# Surface area determination - physisorption and chemisorption

- Motivation
- Physisorption
- Chemisorption
- Outlook

Literature:


1. DIN ISO 9277: BET method
2. DIN 66136: Dispersion measurement of metals
3. DIN 66134: BJH method
4. Rouquerol F, Rouquerol J, Sing K. Adsorption by Powders and Porous Solids. London: Academic Press; 1999.
5. Neimark AV, Sing KSW, Thommes M. Surface Area and Porosity. Handbook of Heterogeneous Catalysis. Wiley-VCH Verlag GmbH & Co. KGaA; 2008.
6. Bergeret G, Gallezot P. Particle Size and Dispersion Measurements. Handbook of Heterogeneous Catalysis. Wiley-VCH Verlag GmbH & Co. KGaA; 2008.
7. Quantachrome manuals


Dirk Rosenthal, Electronic Structure, Department Inorganic Chemistry, Fritz-Haber-Institut der MPG, Berlin, Germany

## What do we obtain?

- specific surface area of a substance
- specific surface area of a part of a substance (i.e. of the metal particles on a support)

## Why do we need such quantities?

- comparability of different charges of the same substance
- comparability of catalyst activity (... not given per gram)

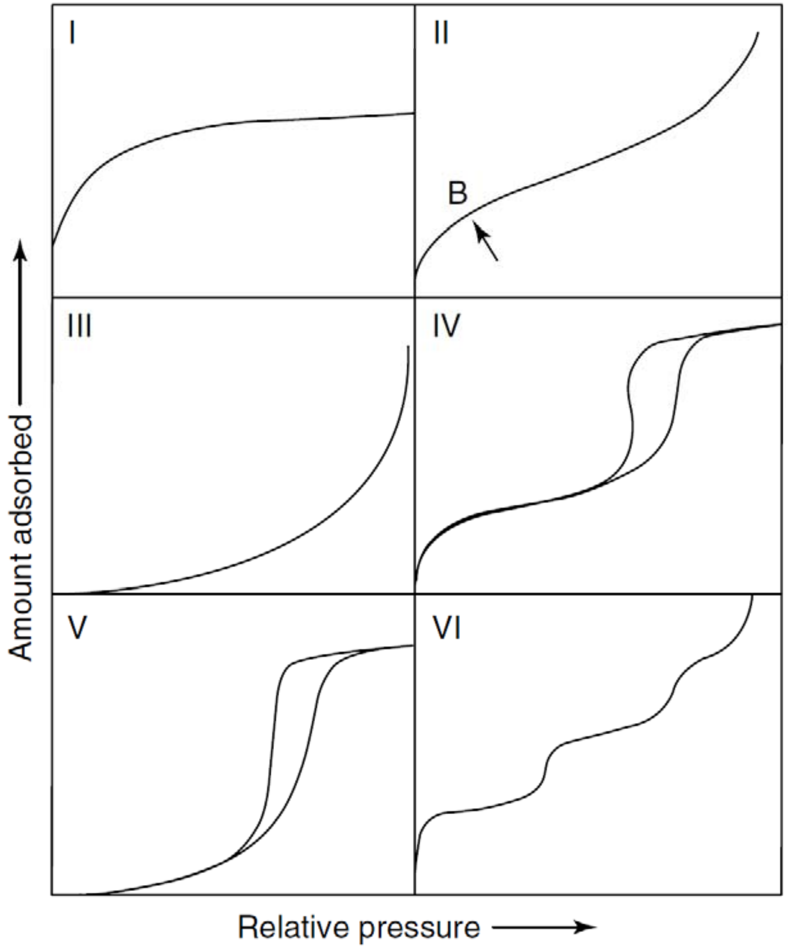
Idea: surface area is a measure for the number of catalytic centers (but for sure not the number of active sites – no one knows how an active site looks like)

Weak adsorbate – adsorbens interactions – first level approximation:

Adsorption energy is constant in the first layer and different but nearly constant in the following multilayers

**We measure the (in principle) whole surface area!**

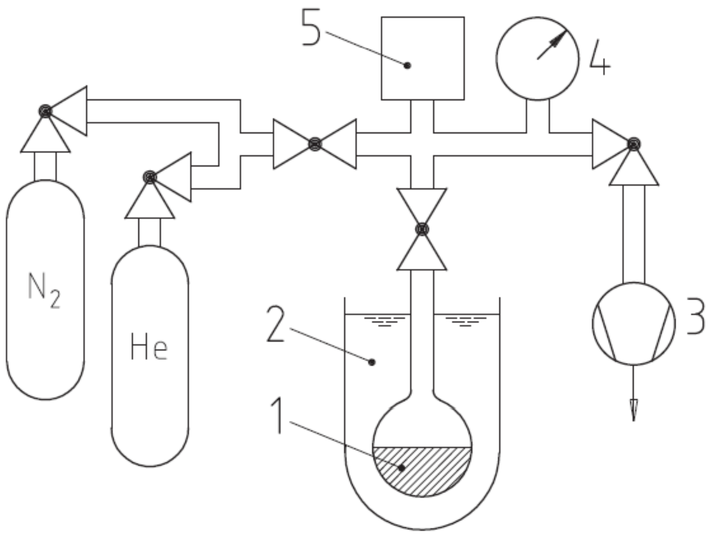
# Physisorption
## What do we measure? - **isotherms**




IUPAC isotherm classification

- Saturation behaviour for high $p/p_0$
- concave – convex
- „sharp knee point“ B

# How do we measure?
# Volumetric measurement



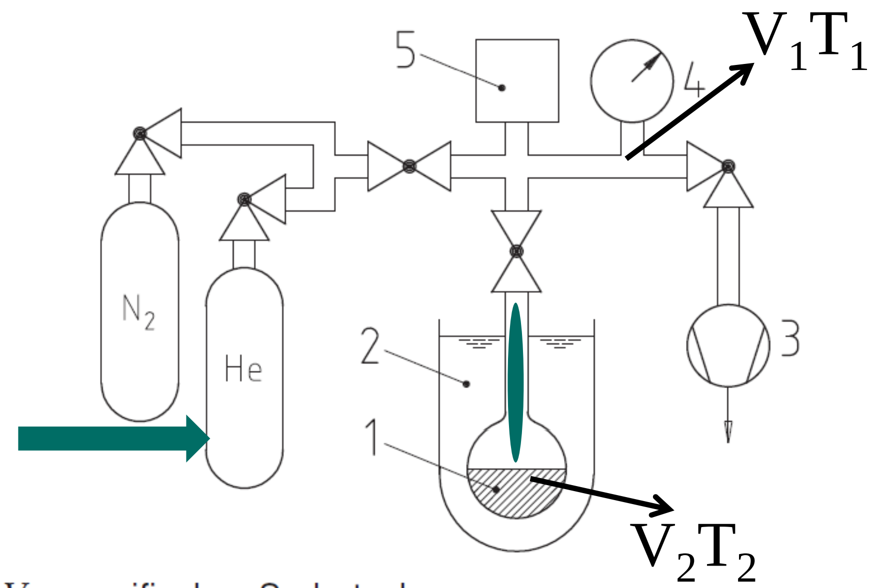

| | | | |
|---|---|---|---|
| $V_a$ | spezifisches Sorbatvolumen | | |
| $p$ | Druck des Sorptivs | | |
| 1 | Probe | 3 | Vakuumaggregat |
| 2 | Dewargefäß mit flüssigem Stickstoff | 4 | Manometer |
| | | 5 | kalibriertes Volumen |

**Bild 6: Volumetrische Apparatur**

**ideal gas law:**

$$pV = nRT$$

# 1. Dead volume measurement with He




$V_a$ spezifisches Sorbatvolumen
$p$ Druck des Sorptivs

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**Bild 6: Volumetrische Apparatur**

Problems:

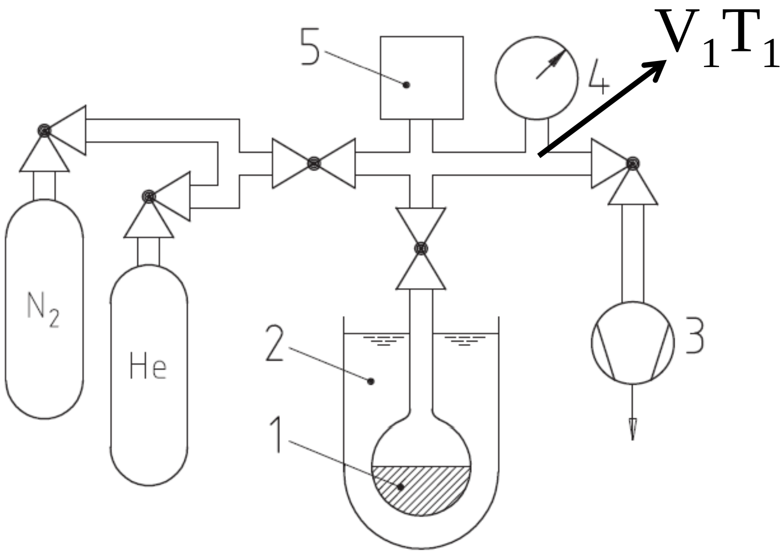
**$V_2$ is unknown, $T_2$ is not well defined:**

Quantachrome :

1. $V_2$ at RT with He
2. Pressure change with and without bath yields volume of „cold“ and „warm“ zone volume in $V_2$

- **Cold and warm zone changeover volume should be minimized!**
- **Some adsorbens absorb also He!**

# 2. Measurement with $N_2$




$V_a$ spezifisches Sorbatvolumen
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1 Probe
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**Bild 6: Volumetrische Apparatur**

1. Certain amount of $N_2$ is dosed in $V_1$
2. Equilibration with $V_2$ yields new (lower) $p_1 = p_2$
3. Step one is repeated until the desired p
4. the lost amount is now in $V_2$, i.e. in the „cold“ and „warm“ zone volume and the residual in the calculation is the adsorbed amount of $N_2$

# Analysis of the isotherms
# the BET method

**B**runauer, **E**mmett and **T**eller in the 1930s

$$\frac{p/p_0}{n_a\left(1-\left(p/p_0\right)\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \bullet \frac{p}{p_0}$$

with $n_a$ : adsorbed amount

$$y = a + bx$$

Monolayer capacity $n_m = \frac{1}{a+b}$

BET constant C: $C = \frac{b}{a} + 1$

Specific surface area $a_s = n_m a_m L$

$a_m = 0.162 nm$ for $N_2$

L: Avogadro number

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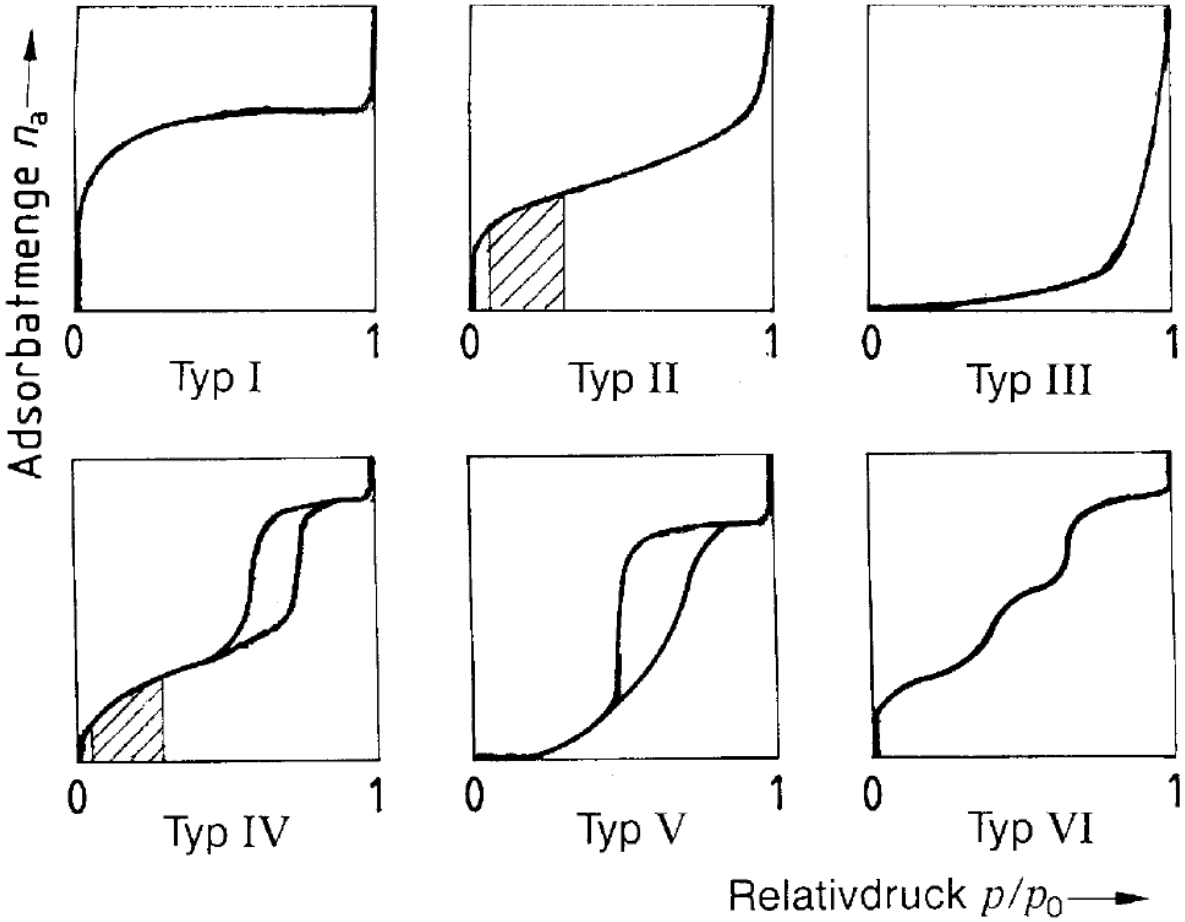
# Analysis of the isotherms
# the BET method




How to do?

Fit with the BET equation in the range of $p/p_0 = 0.05 ... 0.3$

Sometimes even at lower upper limit

# BET equation, BET constant *C*, Langmuir equation as limit for C=1

$$\frac{p/p_0}{n_a\left(1-\left(p/p_0\right)\right)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \bullet \frac{p}{p_0}$$

From the original theory: $C = e^{\frac{E_1 - E_L}{RT}}$

$E_1$ is the adsorption energy of the first layer and
$E_L$ the liquefaction energy,

with $E_1 = E_L$ this transforms into the Langmuir equation

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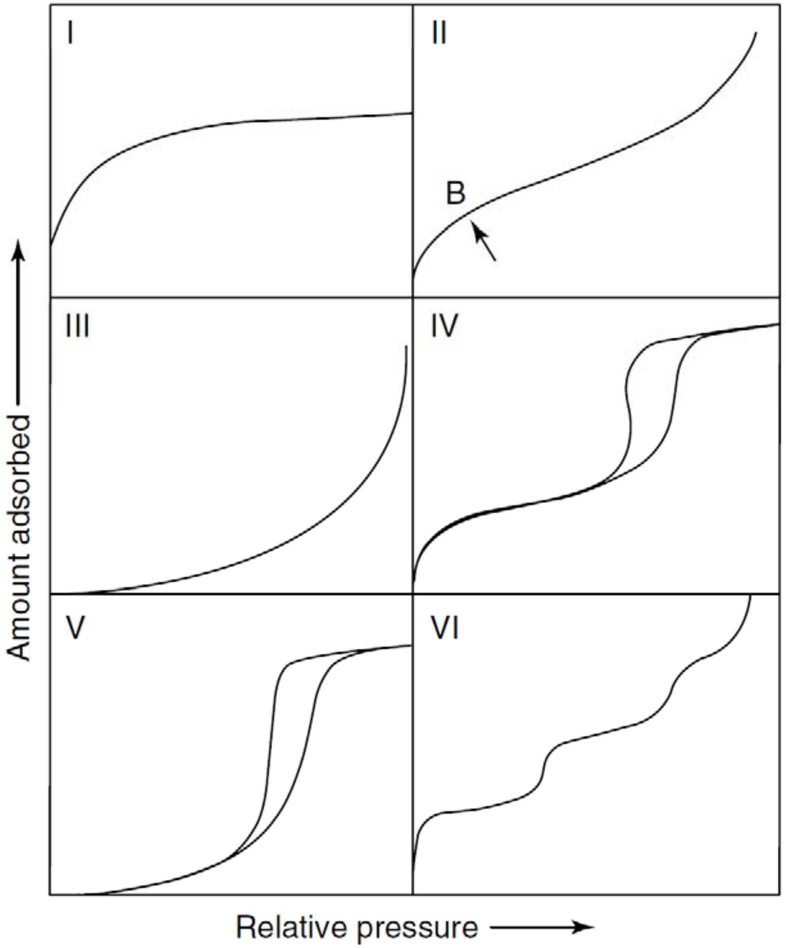
# Isotherm classification

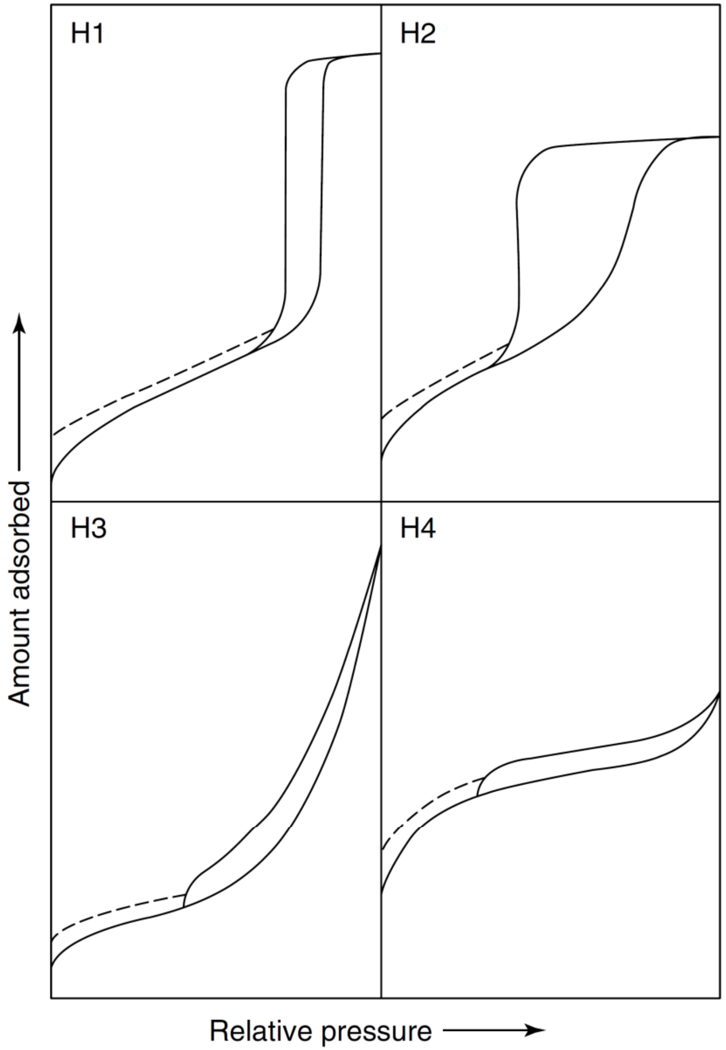



## IUPAC isotherm classification

- Saturation behaviour for high $p/p_0$ (pore filling)
- concave – convex
- „sharp knee point“ B

| | |
|---|---|
| Type I: | Langmuir, „saturation“ |
| Type II: | C > 2, sigmoid (S-shaped)<br>non- or macroporous |
| Type III: | C < 2, weak interactions |
| Type IV: | C > 2, mesoporous, „saturation“ |
| Type V: | C < 2, like III with „saturation“ |
| Type VI: | stepwise (layer by layer) adsorption |

# Adsorption and desorption hysteresis




H1: narrow distribution of relatively uniform (cylindrical-like) pores
-delayed condensation and no network effects, analysis of the desorption branch

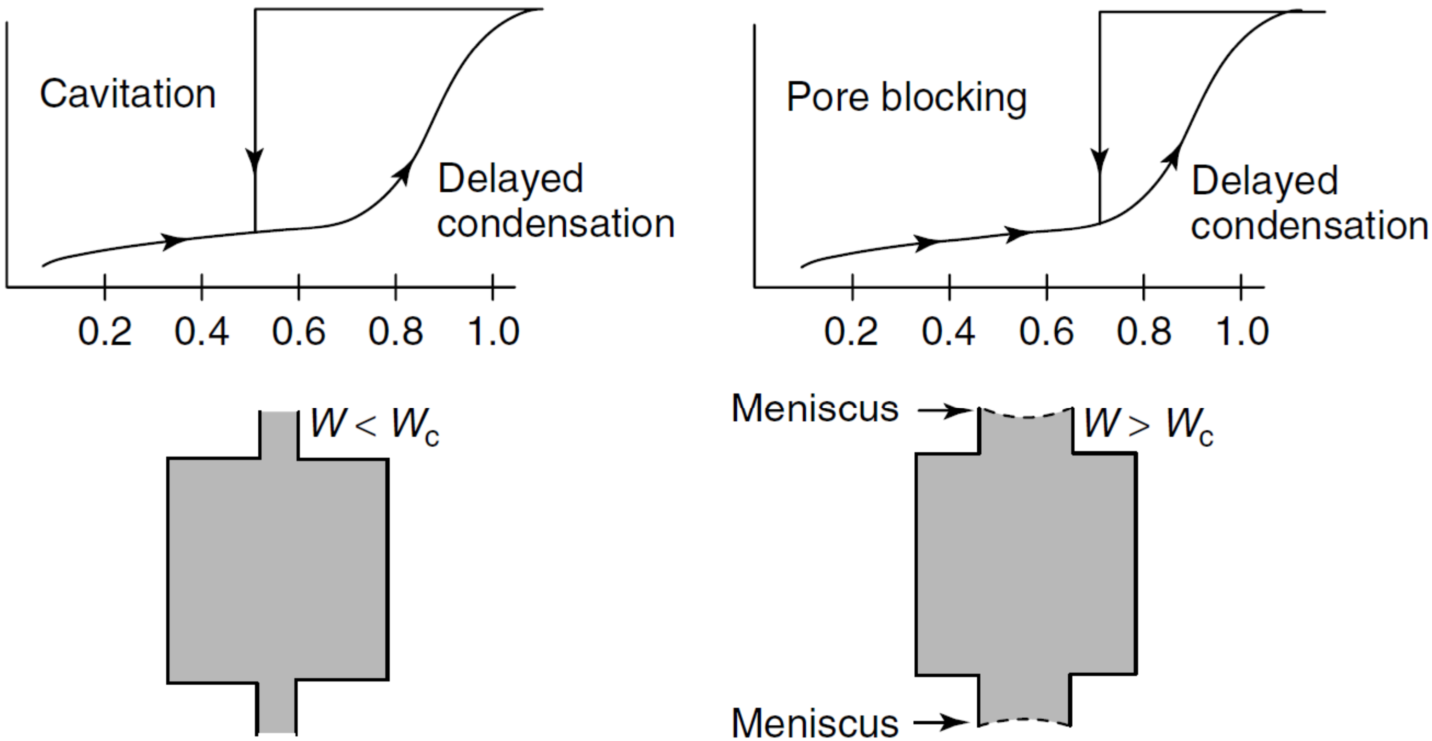
H2: complex pore structure, network effects are important, analysis of the adsorption branch

H3: non-rigid aggregates of plate-like particles or assemblages of slit-shaped pores
- no saturation

H4: complex materials containing both micropores and mesopores

Neimark AV, Sing KSW, Thommes M. Surface Area and Porosity. Handbook of Heterogeneous Catalysis, Wiley; 2008.

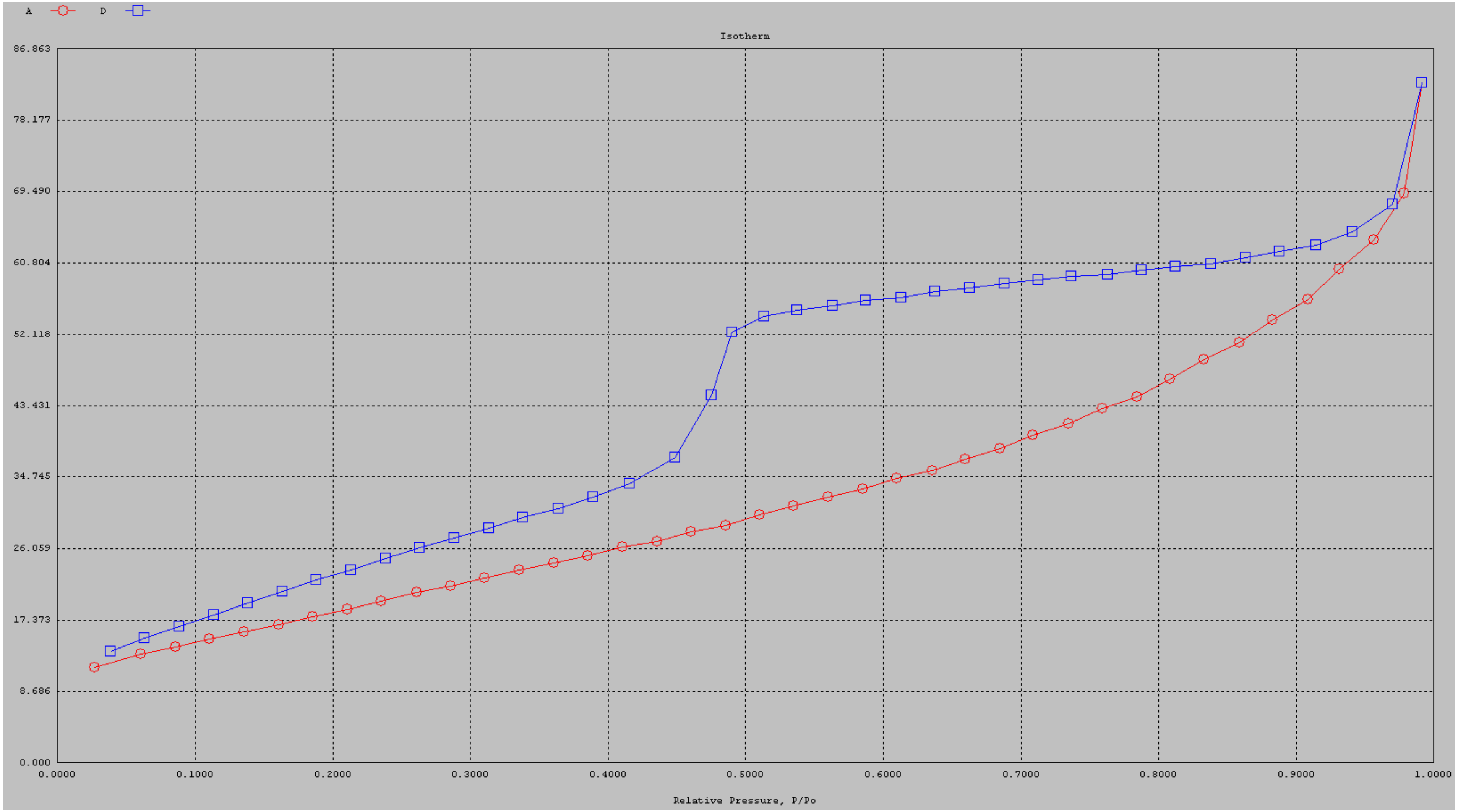
# Adsorption and desorption hysteresis, some effects



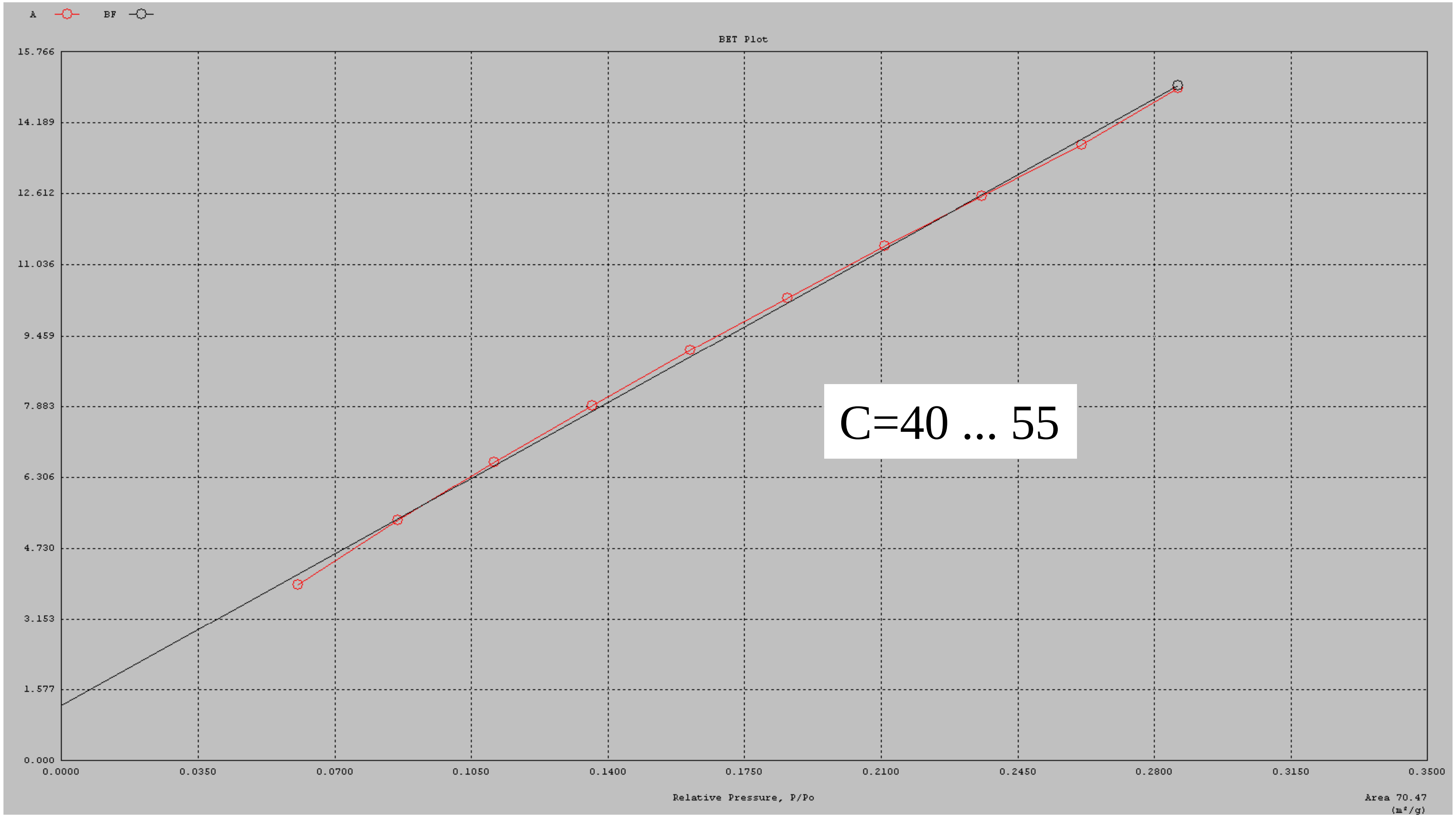

Often at $p/p_0=0.42$ for $N_2$
independent of the adsorbent

Neimark AV, Sing KSW, Thommes M. Surface Area and Porosity. Handbook of Heterogeneous Catalysis, Wiley; 2008.

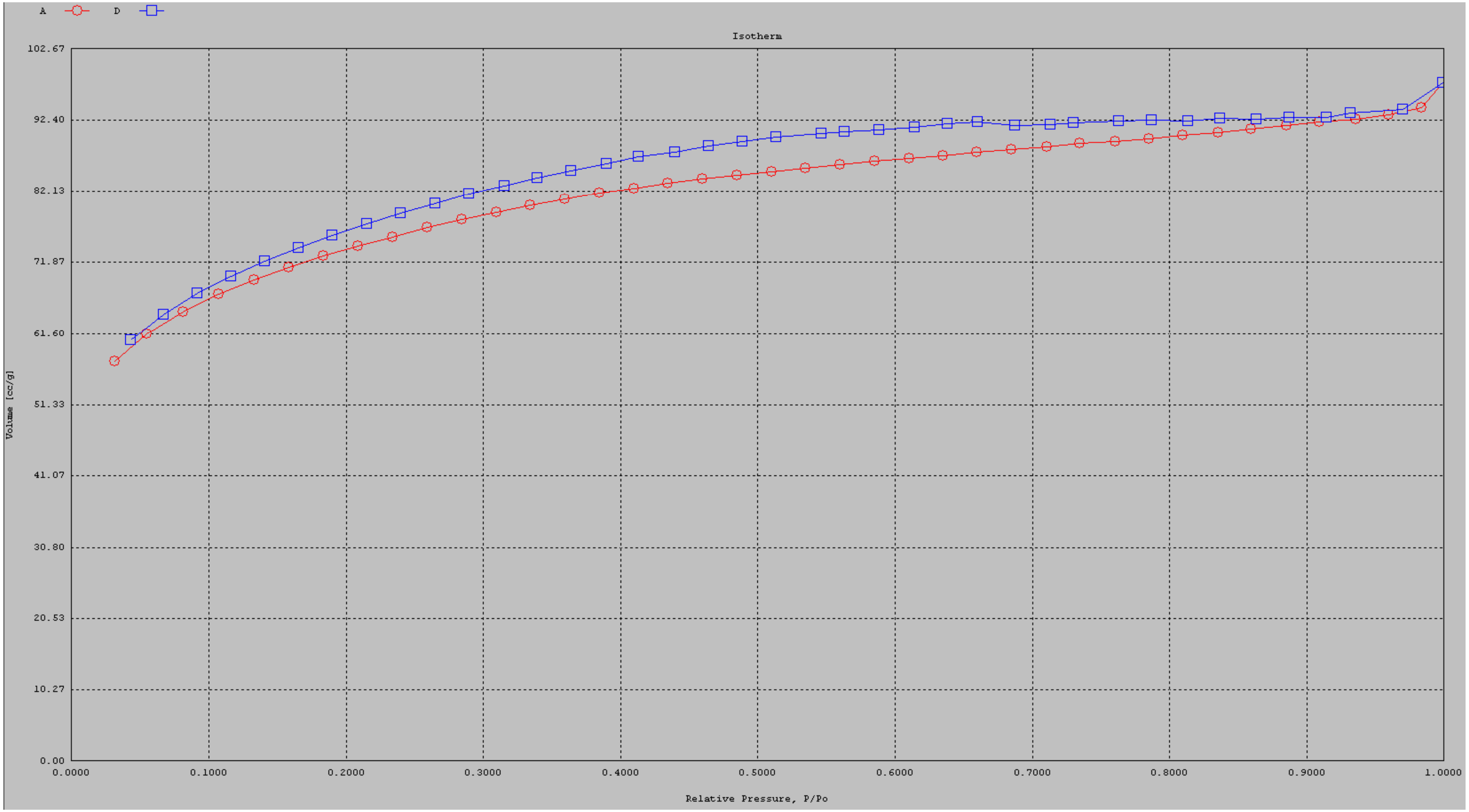
# BET method – example 1
# 10904



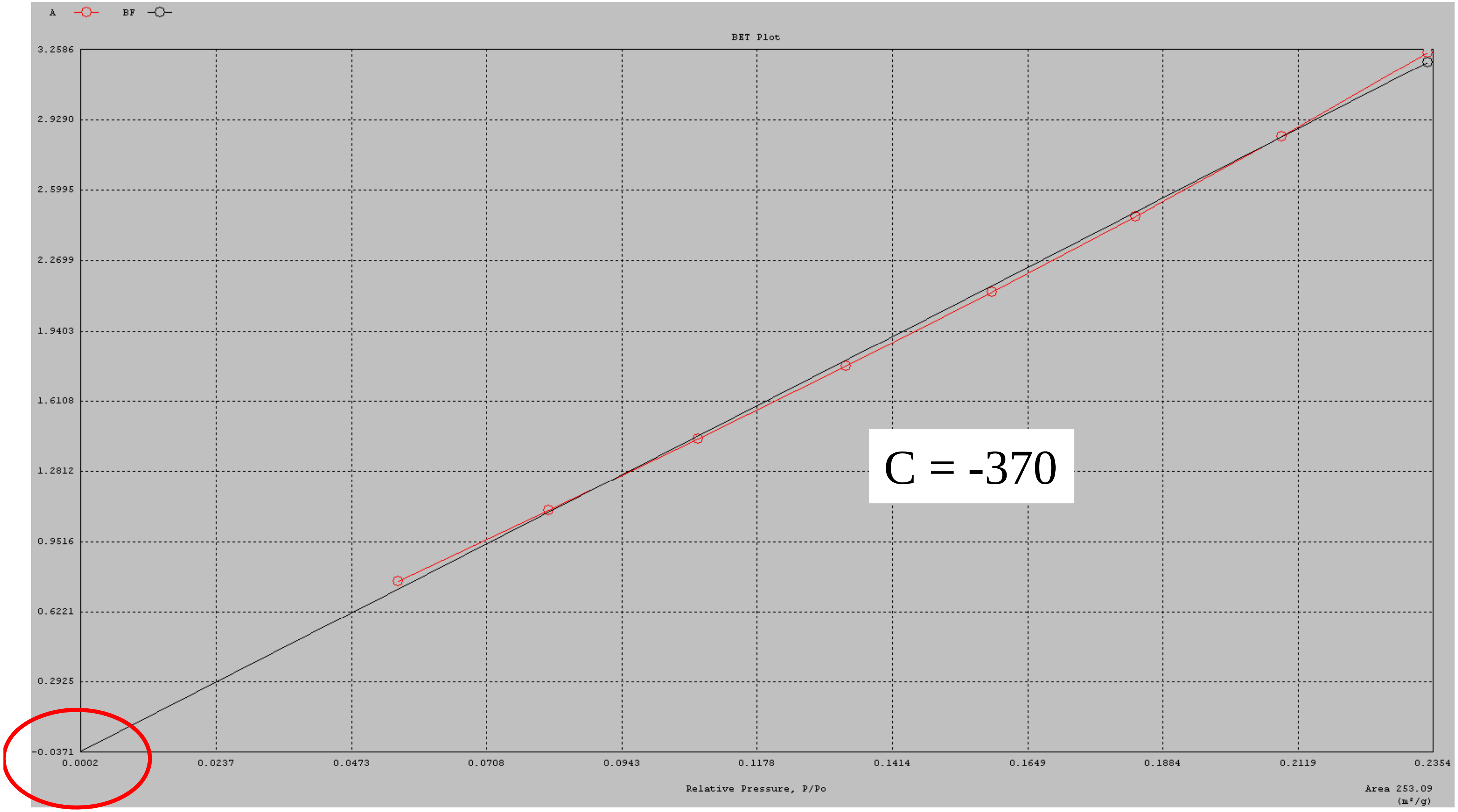
# BET method – example 1
# 10904



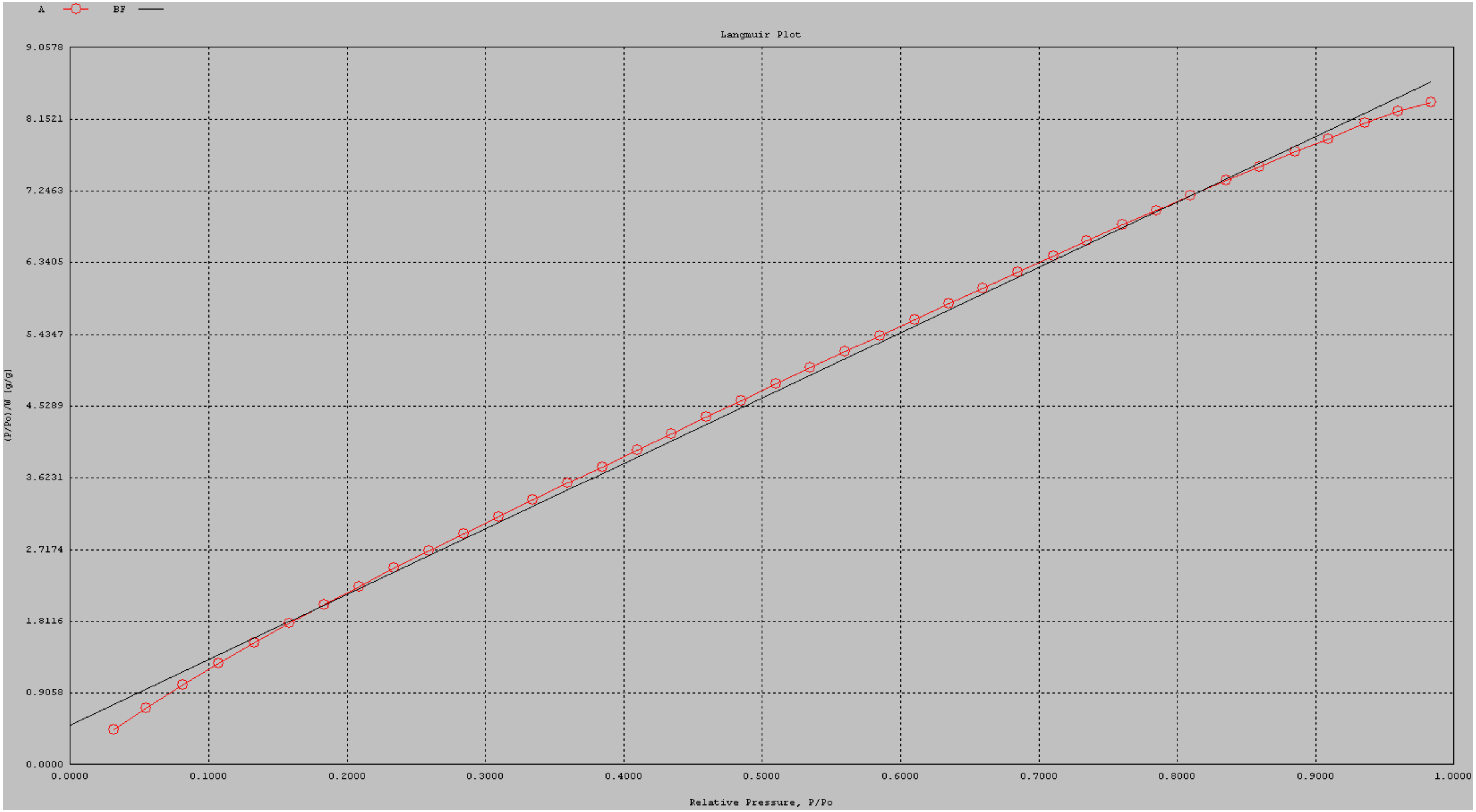
# BET method – example 2
# # 9828



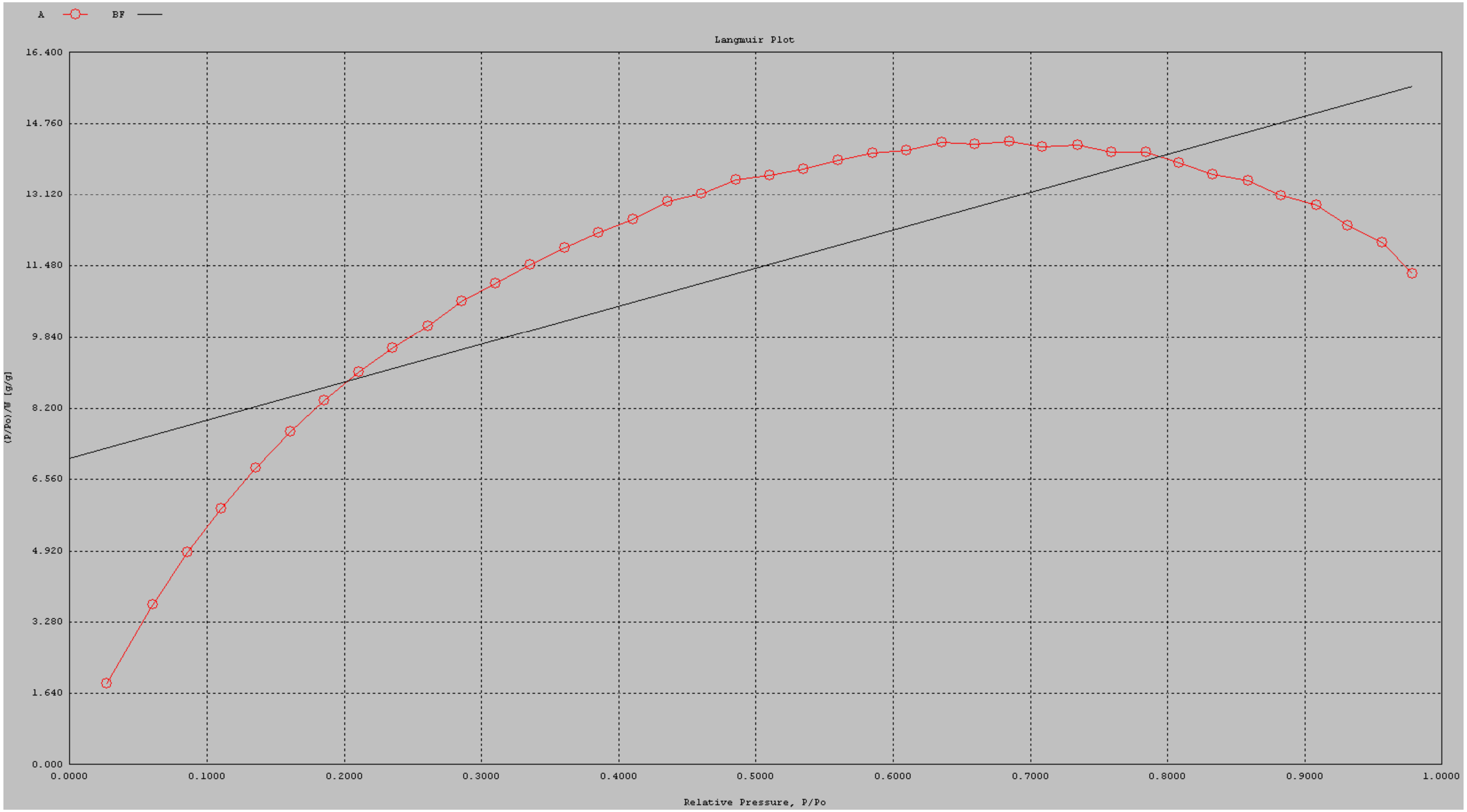
# BET method – example 2
# 9828



# BET method – example 2
# 9828 - Langmuir



# BET method – example 1
# # 10904 - Langmuir



# Reference materials for the BET method, measurement errors

DIN ISO 9277:

measurement errors:

- Instrument (p, V, T, vacuum)
- Scatter of different measurement

**Zertifizierte Referenzmaterialien für das BET-Verfahren**

| Material | Bezeichnung | Bezugs-quelle | Spezifische Oberfläche[a] $m^2g^{-1}$ |
|---|---|---|---|
| Silica[b] | BAM-PM-101 | BAM | 0,177 |
| Alpha-Alumina | BAM-PM-102 | BAM | 5,41 |
| Alumina | BAM-PM-103 | BAM | 156 |
| Alumina | BAM-PM-104 | BAM | 79,8 |
| Alpha-Alumina | BCR-169 | IRMM | 0,104 |
| Alpha-Alumina | BCR-170 | IRMM | 1,05 |
| Alumina | BCR-171 | IRMM | 2,95 |
| Quartz | BCR-172 | IRMM | 2,56 |
| Titania-Rutile | BCR-173 | IRMM | 8,23 |
| Tungsten | BCR-175 | IRMM | 0,181 |
| Carbon black | LGC2101 | LGC | 10,5 |
| Carbon black | LGC2102 | LGC | 69 |
| Silica (nonporous) | LGC2103 | LGC | 142 |
| Silica (mesoporous) | LGC2104 | LGC | 247 |
| Silica/Alumina | SRM 1897 | NIST | 258,32 |
| Silicon nitride | SRM 1899 | NIST | 10,52 |
| Silicon nitride | SRM 1900 | NIST | 2,85 |

[a] Die spezifische Oberfläche ist mit dem Stickstoffadsorptionsverfahren bei 77 K gemessen worden (Ausnahmen sind besonders gekennzeichnet).

[b] Gemessen mit Krypton bei 77 K.

Strong adsorbate – adsorbens interactions – first level approximation for metal on a support:

Adsorption energy on the metal is constant in the first layer and **strongly** exceeds the adsorption energies on the support or in multilayers

**We measure (in principle) the metal surface area!**

# How do we measure?
# Pretreatment, choice of adsorbate

**Pretreatment** is different from physisorption

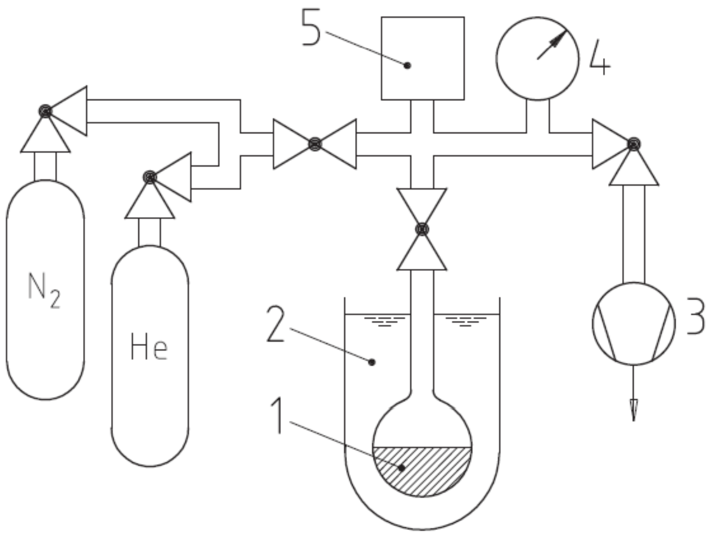
- removal of water
- reduction of the metal (only!)

Quantachrome: Flow cell, reduction with $H_2$/Ar or CO, evacuation

**Choice of adsorbate** is crucial

- only adsorption on the metal
- no irreversibel subsurface absorption
- no volatile reaction products (carbonyles)
- no bulk reaction

# How do we measure?
# Volumetric measurement




$V_a$ spezifisches Sorbatvolumen
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**Bild 6: Volumetrische Apparatur**

**ideal gas law:**

$$pV = nRT$$

# Chemisorption: measurement

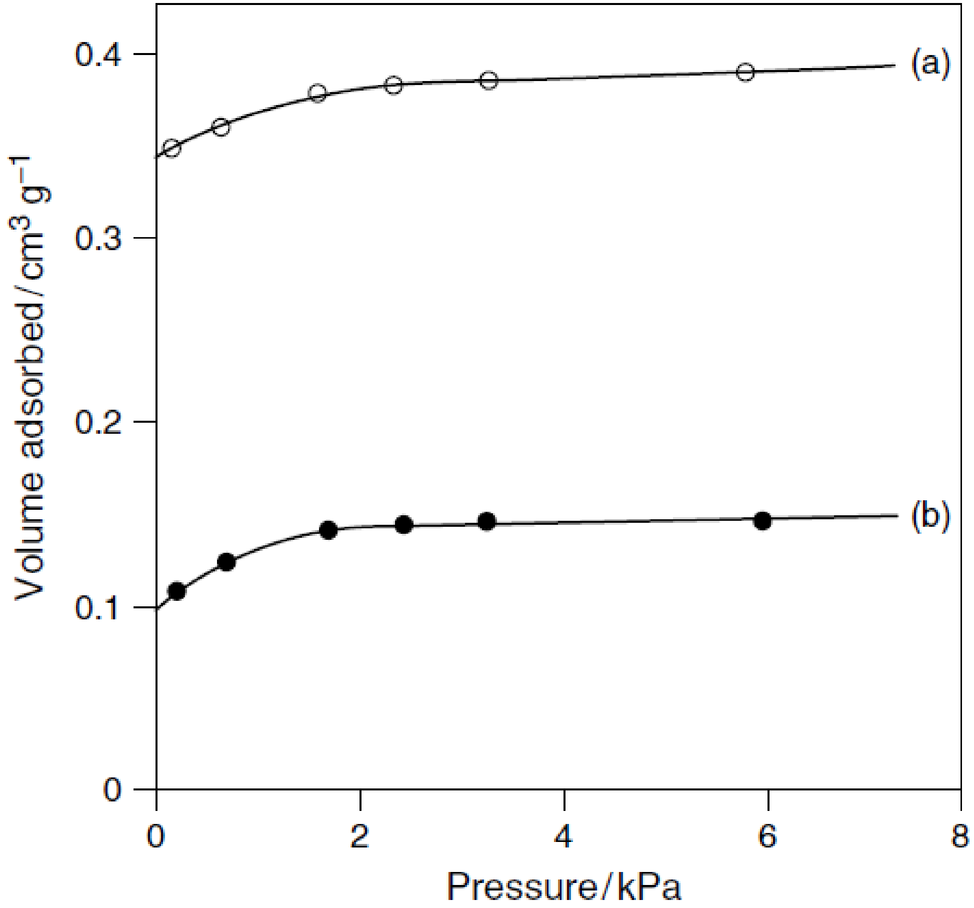
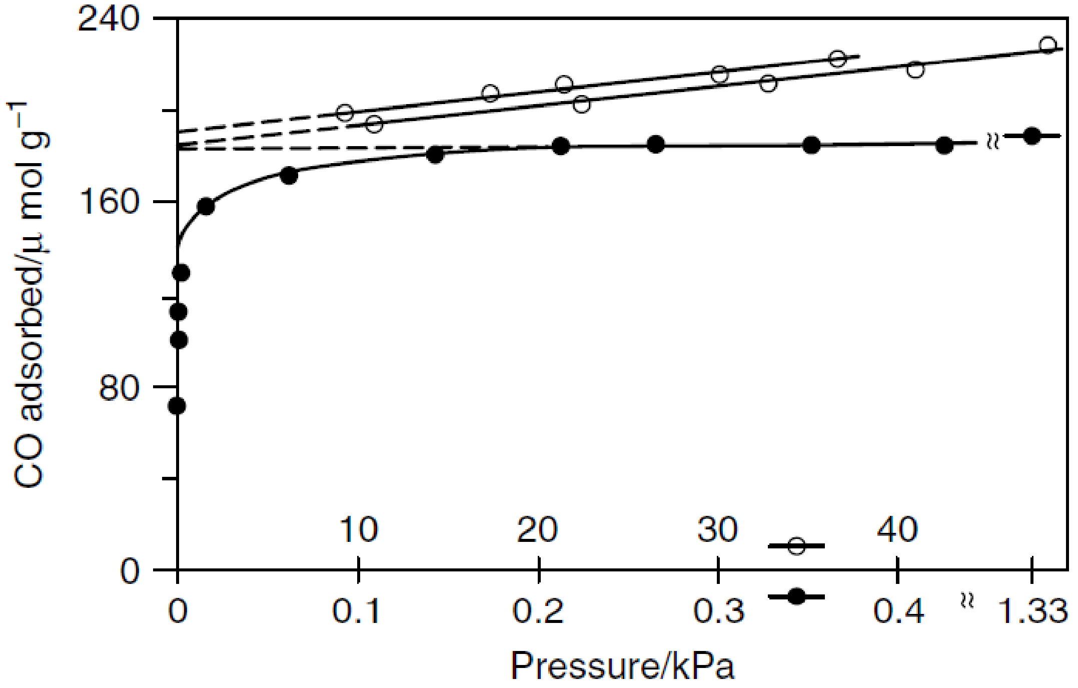



**Fig. 6** Isotherms of $H_2$ adsorption on 0.5% Pt on $\gamma$-alumina at 303 K: (a) total amount of adsorbed $H_2$; (b) amount of reversibly adsorbed $H_2$ after evacuation at room temperature. (Adapted from Ref. [17].)

Two isotherms:

1. Total amount
2. Reversible amount (evacuation after saturation and a second isotherm)

# Chemisorption: analysis




Linear extrapolation to $p = 0$ yields the volume of an adsorbed monolayer $v_m$

**Fig. 4** Isotherms for the adsorption of CO on EUROPT-1 $Pt/SiO_2$ catalyst at room temperature from different laboratories for a pressure range 0–1.33 kPa (solid circles) and 10–50 kPa (open circles). (Adapted from Ref. [14].)

# Chemisorption: analysis

Specific metal surface area: $$A_M = \frac{v_m}{22414} L n \frac{1}{m} a_m \frac{100}{wt} (m^2 g^{-1} metal)$$

metal dispersion: $$D = \frac{v_m n}{22414 m} \bullet \frac{100M}{wt}$$

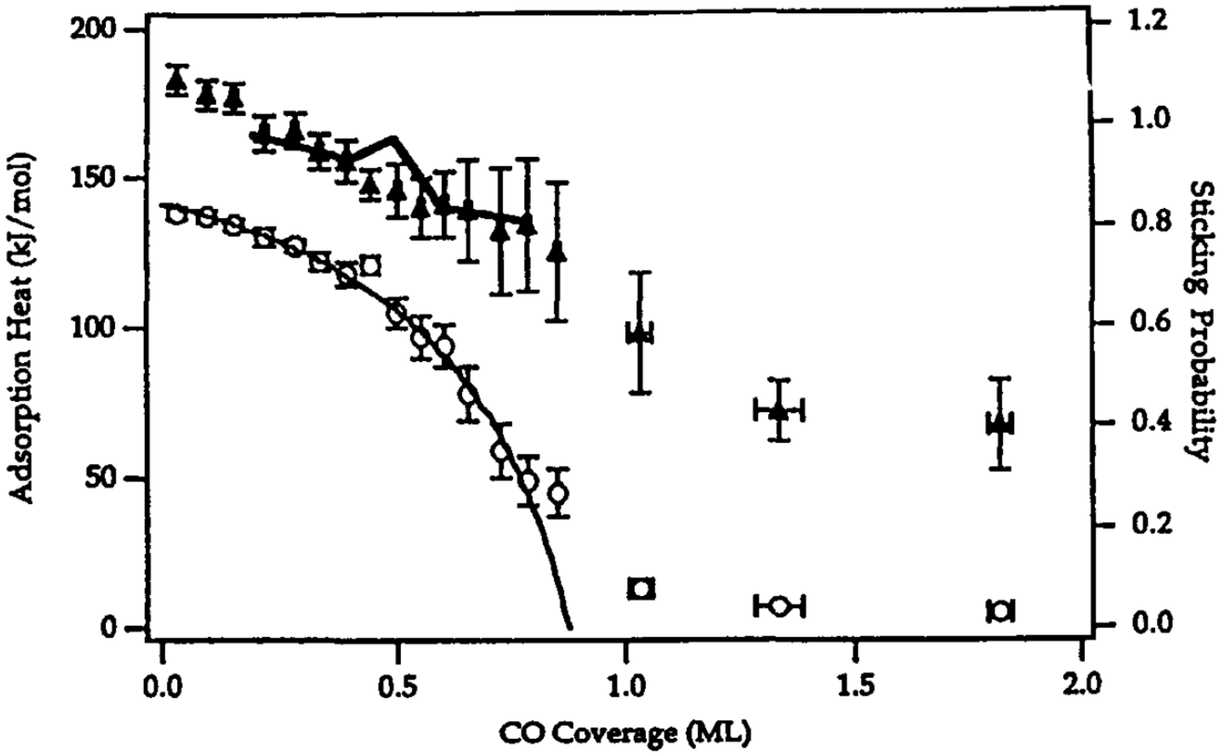
| | |
|---|---|
| Vm | volume of an adsorbed monolayer |
| L | Avogadro number |
| n | chemisorption stoichiometry |
| m | sample mass |
| $a_m$ | surface area occupied by a metal atom |
| wt | metal loading |
| M | atomic mass of the metal |

# Comparison of different adsorptives for Pt, Pd and Rh

| No. | Catalyst Metal/Support | Metal content wt% | Volumetric adsorption H/M | O/M | CO/M[b] | TPR H/M | TEM $\bar{d}_{VA}$(Å) | D[c] from TEM |
|---|---|---|---|---|---|---|---|---|
| 1 | Pt / ALO-1 | 0.50[d] | 1.25 (0.41) | 0.55 | 1.22 (0.60) | 0.98 | 10 | 1.14 |
| 2 | Pt / ALO-4 | 0.50[d] | 1.25 (0.43) | 0.57 | 1.25 (0.52) | 1.06 | 10 | 1.14 |
| 3 | Pt / ALO-4 | 5.1[d] | 1.14 (0.37) | 0.48 | 0.72 (0.15) | 0.83 | 18 | 0.63 |
| 4 | Pt / SIO-2 | 0.50[d] | 0.28 (0.10) | 0.13 | 0.19 (0.026) | 0.33 | 72 | 0.16 |
| 5 | Pt / SAH | 0.64[e] | 0.76 (0.25) | 0.36 | 0.82 (0.33) | 0.68 | 18 | 0.63 |
| 6 | Pt / SAL | 0.72[e] | 0.60 (0.22) | 0.34 | 0.73 (0.30) | 0.56 | 21 | 0.54 |
| 7 | Pt / Z-1 | 0.50[d] | 0.13[f] (0.07) | 0.08[f] | 0.29 (0.15) | 0.04 | 82 | 0.14 |
| 8 | Pd / ALO-4 | 0.50[e] | 0.91 (0.28) | 0.40 | 0.82 (0.27) | 0.90 | 9 | 1.26 |
| 9 | Rh / ALO-4 | 0.50[e] | 0.92 (0.46) | 0.91 | 1.29 (0.30) | 0.79 | 9 | 1.22 |

Kunimori K, Uchijima T, Yamada M, Matsumoto H, Hattori T, Murakami Y. Appl Catal 1982;4(1):67-81.

# Chemisorption – the heat of adsorption




Triangles:
Heat of adsorption for CO/Pt(110) is far from being constant!

Stuck A, Wartnaby CE, Yeo YY, Stuckless JT, AlSarraf N, King DA. An improved single crystal adsorption calorimeter. Surf Sci 1996;349(2):229-40.