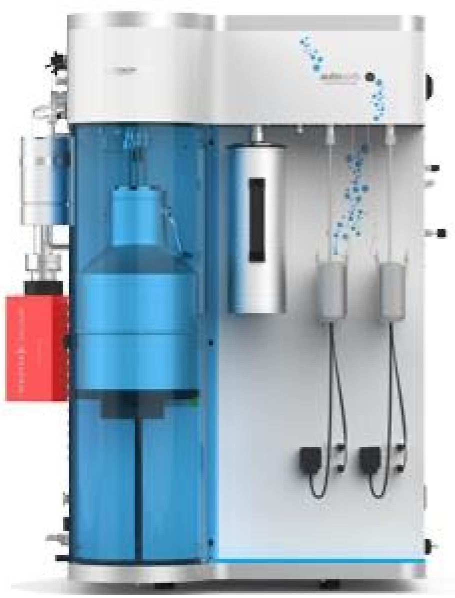
Pore Structure Analysis by Physisorption

The slide was adapted from Quantachrome and other sources only for educational purposes

Example of equipment



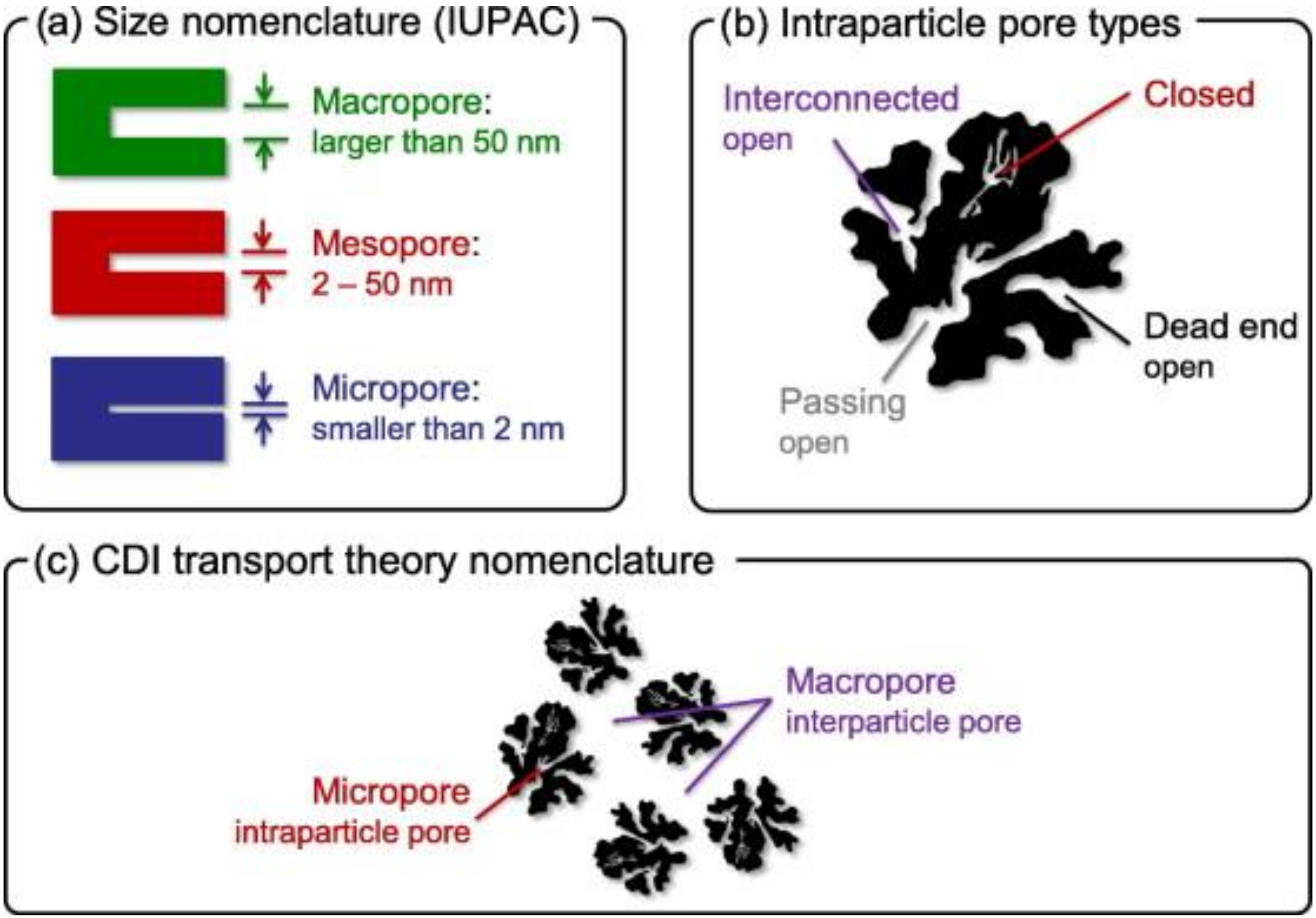
Autosorb

Quadrasorb

NOVA

Quantachrome
INSTRUMENTS

Pores of Porous Solids

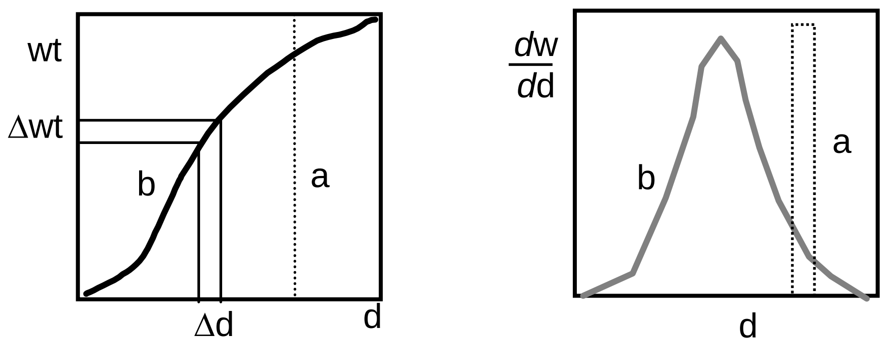


Porada et al., Progress in Materials Science 58 (2013) 1388–1442

Pores of Porous Solids

- **Pore size distribution**
  - Typical curves to characterise pore size:
    - Cumulative curve
    - Frequency curve
  - Uniform size distribution (a) &

    non-uniform size distribution (b)

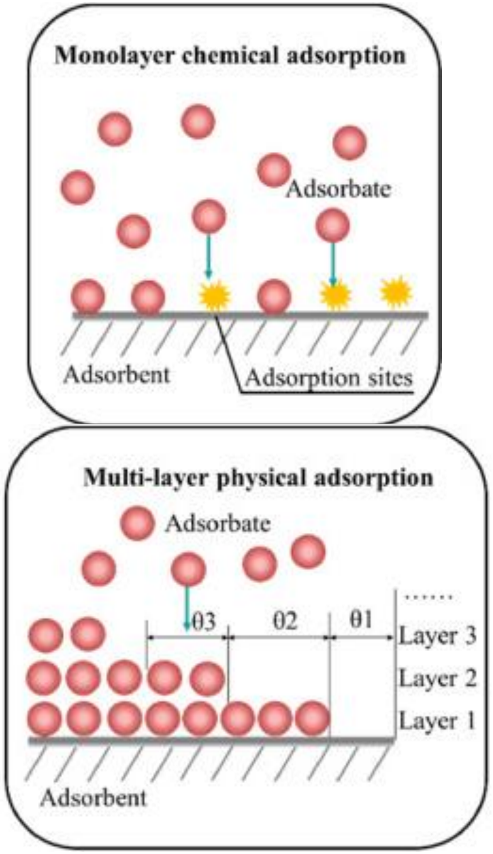


Cumulative curve   Frequency curve

Adsorption – physisorption - chemisorption

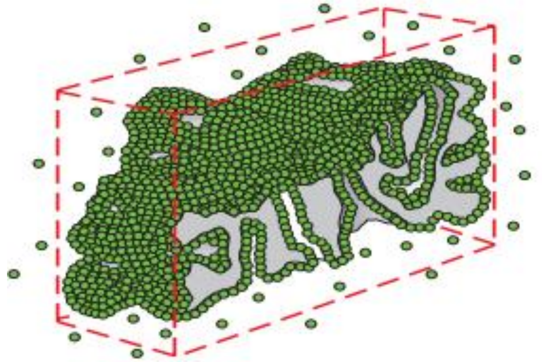
Adsorption is the process in which matter is extracted from one phase and concentrated at the surface of a second phase (Interface accumulation)

Property	Physisorption	Chemisorption
Forces	van der Waals	Chemical bonding
ΔH_{ads} (kJ mol^{-1})	< 40	50-200
E_a (kJ mol^{-1})	Rare	60–100
Isothermal Reversibility	Complete	Slow or none
Extent	Multilayers	Monolayer

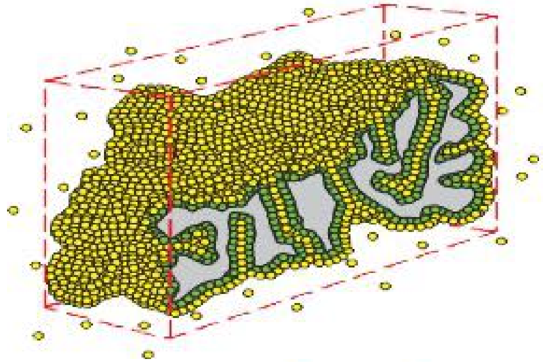


Wang and Guo, Chemosphere, 258, 2020, 127279

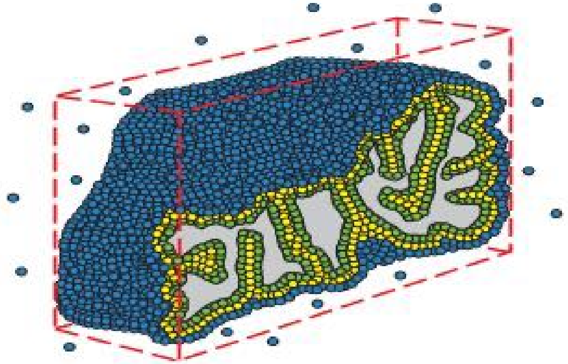
Physisorption



The monolayer of adsorbed molecules; typically, 15 - 20% saturation



The multilayer capillary condensation stage approximately 70% saturation

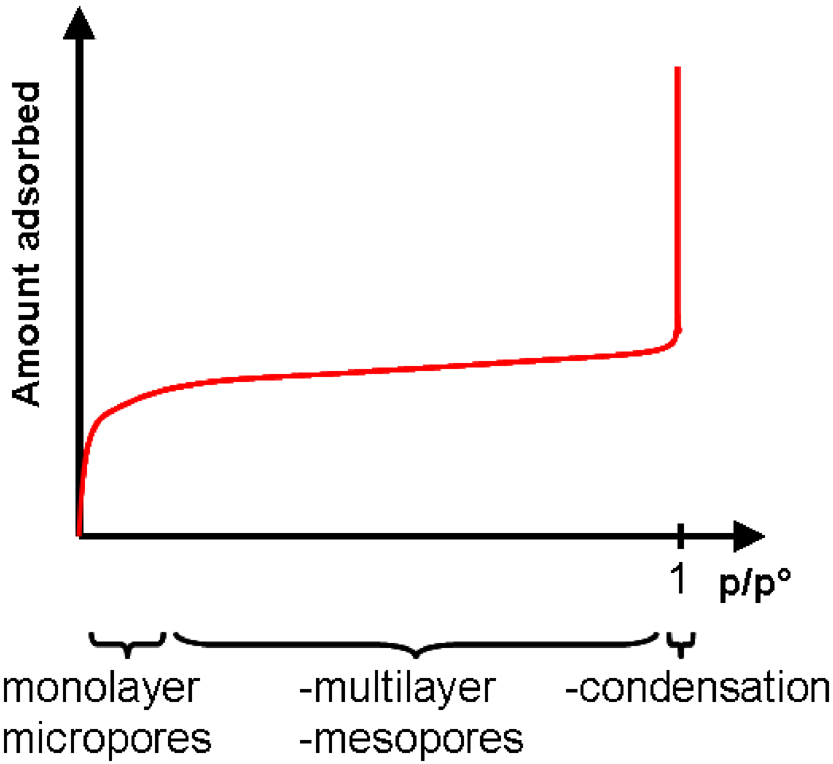


Total pore volume filling; approximately 100% saturation

ADSORPTION ISOTHERM

- amount of N_2 adsorbed versus relative pressure at constant temperature

  - temperature: 77 K: boiling/condensation point of N_2 at p_{atm}=p°



- Amount adsorbed
per unit adsorbent mass:

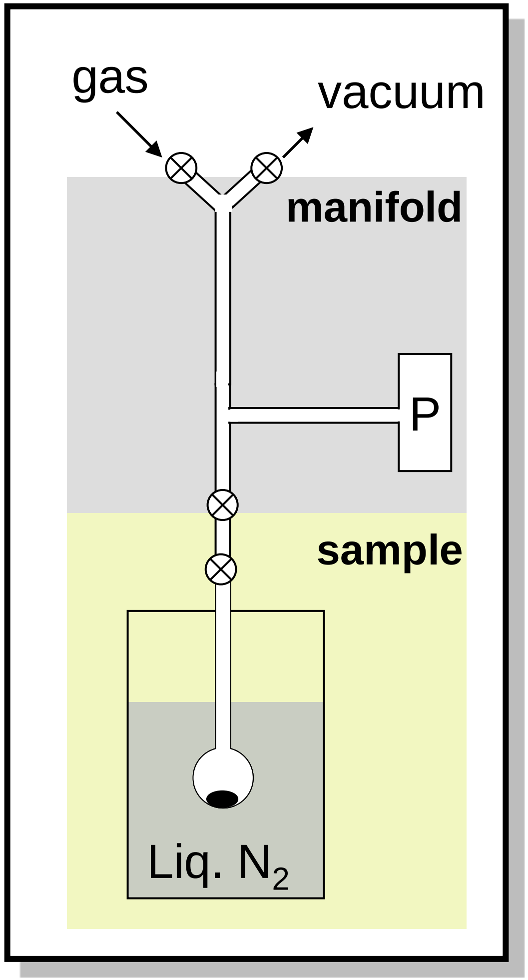
n	mol/g
$V_{ads, STP}$	ml/g = cm^3/g

- STP = 0 °C, 1 bar

$$V_{ads,liq} = \frac{\rho_{N_2,STP}}{\rho_{N_2,liq}} V_{ads,STP}$$

$$= 0.001544 \times V_{ads,STP}$$

how is an adsorption isotherm recorded?

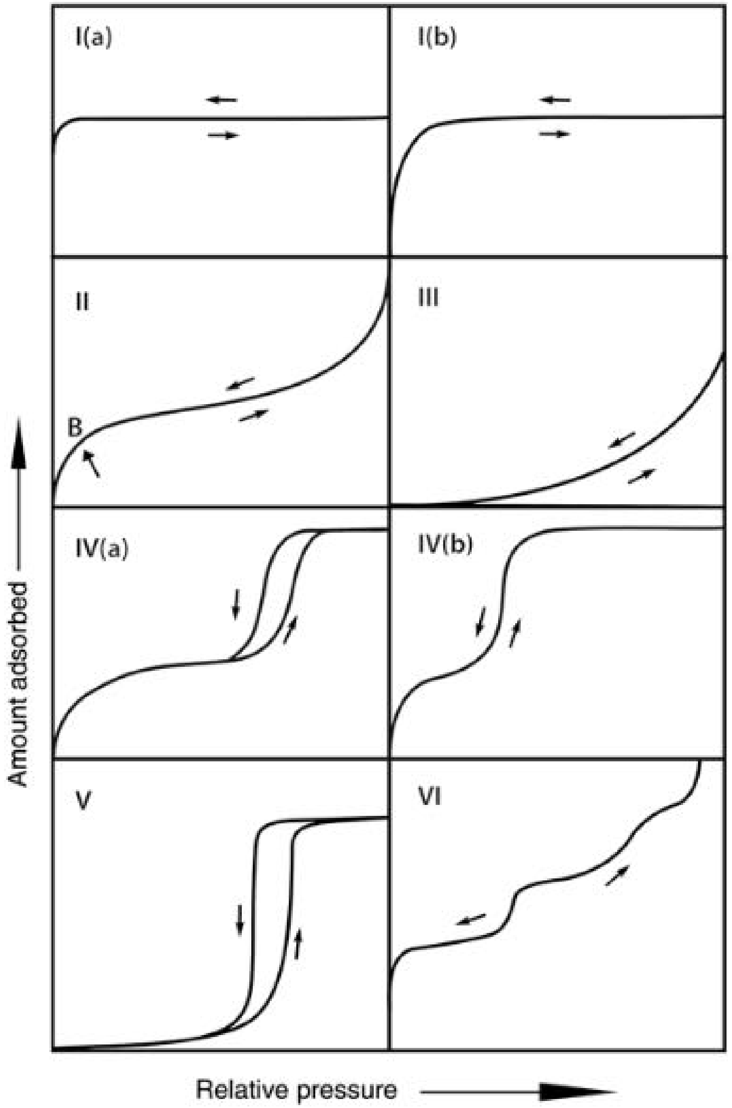


- Total volume of system determined:
  - "manifold" volume known
- System is evacuated
- Start of adsorption:
  - amount of gas dosed in manifold
  - *p* measured → quantity known
  - gas expanded into sample volume
  - equilibrium *p* measured; compared to calculated *p*
  - difference → amount adsorbed at *p*
- p° measured to account for temp changes in liq. N_2

Lower p/p° limit: determined by pump and pressure measurement

Adsorption on Solid Surface

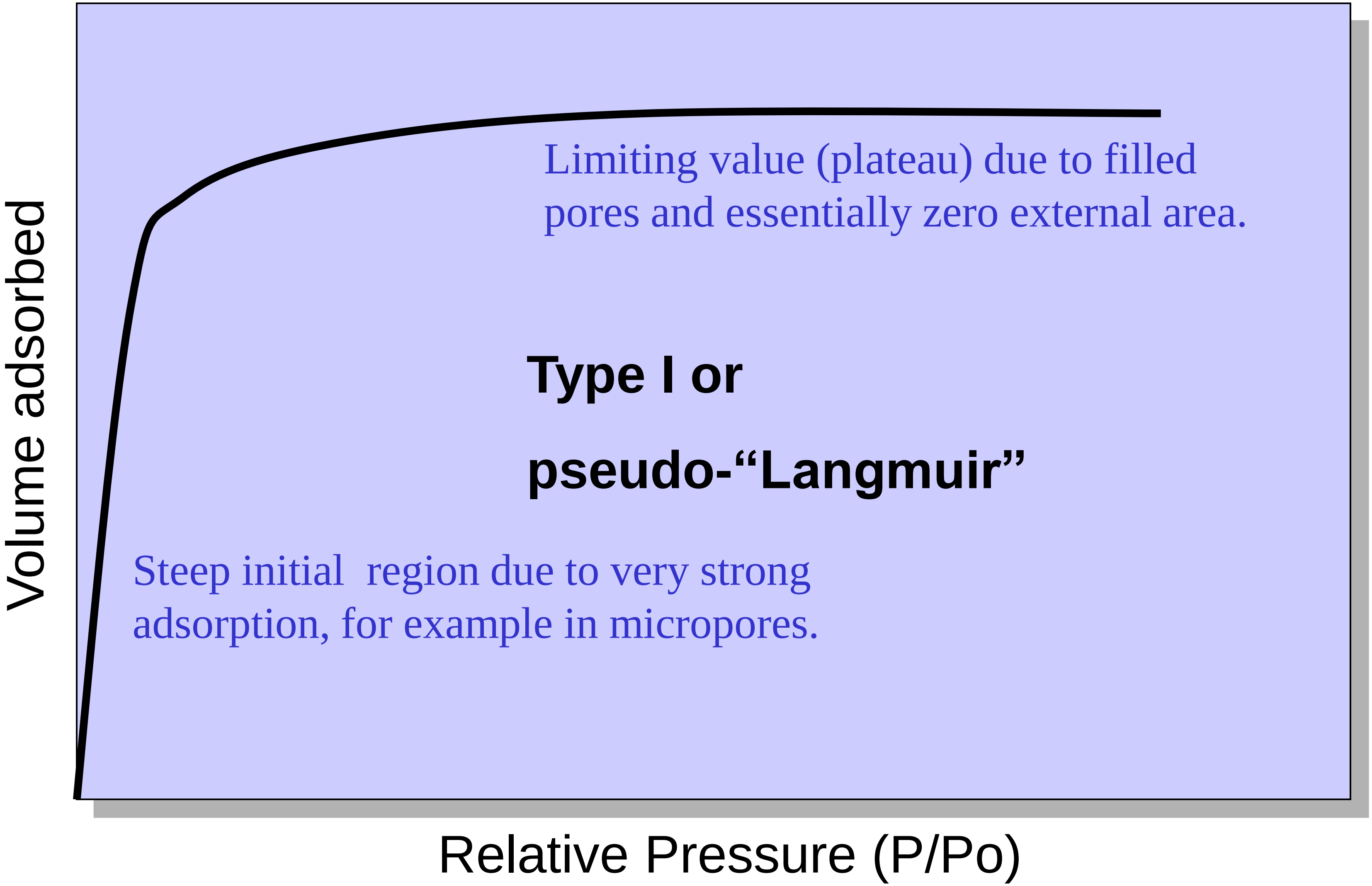
- **Six types of physisorption isotherms are found over all solids**



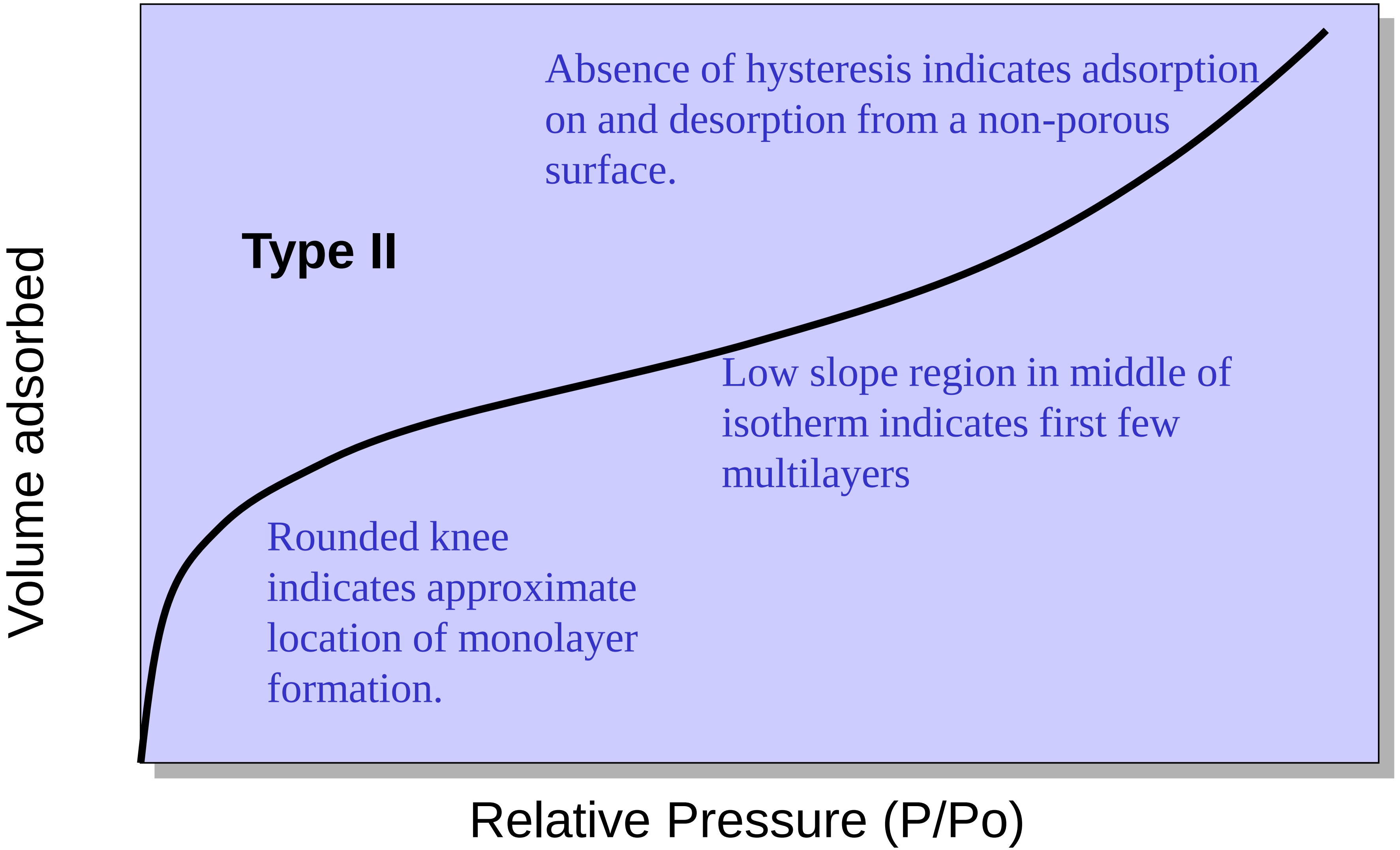
Thommes et al, IUPAC Technical Report, 2015

Pure Appl. Chem. 2015; 87(9-10): 1051–1069

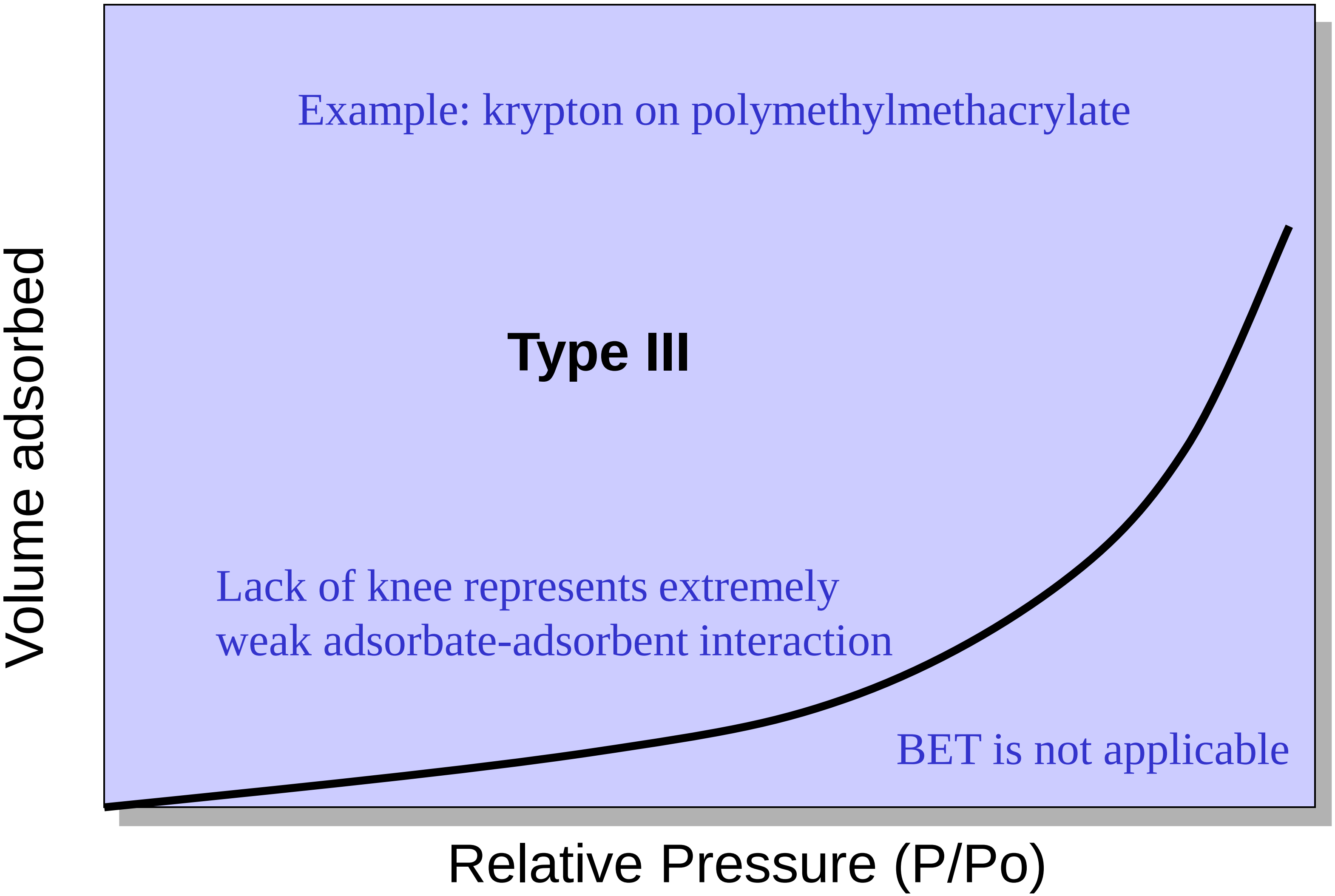
Types of Isotherms



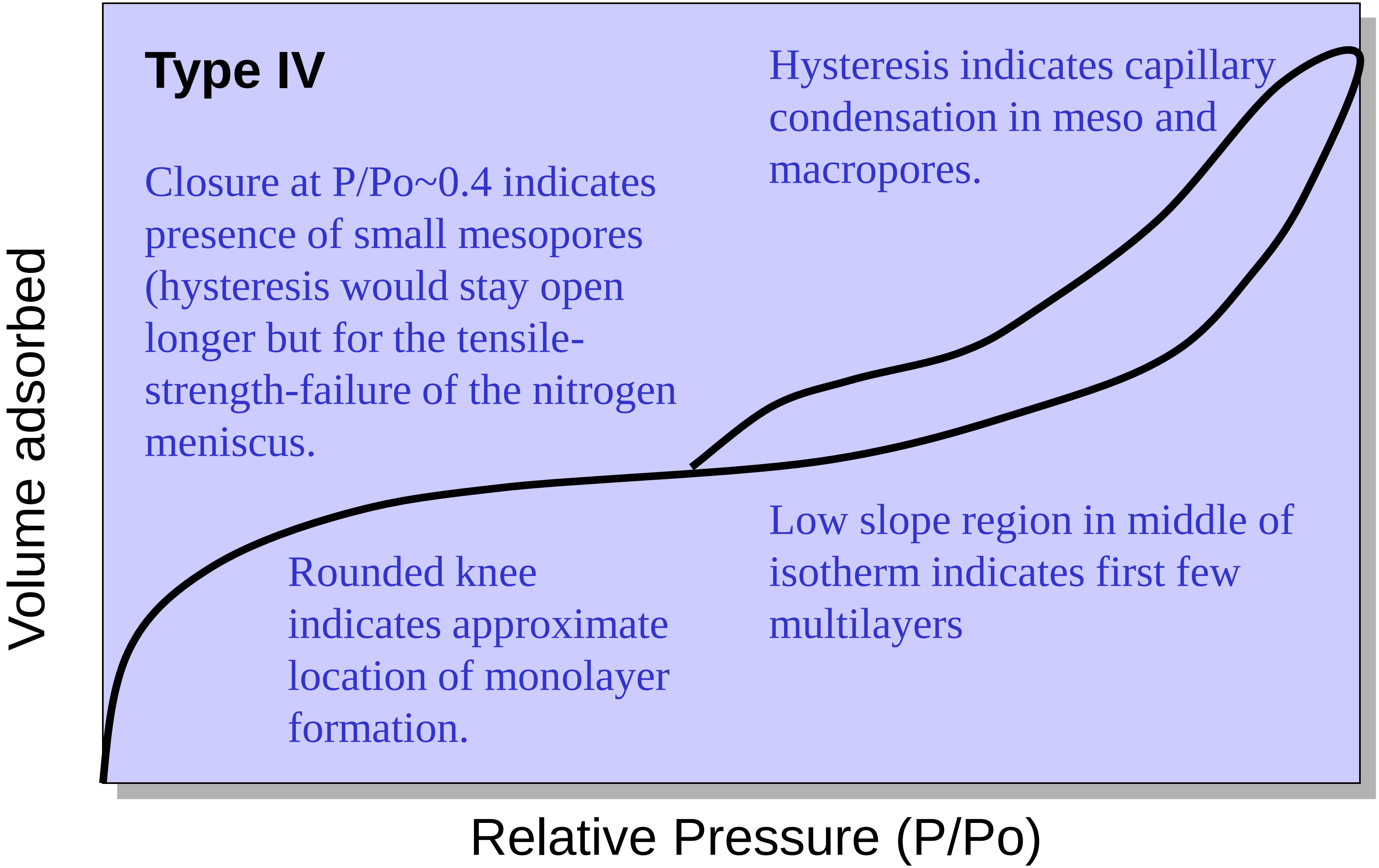
Types of Isotherms



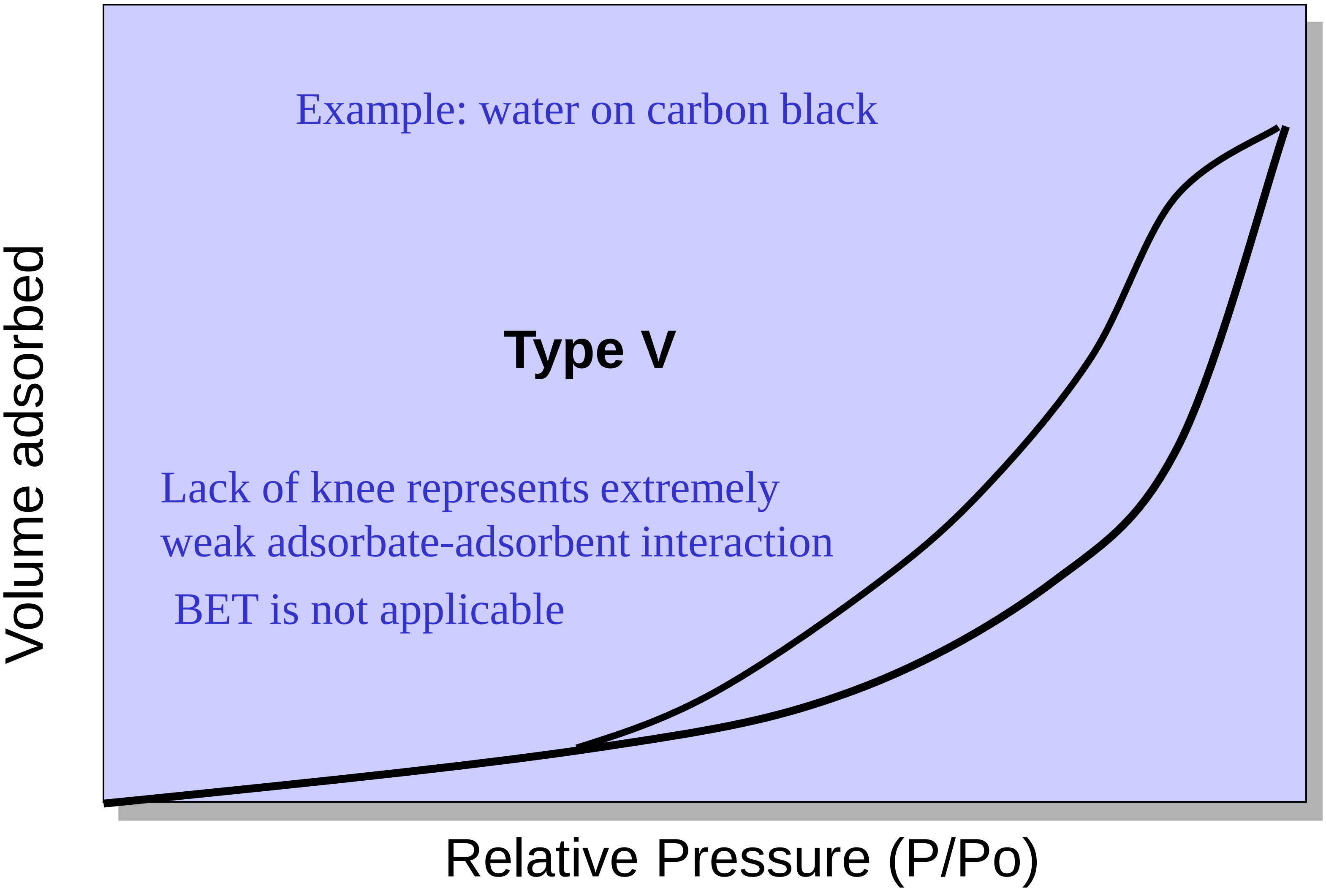
Types of Isotherms



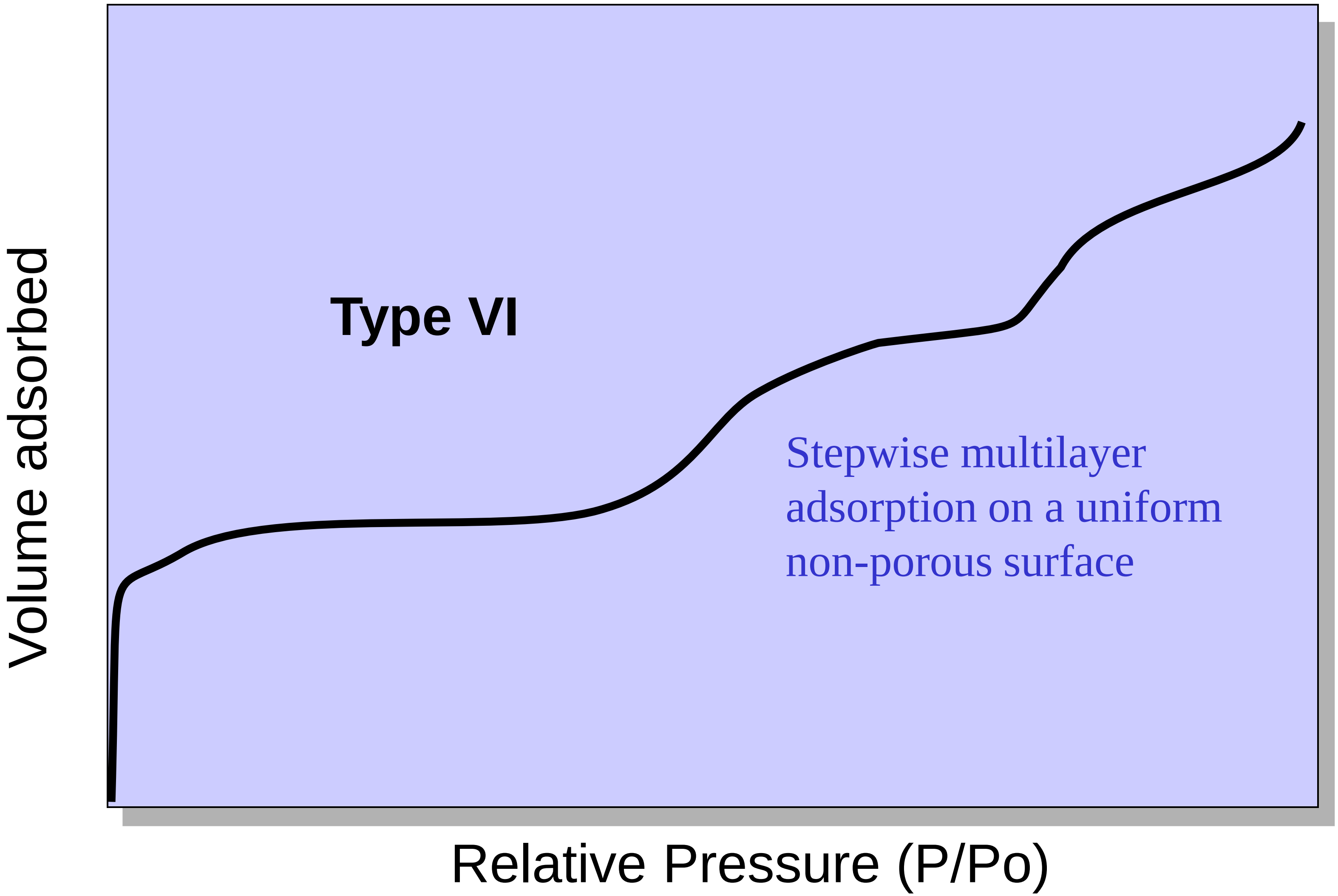
Types of Isotherms



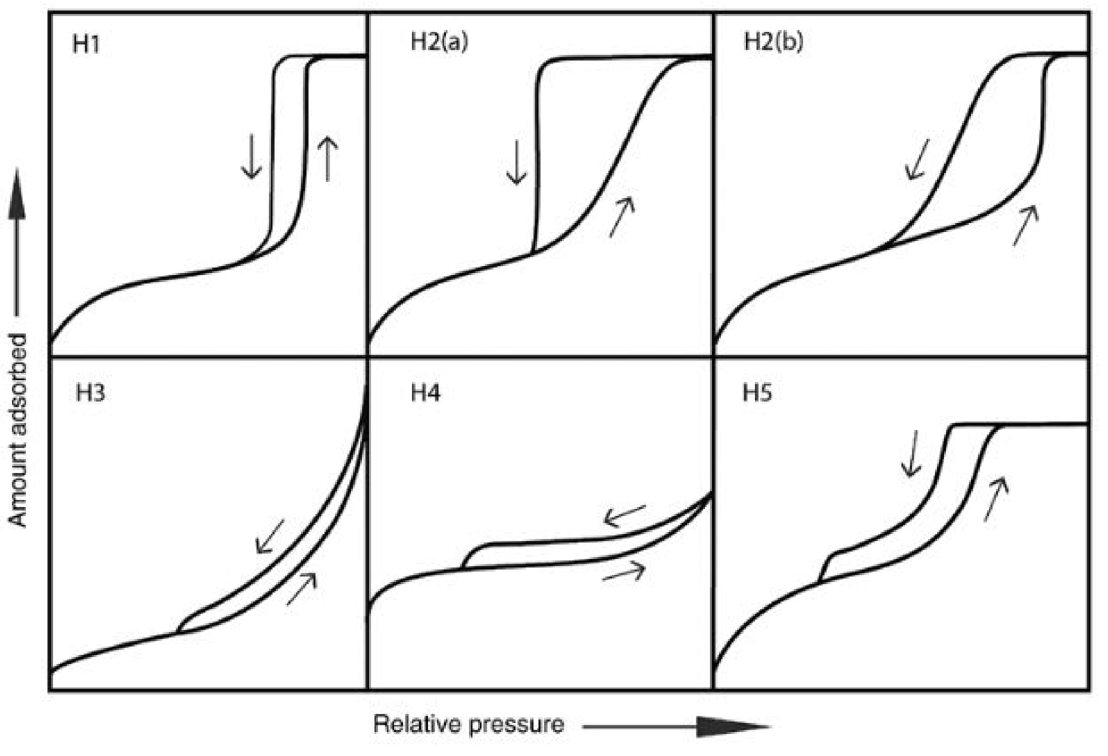
Types of Isotherms



Types of Isotherms



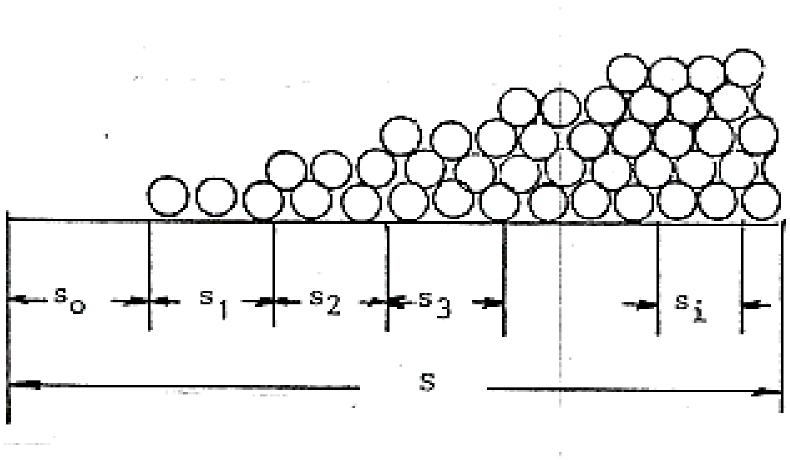
Types of Hysteresis



Thommes et al, IUPAC Technical Report, 2015

- H1: a narrow range of uniform mesopores (e.g. MCM 41, MCM 48)
- H2: complex pore structures (e.g. pore blocking)
- H3: typical for plate-like particles or pore network consists of macropores
- H4: typical micro-mesopores
- H5: unusual, typically open and partially blocked mesopores

The BET isotherm



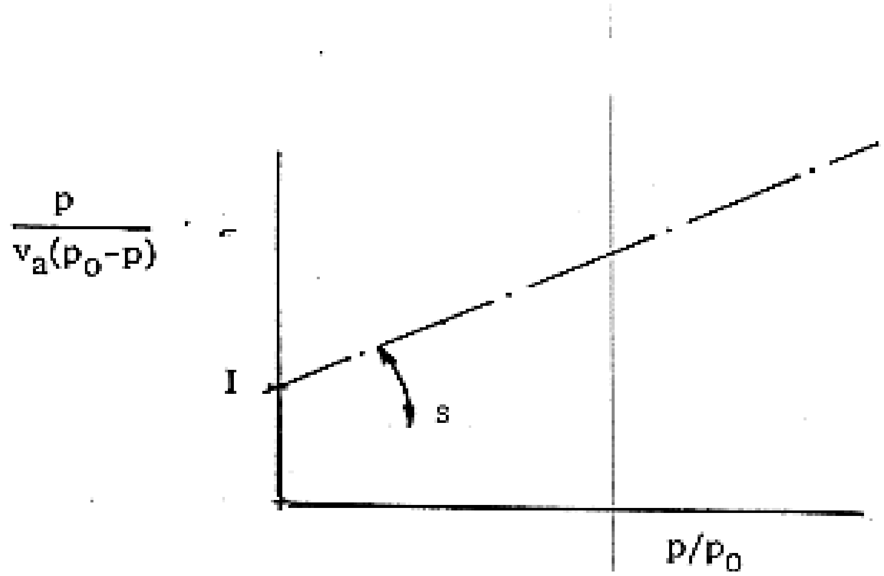
- Theoretical development based on several assumptions:
  - multimolecular adsorption
  - 1st layer with fixed heat of adsorption H_1
  - following layers with heat of adsorption constant (= latent heat of condensation)
  - constant surface (i.e. no capillary condensation) gives

$$\frac{p}{v_a(p_0 - p)} = \frac{1}{v_m \cdot C} + \frac{C-1}{v_m \cdot C} \cdot \frac{p}{p_0}$$

or

$$\frac{p}{v_a(p_0 - p)} = I + s \cdot \frac{p}{p_0}$$

The BET isotherm, cont.



- Plot of left side vs. p/p_0 should give straight line with slope s and intercept I

$$\frac{p}{v_a(p_0 - p)} = I + s \cdot \frac{p}{p_0}$$

- Reorganizing gives

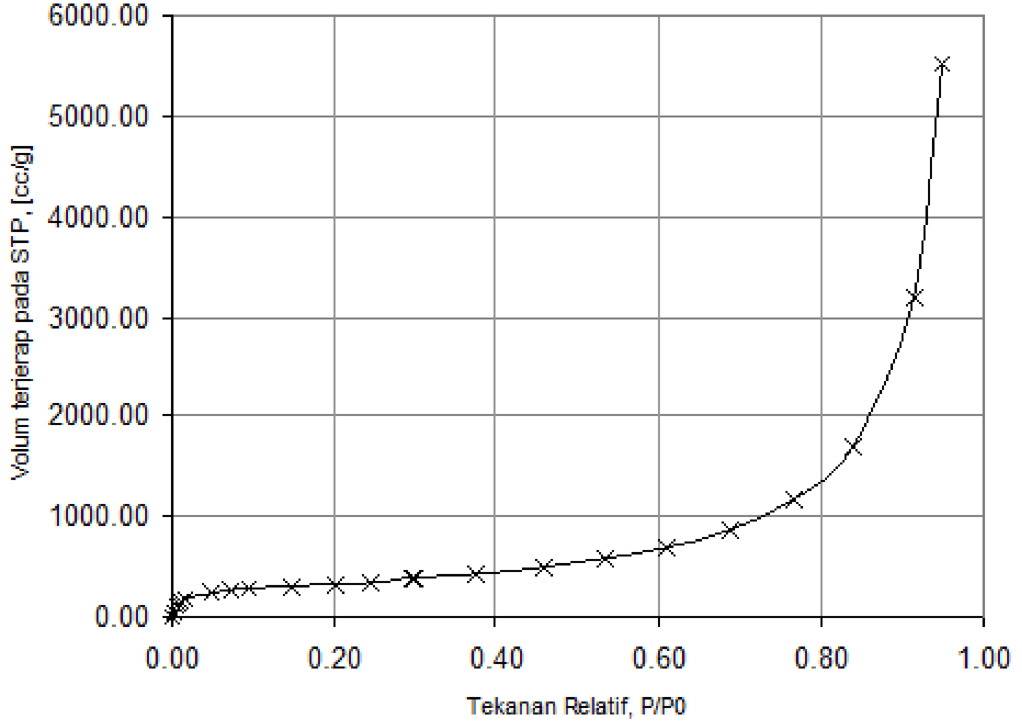
$$v_m = \frac{1}{s+I} \text{ and } C = \frac{I+s}{I}$$

- Knowledge of S_0 (specific area for a volume of gas then allows the calculation of the specific surface area Sg:

$$S_g = \frac{v_m \cdot S_0}{m_p}$$

where m_p is the mass of the sample

Example SSA calculation



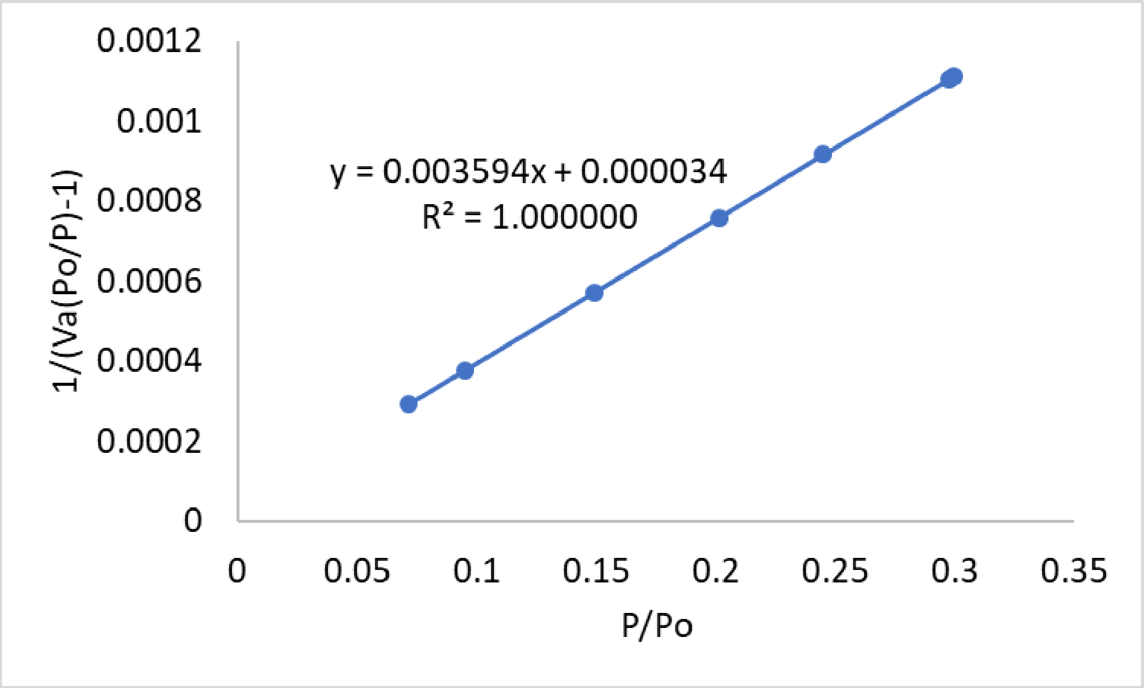
Determine the specific surface area of activated carbon, which an N_2-isotherm curve at 77 K as shown in the figure!

Standard range for BET model: P/P0: 0.05 – 0.30

P/Po	Volume of adsorbate V (cm^3/g), at STP	1/(Va(Po/P-1))
0,0715	264,6179	0,00029101
0,0953	279,7367	0,00037656
0,1493	307,5930	0,00057057
0,2013	332,7449	0,00075744
0,2452	354,9241	0,00091528
0,2976	383,9286	0,00110357
0,2996	385,1396	0,00111065

$$\frac{p}{v_a(p_0 - p)} = I + s \cdot \frac{p}{p_0}$$

Standard range for BET model: P/P0: 0.05 – 0.30



$$\frac{p}{v_a(p_0 - p)} = I + s \cdot \frac{p}{p_0}$$

Specific surface area then can be calculated:

$$v_m = \frac{1}{s + I} \quad \text{and} \quad C = \frac{I + s}{I}$$

$$S_g = \frac{v_m \cdot S_0}{m_p}$$

Adsorbates

- An adsorbate molecule covers an area σ, calculated assuming dense packing of the molecules in the multilayer. The corresponding area per volume gas is S_0:

Gas	**Temp. [K]**	**σ [Å²/molecule]**	**S_0 [m²/cm³ gas (STP)]**
N_2	77,5	16,2	4,36
Kr	77,5	19,5	5,24
Ar	77,5	14,6	3,92
H_2O	298	10,8	2,90
C_2H_6	90	22,5	6,05
CO_2	195	19,5	5,24

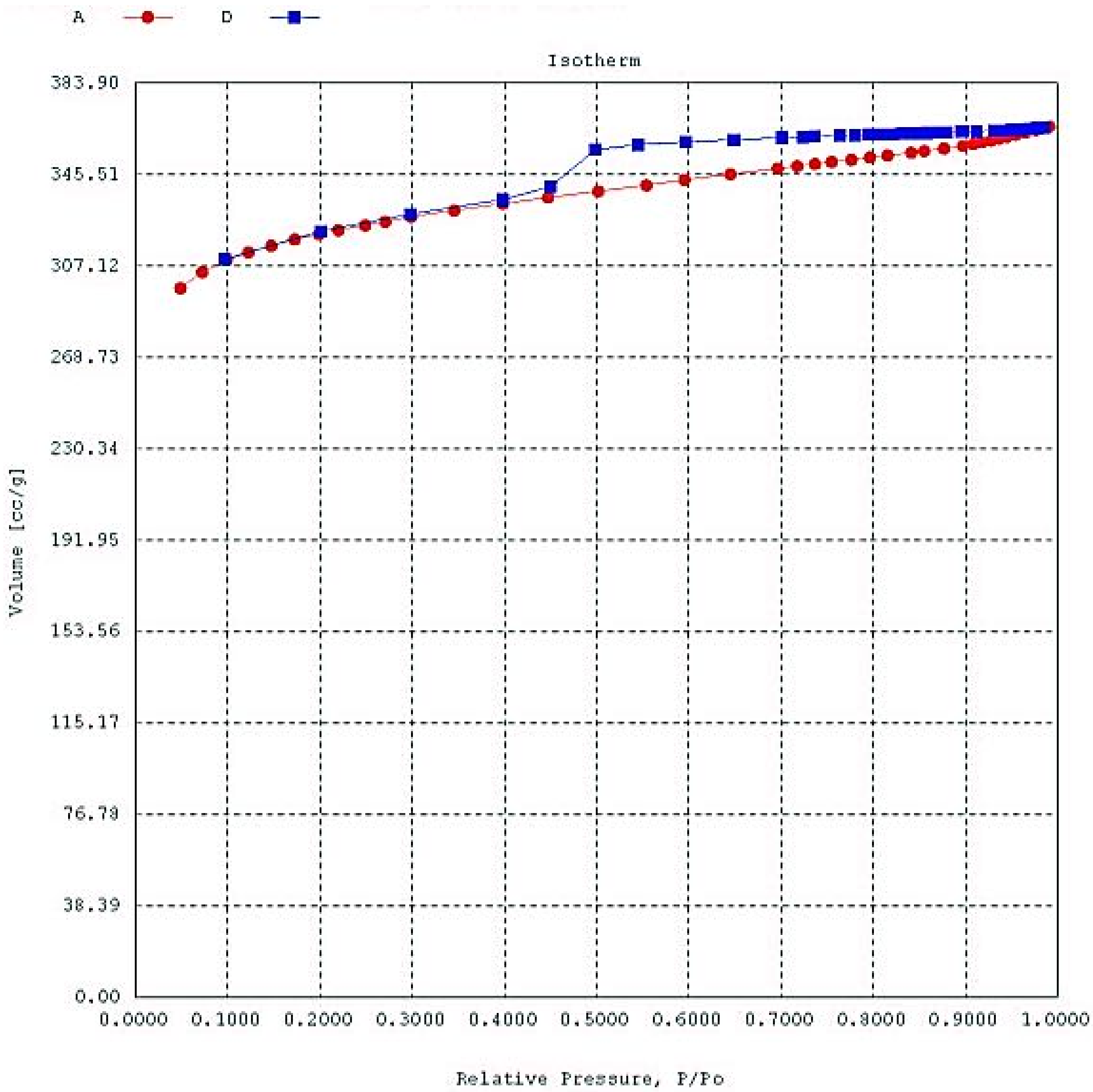
Calculation Models

Comparisons

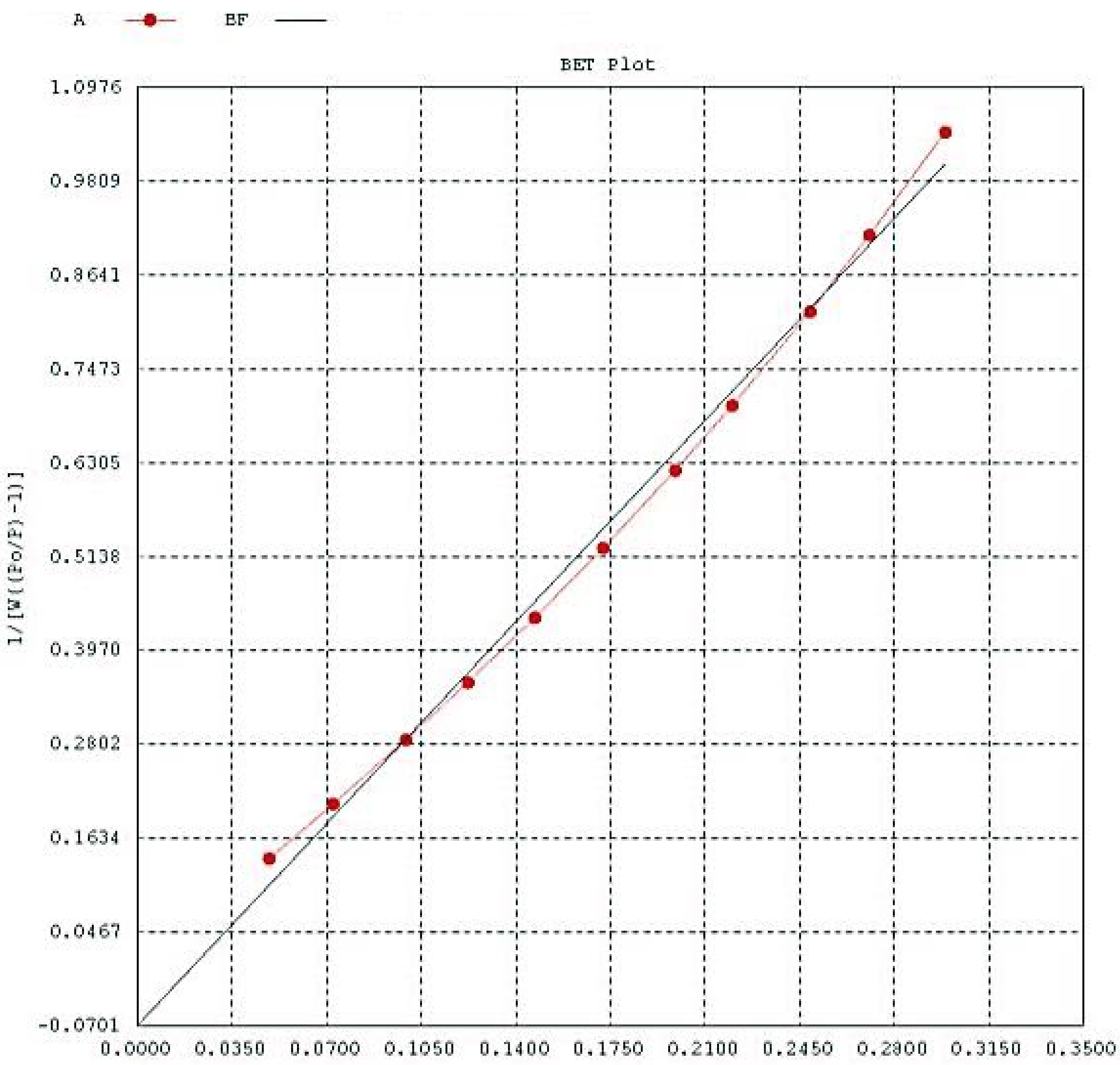
- **Gas Sorption Calculation Methods**

P/Po range	Mechanism	Calculation model
$1x10^{-7}$ to 0.02	micropore filling	DFT, GCMC, HK, SF, DA, DR
0.01 to 0.1	sub-monolayer formation	DR
0.05 to 0.3	monolayer complete	BET, Langmuir
> 0.1	multilayer formation	t-plot (de-Boer,FHH),
> 0.35	capillary condensation	BJH, DH
0.1 to 0.5	capillary filling in M41S-type materials	DFT, BJH

Example Data : Microporous Carbon



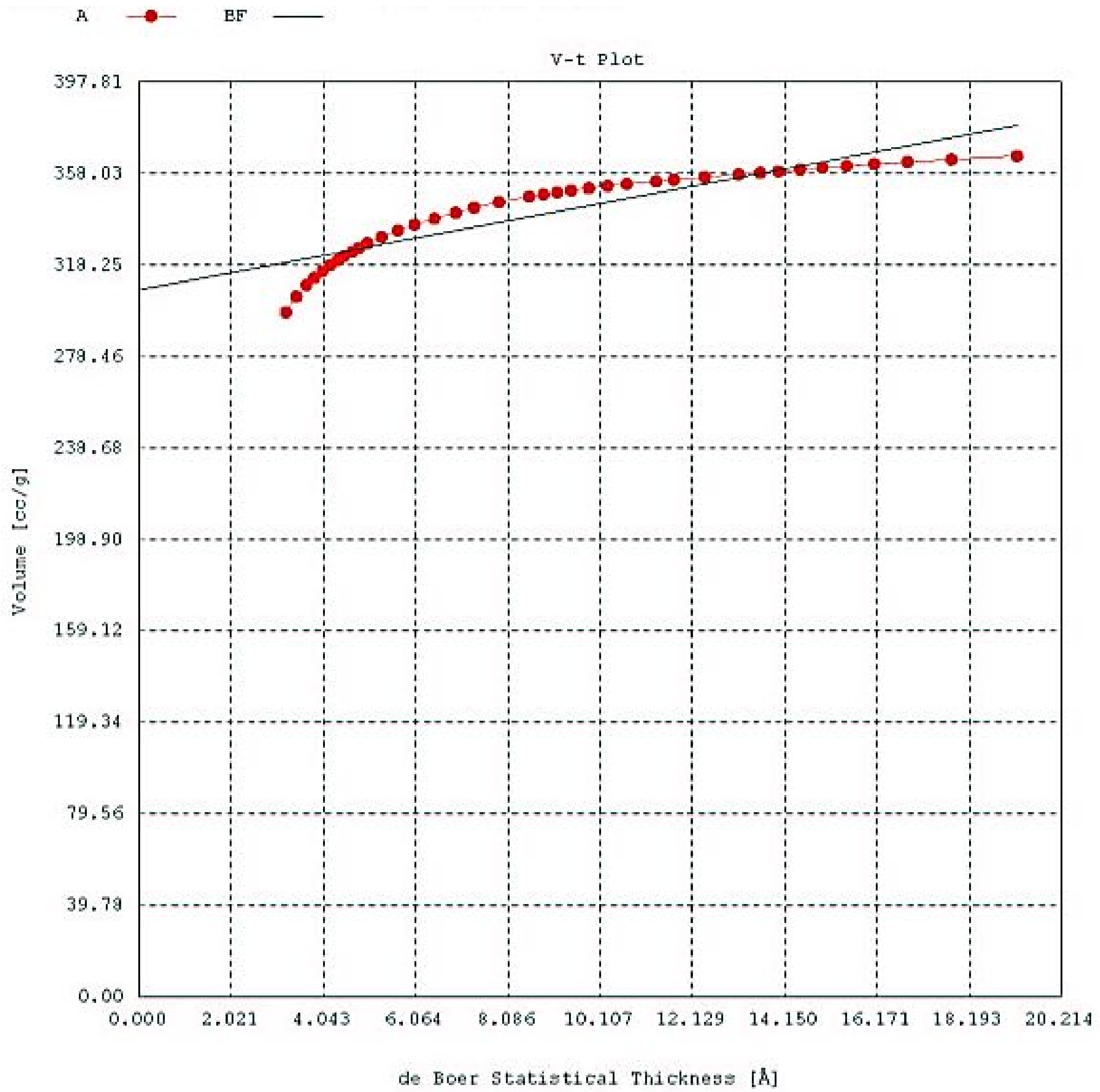
BET : Not strictly applicable



P/Po

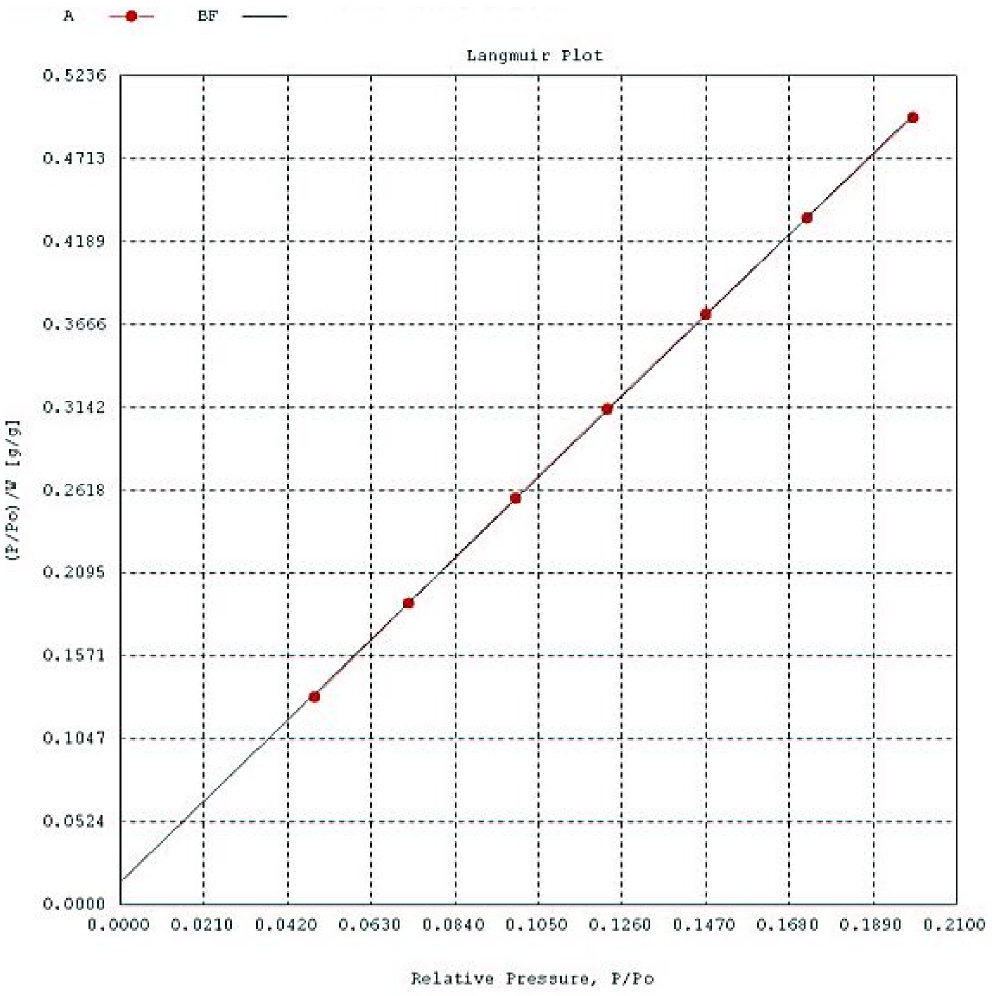
Example Data : Microporous Carbon

- Tag all adsorption points
- Analyze behavior
- Note knee – transition from micropore filling to *limited* multilayering (plateau).



Example Data : Microporous Carbon

- Use Langmuir (Monolayer model) / DR for Surface Area, Micropore Volume
- Usue Langmuir in range of 0.05 -> 0.2 (monolayer)



Example Data : Microporous Carbon

- Langmuir Surface Area

P/Po	P/Po/W
4.8787e-02	1.312E-01
7.2426e-02	1.904E-01
9.9303e-02	2.568E-01
1.2234e-01	3.131E-01
1.4707e-01	3.730E-01
1.7250e-01	4.339E-01
1.9907e-01	4.973E-01

Langmuir surface area = 1.430E+03 m²/g

Slope = 2.435E+00

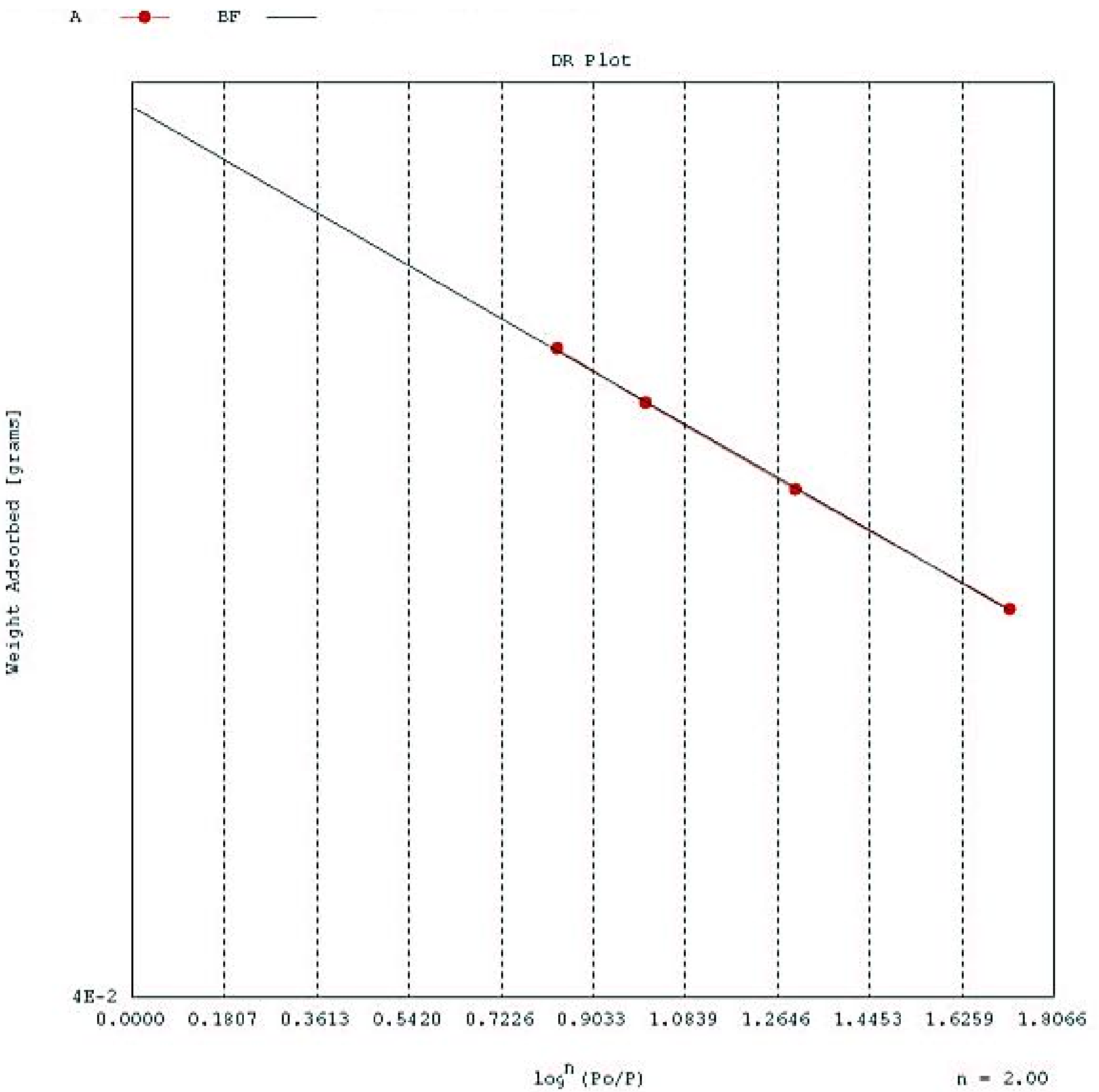
Y - Intercept = 1.398E-02

Correlation Coefficient = 0.999961

Langmuir constant K = 1.7422E+02

Example Data : Microporous Carbon

- DR Method for surface area, micropore volume
- Choose low relative pressure points (up to P/P0 = 0.2)



Example Data : Microporous Carbon

- Reports micropore surface area, and micropore volume.
- Note Langmuir, DR surface areas very close (1430 m^2/g vs. 1424 m^2/g)

log^2.00(Po/P)	Weight Adsorbed [grams]
1.72055E+00	4.304E-02
1.29984E+00	4.402E-02
1.00608E+00	4.475E-02
8.32544E-01	4.521E-02

Slope = -2.399E-02

Y - Intercept (anti-log) = 4.732E-02

Correlation Coefficient = 0.999033

Affinity coefficient (ß) = 0.389343

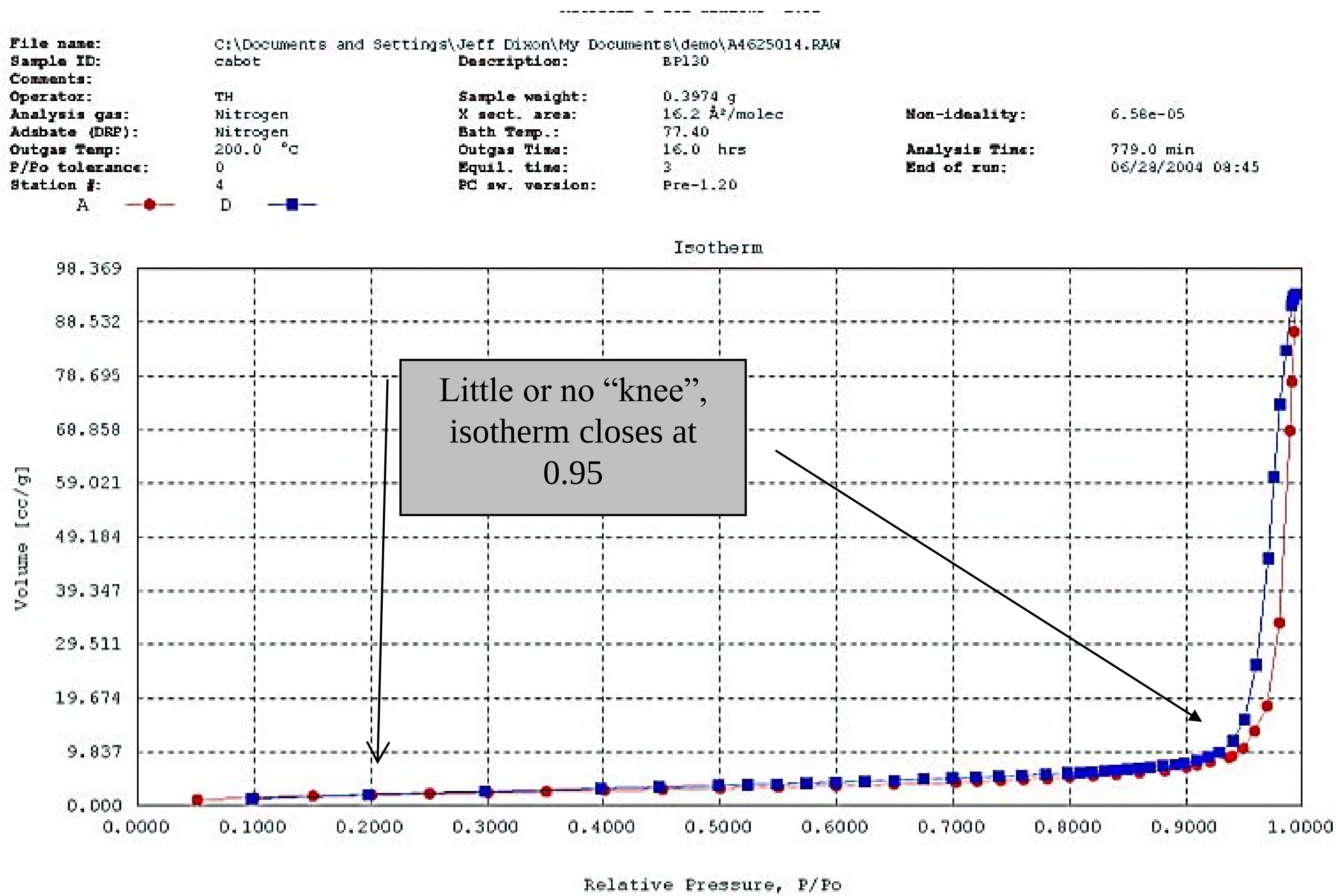
Average Pore Width = 8.032E-01 nm

Adsorption Energy (Eo) = 1.619E+01 kJ/mol

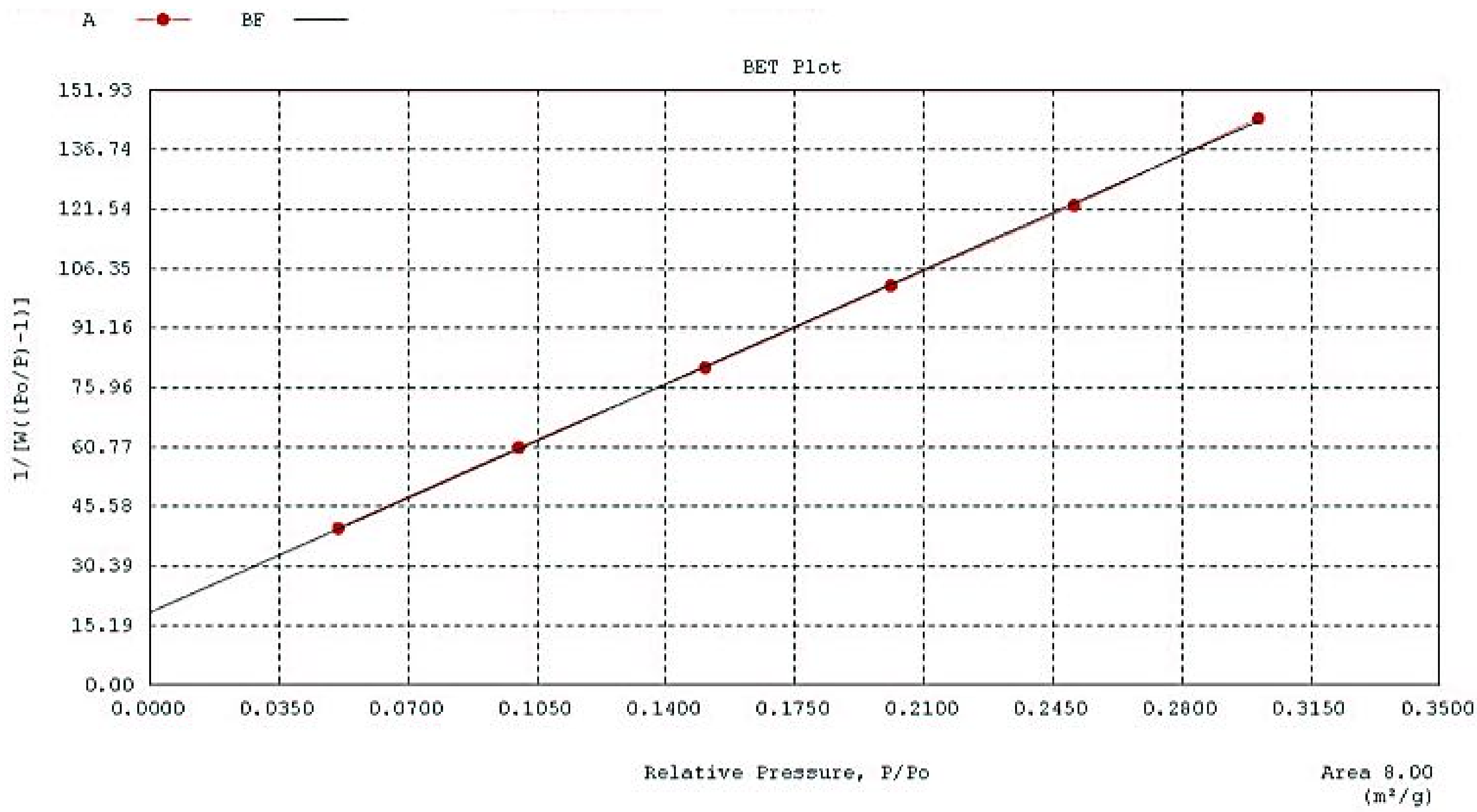
Micro Pore Volume = 5.030E-01 cc/g

Micro Pore Surface Area = 1.424E+03 m²/g

Example Data : Macroporous Sample

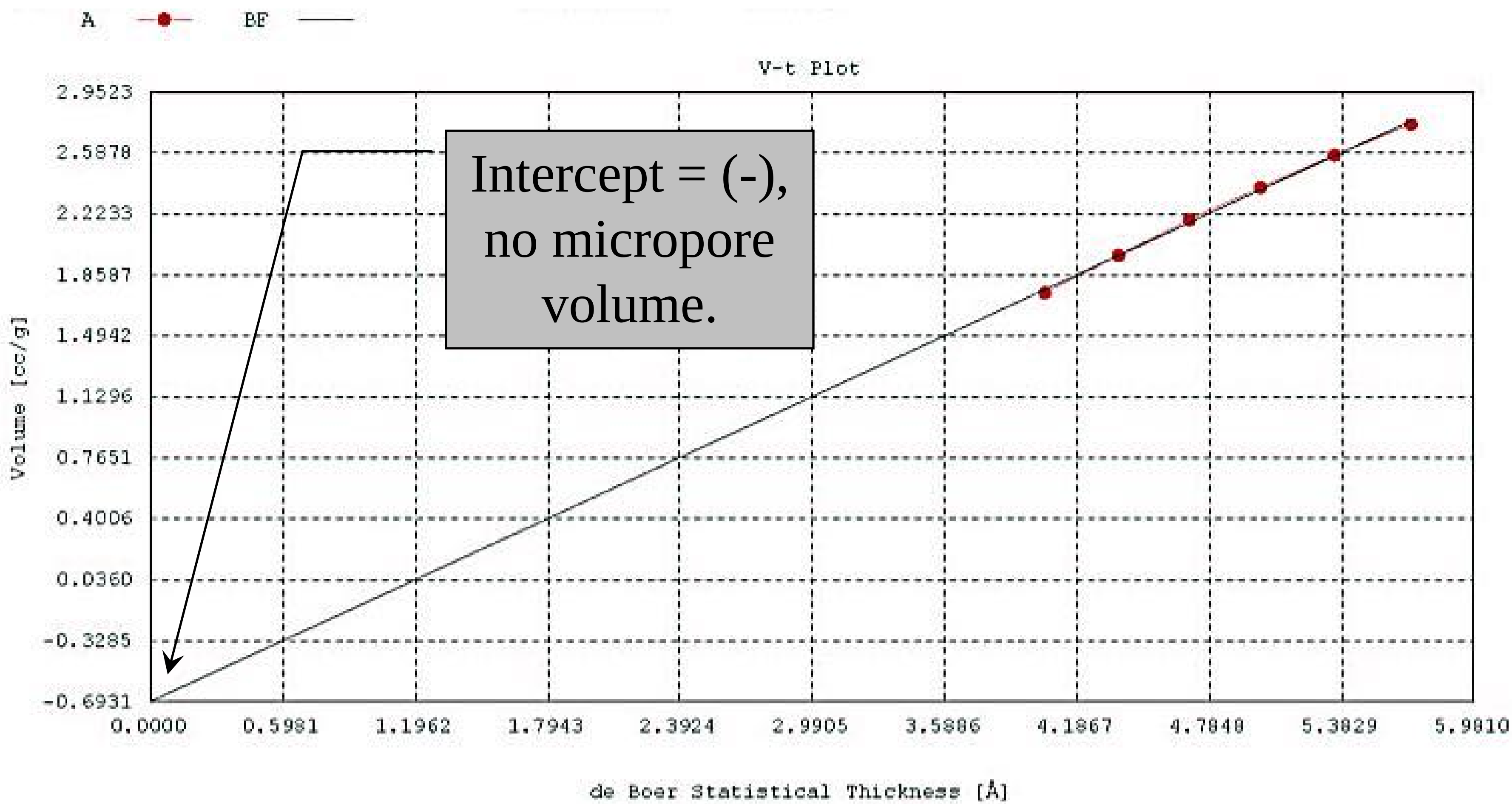


Example Data : Macroporous Sample

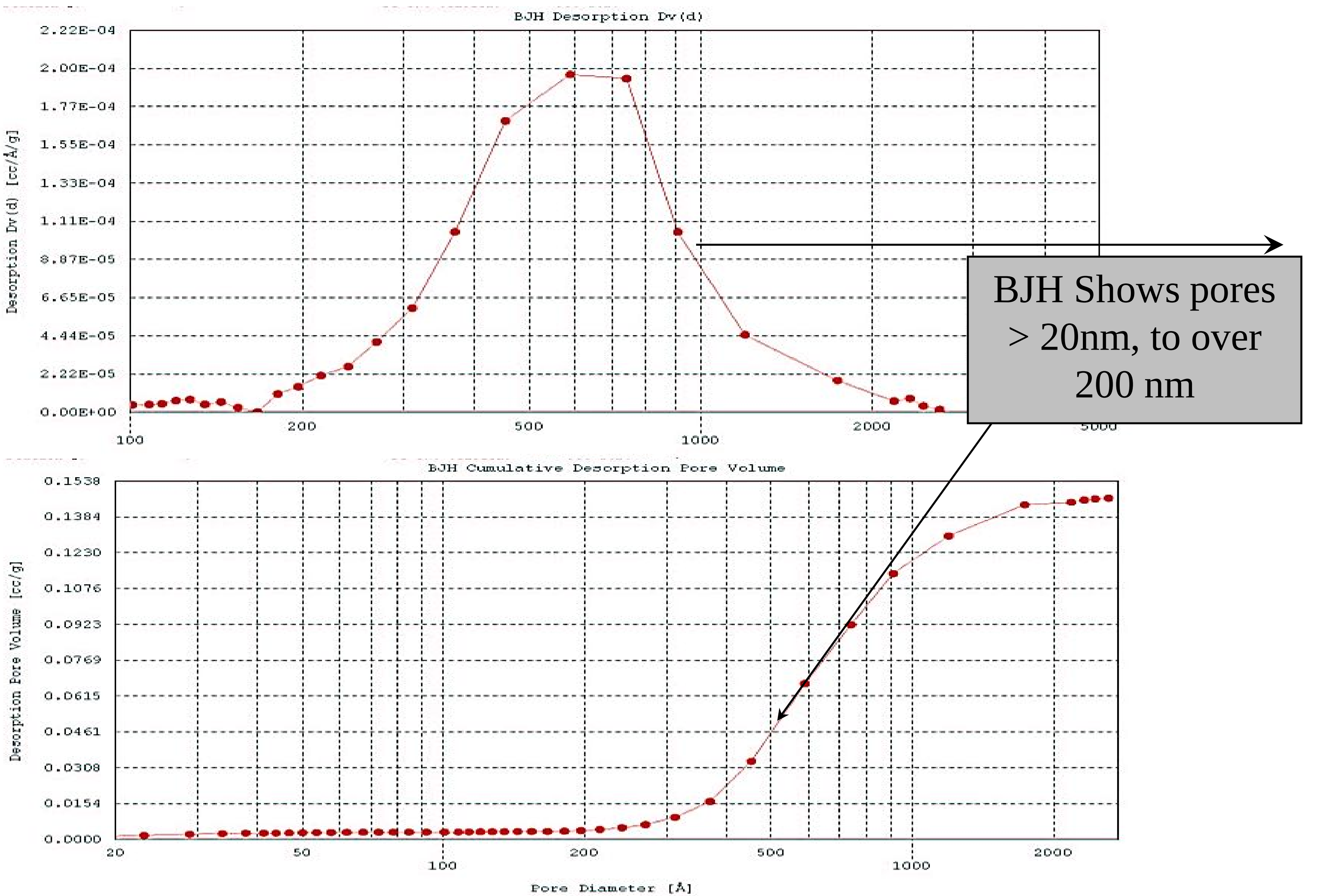


- BET Plot = OK
- Surface area ca. 8m^2/g (low)
- Note hysteresis above P/P0 = 0.95 ∴ Pores > 35 nm

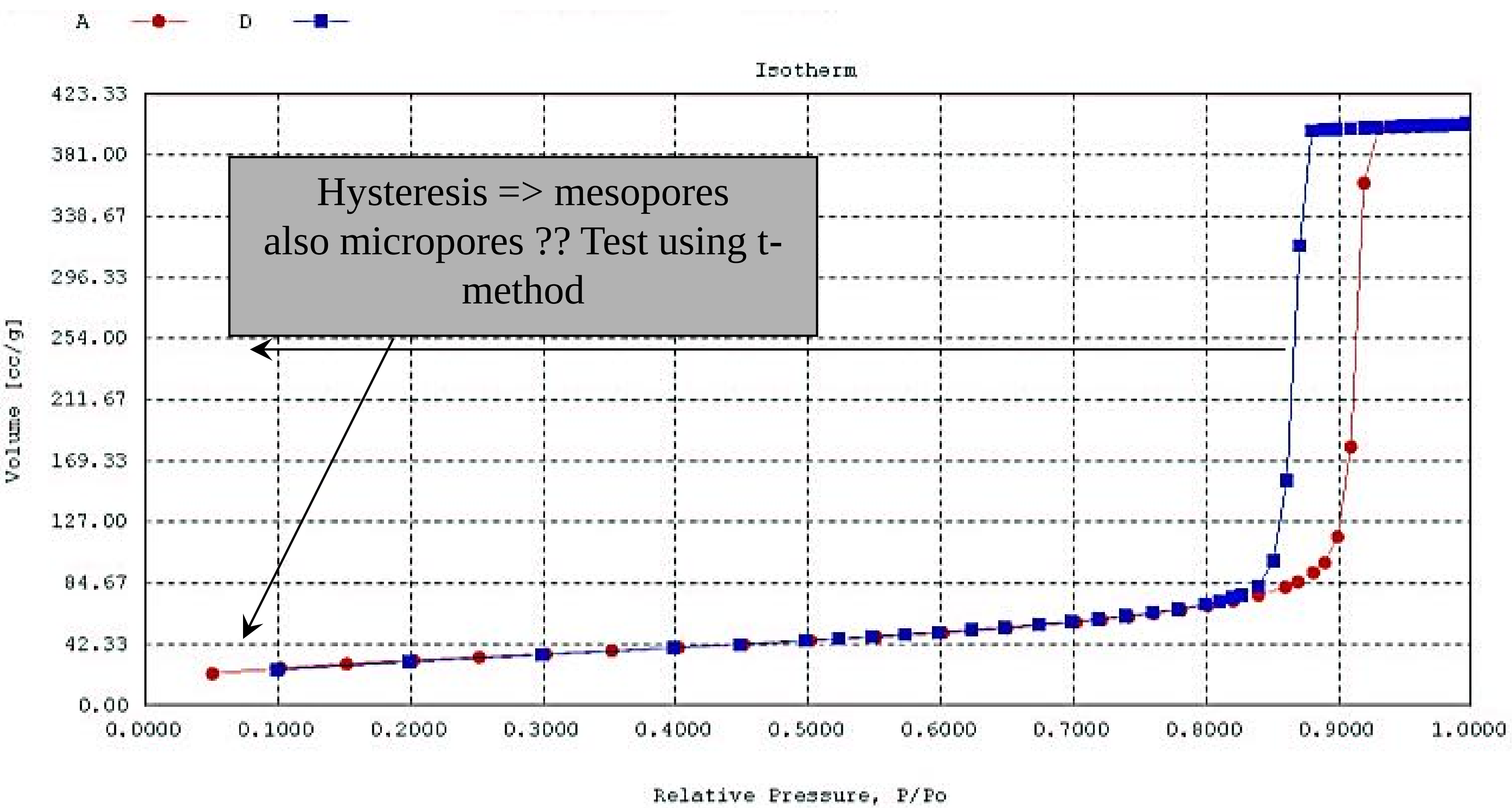
Example Data : Macroporous Sample



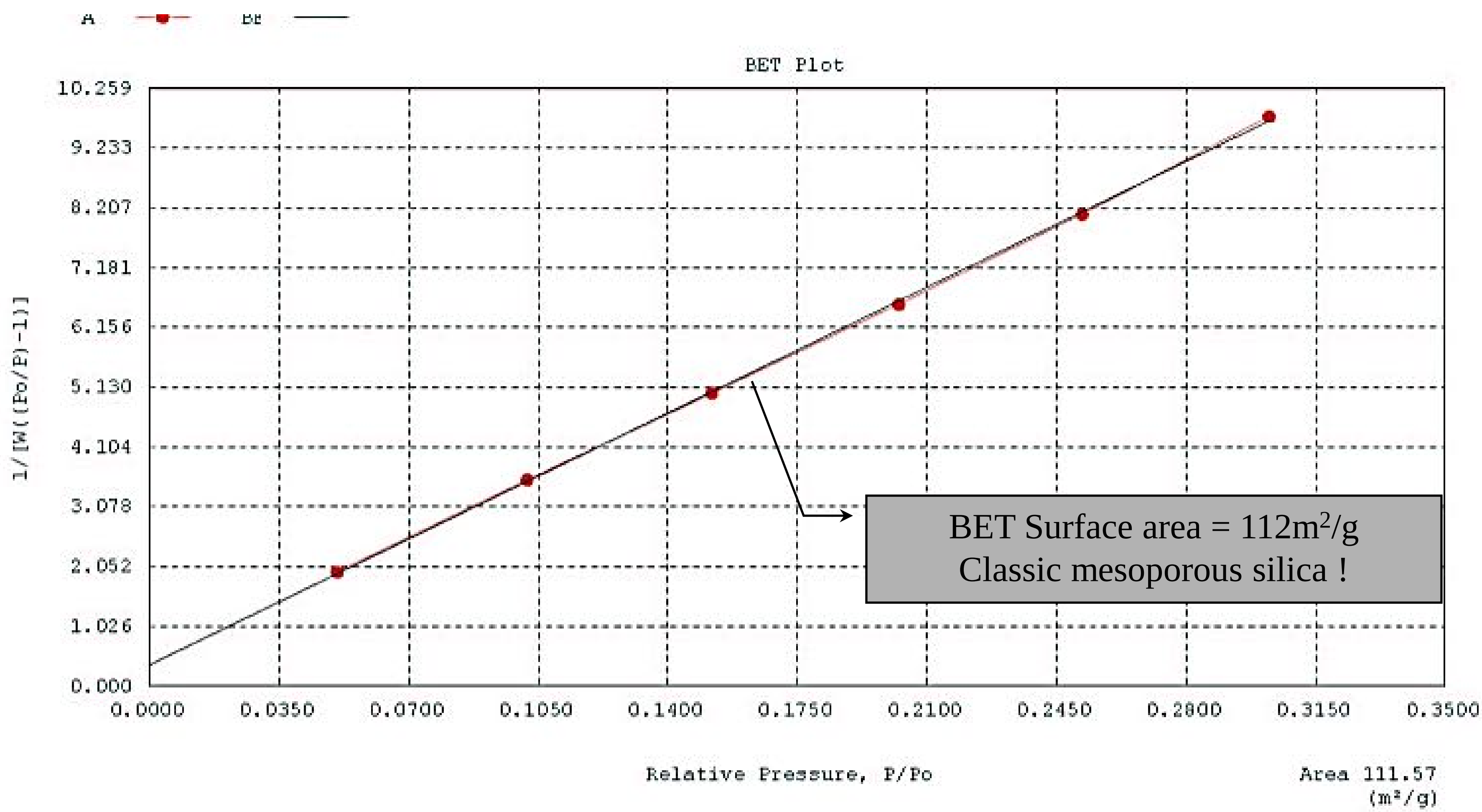
Example Data : Macroporous Sample



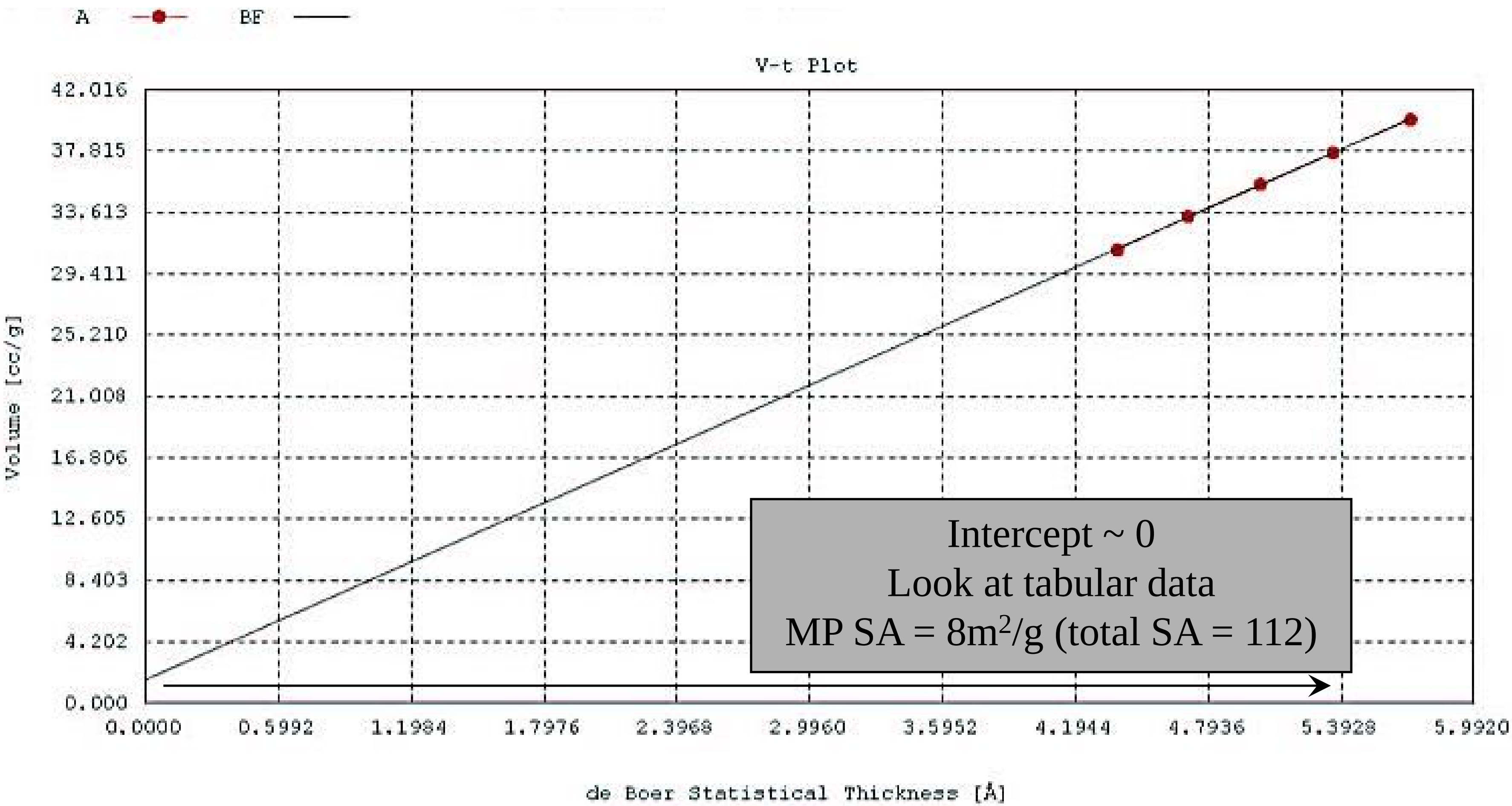
Example Data : Mesoporous Silica



Example Data : Mesoporous Silica

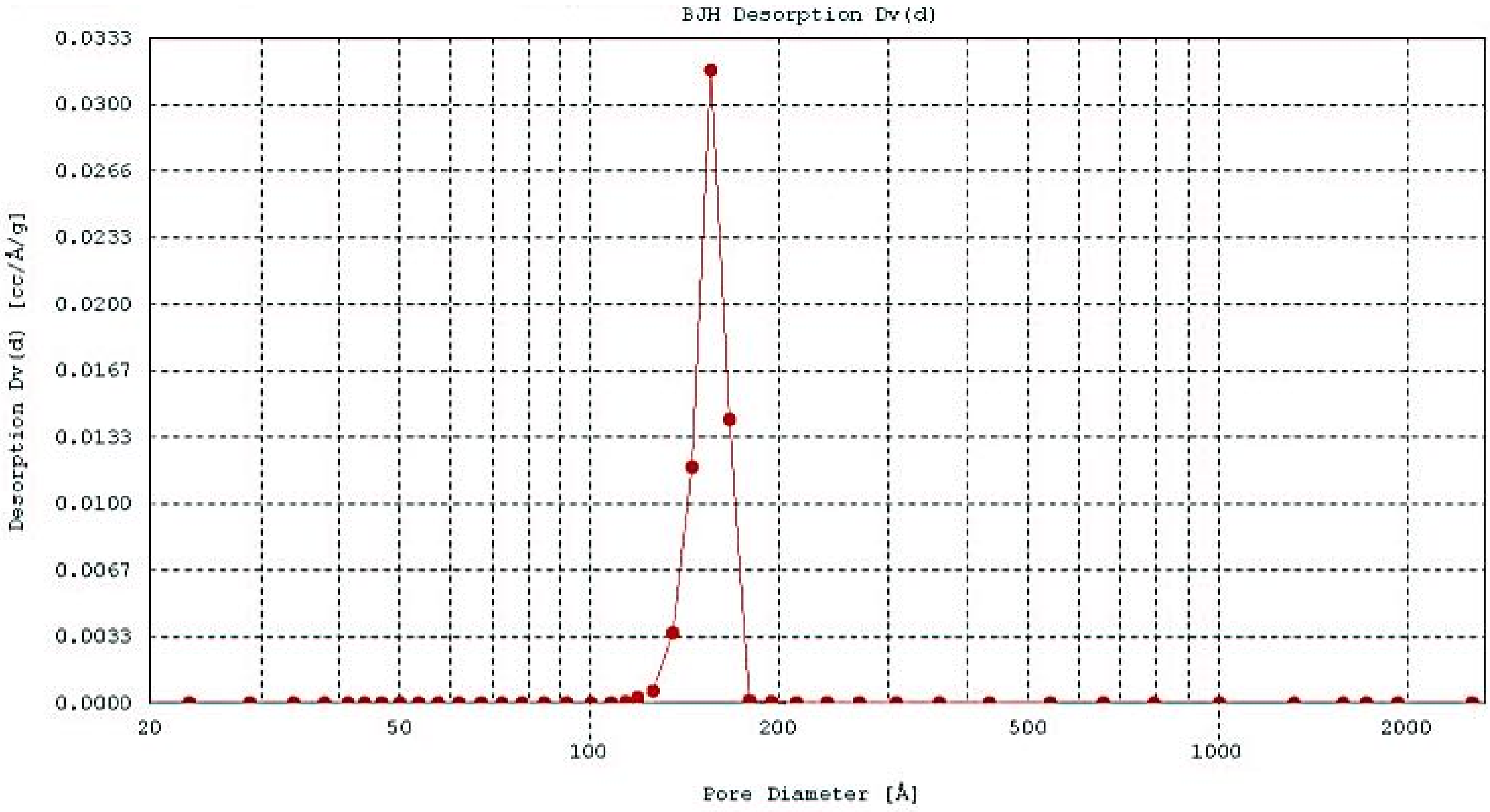


Example Data : Mesoporous Silica



Statistical Thickness => Use de Boer for oxidic surfaces = silicas

Example Data : Mesoporous Silica



Use BJH – shows narrow pore size distribution in 14-17nm range (mesopores)

Thank you