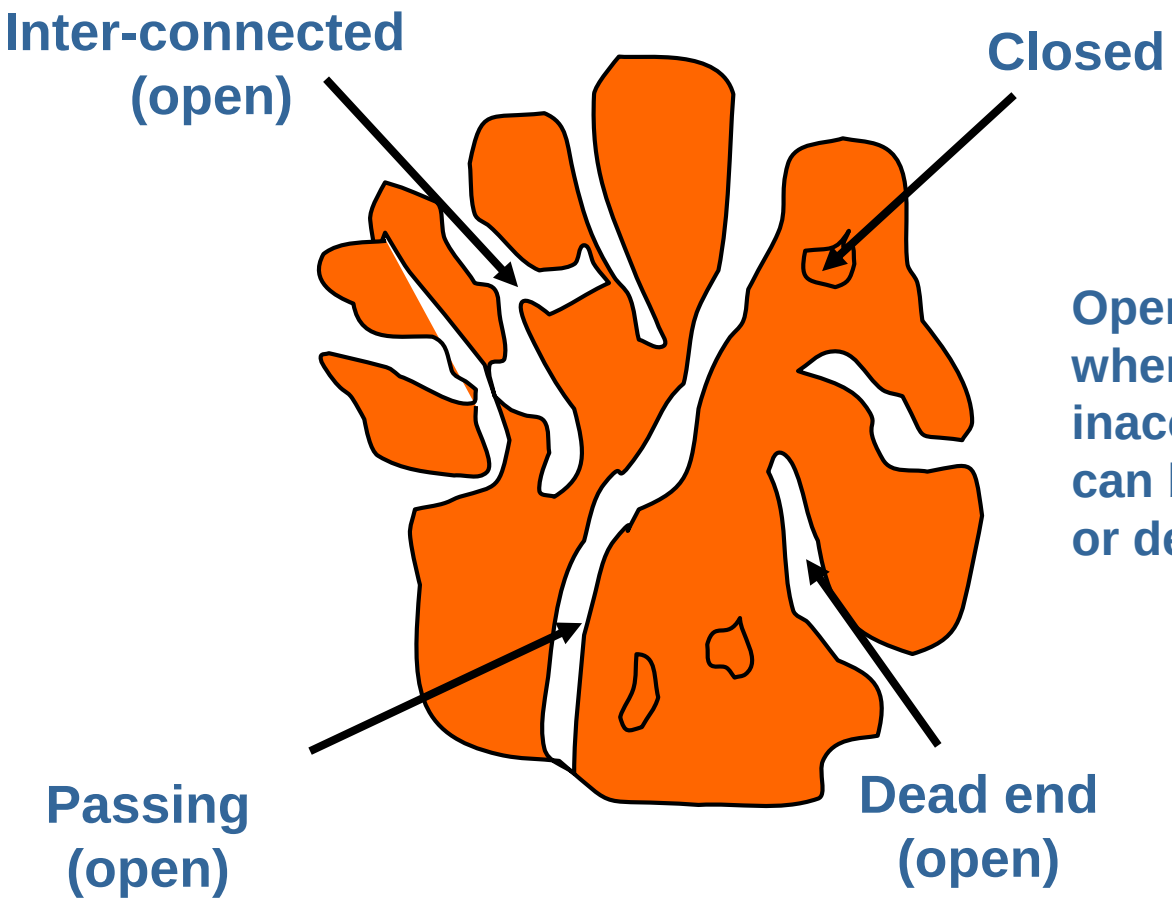
II. Caractérisation de la porosité par adsorption/désorption de gaz

Concept of Porosity: Open vs. Closed Pores



Open pores are accessible whereas closed pores are inaccessible pores. Open pores can be inter-connected, passing or dead end.

F. Rouquerol, J. Rouquerol, K. S. W. Sing, Adsorption by Powders and Porous Solids, Academic Press, 1-25, 1999

Classification des isothermes d'adsorption d'azote suivant l'IUPAC

Les isothermes de type I sont typiques d'une adsorption en monocouche, ou correspondant au remplissage de micropores avec saturation lorsque le volume à disposition est totalement rempli. Ce type d'isothermes est caractéristique pour l'adsorption sur les charbons microporeux et les zéolithes.

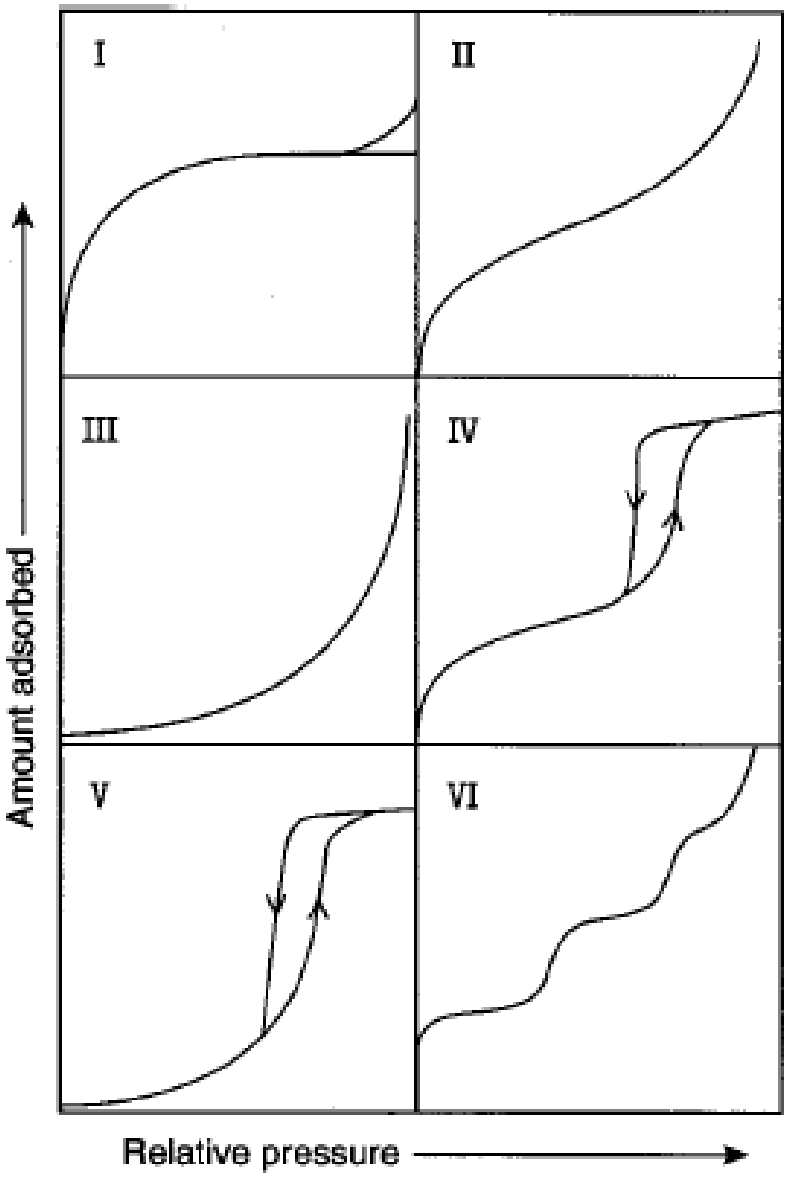
Les isothermes de type II, au contraire, correspondent en général à l'adsorption multicouche sur des surfaces ouvertes. Cependant, une isotherme de type II peut aussi résulter d'une somme d'isothermes I + II (remplissage de micropores suivi d'une adsorption multicouche sur une surface externe).

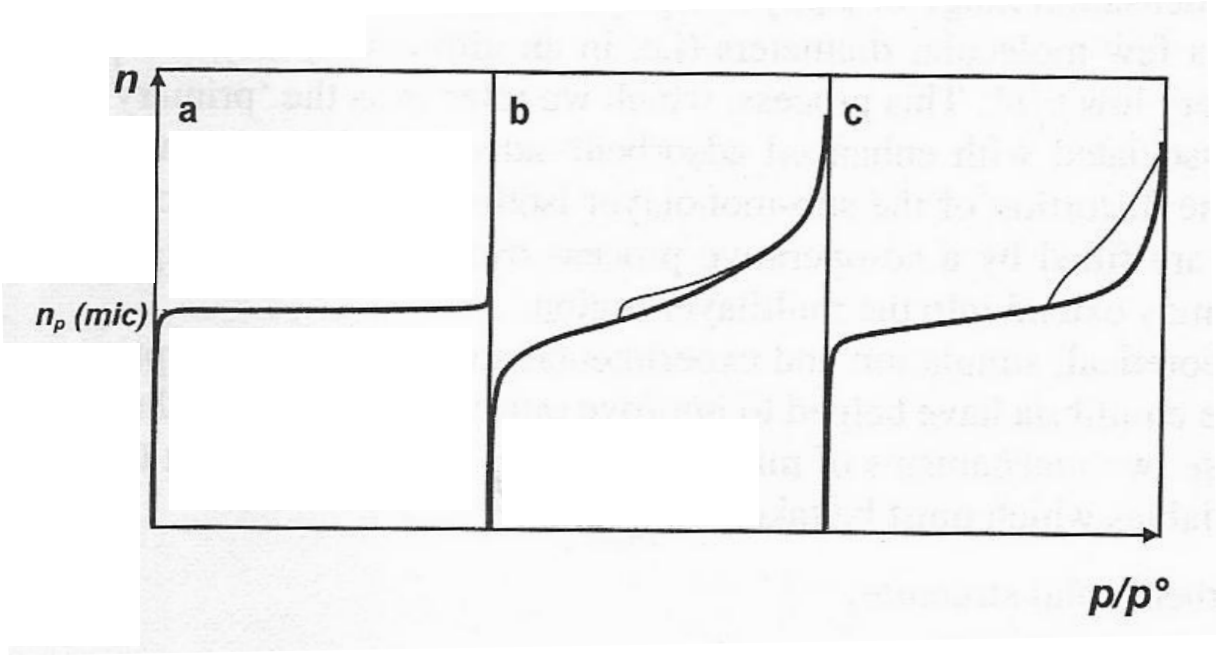
Les isothermes de type III reflètent un manque d'affinité entre l'adsorbat et l'adsorbant, et des interactions adsorbat-adsorbat relativement fortes. C'est le cas de l'adsorption de l'eau sur des surfaces hydrophobes (par exemple graphite ou charbons actifs contenant peu d'oxygène).

Les isothermes de type IV peuvent résulter de la combinaison d'une isotherme de type I (adsorption forte, mais limitée) et de type V. C'est le cas de l'eau sur les carbones riches en oxygène [4,5].

Les isothermes de type V reflètent aussi une forte interaction entre les adsorbats. De plus, l'existence d'une hystérèse au cours de la désorption reflète la présence de mésopores dans lesquels la vapeur se condense en formant un ménisque de forte courbure.

Les isothermes de type VI présentent des marches caractéristiques d'une adsorption multicouche sur une surface non-poreuse très homogène.





Adsorption d'azote dans (a) des ultramicropores; (b) dans des larges micropores (supermicropores) et sur la surface externe; (c) dans des micropores et de larges mésopores

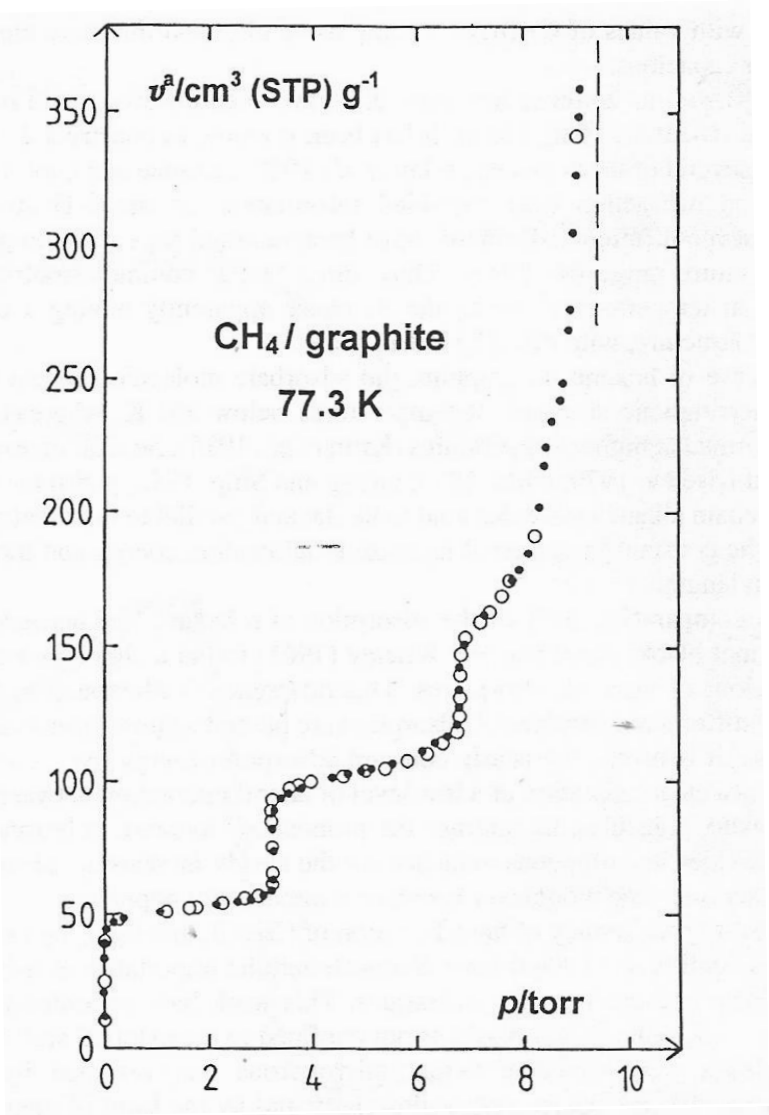
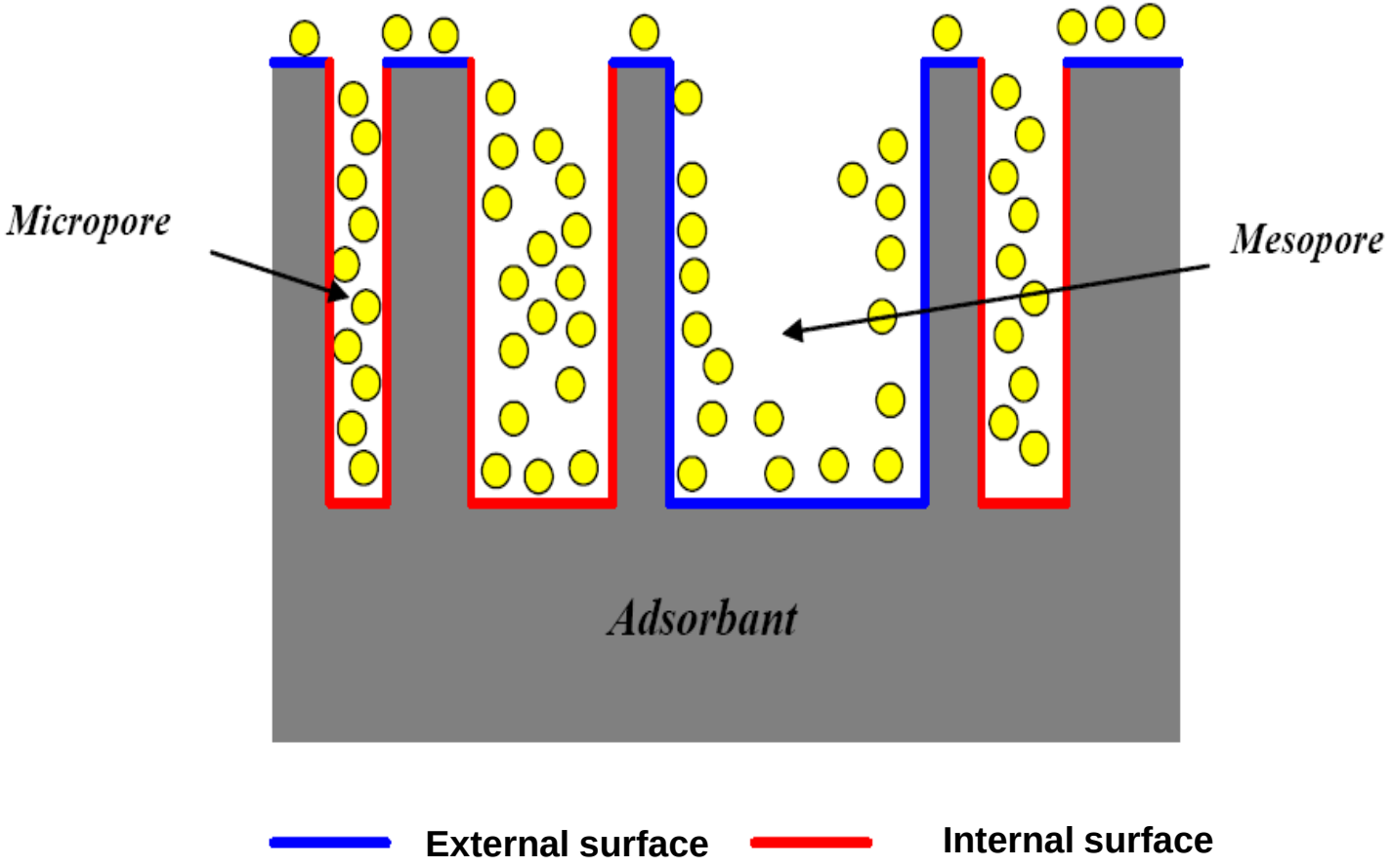


Figure 9.9. Stepwise isotherm of CH_4 on graphite foam (open circles) and exfoliated graphite (solid circles) at 77.3 K (reproduced courtesy of Bienfait *et al.*, 1990).

External surface by t and α_S method



Schematic representation of the external and internal surface of an activated carbon

1. t-method determination of microporous volume (de Boer, 1965)

- The adsorbed volume (or number of adsorbed moles) is plotted as a function of t, thickness of the adsorbed layer

- “de Boer” has shown that the curve giving $t = f(P/P_0)$ is universal on a non porous solids of a given chemical nature (example : oxides).

- Thus, according to “de Boer” the thickness t, of the adsorbed layer on an adsorbent can be obtained from the t value on a non porous solid of reference (and of similar nature).

[Lippens, B.C. and de Boer, J. H., Journal of Catalysis 4(3), 1965
“Studies on pore systems in catalysts. V. The t method”]

- “de Boer” calculated t from non porous solid isotherms using the relation :

$$\mathbf{t = (n/n_m)\times d'}$$

n : number of adsorbed moles

n_m : number of moles in the monolayer (**n_m obtained by the BET equation**)

d’ : effective monolayer thickness

$$\mathbf{d'=M/(\sigma \times N_A \times \rho)}$$

M : molar mass

σ : average surface occupied by the molecule

ρ : specific weight of adsorbed liquid

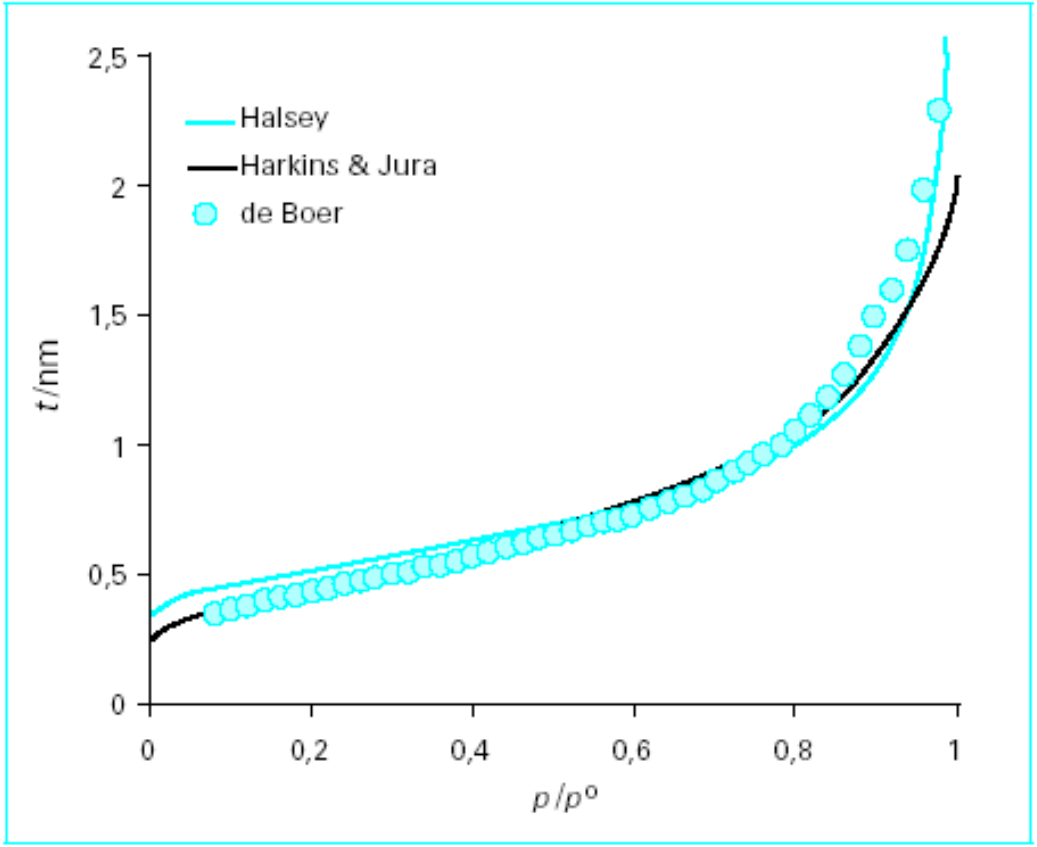
N_A : number of Avogadro

For Nitrogen adsorption at 77K, M=28 g.mol^{-1} ; σ_{N_2}=0.162 nm^2 ; ρ=0.809 g/cm^3

so that d’=0.354 nm and t(nm) = $(n/n_m)\times 0.354$

• t can be simulated by the equation of Harkins and Jura $t/\mathrm{nm} = \left(\frac{0{,}1399}{0{,}034 - \lg(p/p^{\circ})}\right)^{0{,}5}$ or Hasley :

$$t/\mathrm{nm} = 0{,}354\left(\frac{-5}{\ln(p/p^{\circ})}\right)^{0{,}333}$$



Universality of this curve

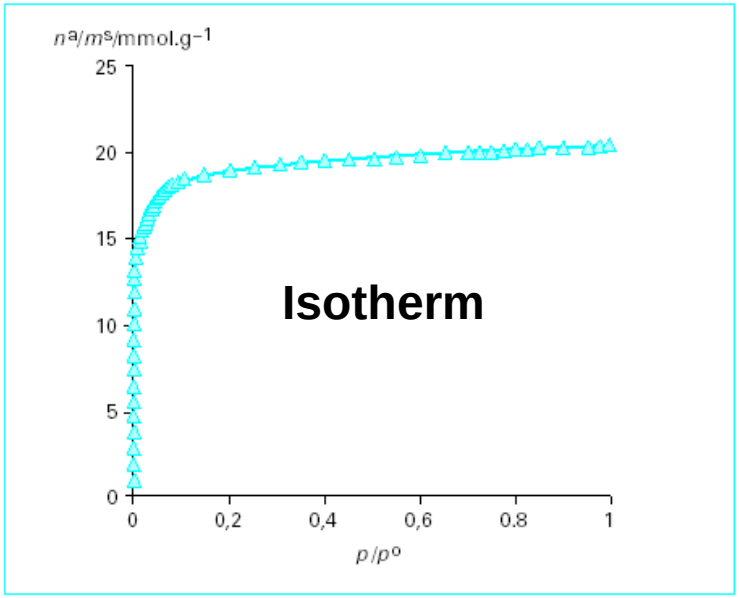
Variation of the thickness t of the multilayer as a function of the relative pressure for Nitrogen at 77K
("de Boer" experimental curve and the calculations of Harkins & Jura and Hasley)

Isotherm ⟶ Transformed t-plot (transformed plot)

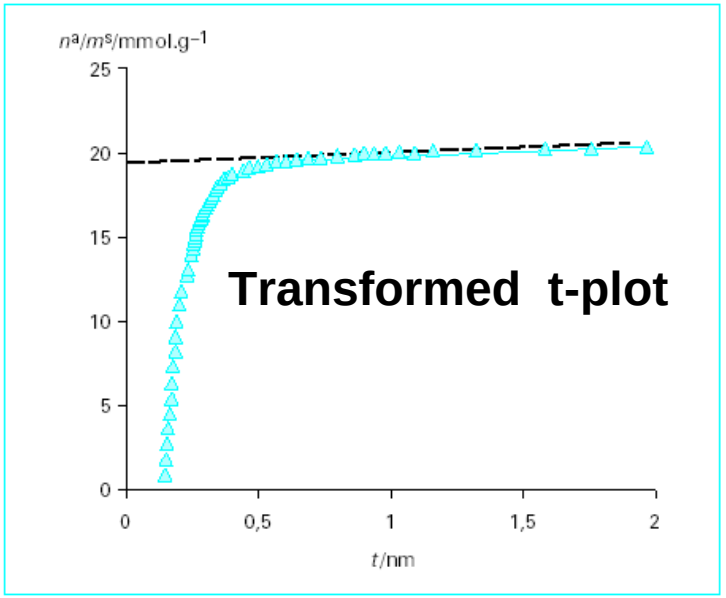
(i) the slope of the linear domain of t-plot gives the external surface slope= $n_m/0.354$ and $S_{external} = n_m \times \sigma N_2 \times N_a$

If slope unity is $\mu mol.g^{-1}.nm^{-1}$ and $S_{external}$ unity is m^2/g
$S_{external} = (slope/\ \mu mol.g^{-1}.nm^{-1}) \times 0.354 \times \sigma N_2 \times N_a \times 10^{-6} = slope \times 0.0346$

(ii) the intercept point gives the microporous surface (or volume)

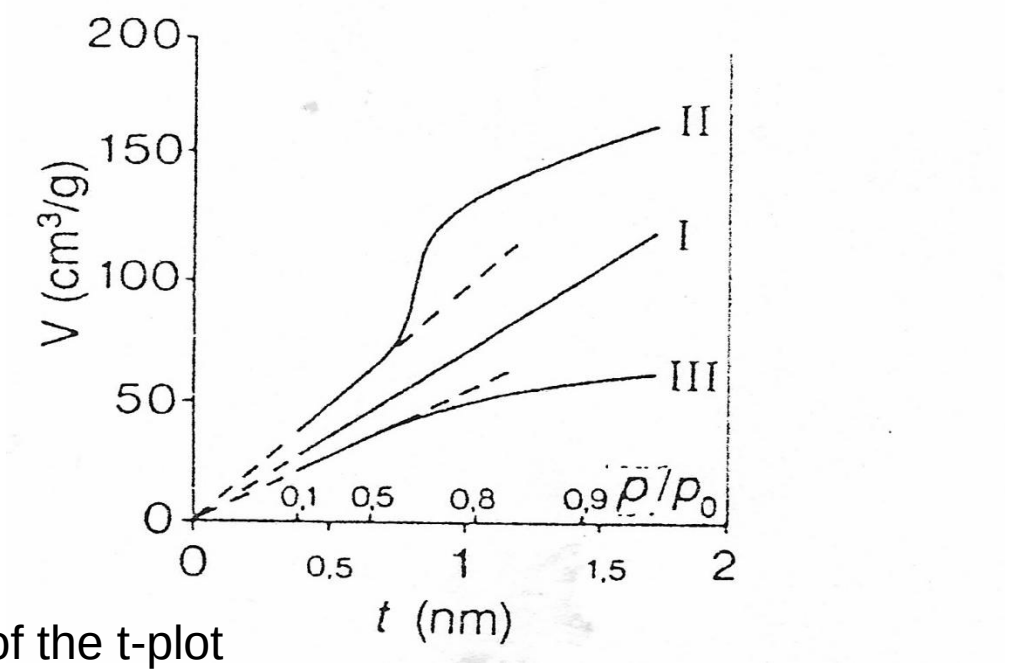


Isotherm of N_2 adsorption at 77 K of a microporous carbon



Transformed t-plot of the N_2 adsorption isotherm at 77 K of the same microporous carbon

Problems of t-method method : linear domain depends on the user's choice



Various forms of the t-plot

- type I excusively microporous
- Type II microporous and mesoporous
- Type II limited linear domain (various kind of micropores)

t-plot method is not precise and not reproducible

2. α_S method for microporosity determination (Sing 1968, 1970)

- Definition of α_S

$\alpha_S = N_{ref.\ (adsorbed)} / N_{ref.\ (0.4)}$

Reference : a non porous solid of the same nature

$N_{ref.\ (adsorbed)}$, from an isotherm of reference,

$[N_{ref.\ (0,4)}]$: $N_{ref.\ (adsorbed)}$ at $P/P_0=0.4$

Advantage : N_m not needed (BET monolayer adsorption not required).

- Transformed α_S plot : number of adsorbed moles ($N_{adsorbed}$) as a function of α_S

- Determination of specific surface area

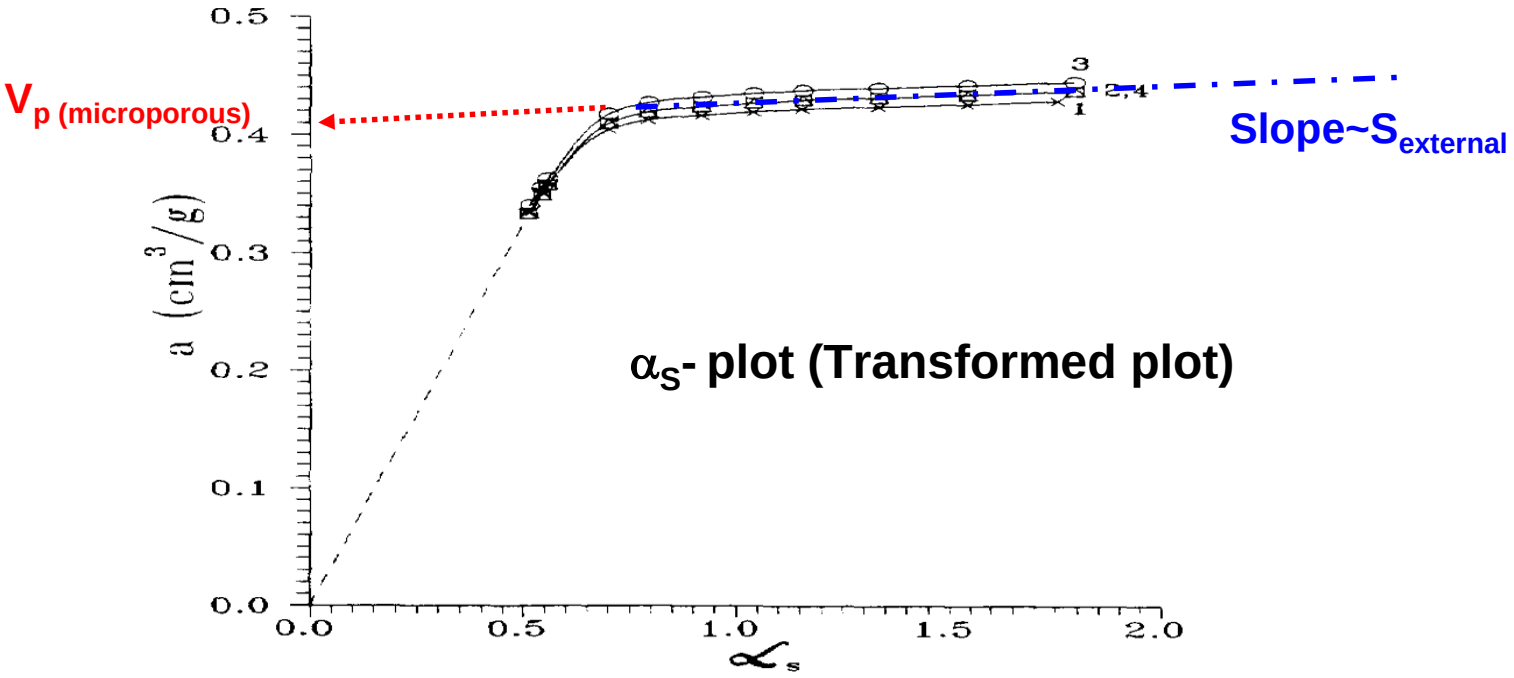
$S_{test}/S_{ref.} = [N_{test\ (adsorbed)}/ N_{ref.\ (0.4)}]/ [N_{ref.\ (adsorbed)} / N_{ref.\ (0.4)}]$ London, 1970

⇓

$S_{test} = S_{ref.}\ [N_{test\ (adsorbed)}/ \alpha_S/ N_{ref.\ (0.4)}] = S_{ref.}\ [slope / N_{ref.\ (0.4)}]$

S_{test} : specific surface of the tested material
$S_{ref.}$: specific surface of the reference
$N_{test\ (adsorbed)} / \alpha_S$: slope of the α_S plot (transformed plot)

[Sing, K. S. W., in D. H. Everett and R. H. Ottewill, Eds. "Surface Area Determination," Butterworths, London]



- **External surface calculated from the linear part (slope) of α_S- plot (multilayer adsorption)**

$$S_{external} = S_{ref.}\ [N_{test\ (adsorbed)} / \alpha_S / N_{ref.\ (0.4)}] = S_{ref.}\ [slope / N_{ref.\ (0.4)}]$$

Slope of the α_S plot : $N_{test\ (adsorbed)} / \alpha_S$
$S_{external}$: specific external surface area of tested material
$S_{ref.}$: specific surface area of reference material

- **$N_{ads,mic}$. number of adsorbed moles in the micropores from Intercept point**

Microporous volume: $V_{micro} = N_{ads,mic} \times M/\rho$

Various forms of the α_s-plot

Weakly (non) porous

Mesoporous

Microporous

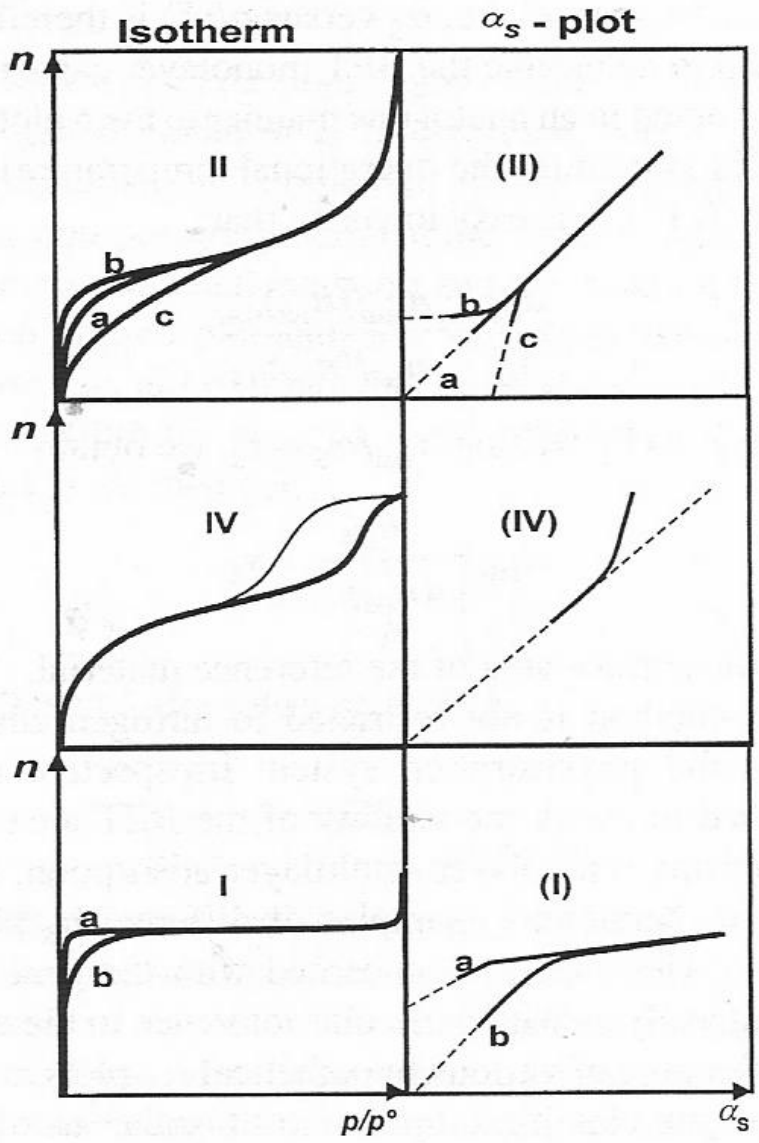


Figure 6.1. Hypothetical α_S-plots (right) and corresponding adsorption isotherms (left). The adsorbent is either non-porous (top), mesoporous (middle), or microporous (bottom).

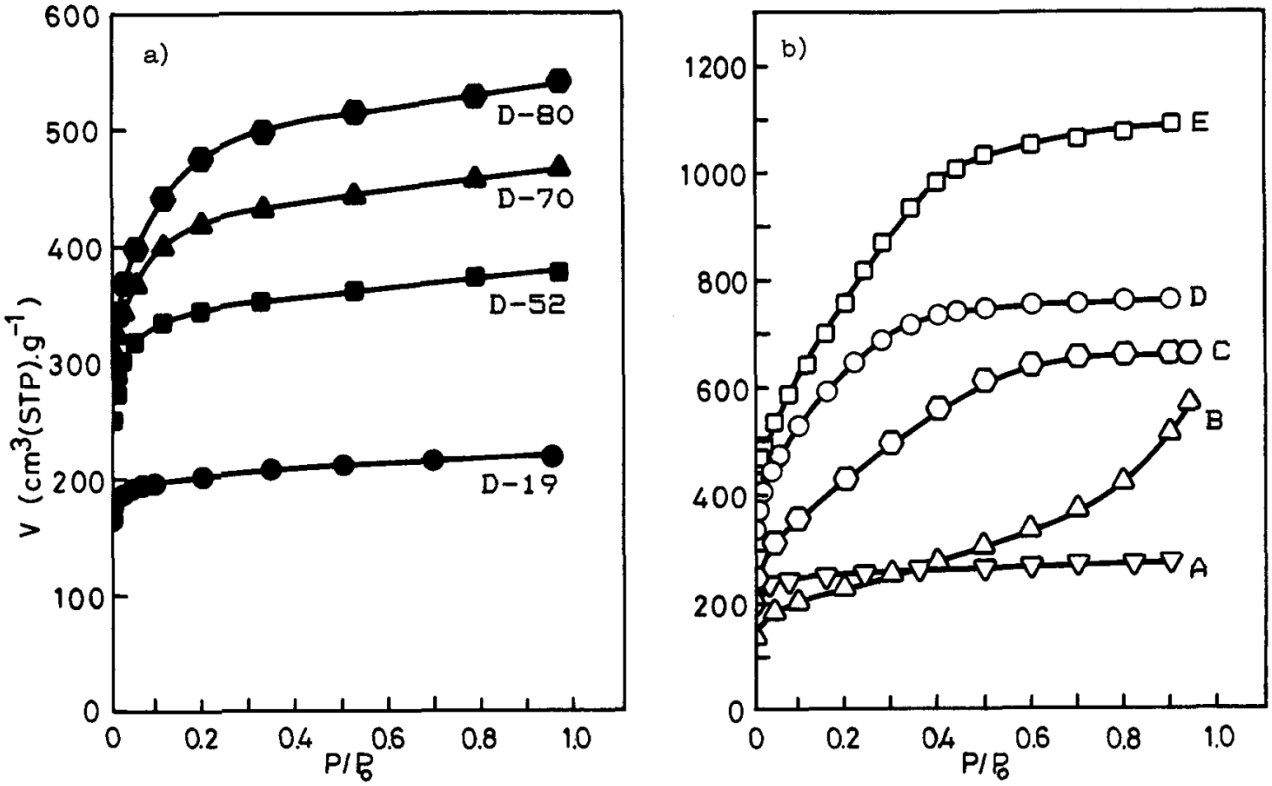


Fig. 1.- Nitrogen adsorption isotherms on: a) some carbons of Series D and b) some activated carbons.

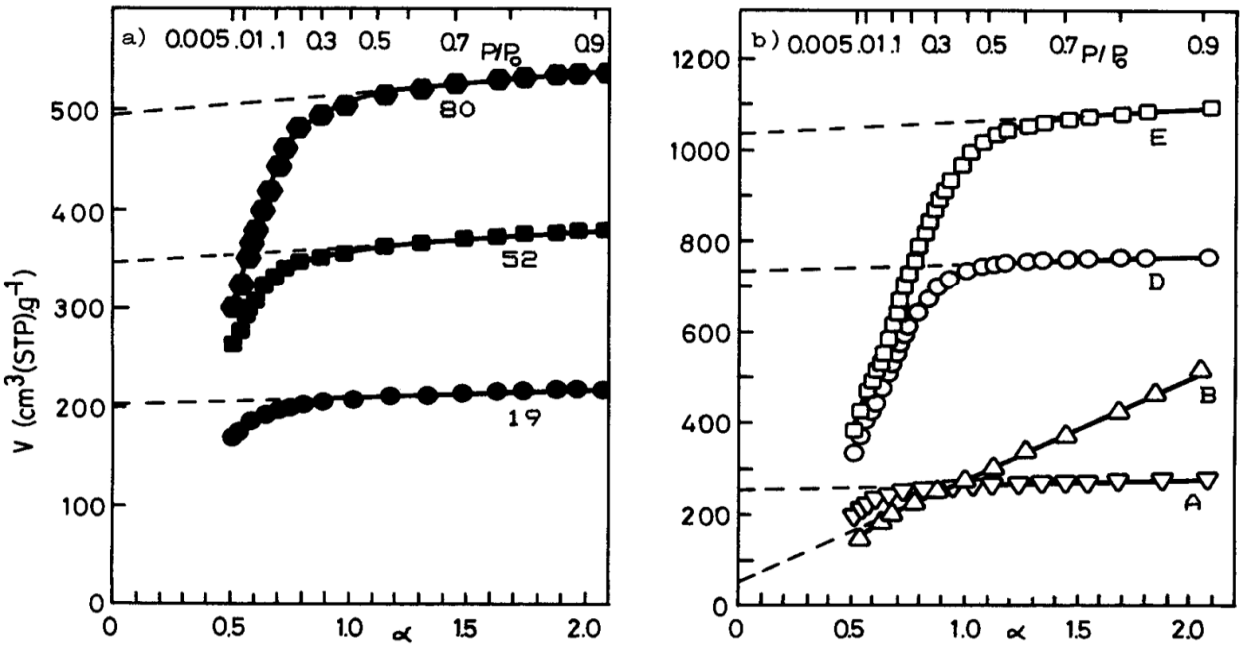


TABLE 1. Micropore volume (cm^3g^{-1}) and external surface area (m^2g^{-1}) of activated carbons.

Sample	N_2(77K)		CO_2(273K)	n-nonane preadsorption		S_{ext}
	DR	α	DR	V_{NP}	V_{np}	
D-19	0.31	0.31	0.30	0.31	0.24	24
D-52	0.50	0.53	0.41	0.51	0.41	41
D-70	0.57	0.64	0.48	0.52	0.47	58
D-80	0.62	0.76	0.51	0.52	0.50	56
A	0.39	0.39	0.36	0.38	0.31	39
B	0.32	0.08	0.09	--	--	577
C	0.49	1.01	0.27	0.20	0.25	10
D	0.75	1.12	0.48	0.46	0.51	34
E	0.92	1.61	0.51	0.49	0.52	53

Example α_s-plot

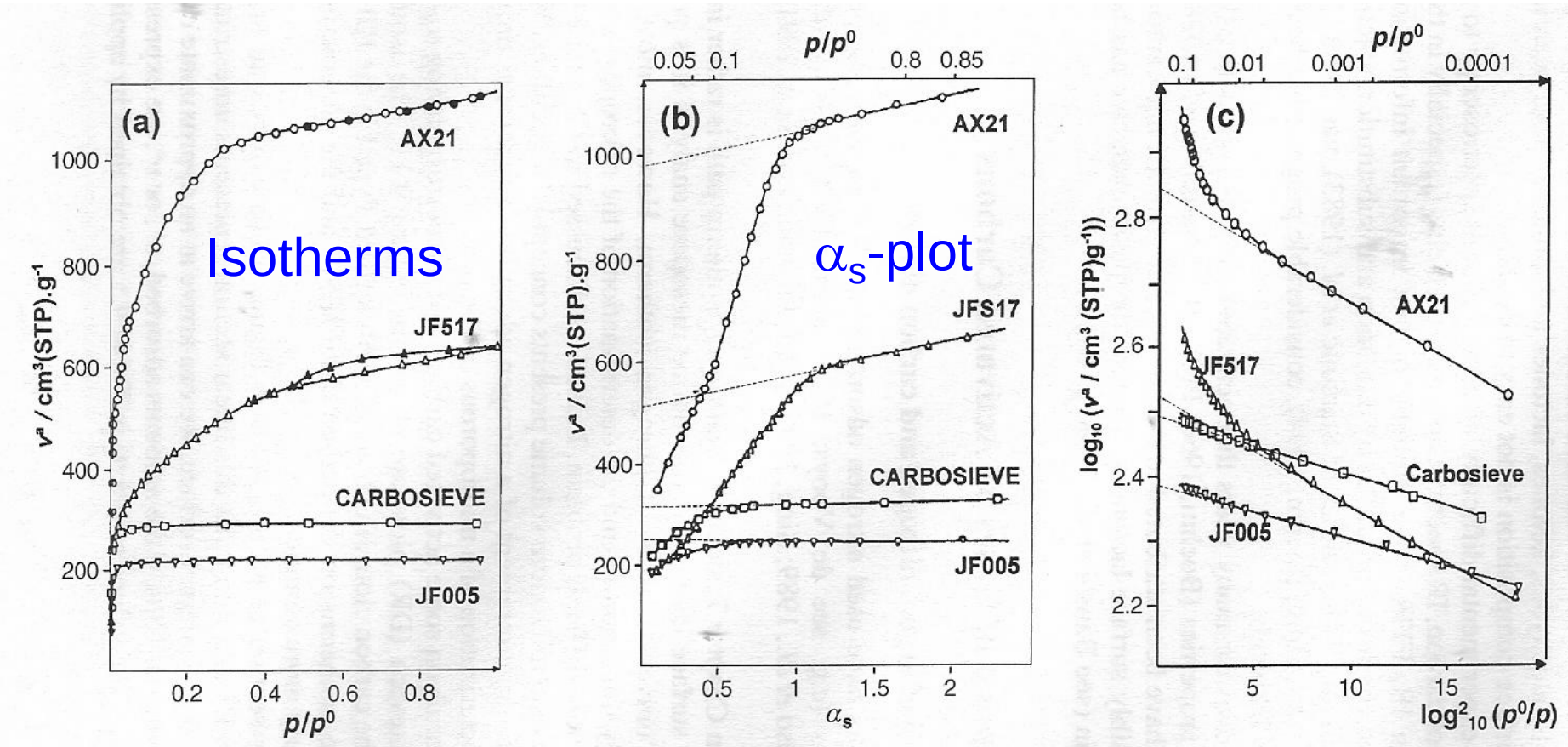


Figure 9.11. (a) Adsorption isotherms on microporous carbons (open symbols adsorption; solid symbols, desorption); (b) α_S-plots for microporous carbons; (c) DR plots for microporous carbons (after Carrott *et al.*, 1987).

Reference of activated carbon for α_s-plot :
often carbon black (as non porous)

Table 9.1. Surface areas and pore volumes of some microporous carbons (N_2)

Carbon	a(BET) ($m^2\,g^{-1}$)	a(ext) ($m^2\,g^{-1}$)	v_p(mic, S) ($cm^3\,g^{-1}$)	v_p(mic, D) ($cm^3\,g^{-1}$)
PX21	3700	178	1.75	0.99
AX21	3393	233	1.52	1.00
JF516	2053	246	0.98	
JF517	1657	218	0.76	0.47
JF142	1479	54	0.55	
Carbosieve	1179	41	0.43	0.45
JF005	882	19	0.33	0.35

α_s

Dubinin-Raduskevitch

Ref. for α_s-plot method : [Bhambhani, M. R, Cutting, P. A, Sing, K. S. W, Turk, D. H., Journal of Colloid and Interface Science, 38, 1, 1972, ***Analysis of nitrogen adsorption isotherms on porous and nonporous silicas by the BET and αs methods****]*

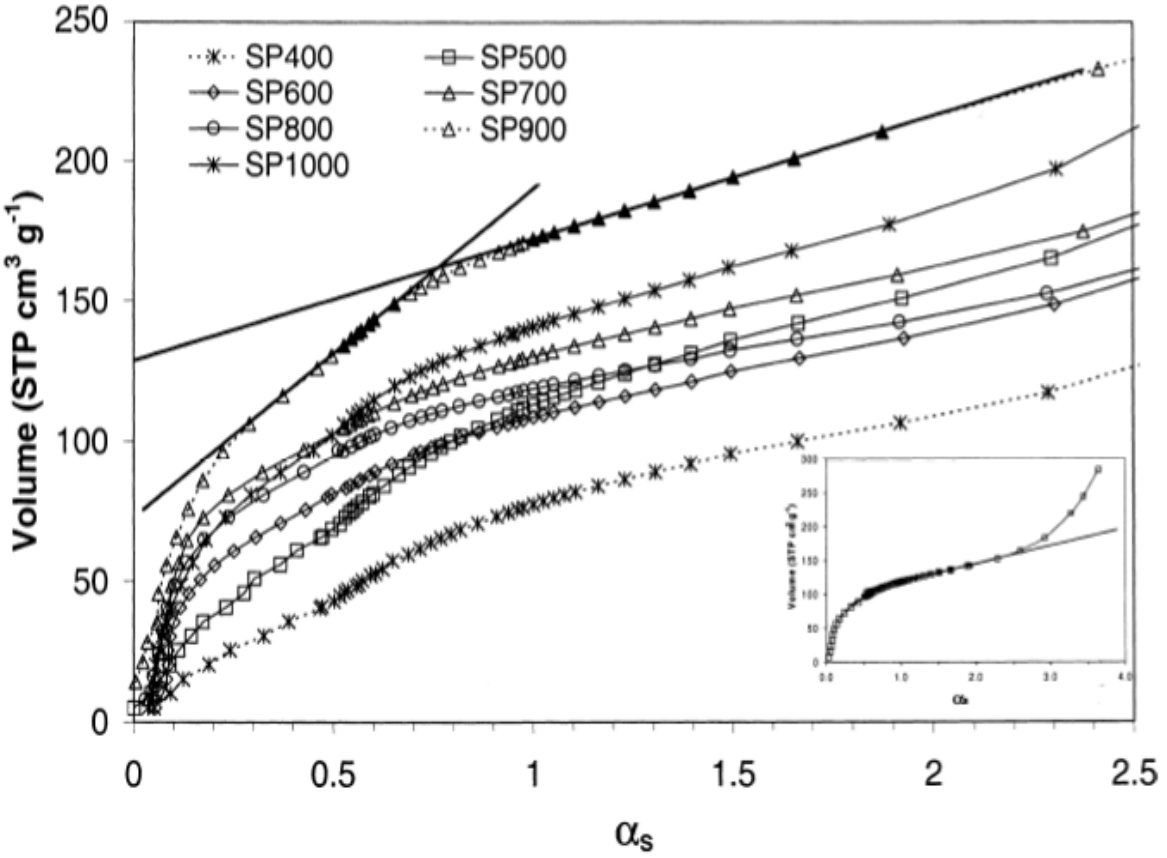


Fig. 2. α_s plots drawn from N_2 adsorption isotherms at -196 °C on synthetic activated carbons prepared at different temperatures. Insert, α_s plot for SP800 carbon including data at $\alpha_s > 2.5$.

Assesment of ultramicroporosity by α_s-plot

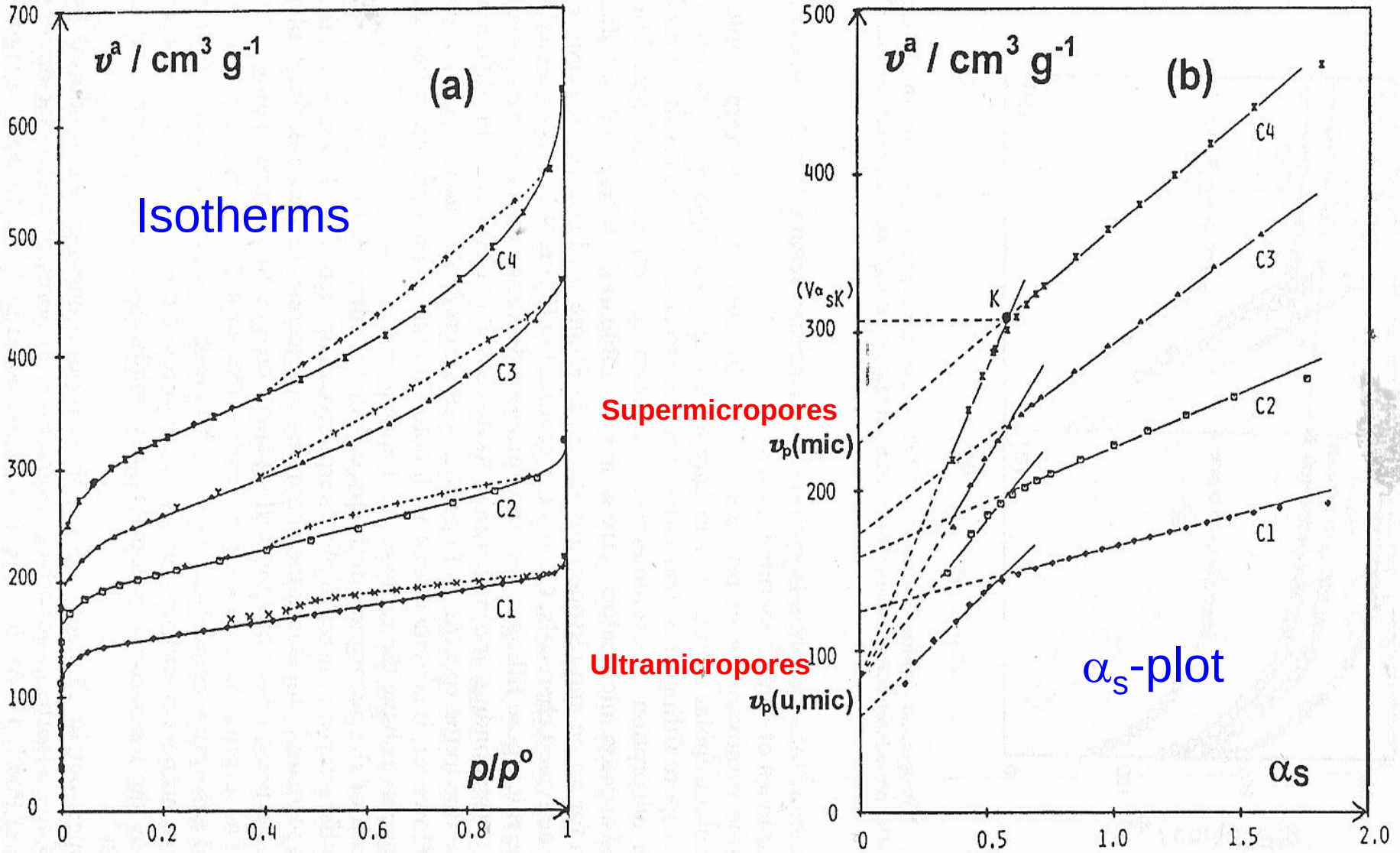


Figure 9.12. N_2 adsorption isotherms at 77 K (a) and corresponding α_S plots (b) on four activated carbons (Fernandez-Colinas *et al.*, 1989a).

Carbones activés issus de l'activation phosphorique de pulpe de pomme

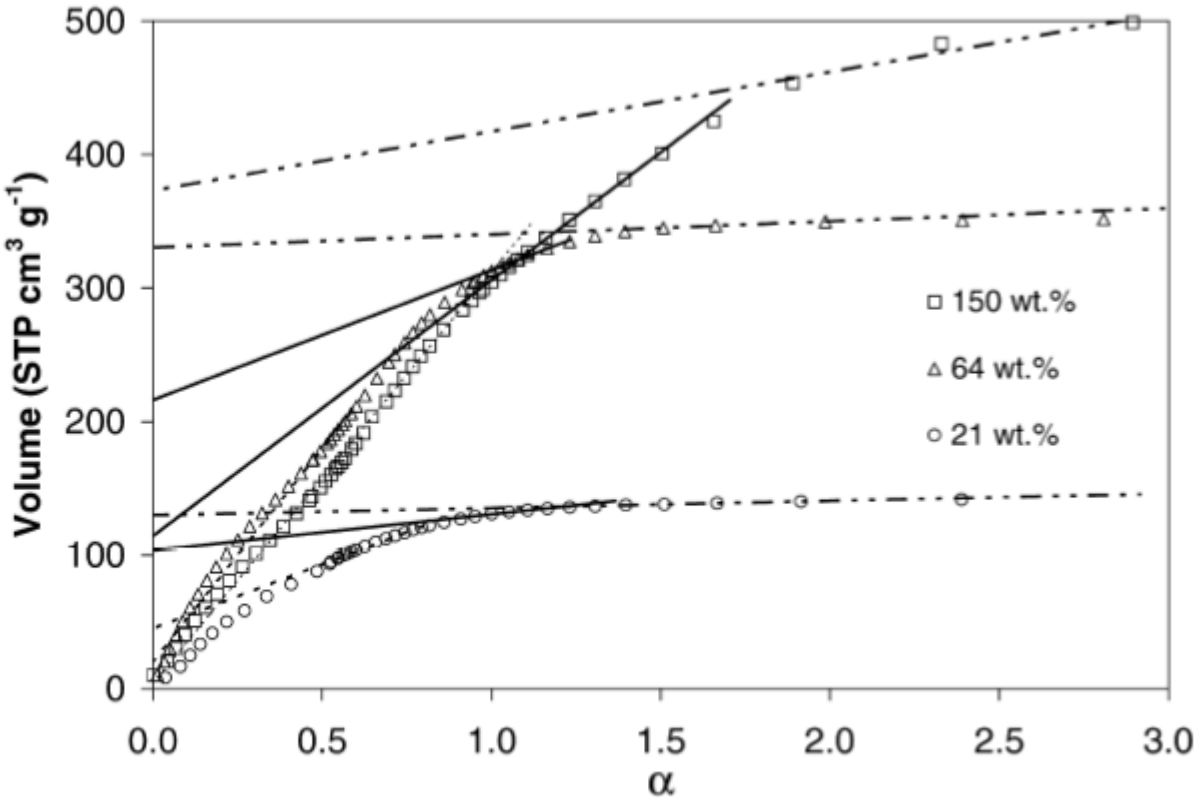
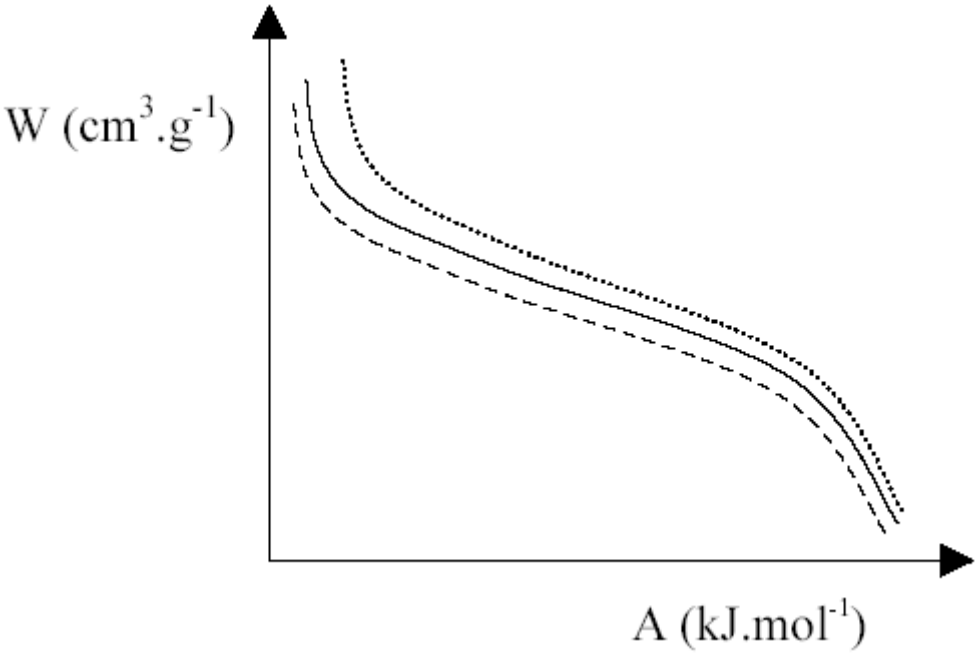


Fig. 2. α_s-plots drawn from N_2 adsorption isotherms on ACs with impregnation ratios of 21, 64 and 150 wt.%.

3. DR (Dubinin-Radushkevich) method for determination of microporous volume

Postulat de Dubinin : quantité N_a de vapeur adsorbée par un solide microporeux est une fonction du potentiel thermodynamique.

Tests expérimentaux suggèrent uneexpression Gaussienne décrivant la courbe caractéristique W=f(A) d'un solide microporeux (W : volume adsorbée).



- Courbes caractéristiques uniques pour un système adsorbat-adsorbant donné quelle que soit sa température.

- Pour le même adsorbant mais pour un adsorbat différent, courbes différentes affines entre elles, ce qui signifie que l'on passe de l'une à l'autre par un facteur multiplicatif spécifique β .

Représentation des courbes caractéristiques de trois adsorbats (—,– –,···) différents adsorbés sur le même adsorbant.

Dubinin et Radushkevich ont proposé l'expression :

$$W = N^a V_m^a = W_0 \exp\left\{-\left[\left(RT/\beta E_0\right)\ln\left(P_s/P\right)\right]^2\right\}$$

Où W ($cm^3.g^{-1}$) est le volume adsorbé.

$$W_0 = N_0^a V_m^a$$

N^a_0 est la quantité limite adsorbée possible en $mol.g^{-1}$ pour un adsorbant donné.
V^a_m est le volume molaire ($cm^3.mol^{-1}$) en phase adsorbée.

E_0 est l'énergie caractéristique du solide en $J.mol^{-1}$. L'énergie caractéristique E d'un système adsorbat/adsorbant est reliée aux paramètres β et E_0 par la relation : $E = \beta E_0$.

Le paramètre β (coefficient d'affinité) prend en compte la nature de l'adsorbat. Le benzène a été choisi comme référence et $\beta benz = 1$.

L'équation de Dubinin et Radushkevich (DR) peut aussi s'écrire sous la forme :

$$\log_{10}[W/W_0] = -D\,(\log_{10}[P_0/P])^2$$

Soit dans le cas d'un solide microporeux :

$$\log_{10}[n_{ads}] = \log_{10}[n_p(\text{microporeux}] - D\,(\log_{10}[P_0/P])^2$$

$$\log_{10}[n_{ads}] = \log_{10}[n_p(\text{microporeux}] - D\,(\log_{10}[P_0/P])^2$$

D est une constante empirique

le graphique de $\log_{10}[W]$ en fonction de $(\log_{10}[P_o/P])^2$ est linéaire avec une pente -D et intercepte $\log_{10}$ $[V_p(\text{microporeux})]$ à l'origine.

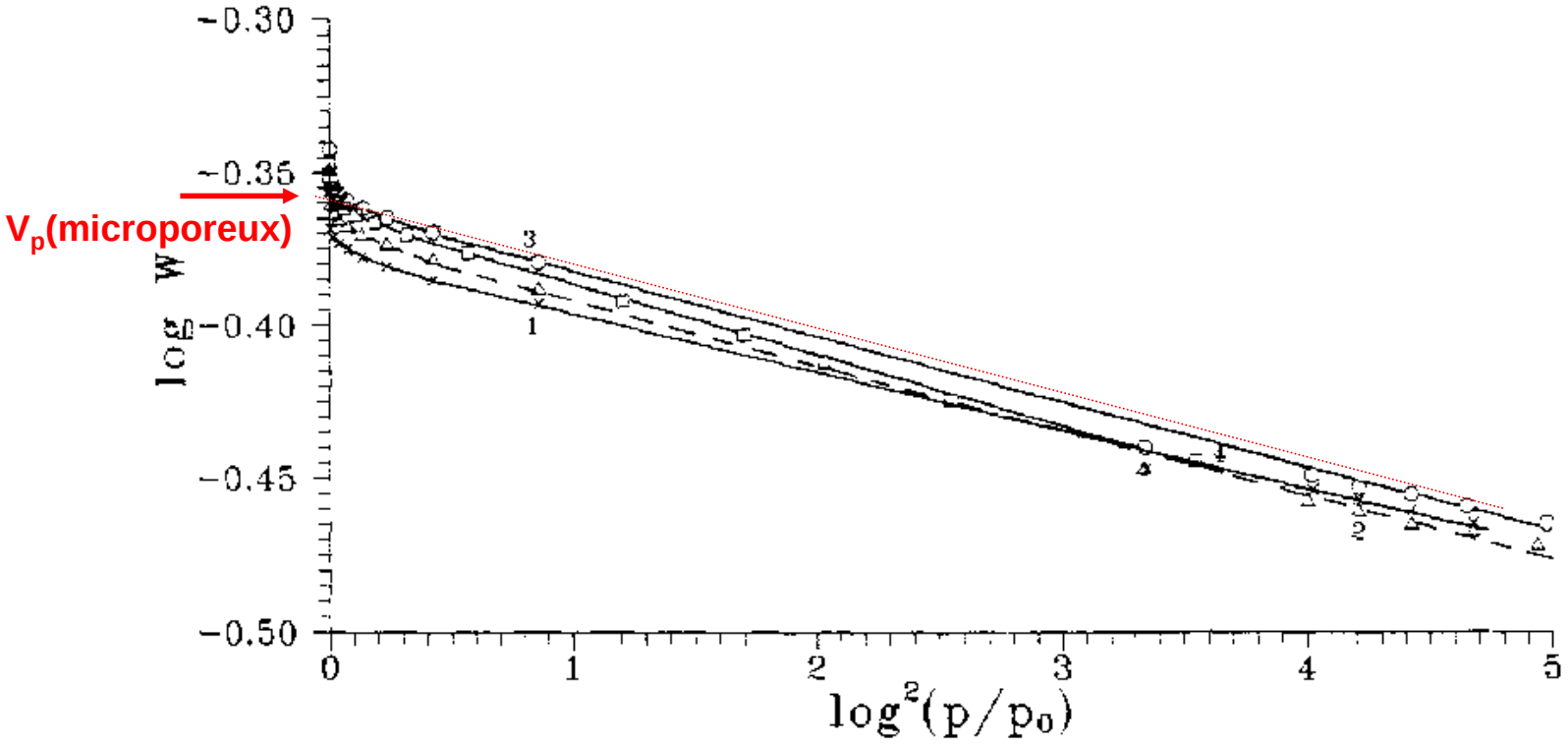
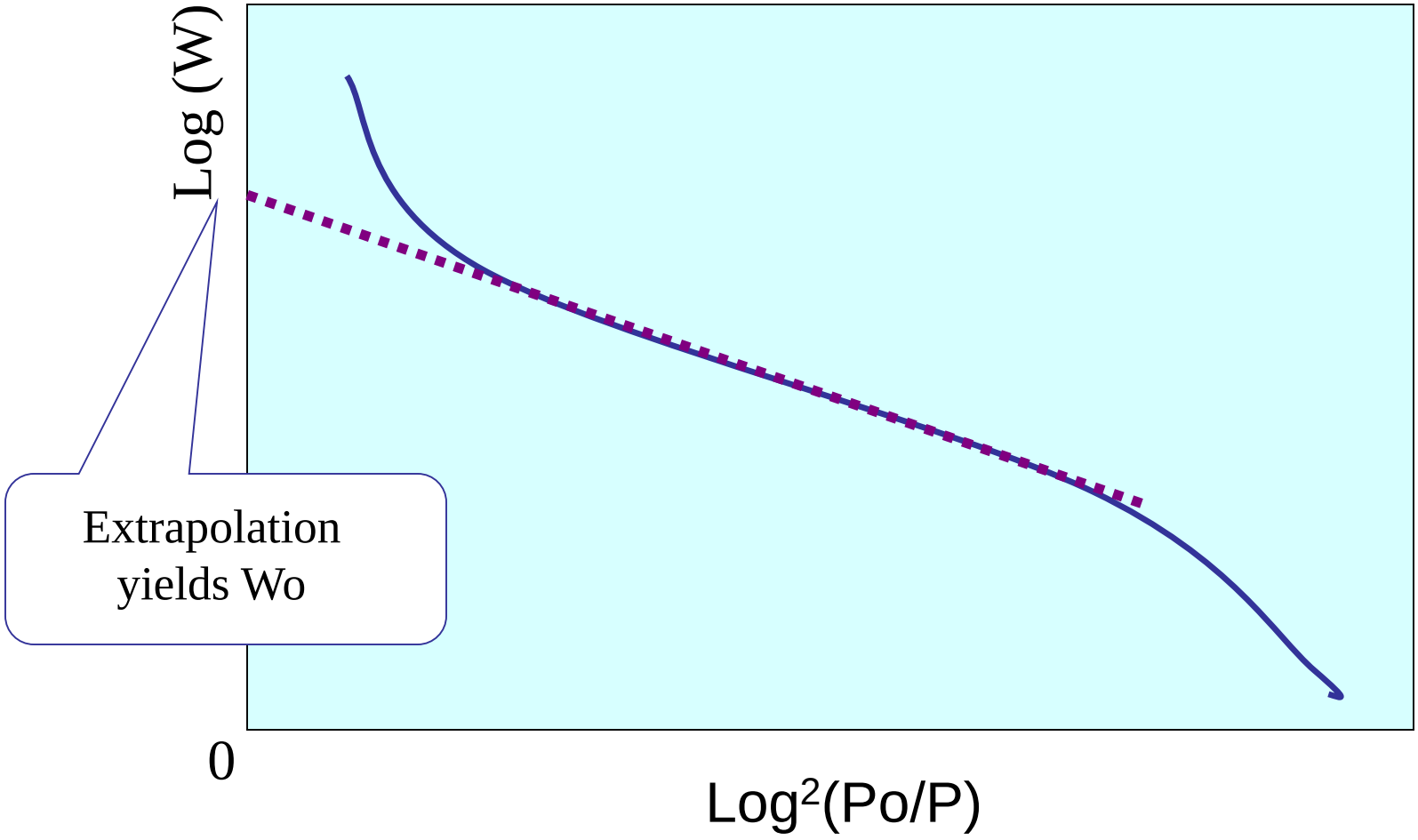


Fig. 2. Dubinin–Radushkevich plots for nitrogen adsorption at 77.5 K onto A (1), B 493 (2), B 523 (3) and B 573 (4) carbons.

Estimation of Micropores
Dubinin-Radushkevich (DR) Plot



Example of DR (Dubinin-Radushkevich) plot for determination of microporous volume

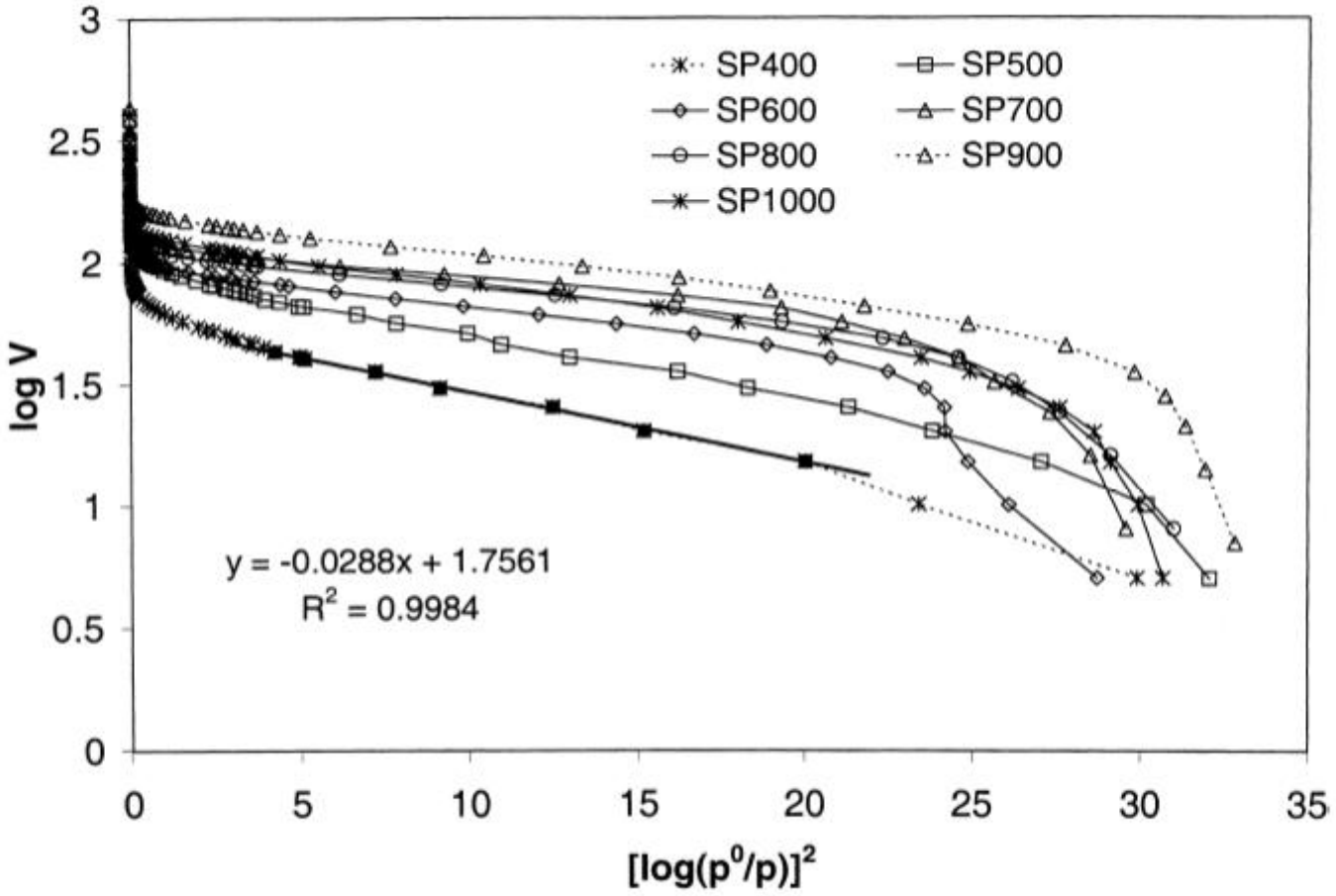


Fig. Dubinin-Radushkevich plots for N_2 isotherms at 77 K on synthetic activated carbons prepared at different temperatures

Mesoporosity determined by the method of Barrett-Joiner-Halenda (BJH)

The assumptions relating to this method are :

- Kelvin's equation is applicable over the entire mesoporous domain.
- $\theta=0°$ and the radius of curvature of the meniscus is controlled by the pore size and shape only.
- The pores are rigid and of well-defined shape (cylindrical, parallel planes, stack of spheres).
- We only have mesopores as a type of pore.
- The filling of a pore does not depend on its location in the pore network.
- Adsorption in the pore occurs according to the same principles as it would on an open surface.

4. Barrett-Joiner-Halenda method (BJH)

The pore size x_k is calculated from the Kelvin equation and the selected statistical thickness (t-curve) equation

$$v_{ads}(x_k) = \sum_{i=1}^{k} \Delta V_i\left(r_i \le r_c\left(x_k\right)\right) + \sum_{i=k+1}^{n} \Delta S_i t_i\left(r_i > r_c\left(x_k\right)\right)$$

$v_{ads}(x_k)$ is the volume of (liquid) adsorbate [cm^3/g] at relative pressure x_k
V pore volume is given in [cm^3/g]
S is surface area [m^2/g]
t is the thickness of adsorbed layer (in appropriate units).

The desorbed amount at k-th point of desorption isotherm originates from two distinct parts:

(1) the volume of condensate gas in all the pores smaller than some characteristic size depending on current relative pressure, $r_c(x_k)$,

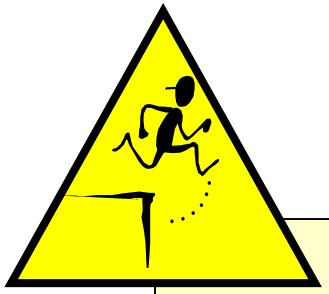
(2) a 2nd volume corresponding to the adsorbed film on all larger pores whose thickness is decreasing together with pressure. This volume is calculated by a sum of terms: Σ (pore surface) ×(thickness of film)

BJH Pore Size Distribution

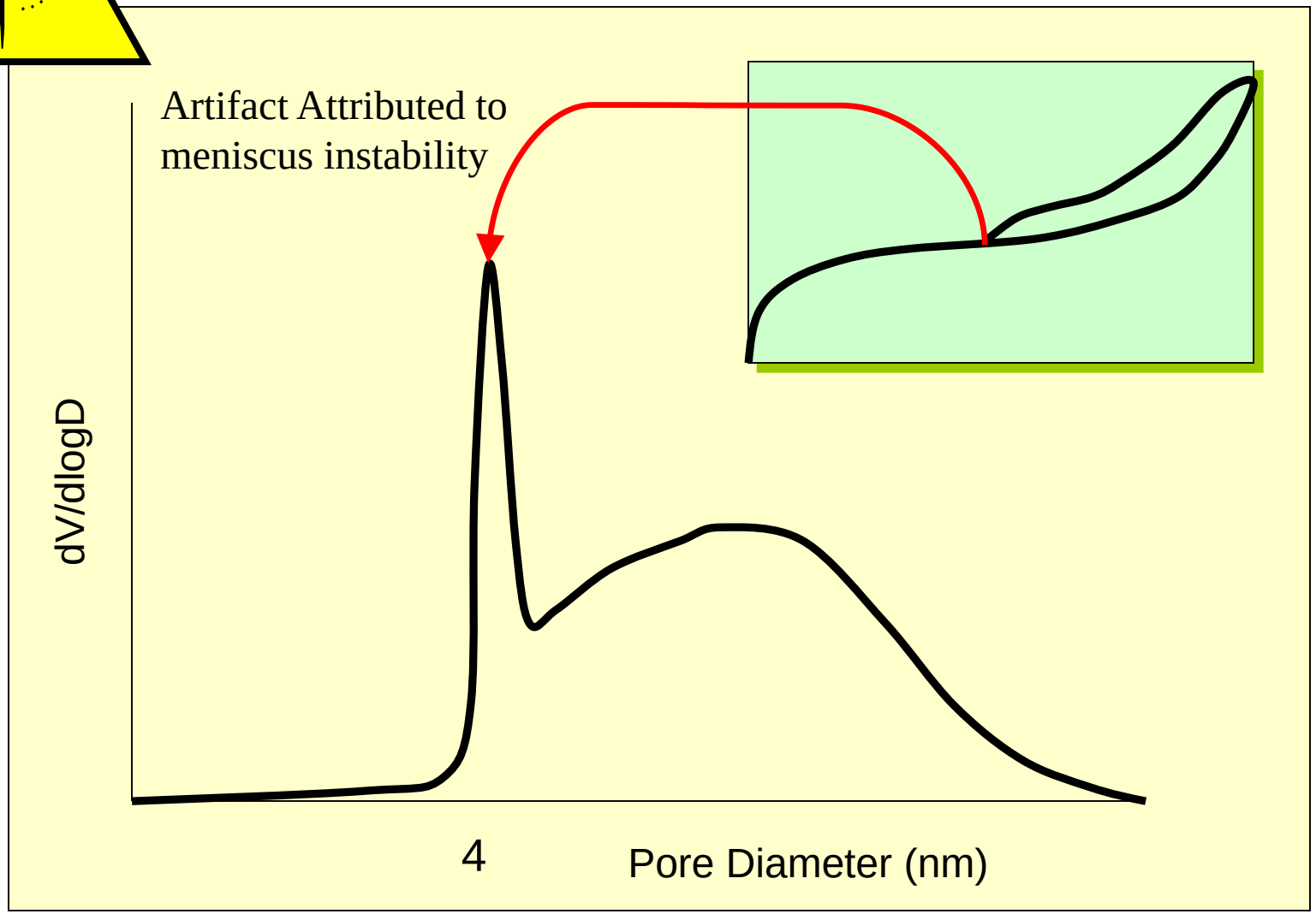
- Hypothesis : the knowledge of t (Harkins-Jura law, for example), Kelvin equation, and an hypothesis about the pore shape
- Calculation by recurrence of the surface area of pore wall and the pore volume of each pore category.
- The sum of these values gives a cumulated specific surface area and a cumulated porous volume.
- Applied in the P/P_0 hysteresis domain and preferentially on the desorption branch (if it exists) because equilibrium conditions are better

Pore volume requires also assumption of liquid density!

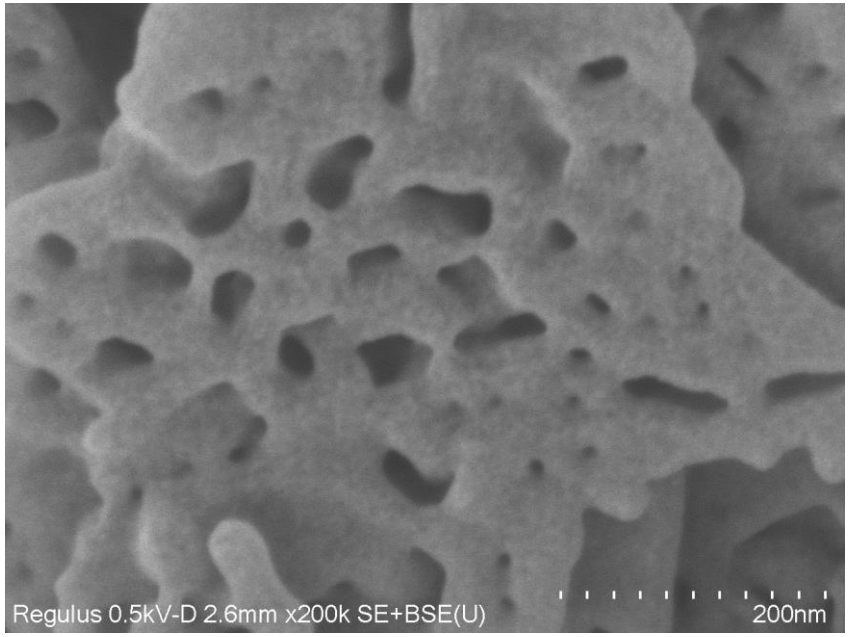
[Elliott P. Barrett, Leslie G. Joyner, Paul P. Halenda, J. Am. Chem. Soc. 73(1), 1951, ***The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms****]*



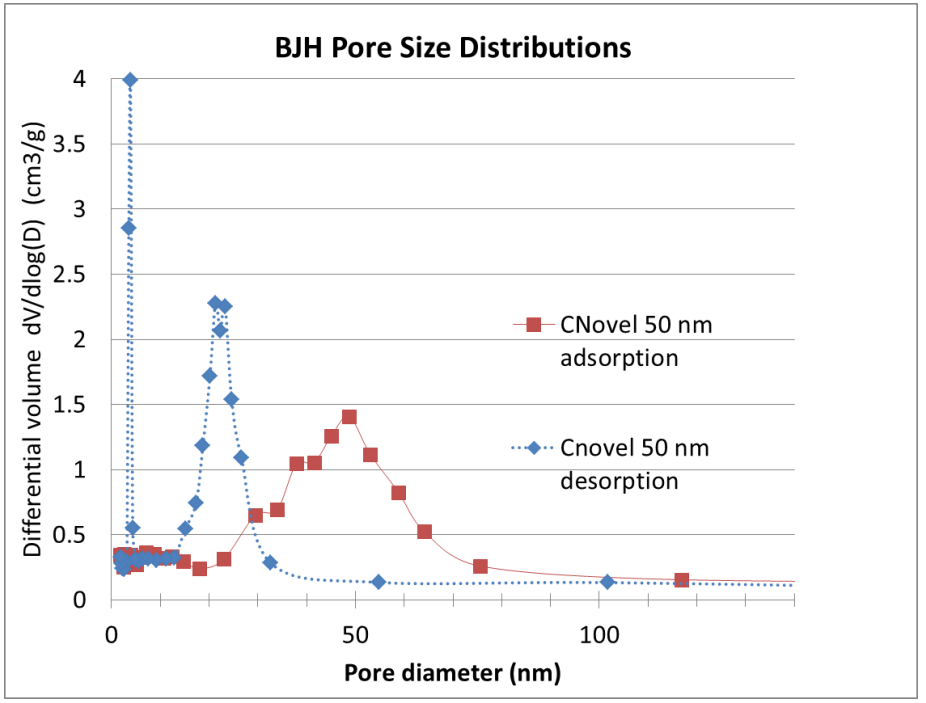
BJH Pore Size Distribution



MgO templated activated carbon



SEM-FEG Image of
CNovel 50 nm (mesopores)



5. Pore Size Distribution by DFT (Density of Functional Theory)

For a given adsorbate-adsorbent system, DFT calculates the most likely summation of "ideal isotherms“ calculated from "ideal pores" of fixed sizes needed to match the experimental results.

The ideal isotherms are calculated from the grand potential

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \int d\mathbf{r}\,\rho(\mathbf{r})[\mu - V_{ext}(\mathbf{r})]$$

r : coordinate

ρ(r) : fluid density

F : free enthalpy of the system, taking into account the interactions between fluid particles

μ : chemical imposed potential which determines which the equilibrium state

V_{ext} : wall/molecule interaction potential dependent on the system shape

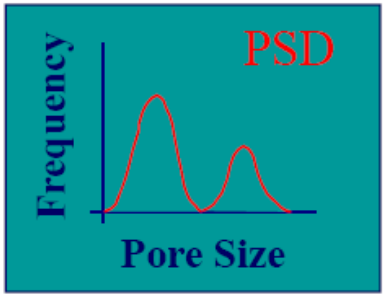
The system equilibrium for a given pressure is obtained from the minimum of the grand potential function

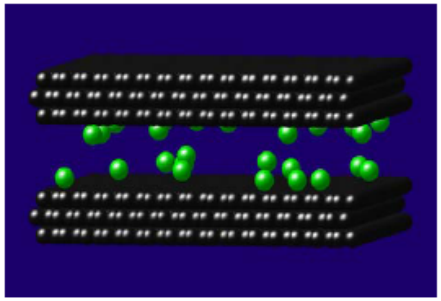
A network of adsorption reference isotherms for different pore size is used (kernel). For fitting the experimental isotherm this equation is solved :

Predicted isotherm **PSD** **Simulated model-pore isotherm**

$$N(P) = \int_0^{\infty} f(w)\ \rho(w, P)\, dw$$

?





N number of adsorbed moles, is known for each size w.
The distribution f(w) of each size is deduced.

[Olivier J. P., Modeling physical adsorption on porous and nonporous solids using density functional theory, Journal of Porous Materials, Vol. 2, 1995, pp. 9-17.]

Activated Carbons obtained by phosphoric activation of coffee hulls

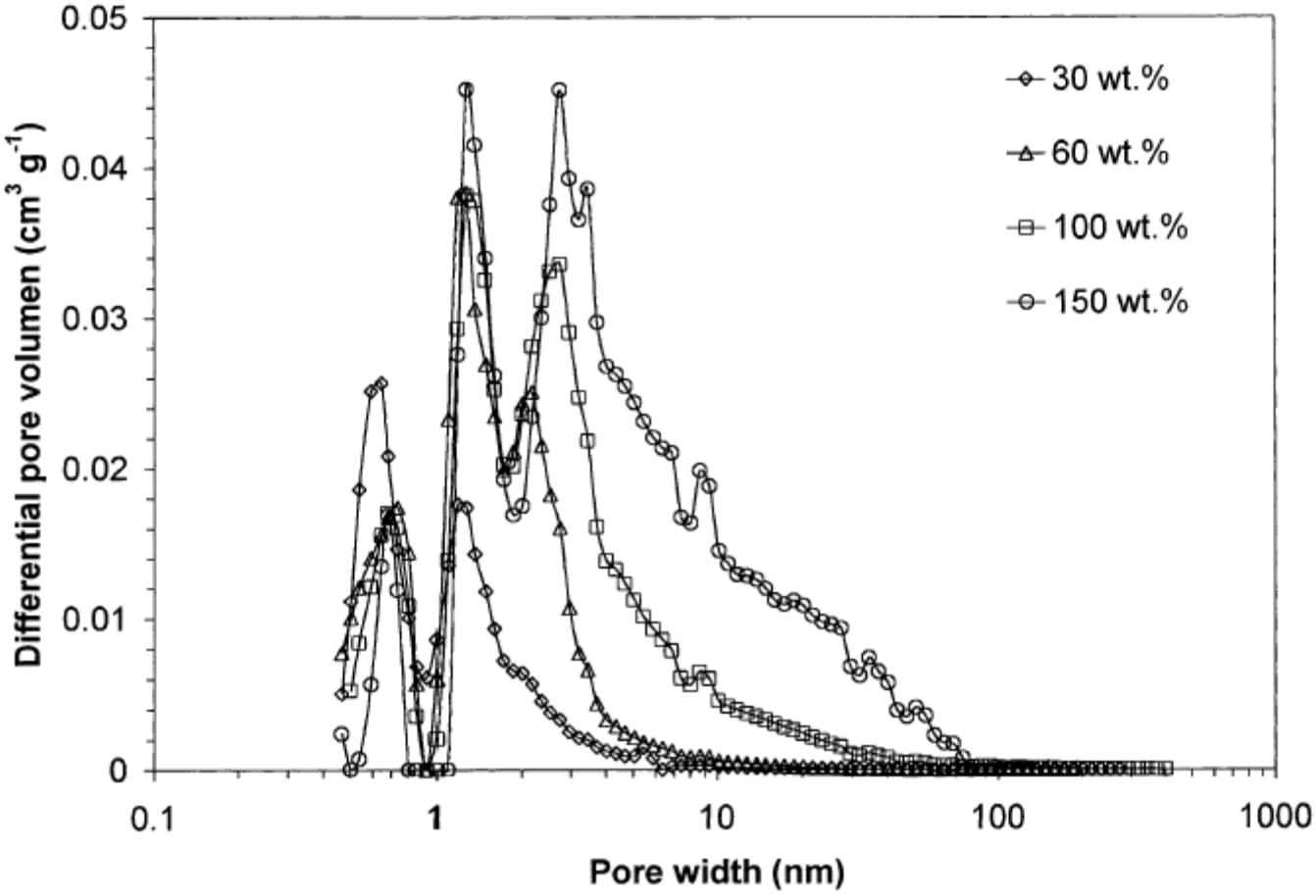


Fig. 2. PSDs obtained by applying the DFT theory to N_2 adsorption data at 77 K.

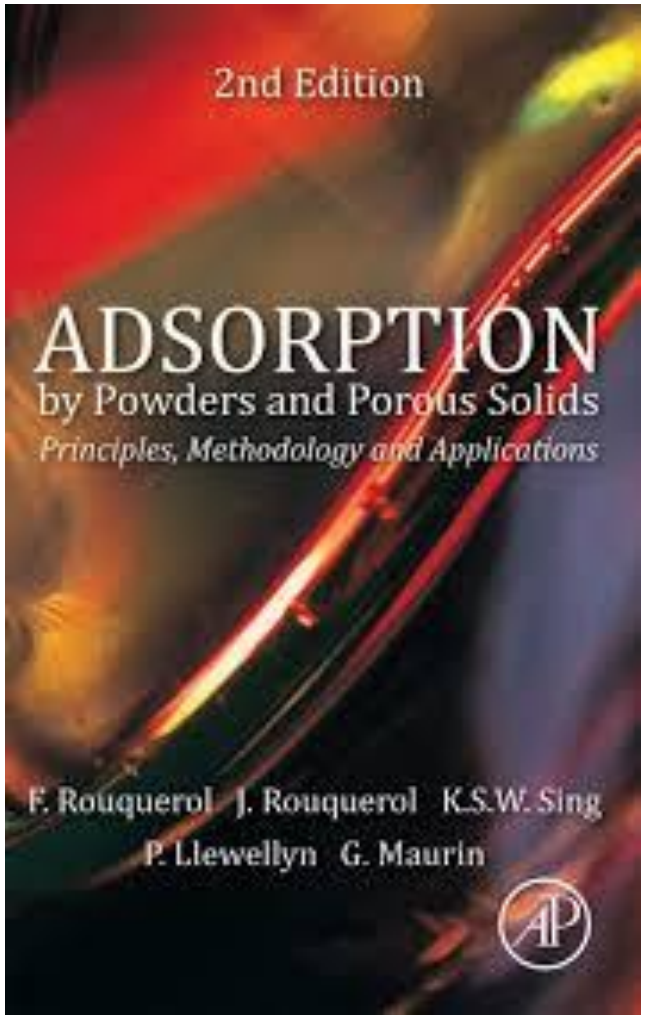
Reference of book

“Adsorption by Powders and Porous Solids
Principles, Methodology and Applications”

Second edition

<u>Authors</u> : F. Rouquerol, J. Rouquerol, K.S.W. Sing, P. Llewellyn and G. Maurin

Academic Press



III. Caractérisation de la macroporosité

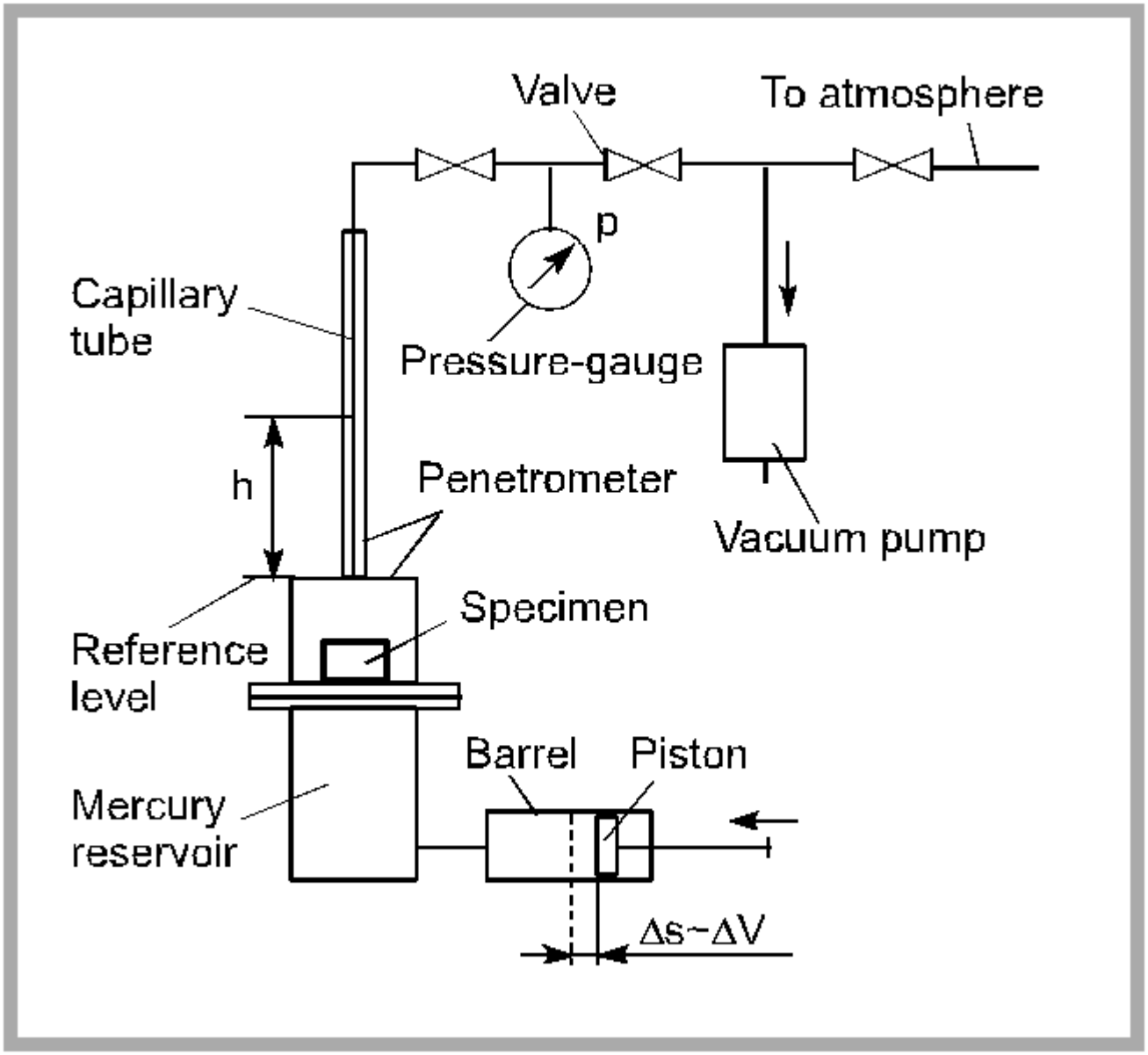
Porosimétrie Mercure

La méthode de mesure est basée sur **la loi de Washburn** qui permet de déterminer la force nécessaire pour faire pénétrer un liquide non mouillant dans un pore de section circulaire r.

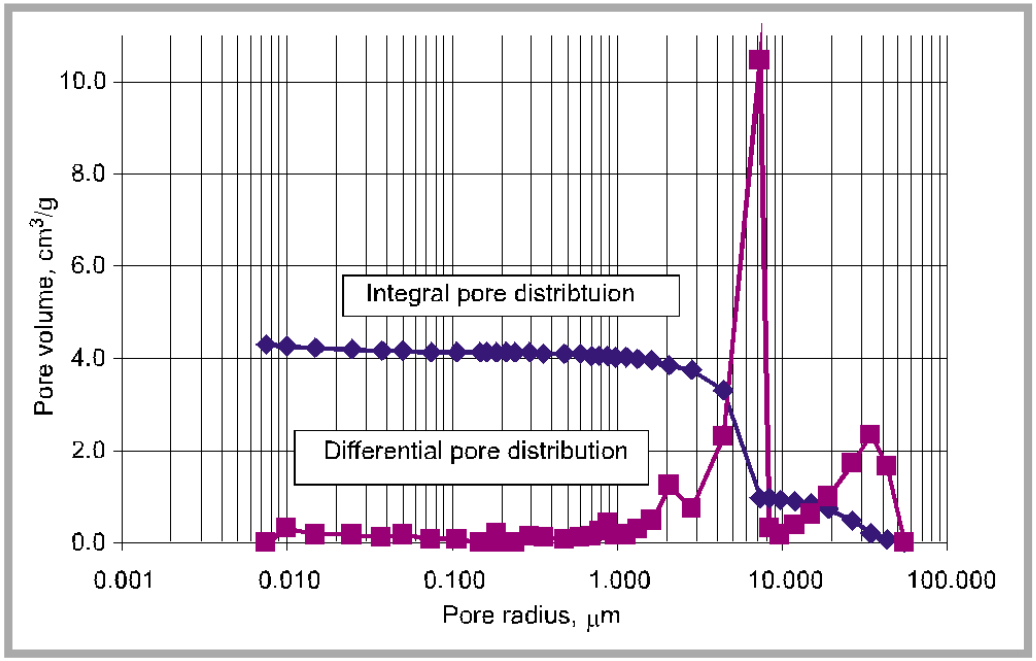
$$P.r = - 2 \gamma . \cos \theta$$

avec : r = rayon hydraulique des pores,
p = pression nécessaire pour faire pénétrer le mercure dans les pores,
γ = tension superficielle du mercure,
θ = angle de contact du mercure avec le solide étudié.
On adopte en général : γ = 0,480 N/m et θ = 142° .

En exprimant r en microns et P en bars, on obtient la relation généralement utilisée en porosimétrie : P.r = 7,5.


Valve
To atmosphere
p
Capillary tube
Pressure-gauge
h
Penetrometer
Vacuum pump
Specimen
Reference level
Barrel
Piston
Mercury reservoir
Δs~ΔV

Pour déterminer la courbe de distribution des rayons hydrauliques des pores on effectue une montée en pression par paliers entre la pression atmosphérique et la pression maximale de l'installation. A chaque palier de pression, on détermine le volume de mercure injecté dans les pores.



A partir de ces résultats, on détermine soit
la variation du volume poreux en centimètres cubes par gramme d'échantillon en fonction des rayons des pores (distribution intégrale), soit la distribution différentielle des pores (dV/dr en fonction de r).

Monolithic organic aerogels prepared by sol–gel polymerization reaction of resorcinol (R) and formaldehyde (F) in water (W) using Na_2CO_3 and K_2CO_3 catalyst

[D. Fairen-Jimenez et al. / Carbon 44 (2006) 2301–2307]

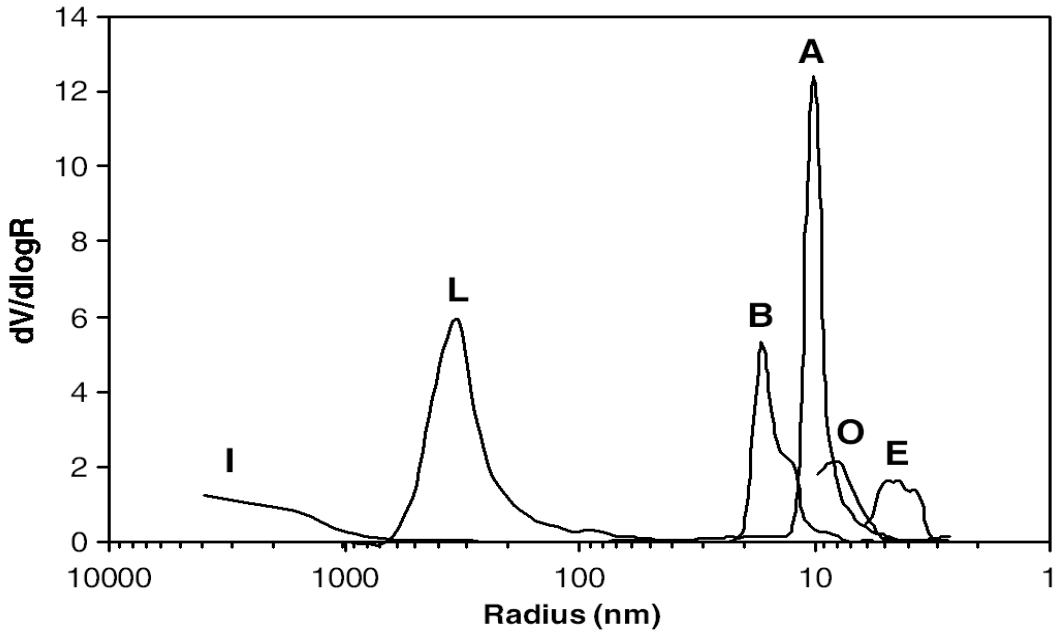


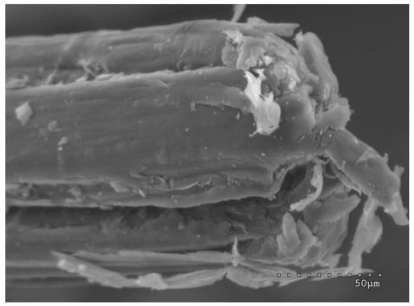
Fig. 2. Pore size distributions of carbon aerogels from mercury porosimetry.

Table 2
Particle density and pore texture (from mercury porosimetry) of carbon aerogels prepared using Na_2CO_3 (A and O) and K_2CO_3 (L and B) as catalysts

Sample	R/W	ρ g/cm^3	V_P cm^3/g	d nm
A	0.08	0.48	1.30	20
O	0.13	0.70	0.39	16
L	0.08	0.38	1.67	666
B	0.13	0.62	0.79	34

Kenaf activated fibers prepared by carbon dioxide activation

(Kenaf is an herbaceous annual plant that belongs to the family of Malvaceae)



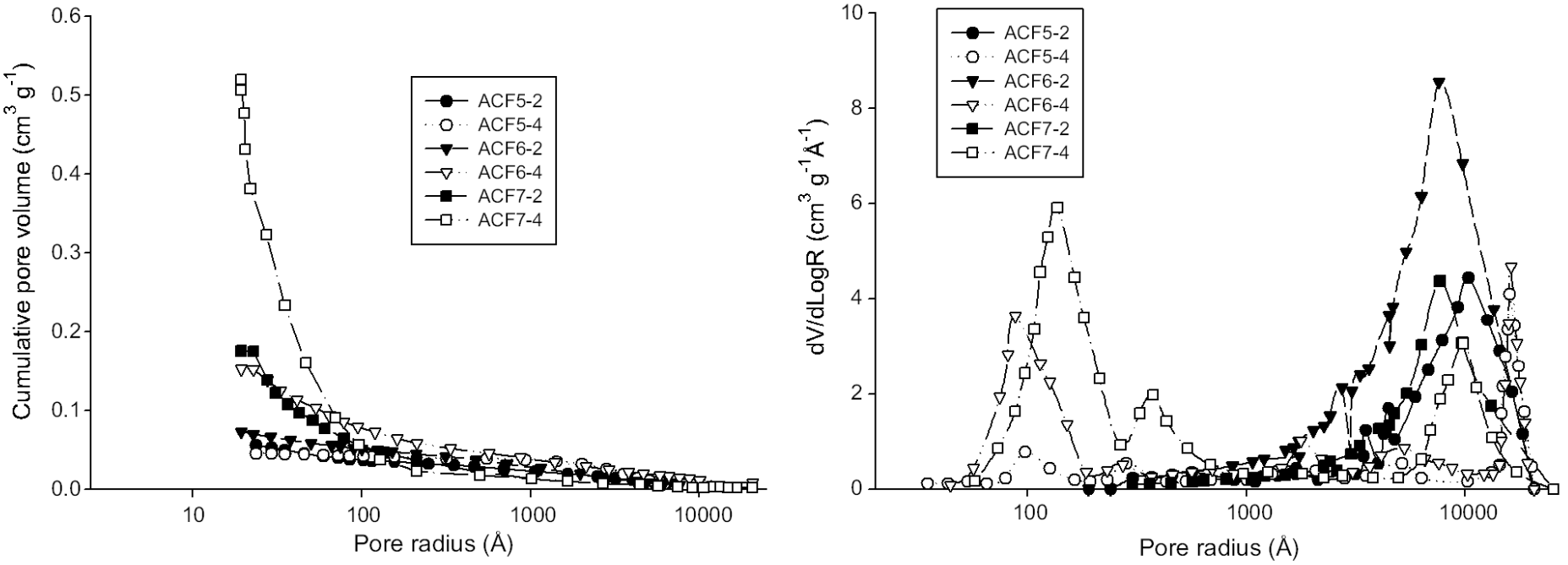


Fig. 6. Mercury intrusion curves (left) and meso- and macropore size distributions (right) of the activated samples.

[E.M. Cuerda-Correa et al. / Microporous and Mesoporous Materials 111 (2008) 523–529]

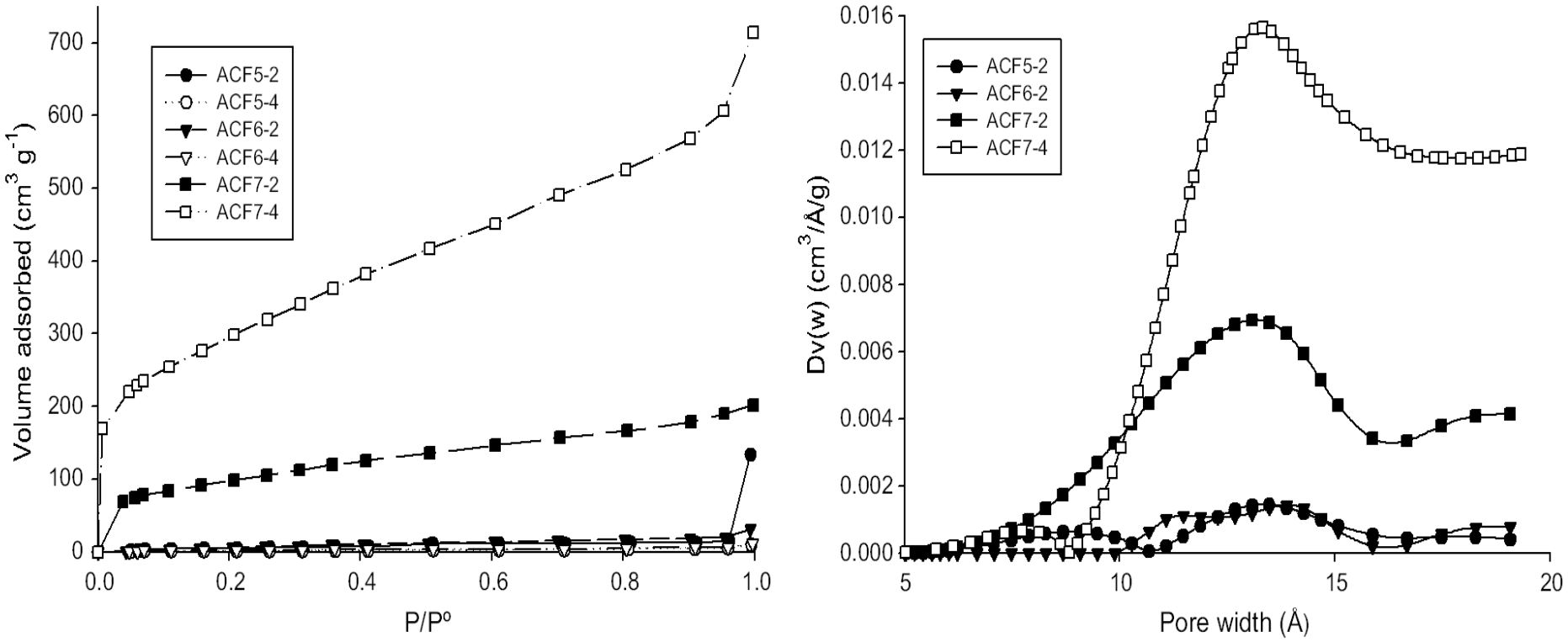


Fig. 5. Adsorption isotherms (left) and micropore size distributions (right) of the activated samples.

Tomographie X

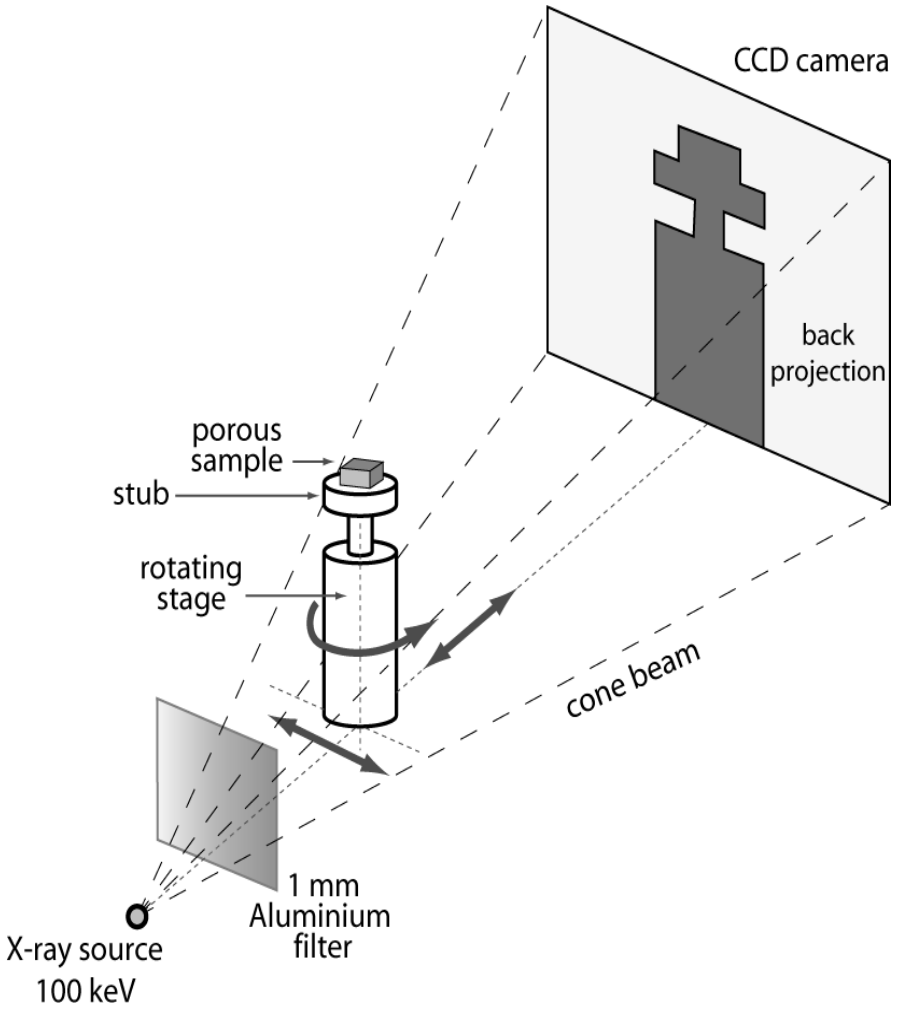


Fig. 9. Schematic of experimental set-up for collecting two-dimensional radiographs of bonded fibre networks, using a cone-beam X-ray arrangement. The set-up resides within an enclosed X-ray compartment.

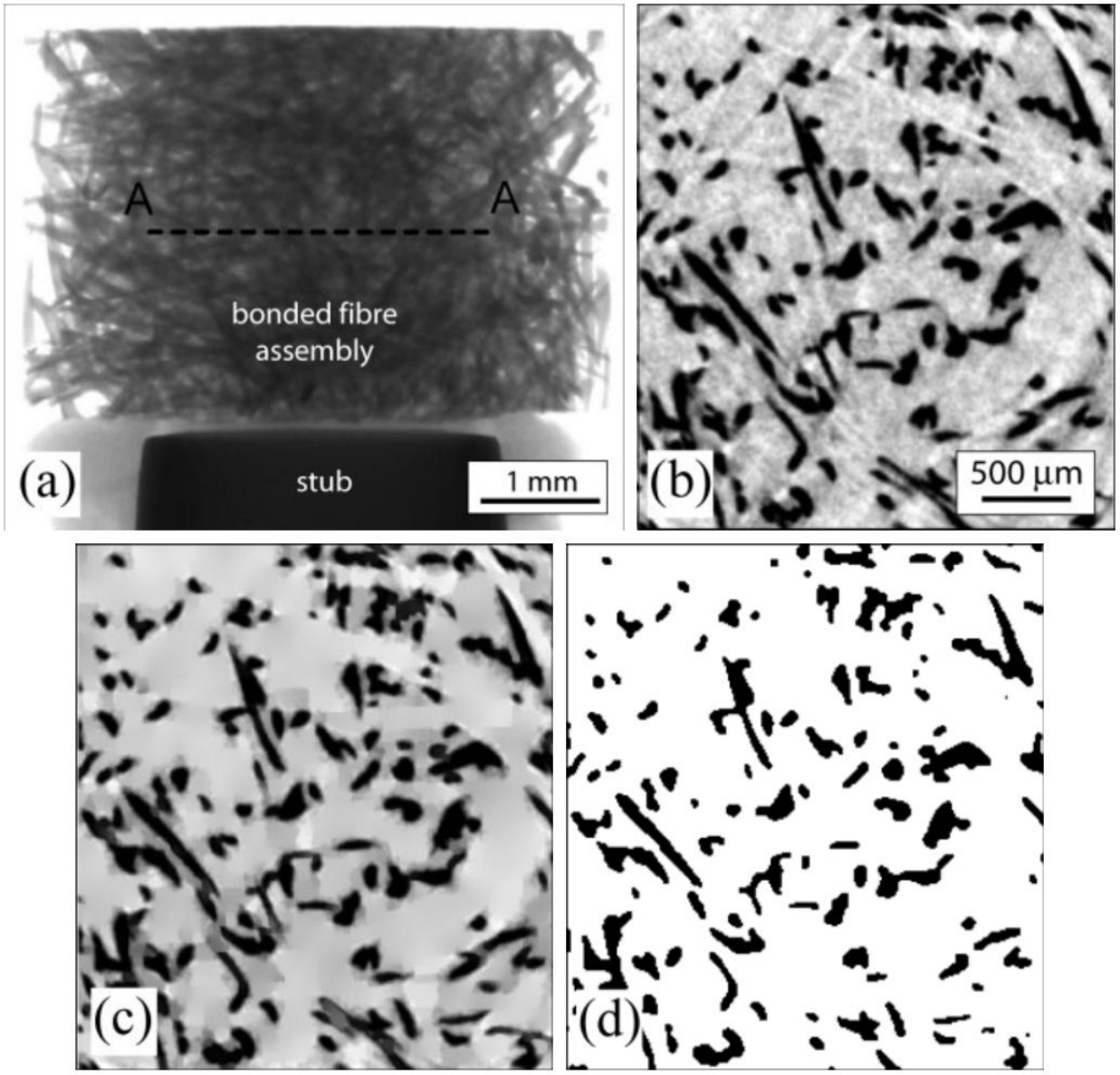


Fig. 2. A typical X-ray absorption radiograph of network A material, (b) a reconstructed 2-D slice through position A-A, (c) the greyscale image after anisotropic diffusion smoothing, and (d) the segmented slice after simple thresholding.

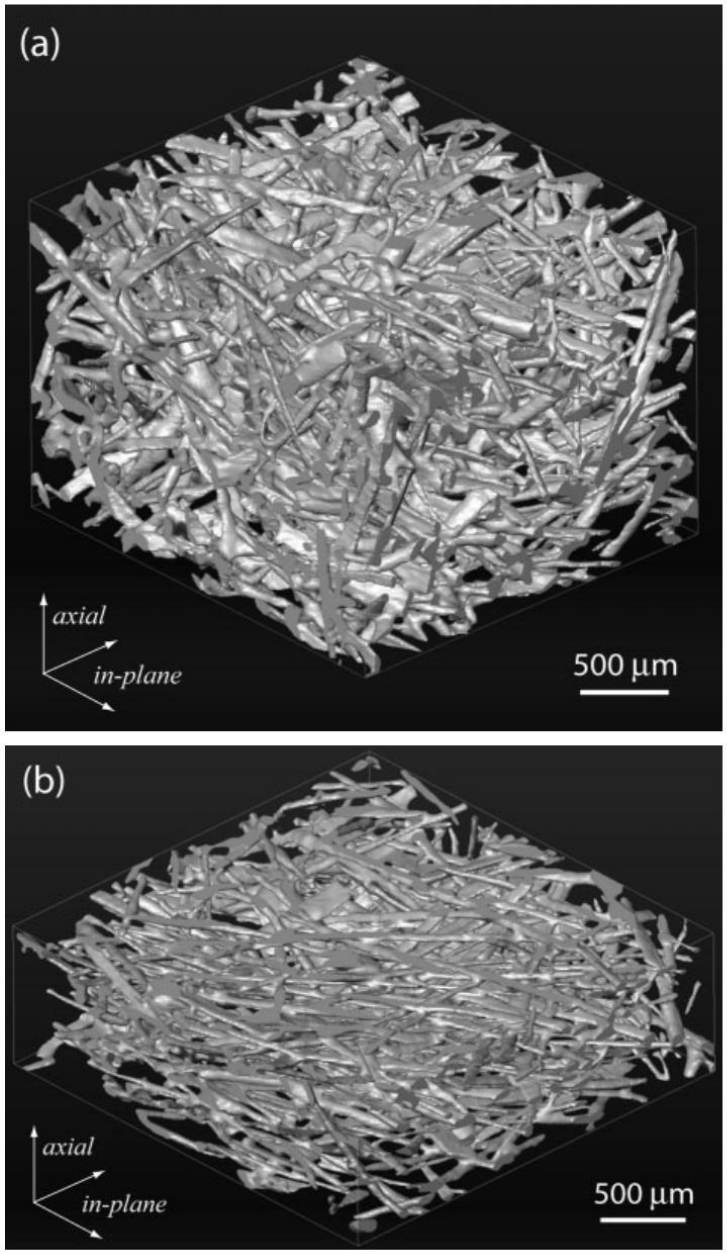
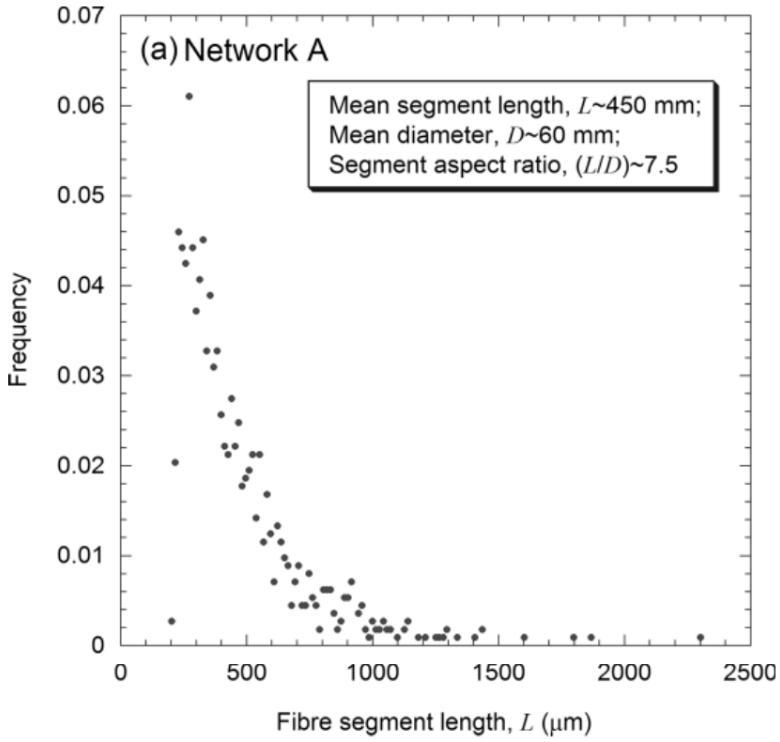


Fig. 3. Three-dimensional tomographic reconstructions of the two types bonded fibre networks being investigated: (a) network A and (b) network B.



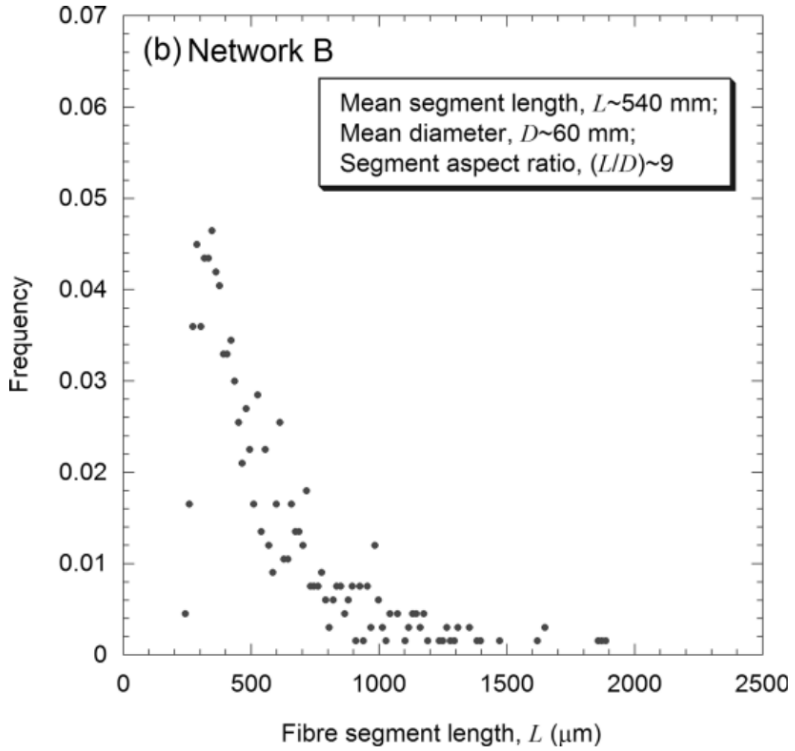
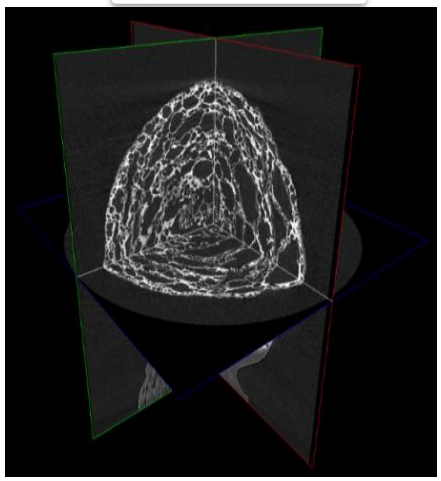


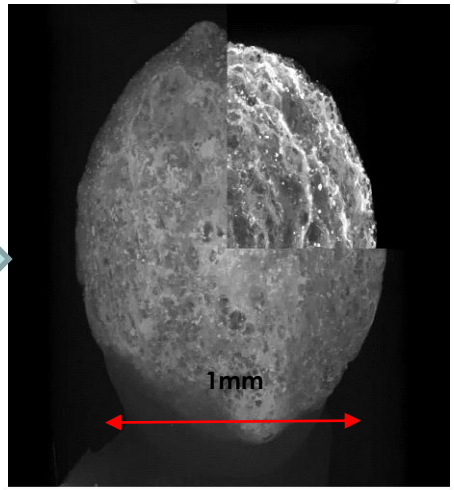
Fig. 6. Fibre segment length (B-B path) distributions for (a) network A and (b) network B materials.

X-ray tomography

Various sections



Résolution 2 **µm**



Sample : Cu KOH 63% 700°C

Resolution 0.4 **µm**

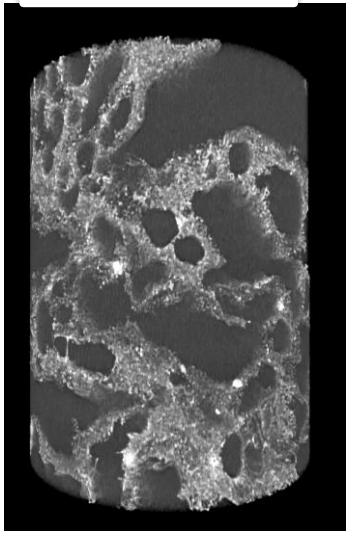


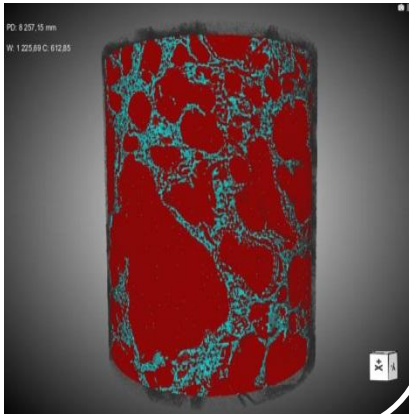
Image rebuilding Dragonfly ORS

Estimation of macroporous volume

Samples	CS+Cu KOH	CS+Cu NH_3	Raw Cs NH_3
Total macroporous volume (cm^3/g) Dragonfly	0.63	1.20	0.96

Cu nanoparticle distribution

Interconnectivity of macroporosity



IV. Détermination de l’énergie d’adsorption

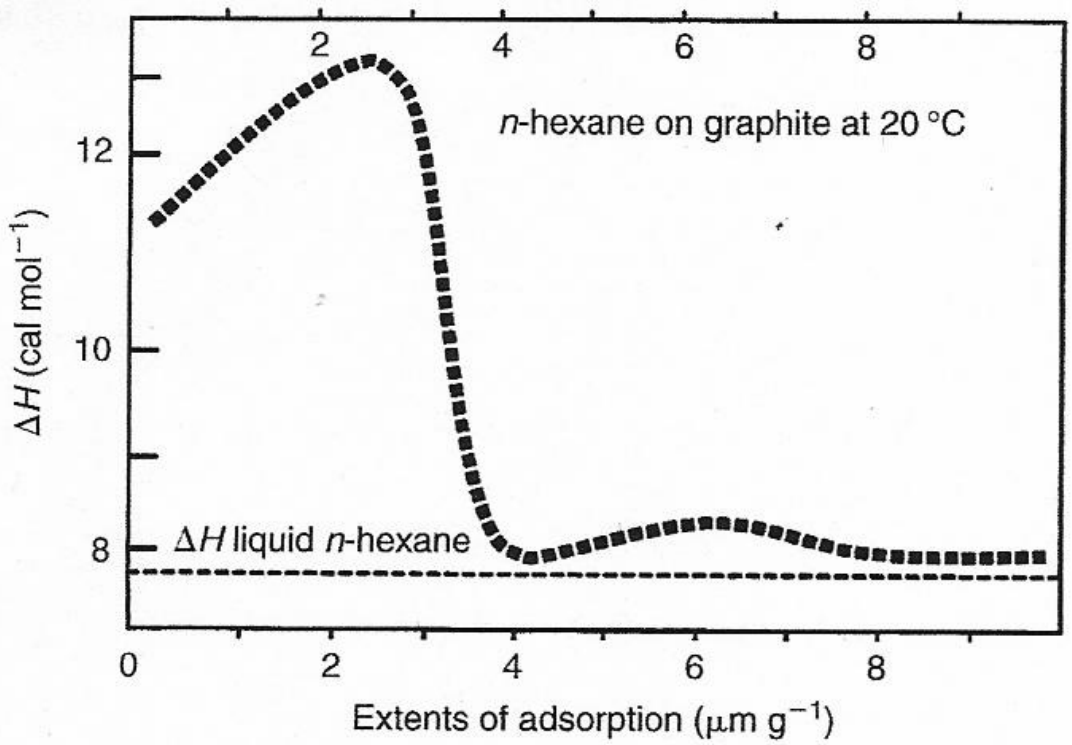
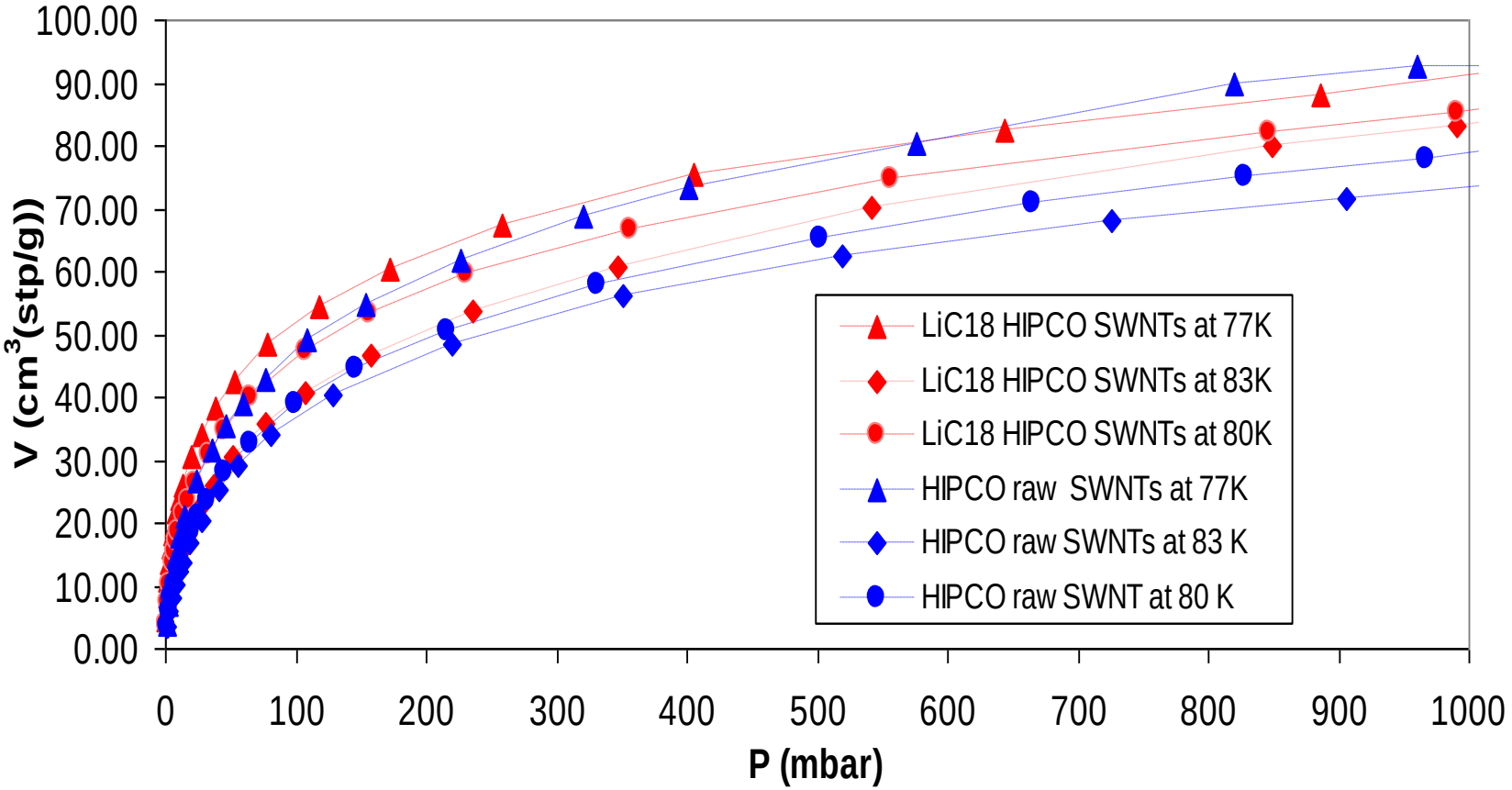


Figure 4.43. The variation of differential heats of adsorption (ΔH in cal mol^{-1}) of *n*-hexane at 20 °C on a graphitized carbon black, with coverage, (μmol m^{-2}) (Isirikyan and Kiselev, 1961) (1 cal = 4.2 J).

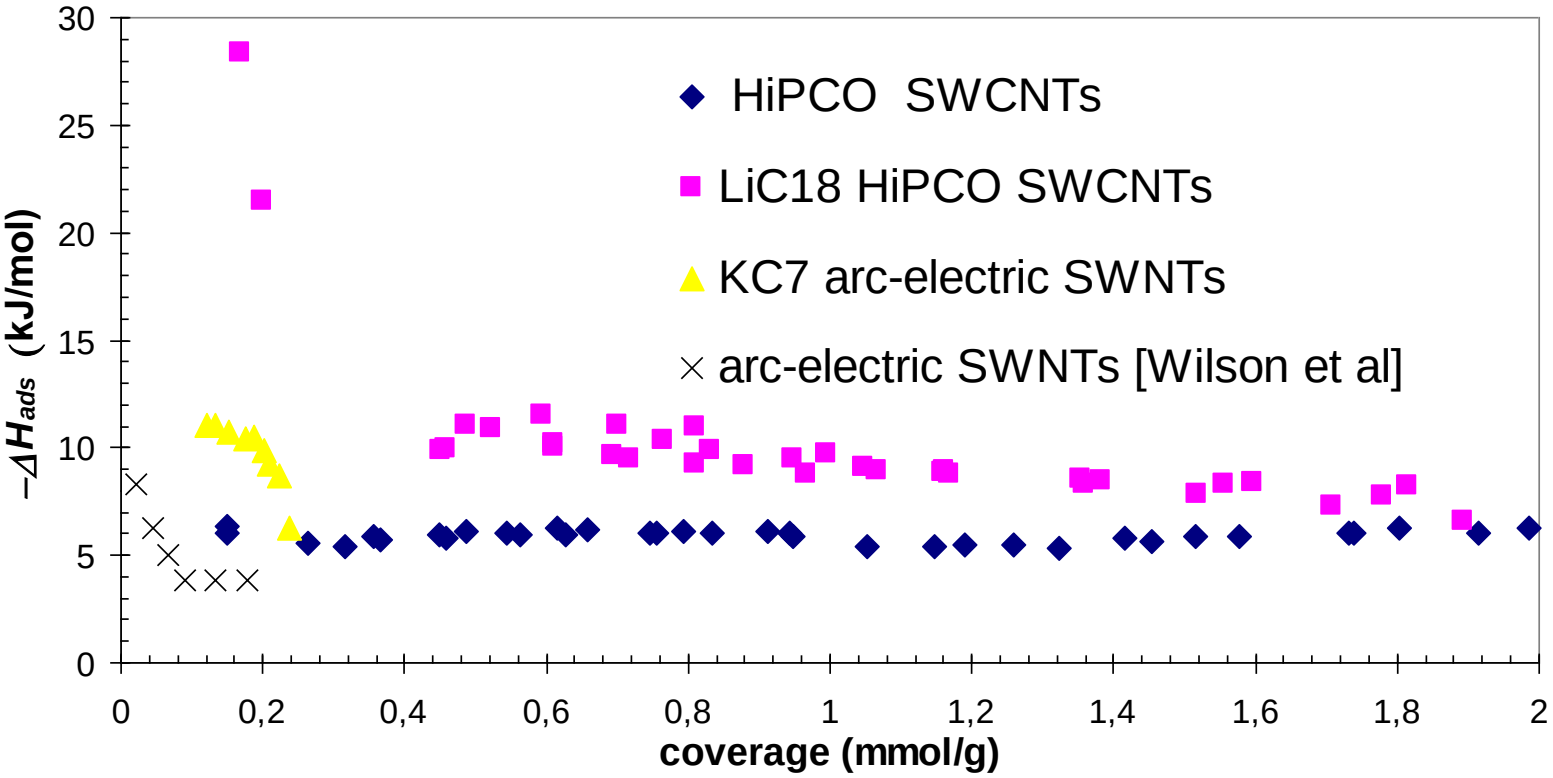
D_2 adsorption isotherms of pristine and doped (LiC_{18}) HiPCO nanotubes at 83 K, 80 K et 77 K



Isosteric heats of D_2 adsorption in doped and pristine SWNTs from the isotherms at T~80K

Clausius Clapeyron Law : $Ln(P)=\Delta H°_{ads}/RT-\Delta S°/R$

$q_{st}=-\Delta H°_{ads}$



[T. Wilson, A. Tyburski, M. M. R. DePies, O. E. Vilches, D. Becquet, M. Bienfait, J. Low Temperature Phys. 126 (2002) 403-408.]