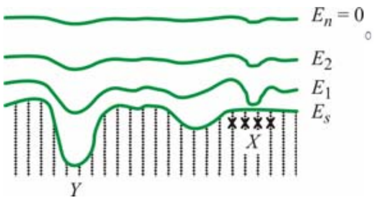
The corresponding text from Physical chemistry of surfaces Part 1 (CH server)

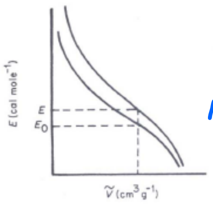
1) p. 41-52 (till Table 3.4, inclusive)
2) p. 52 (from 3.7.2) till p. 59

3. Dubinin-Radushkevich (DR) model

Pore filling $\Theta = \frac{W}{W_0}$

Adsorption potential of the vapour (M.) $A = -RT\ln\left(\frac{p}{p_0}\right)$





M. Polanyi

$$\frac{W}{W_0} = exp\left[-\left(\frac{A}{E}\right)^2\right]$$

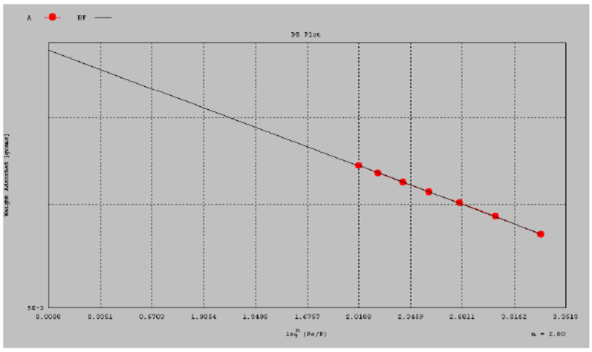
Characteristic adsorption energy of the surface, Gaussian distribution

$$\frac{W}{W_0} = exp\left[-\frac{(RT)^2 \cdot ln^2\left(\frac{p_0}{p}\right)}{E^2}\right]$$

DR- plot

$$\frac{W}{W_0} = exp\left[-\frac{(RT)^2 \cdot ln^2\left(\frac{p_0}{p}\right)}{E^2} \right]$$

lnW



$ln^2(p_0/p)$

3

Interpretation of the fitted parameters

1. Derivation of specific surface area from monolayer capacity

$$S_A = n_m \cdot N_A \cdot a_s \qquad \frac{m^2}{g}$$

CONDITIONS!!!!

n_m: Monolayer capacity

N_A: Avogadro's number

a_s: Area occupied by a single adsorbent

1) (Most often) N_2, 77 K
2) Initial part of the isotherm (p/p_0=0.05-0.35)
3) n_m from the linear plot of minimum 5 measured points
4) a_s=0.162 nm^2

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Surface area of selected solids

Activated carbon	600-1400 m^2/g
Silica	300- 600 m^2/g
Catalysts	50- 300 m^2/g
Dust (particle diameter 0.1 mm)	0.1-0.5 m^2/g

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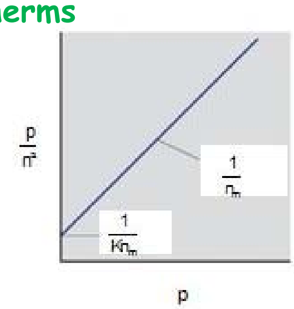
2. The adsorption energy

- Can be measured directly (calorimetry)
- Indirect info from the isotherms

Langmuir model

$$\frac{p}{n^s} = \frac{1}{Kn_m} + \frac{p}{n_m}$$



$$-RT \ln K = \Delta G$$

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

BET model

$$C = e^{\frac{(E_a - E_L)}{RT}}$$

DR model

E characteristic adsorption energy

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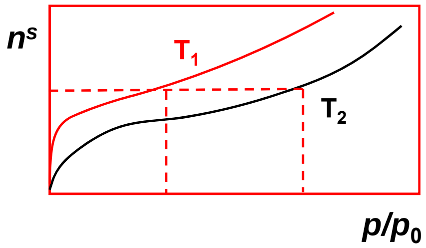
3. Isosteric heat of adsorption

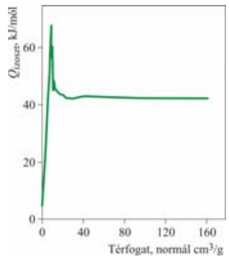
$$\left(\frac{\partial \ln p}{\partial T}\right)_{n^s} = \frac{\Delta H_m^{ads}}{RT^2}$$

lnp vs. 1/T

→ ΔH_m^{ads}



$$\Delta H_m^{ads} \approx Q_{izost} = f(n^s)$$



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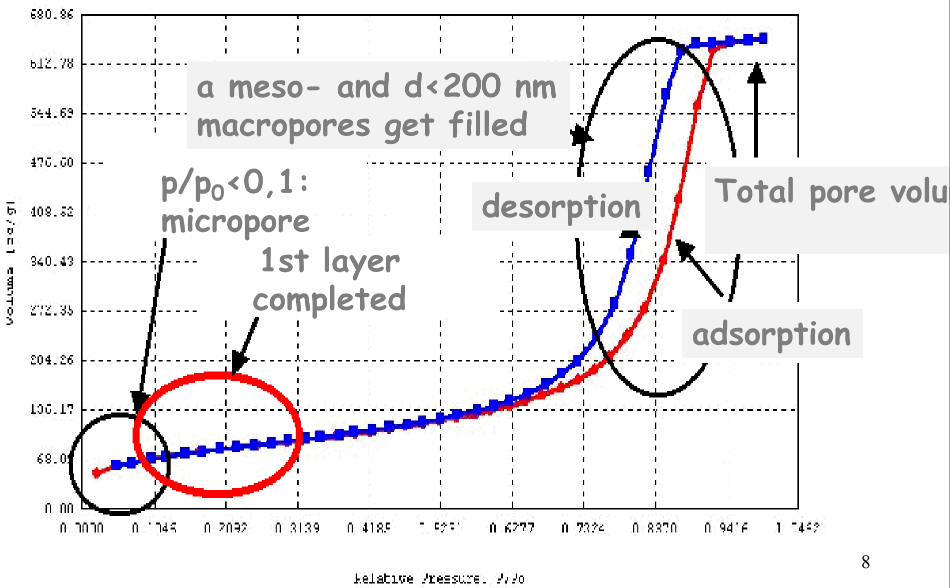
The story told by the adsorption isotherm



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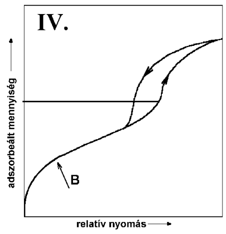
Adsorption hysteresis:



$$\Delta G_{ads} = -RT \ln \frac{p_{ads}}{p_0}$$

$$\Delta G_{des} = -RT \ln \frac{p_{des}}{p_0}$$

$$\Delta G_{des} < \Delta G_{ads}$$

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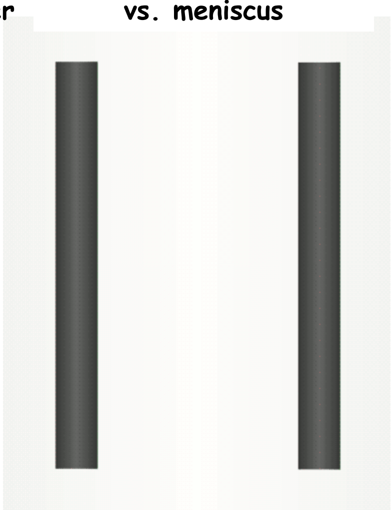
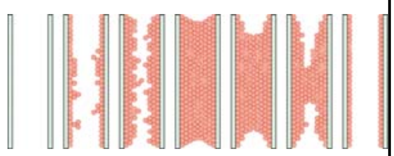
Adsorption/desorption in mesopores::

adsorption and desorption

layer vs. meniscus





$$r_p = r_K + t$$

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Capillary condensation

layer | meniscus

The change of volume and surface area in a

cylindrical pore with a radius r | semi-sphere wits a radius r

Adsorption: on the surface of a cylinder: $r \rightarrow (r\text{-}dr)$

$$V = r^2 \pi l \qquad A_s = 2r\pi l$$

$$dA_s = -2\pi l dr$$

$$dV = -2\pi r l dr$$

$$\frac{dV}{dA_s} = r$$

Desorption:

$$V = \frac{4r^3\pi}{3 \cdot 2} \qquad A_s = \frac{4r^2\pi}{2}$$

$$dA_s = -4\pi r dr$$

$$dV = \frac{-12\pi r^2 dr}{6} = -2\pi r^2 dr$$

$$\frac{dV}{dA_s} = \frac{r}{2}$$

GEOMETRY

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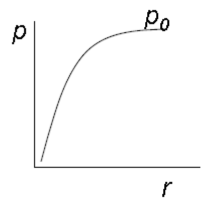
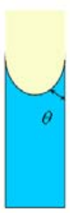
POSSIBLE REASONS OF THE HYSTERESIS:

1. The different mechanism of ads/des

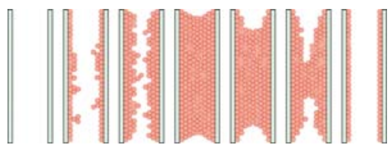
Saturation pressure in a cylindrical capillary of radius r_K:



$$\ln \frac{p}{p_0} = -\frac{2\gamma^{LV} V_m^L}{r_K RT}$$ **Kelvin equation**



$\cos\Theta = 1$



$$r_p = r_K + t$$

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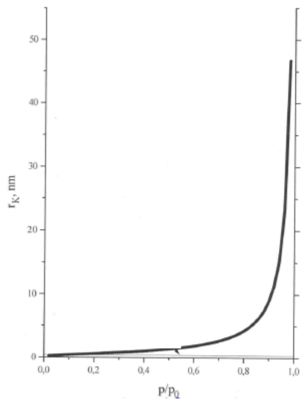
➨ Pore size distribution can be deduced with the Kelvin equation

$$\ln\frac{p}{p_0}=-\frac{2\gamma^{LV}V_m^L}{r_K RT}$$

Limits of the Kelvin equation:

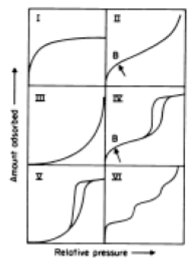
$r_{min}\sim 1nm \qquad r_{max}\sim 25nm$



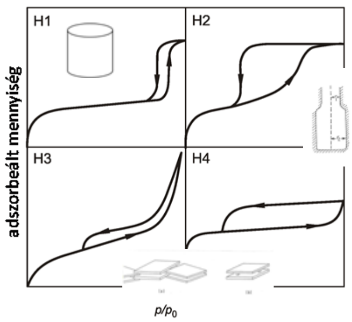
$r=f(p/p_0)$

$V=f(p/p_0)$

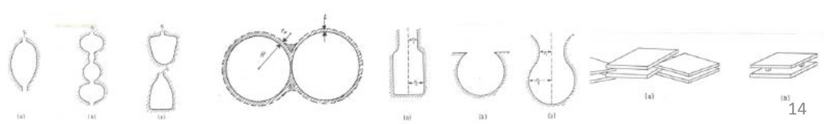
$V=f(r)$



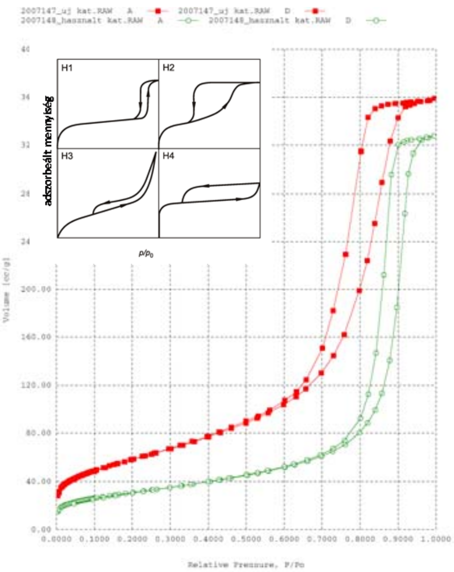
2. Influence of the pore structure/shape (interactions, diffusion, network effect)



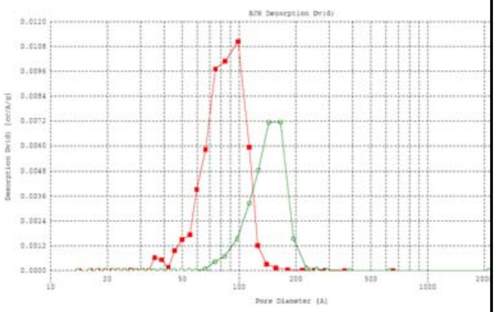
H1 cylinder
H2 network, ink-bottle
H3-H4 slit-like



Example: ageing of an Alumina supported Ir catalyst



Sample	S_{BET}, m^2/g	V_{tot}, cm^3/g
fresh	210	0,556
used	109	0,508



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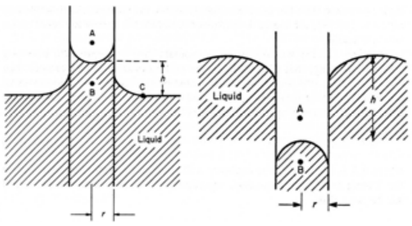
What shall we do with the macropores?

The range of Kelvin is limited

$$\ln\frac{p}{p_0} = -\frac{2\gamma^{LV}V_m^L}{r_k RT}\cos\theta \qquad r_{min} \sim 1nm \qquad r_{max} \sim 25nm$$

Mercury porosimetry



Capillary attraction $\theta < 90°$ repulsion $\theta > 90°$

Volumetric work: $W = V\Delta P$ $\Delta P = hg(\rho_f - \rho_g)$

Work of wetting: $\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$

$W = \gamma_{SL}\Delta A - \gamma_{SG}\Delta A = -\Delta A\gamma_{LG}\cos\theta$

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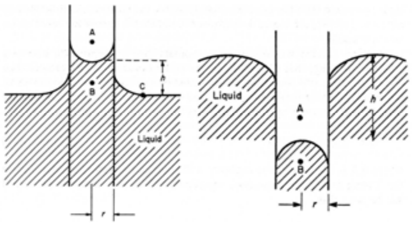
How to measure macroporosity?

Mercury porosimetry



Cylindrical pores:

$$P \cdot r = -2 \cdot \gamma \cdot \cos\theta \qquad \text{Washburn-equation}$$

$\gamma_{Hg} = 480 \frac{N}{m}$ és $\theta = 140^\circ$ $\quad P$ excess pressure

Commercial instruments:

7.5 μm	atmospheric pressure
3.5 nm	P=2000 bar
1.5 nm	P=5000 bar

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$-\Delta A \gamma_{LG} \cos\theta = V \Delta P$

For cylindrical pores:

$$P \cdot r = -2 \cdot \gamma \cdot \cos\theta \qquad \text{Washburn-equation}$$

$\gamma_{Hg} = 480 \frac{N}{m}$ és θ=140 ° $\quad P$ excess pressure

Commercial instruments:

7.5 μm	atmospheric pressure
3.5 nm	P=2000 bar
1.5 nm	P=5000 bar

Drawback:
- environmental
- contamination of the sample
- damage of the sample

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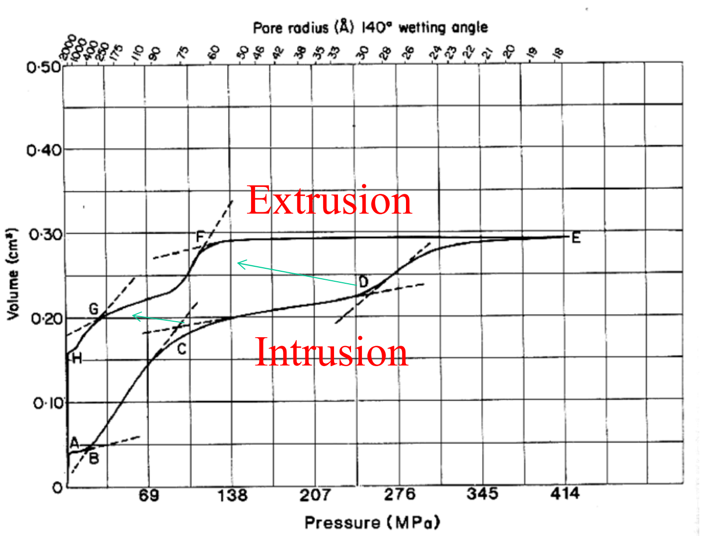
Porogram



B: 500 Å
C: 75 Å
D: 29 Å

Porous Al_2O_3 powder

Various methods for the determination of pore size distribution