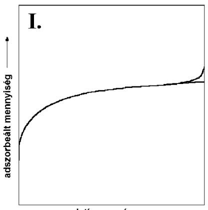
Answers will be given to

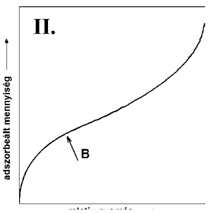
Adsorption capacity
Pore shape and pore size distribution
The role of the surface in diffusion limited processes
Activity of catalysts
Stability, properties of composites
(e.g. rubber – carbon black)

1

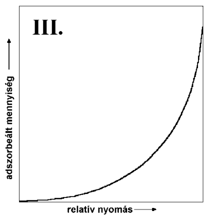
Classification of the S/G isotherms (IUPAC)



Microporous materials with low external surface e.g. activated carbon, zeolite, molecular sieve, some porous oxides. Chemisorption



Reversible isotherm, nonporous or macroporous materials



Reversible isotherm, convex in the total p/p_0 range

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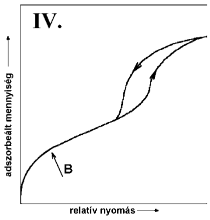
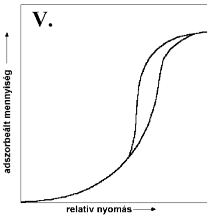
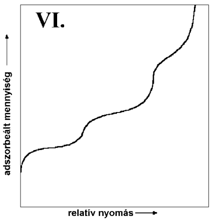


Irreversible isotherm, mesoporous sorbents



Rare, symilar to Type III,
weak adsorbent – adsorbate interaction



Stepwise multilayer adsorption.
Well defined, ordered solid surface.
E.g., Ar or Kr on graphite at 77 K

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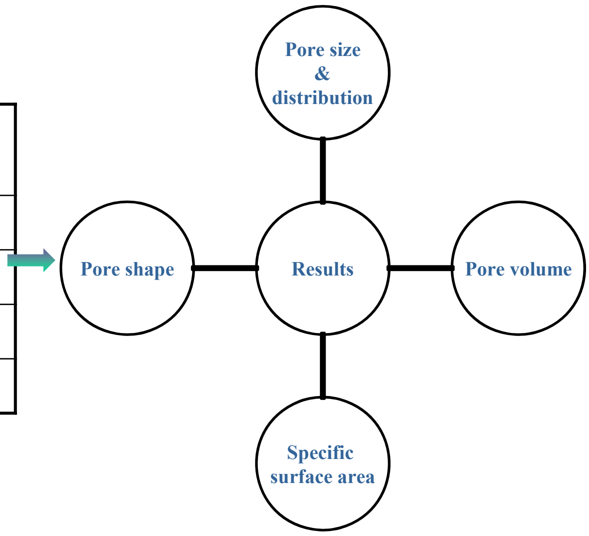
3. Interpretation

Points	P/P^o	Volume adsorbed
1		
2		
3		

OUTPUT

Weight of sample



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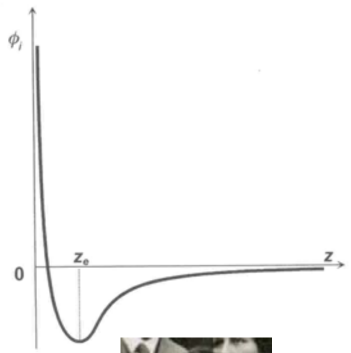
Physisorption interactions



$$\varepsilon_D(r) = -C/r^6$$ London, 1930

$$\varepsilon_R(r) = B/r^m$$ polarizability

$$\varepsilon(r) = B/r^{12} - C/r^6$$

The pair interactions are additive:

$$\phi_i(z) = \sum_j \varepsilon_{i,j}(r_{i,j})$$

Fritz Wolfgang London
1900-1954

John Edward Lennard-Jones
1894-1954

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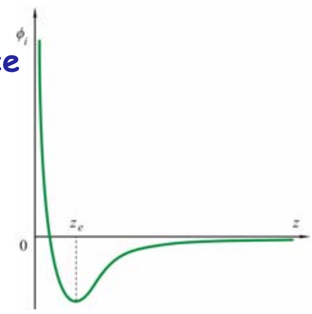
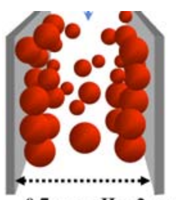
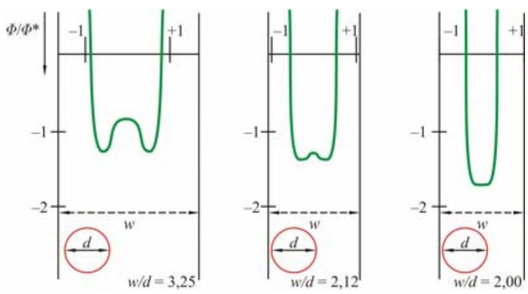
Mechanism of adsorption

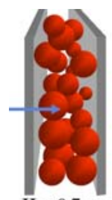
Planar surface





In pores





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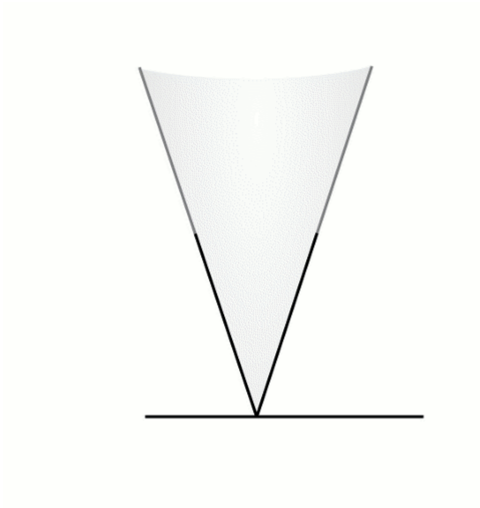
Effect of the pore size



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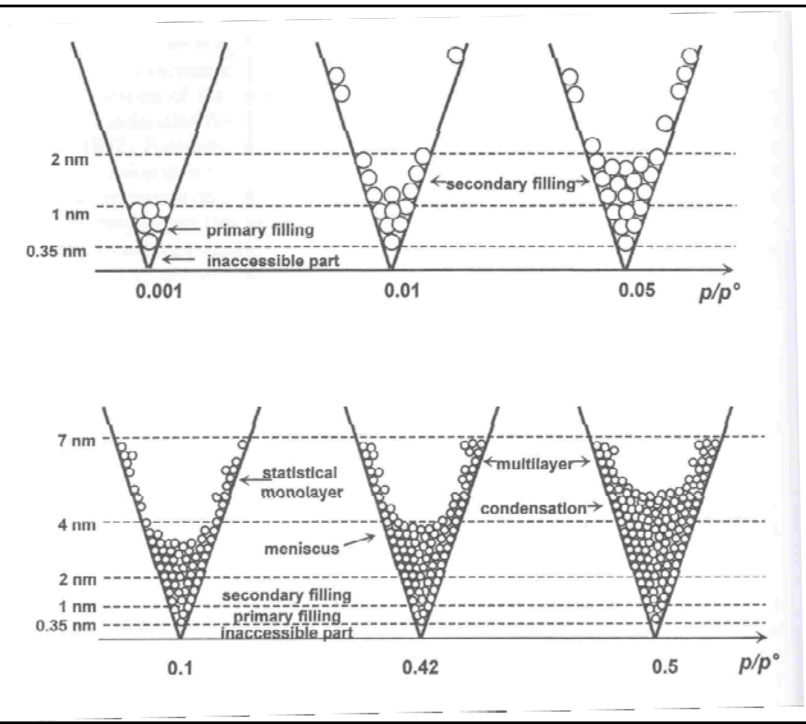
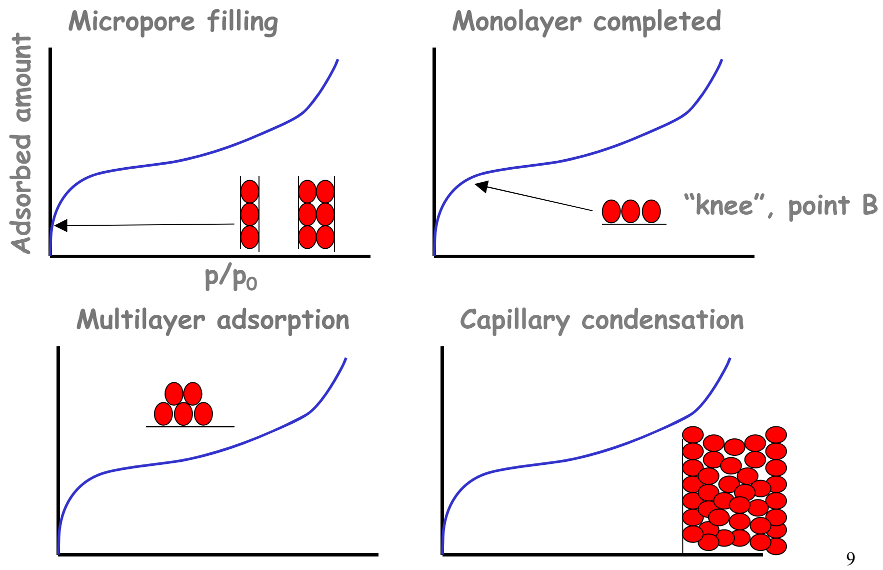


Regions of the adsorption isotherm



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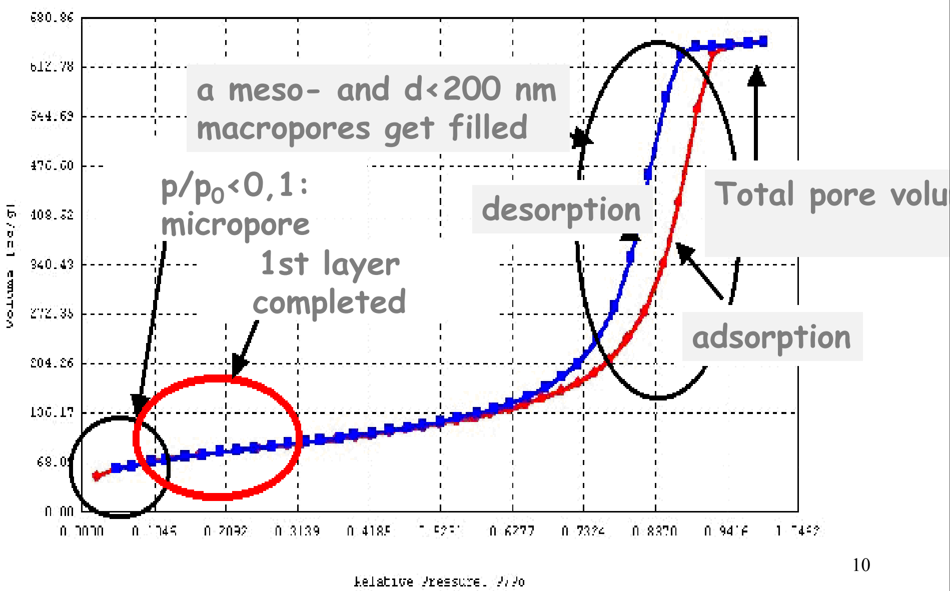
Information from the adsorption isotherm



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Models

Without a model: shape, total pore volume (all the pores are filled with liquid N_2)

p/p_0	Mechanism	Model
10^{-7}-0.02	Micropore filling	GCMC, HK, SF, DA, DR, MP
0.01- 0.3	Development of the monolayer	DR
0.05- 0.3	Complete monolayer	BET, L
> 0.1	Multilayer adsorption	t-Plot (de-Boer, FHH), α-Plot
> 0.35	Capillary condensation	BJH, DH, DFT

BET: Brunauer, Emmett & Teller, BJH: Barrett, Joyner & Halenda, DA: Dubinin-Astakhov, DFT: density function theory, DH: Dollimore-Heal, DR: Dubinin-Radushkevich, GCMC: Grand Canonical Monte Carlo, HK: Horváth-Kawazoe, L: Langmuir, MP: mikropórus-módszer, SF: Saito-Foley

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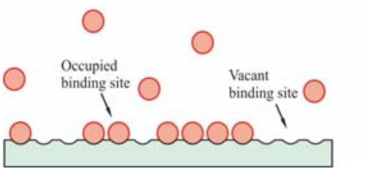
Langmuir model



*Planar surface
*Binding sites of equal energy
*Monolayer coverage

$$A(g) + S \rightleftharpoons AS \qquad \Theta = \frac{N_{occupied}}{N_{total}}$$

$$v_a = k_a(N_{total} - N_{occupied})p$$

$$v_a = k_a N_{total}(1-\Theta)p$$

$$v_d = k_d N_{occupied} = k_d \Theta N_{total}$$

In equilibrium: $v_a = v_d$

$$\frac{N_t\theta}{N_t(1-\theta)p} = \frac{k_a}{k_d} = K$$

Irving Langmuir (1881-1957)

1932: Nobel Prize in Chemistry

in for his work in surface chemistry

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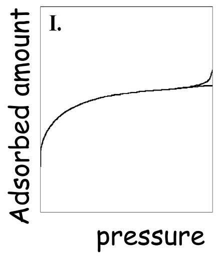
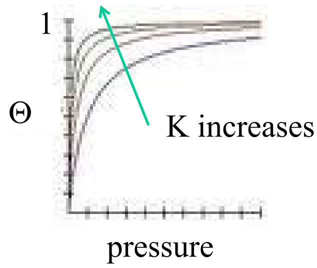
$$\Theta = \frac{K \cdot p}{1 + K \cdot p} \qquad K = \frac{k_a}{k_d}$$



n^s: adsorbed gas/g adsorbent
n_m: monolayer capacity

$$\Theta = \frac{n^s}{n_m}$$

$$n^s = \frac{n_m \cdot K \cdot p}{1 + K \cdot p} = \frac{n_m \cdot K \cdot p / p_0}{1 + K \cdot p / p_0}$$



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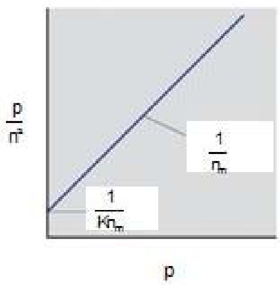
Determination of the Langmuir parameters

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

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



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variations

Virial equation

$$n^a = \frac{n_m K x}{1 + Kx}\left[1 + \frac{x}{1+x} + \left(\frac{x}{1+x}\right)^2 + \ldots\right] \qquad x = p/p_0$$

Toth (surface heterogeneity)

$$n^a = \frac{n_m K p}{[1 + (Kp)^t]^{1/t}}$$

$0 \le t \le 1$
heterogeneity parameter

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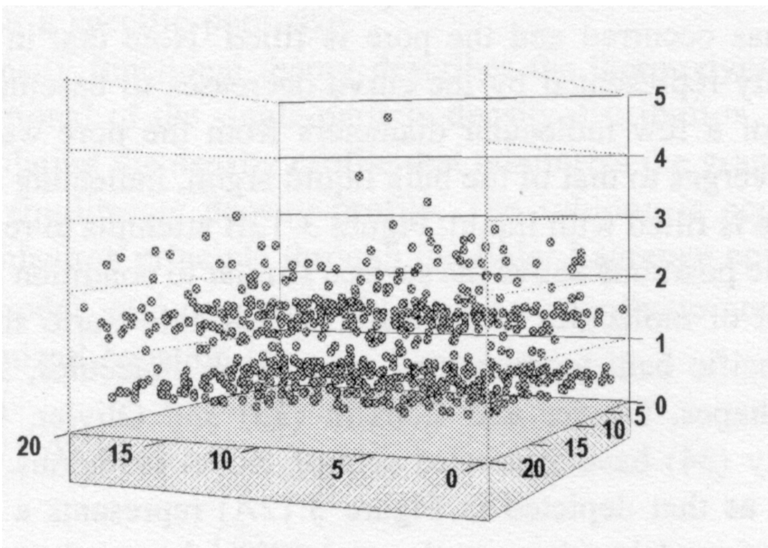

Monte Carlo simulation of multilayer adsorption

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