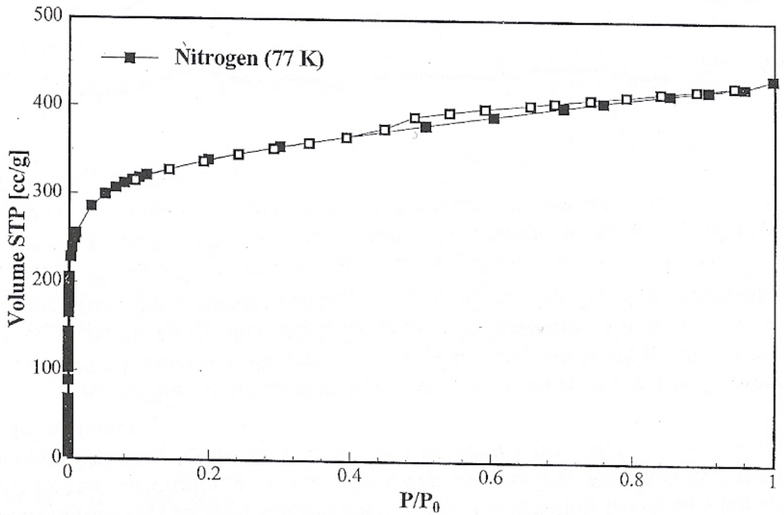


Figure 4.2 Nitrogen adsorption at 77.35 K on an active carbon sample, which contains, in addition to its microporosity, some mesoporosity indicated by the occurrence of hysteresis and the fact that the adsorption isotherm does not reveal a truly horizontal plateau at relative pressures > 0.1; the observed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

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

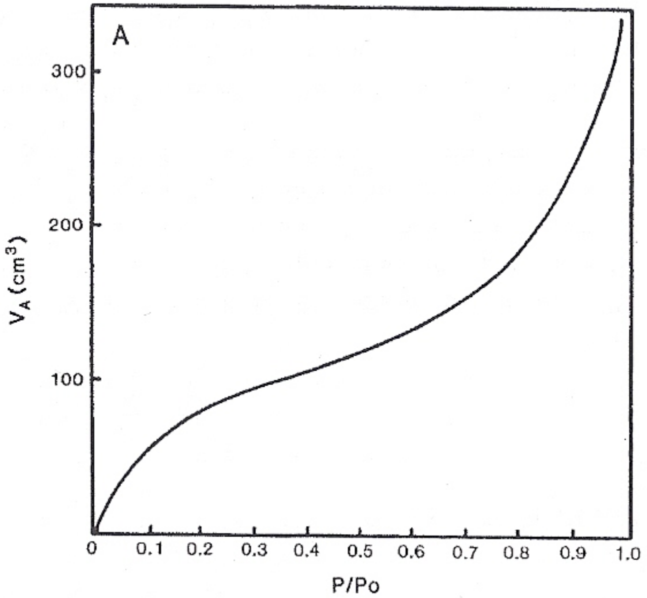
Concept of V-t curves

Assumption

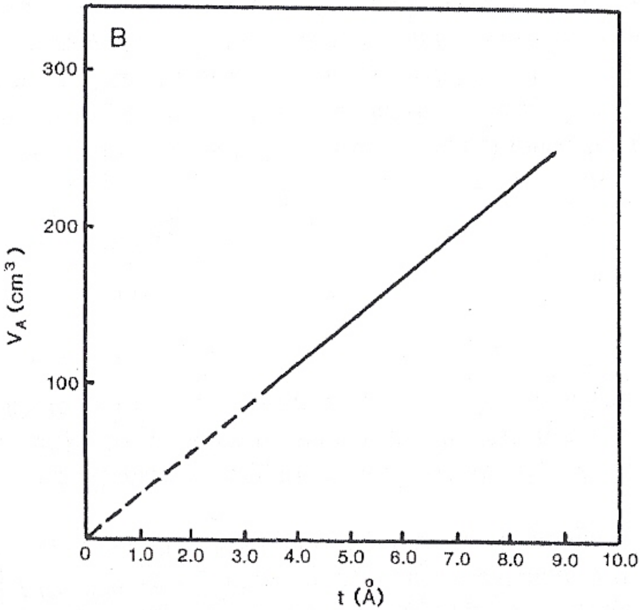
The thickness of the absorbed film on pore walls is uniform → statistical thickness *t*

$$t = 3.54\frac{W_a}{W_m}\,\mathring{\mathrm{A}} = \frac{V_{liq}}{S}\times 10^4\,\mathring{\mathrm{A}} \qquad (N_2,\ 77\ \mathrm{K})$$

It has been shown for type II isotherms that a plot of the volume adsorbed versus t gives a staight line throug the origin



V-t curve



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

The t-method

Principle

- Comparing an isotherm of a microporous material with a standard type II isotherm of a nonporous absorbent with BET C constants similar to that of the microporous sample
- Plot of the reference isotherm as a t-curve: $V_{ads}=f(t)$
- The t values are in practice calculated with the help of thickness equations that desribe the particular standard reference curve

Siliceous materials

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

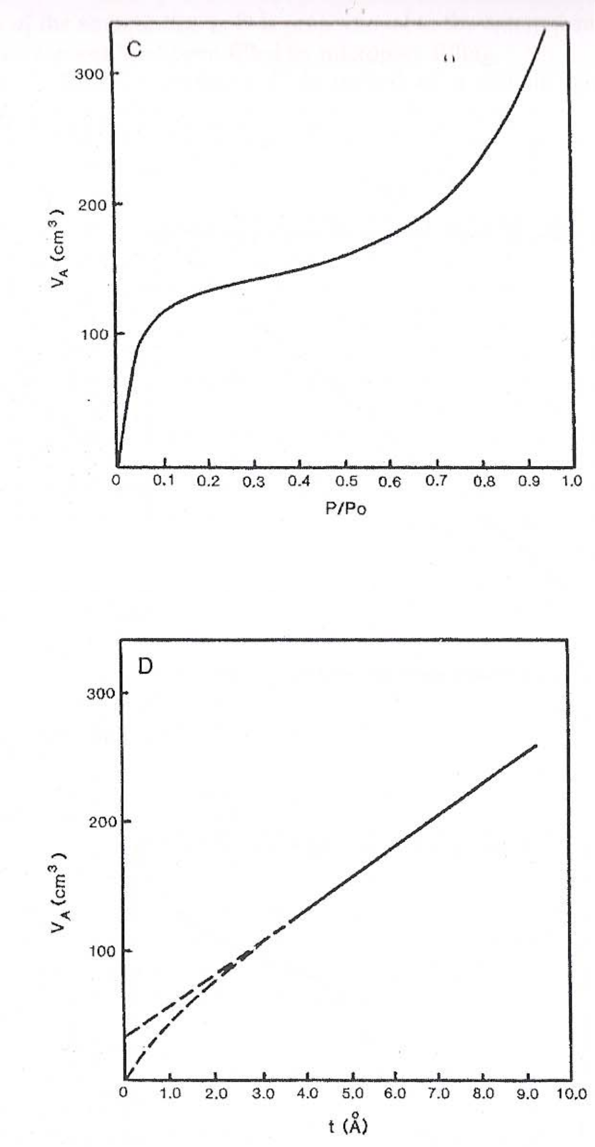
J.H.De Boer *et al.,* J. Colloid Interface Sci. 21 (1966) 405.

C-like materials

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

ASTM standard D-6556-01

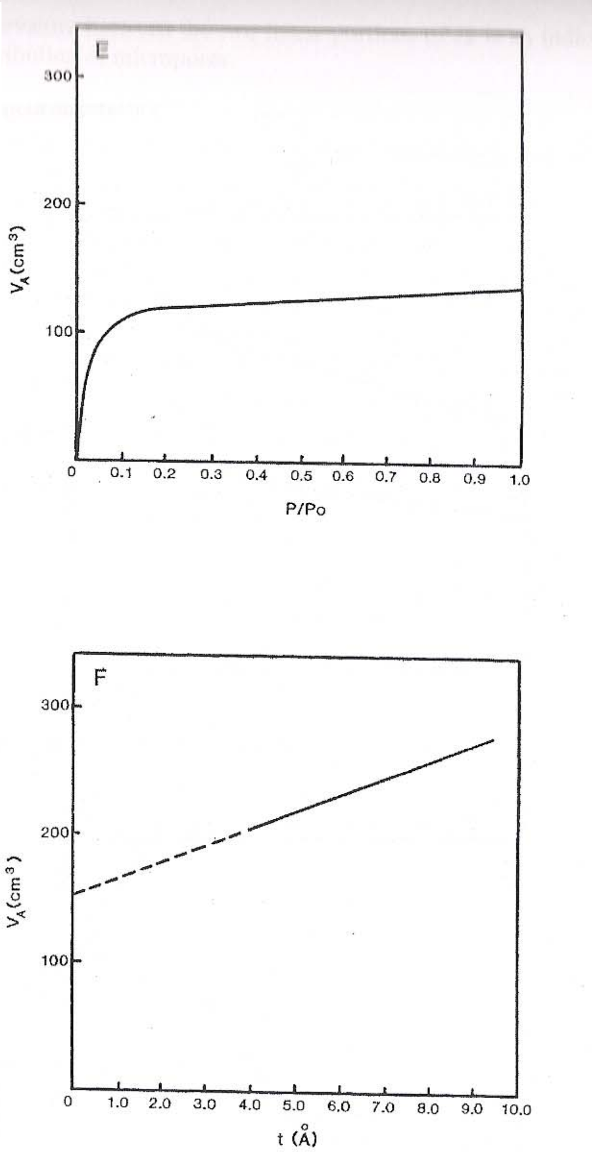
The t-method



Differences between the shape of the experimental isotherm and the standard isotherm result in nonlinear regions of the t-plot and positive or negative intercepts, which can be used to obtain information about micropore volume and surface

$$V_{MP} = i \times 0.001547\ \text{cm}^3$$

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



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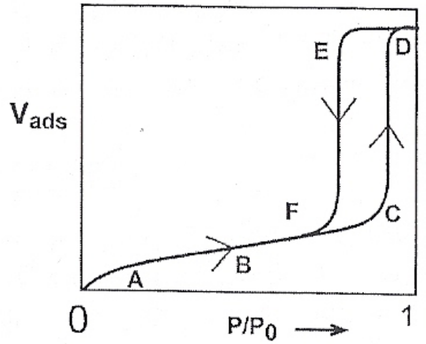
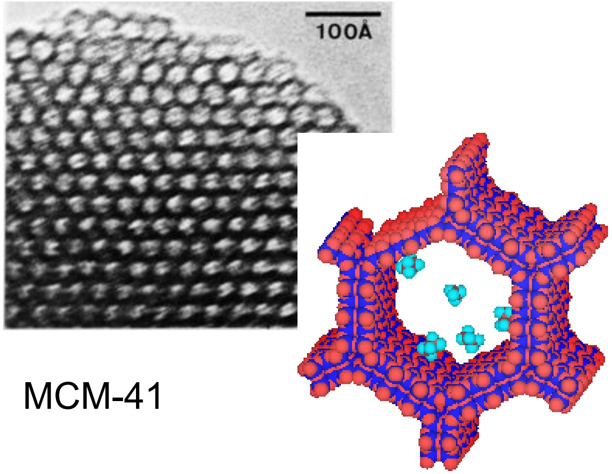
Capillary condensation in mesopores (2 – 50 nm)

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

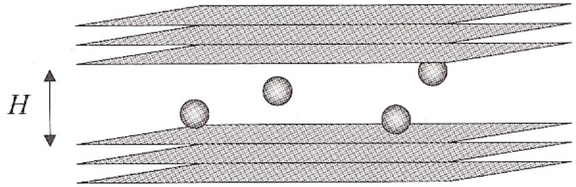
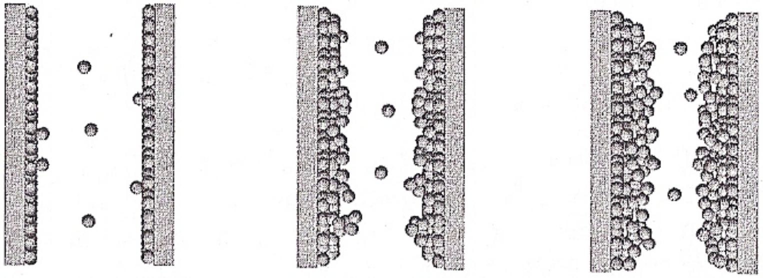


Fig. 3. The slit pore model. Each layer represents a graphene layer.



A Monolayer formation

B Multilayer adsorption

C Critical film thickness reached

D Capillary condensation

E Pore evaporation

F multilayer film

Classification of the hysteresis loops*

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

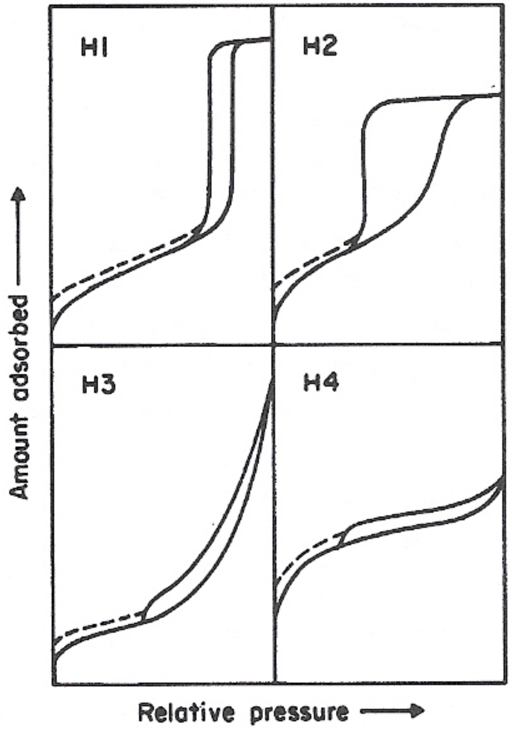


Fig. 3. Types of hysteresis loops

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

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

γ	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

Consideration of fluid-wall interactions (modified Kelvin equation):

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

(N_2, 77 K)

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

$$r_p = r_k + t$$

Total pore volume and average pore radius

$p/p_0 = 0.95$

$$V_p = \frac{W_a}{\rho_l}$$

$$\bar{r}_p = 2V_p / S_{BET}$$

Pore size distribution

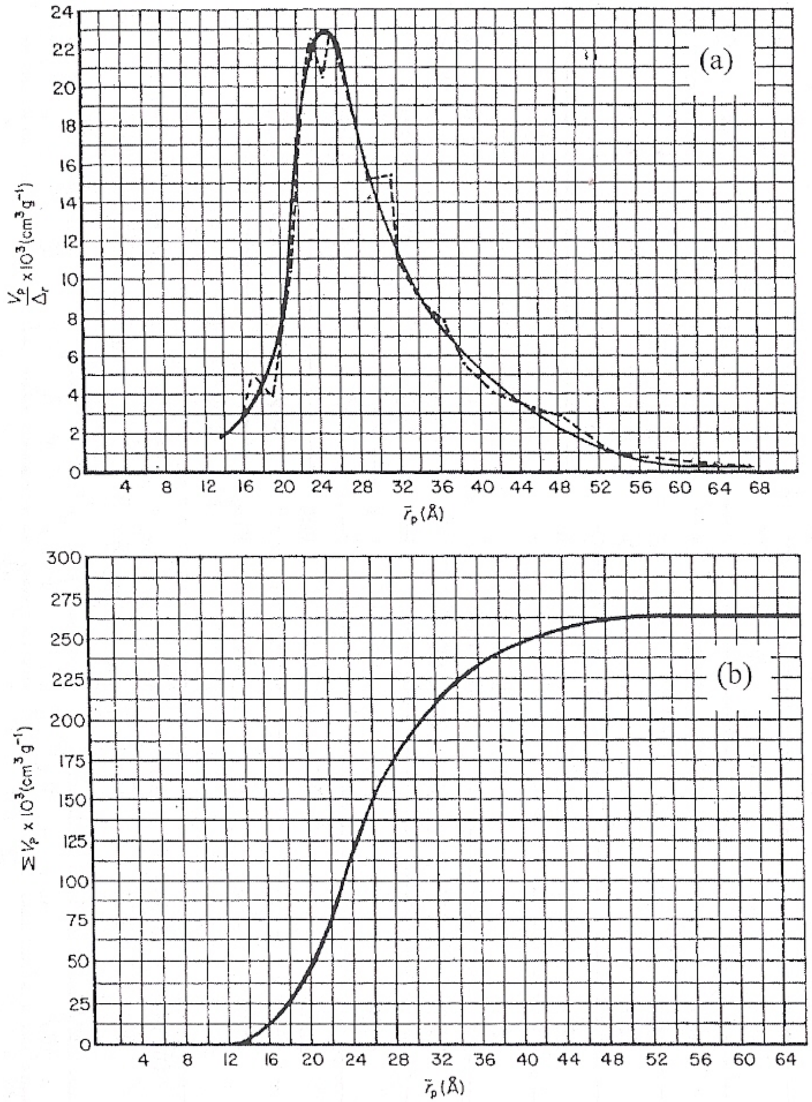


Figure 8.1 (a) Pore size distribution curve from table 8.1. Raw data: --------; smoothed data ————; (b) Cumulative pore volume plot from table 8.1.

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“

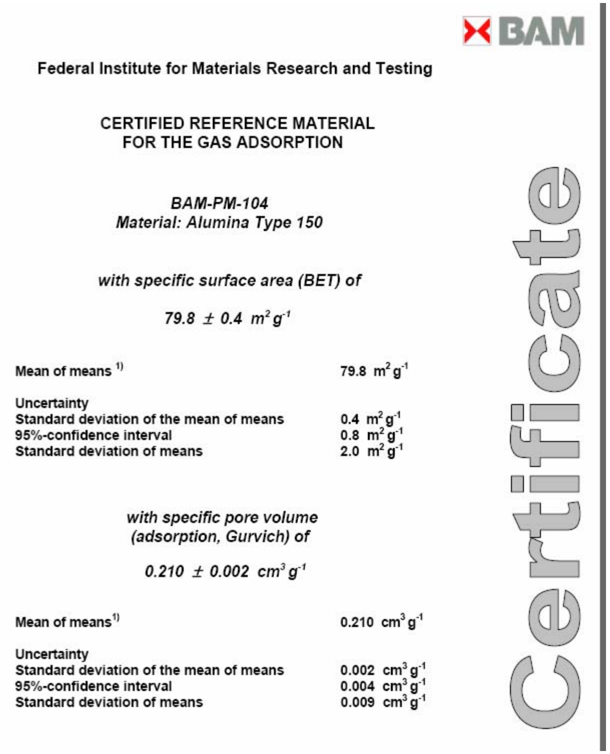
- Pore condensation is associated with metastable states of the pore fluid in ordered materials
- The **desorption branch** of the hysteresis loop reflects the equilibrium phase transition
- Methods, which describe the equilibrium phase transition (**BJH**) have to be applied to the desorption branch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

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)

Available in our laboratory: BAM-PM-104 (mesoporous alumina)



BAM

Federal Institute for Materials Research and Testing

CERTIFIED REFERENCE MATERIAL
FOR THE GAS ADSORPTION

BAM-PM-104
Material: Alumina Type 150

with specific surface area (BET) of

79.8 ± 0.4 $m^2 g^{-1}$

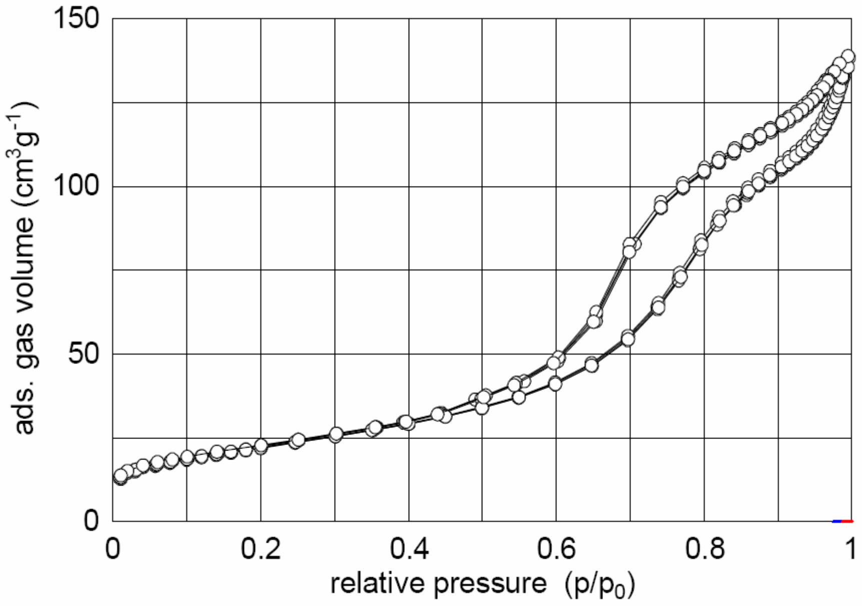
Mean of means [1]	79.8 $m^2 g^{-1}$
Uncertainty	
Standard deviation of the mean of means	0.4 $m^2 g^{-1}$
95%-confidence interval	0.8 $m^2 g^{-1}$
Standard deviation of means	2.0 $m^2 g^{-1}$

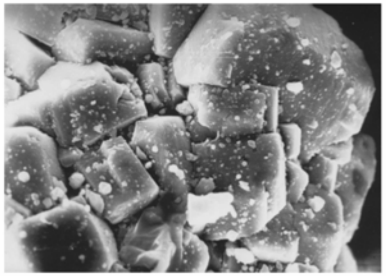
with specific pore volume
(adsorption, Gurvich) of

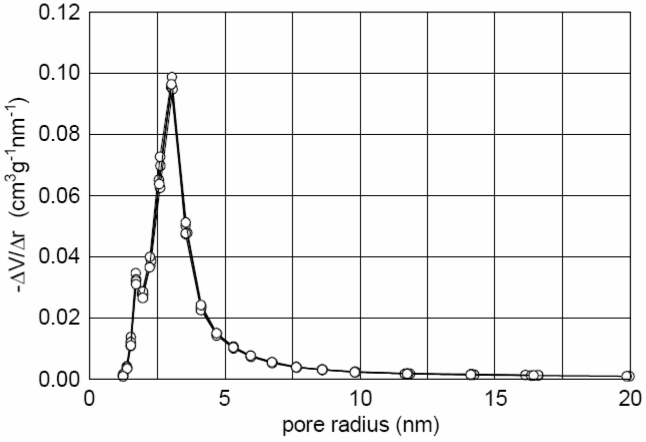
0.210 ± 0.002 $cm^3 g^{-1}$

Mean of means [1]	0.210 $cm^3 g^{-1}$
Uncertainty	
Standard deviation of the mean of means	0.002 $cm^3 g^{-1}$
95%-confidence interval	0.004 $cm^3 g^{-1}$
Standard deviation of means	0.009 $cm^3 g^{-1}$

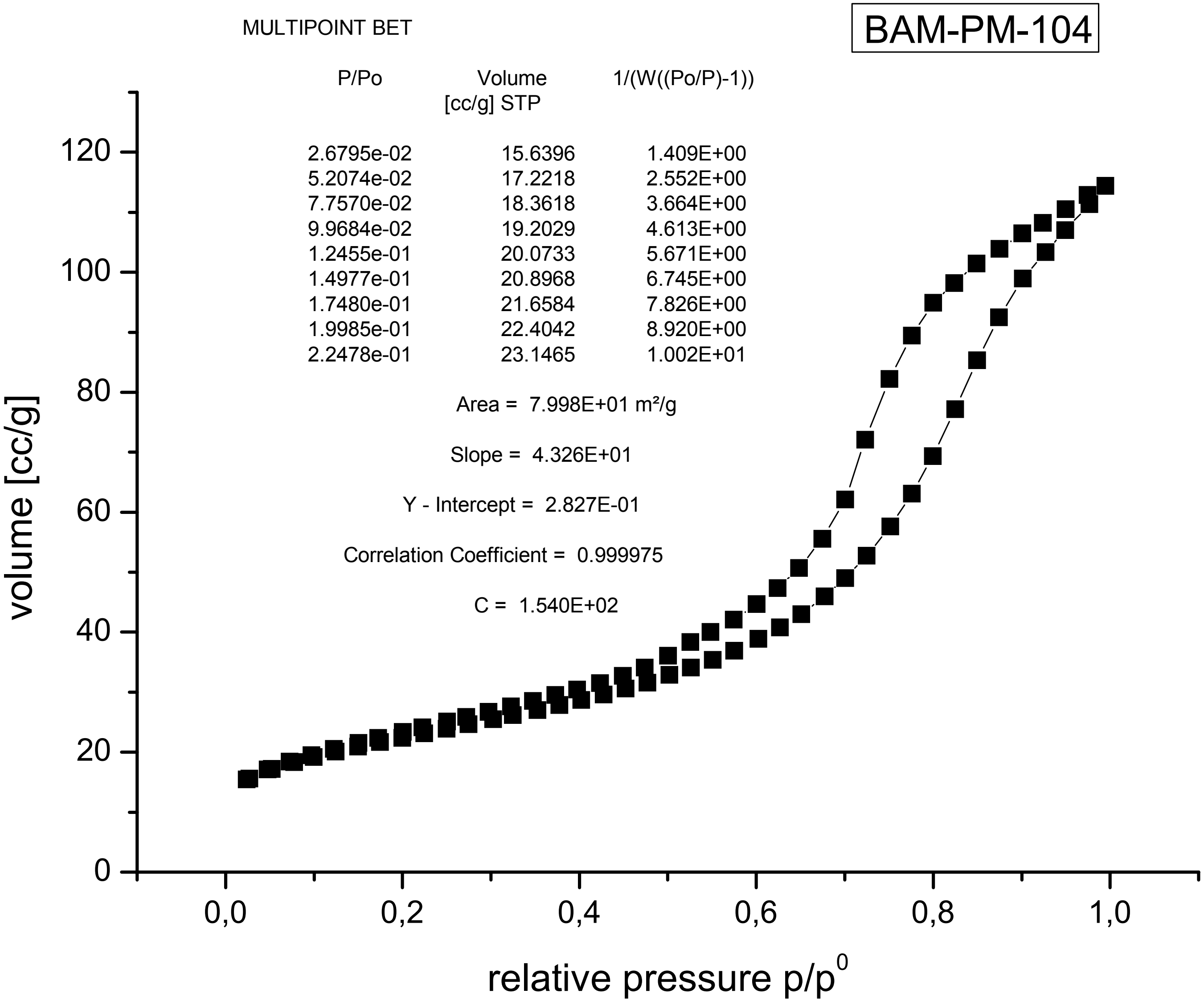
Certificate







BET Standard



MULTIPOINT BET

P/Po	Volume [cc/g] STP	1/(W((Po/P)-1))
2.6795e-02	15.6396	1.409E+00
5.2074e-02	17.2218	2.552E+00
7.7570e-02	18.3618	3.664E+00
9.9684e-02	19.2029	4.613E+00
1.2455e-01	20.0733	5.671E+00
1.4977e-01	20.8968	6.745E+00
1.7480e-01	21.6584	7.826E+00
1.9985e-01	22.4042	8.920E+00
2.2478e-01	23.1465	1.002E+01

Area = 7.998E+01 m²/g

Slope = 4.326E+01

Y - Intercept = 2.827E-01

Correlation Coefficient = 0.999975

C = 1.540E+02

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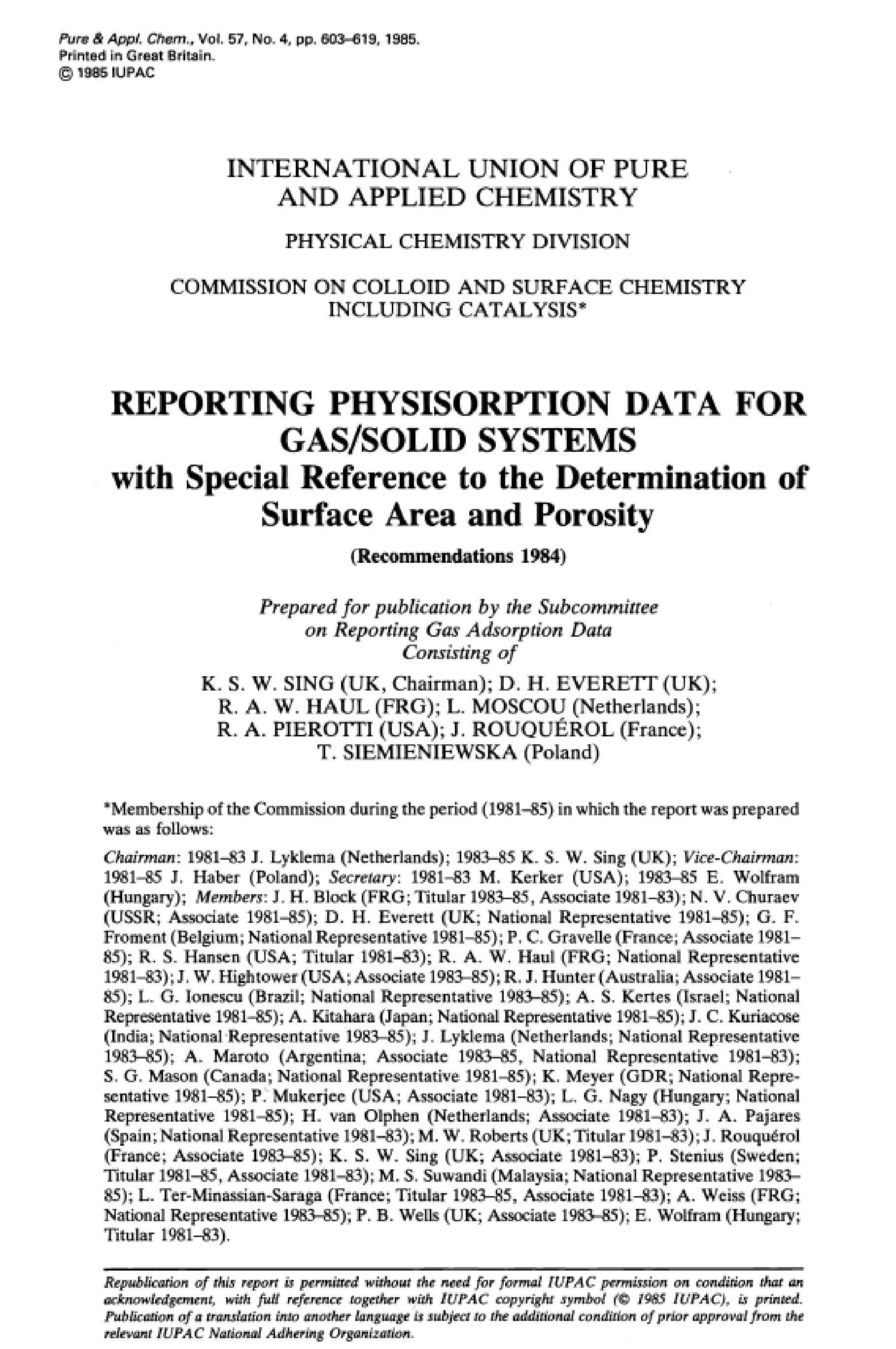
Experimental

Sample preparation:

1. Homogenization
2. Weighing
3. Outgassing adapted to the chemical nature of the sample in vacuum or under flow (repetitive cycling)

Maximun residual pressure:
1 Pa (7.5×10^{-3} Torr)
Micropore analysis: $p < 0.01$ Pa



Pure & Appl. Chem., Vol. 57, No. 4, pp. 603–619, 1985.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY
INCLUDING CATALYSIS*

REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity

(Recommendations 1984)

Prepared for publication by the Subcommittee
on Reporting Gas Adsorption Data
Consisting of

K. S. W. SING (UK, Chairman); D. H. EVERETT (UK);
R. A. W. HAUL (FRG); L. MOSCOU (Netherlands);
R. A. PIEROTTI (USA); J. ROUQUÉROL (France);
T. SIEMIENIEWSKA (Poland)

*Membership of the Commission during the period (1981–85) in which the report was prepared was as follows:

Chairman: 1981–83 J. Lyklema (Netherlands); 1983–85 K. S. W. Sing (UK); *Vice-Chairman*: 1981–85 J. Haber (Poland); *Secretary*: 1981–83 M. Kerker (USA); 1983–85 E. Wolfram (Hungary); *Members*: J. H. Block (FRG; Titular 1983–85, Associate 1981–83); N. V. Churaev (USSR; Associate 1981–85); D. H. Everett (UK; National Representative 1981–85); G. F. Froment (Belgium; National Representative 1981–85); P. C. Gravelle (France; Associate 1981–85); R. S. Hansen (USA; Titular 1981–83); R. A. W. Haul (FRG; National Representative 1981–83); J. W. Hightower (USA; Associate 1983–85); R. J. Hunter (Australia; Associate 1981–85); L. G. Ionescu (Brazil; National Representative 1983–85); A. S. Kertes (Israel; National Representative 1981–85); A. Kitahara (Japan; National Representative 1981–85); J. C. Kuriacose (India; National Representative 1983–85); J. Lyklema (Netherlands; National Representative 1983–85); A. Maroto (Argentina; Associate 1983–85, National Representative 1981–83); S. G. Mason (Canada; National Representative 1981–85); K. Meyer (GDR; National Representative 1981–85); P. Mukerjee (USA; Associate 1981–83); L. G. Nagy (Hungary; National Representative 1981–85); H. van Olphen (Netherlands; Associate 1981–83); J. A. Pajares (Spain; National Representative 1981–83); M. W. Roberts (UK; Titular 1981–83); J. Rouquérol (France; Associate 1983–85); K. S. W. Sing (UK; Associate 1981–83); P. Stenius (Sweden; Titular 1981–85, Associate 1981–83); M. S. Suwandi (Malaysia; National Representative 1983–85); L. Ter-Minassian-Saraga (France; Titular 1983–85, Associate 1981–83); A. Weiss (FRG; National Representative 1983–85); P. B. Wells (UK; Associate 1983–85); E. Wolfram (Hungary; Titular 1981–83).

Experimental – Volumetric measurement

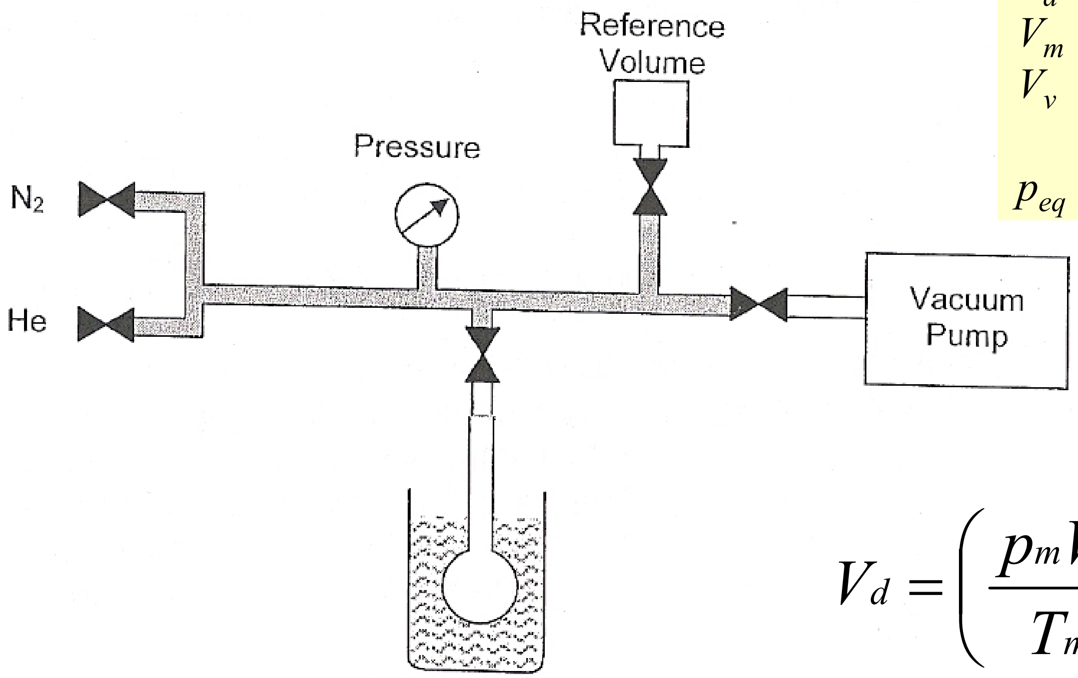


Figure 14.1b Simplified, modern static volumetric apparatus.

V_d	volume of adsorptive dosed
V_m	volume of manifold
V_v	volume of the sample cell, which is not occupied by the adsorbent
p_{eq}	equilibrium pressure after the dose

$$V_d = \left(\frac{p_m V_m}{T_m} - \frac{p_{eq} V_m}{T_{eq}}\right) \times \left(\frac{T_{Std}}{p_{Std}}\right)$$

$$V_s = V_d - \left(\frac{p V_{v\,77\,K}}{p_{Std}}\right)$$

$$T_{std} = 273.15\ \mathrm{K},\ p_{std} = 760\ \mathrm{torr}$$

$$V_{stp}[\mathrm{cm}^3] / 22414\ \mathrm{cm}^3 = n_s$$

Problems

Void volume determination

- He is not adsorbed
- He does not penetrate into regions inaccessible for the adsorptive (He removal procedure for micropore measurements!)

Corrections for non-ideality

Coolant level and temperature control

p_0 determination

Experimental

- p_0 is defined as the saturated equilibrium vapor pressure exhibited by the pure adsorptive contained in the sample cell when immersed in the coolant
- The saturation pressure increases exponentially with T
- Due to dissolved water vapor, oxygen or other gases the T is slightly elevated:

0.1-0.2 K ~ $\Delta p = 10\text{-}20$ torr

- BET plot not very sensitive to p_0
- Broad pressure range for micropore analysis:

$10^{-7} \leq p/p_0 \leq 1$

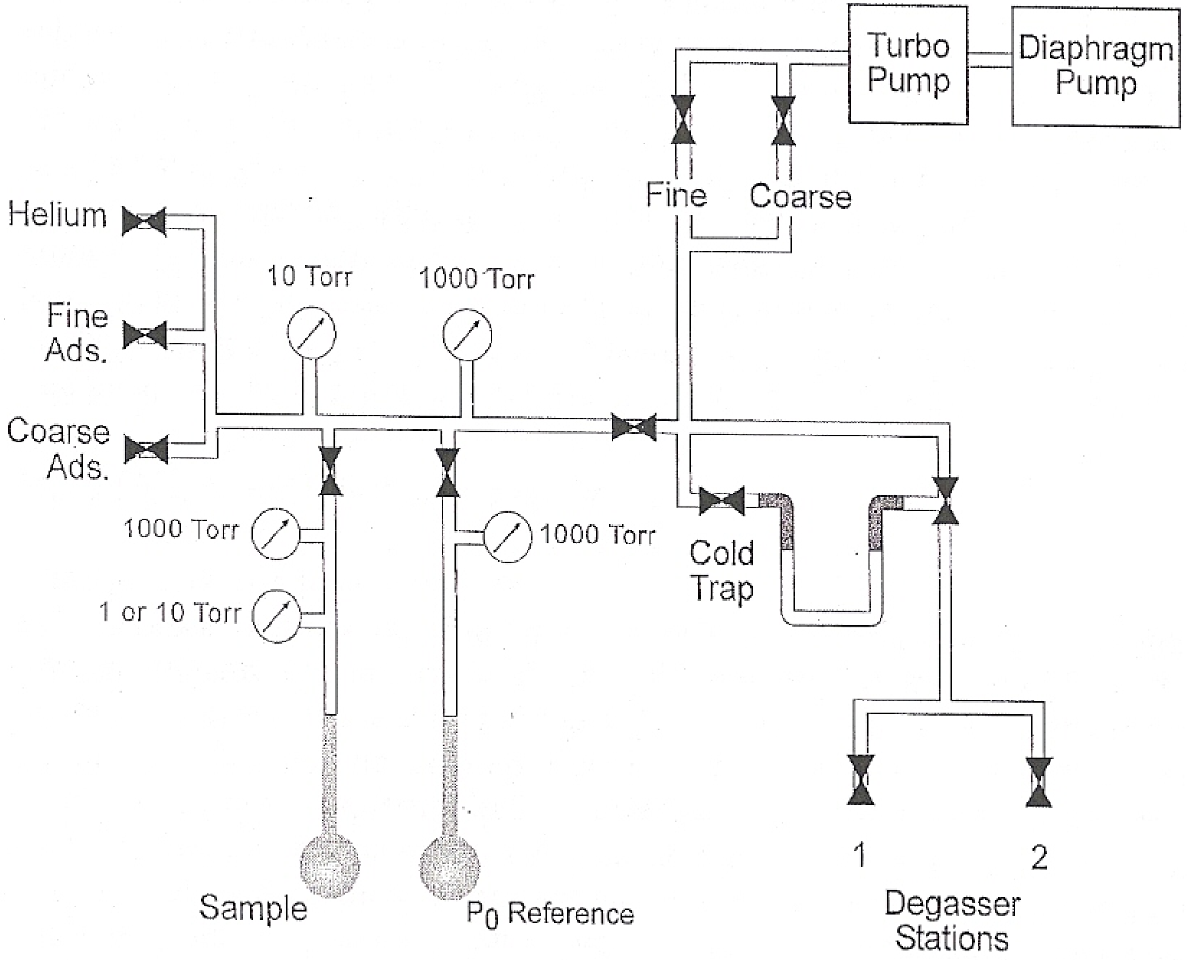


Figure. 14.3 Schematic representation of a high precision volumetric apparatus suitable for pore size analysis of micro- and mesoporous materials as well as for samples with low surface areas.

Acknowledgements

Gisela Lorenz and Kilian Klaeden for gas adsorption measurements

Thank you for your attention