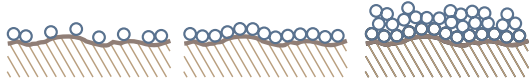


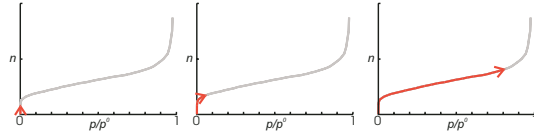
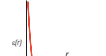
# Some Physical Aspects of Adsorption

## Non-porous Solid



The dispersion forces between the adsorptive molecules and the surface atoms or ions of the adsorbing solid are described by the Lennard-Jones potential [1]:

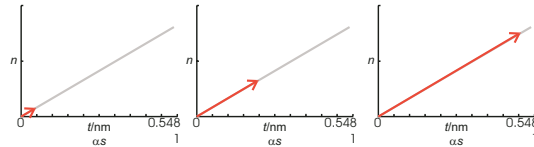
$$e(r) = -Cr^{-6} + Br^{-12}$$



Brunauer, Emmet and Teller [2] developed a model describing the adsorption on surfaces considering multilayers:

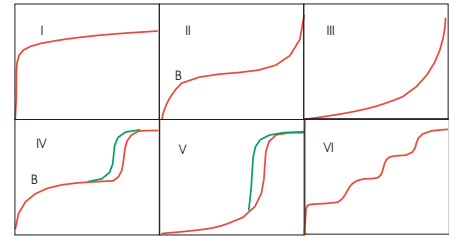
$$V_{ads} = V_m \frac{C(p/p^0)^{-1} - (N+1)(p/p^0)^{-N} N(p/p^0)^{N-1}}{1 - (p/p^0)^{-1} + (C-1)(p/p^0)^{-N} - C(p/p^0)^{-N-1}}$$

This equation can be linearized setting the number of layers to infinite:



Giving the monolayer volume and thus the surface area:

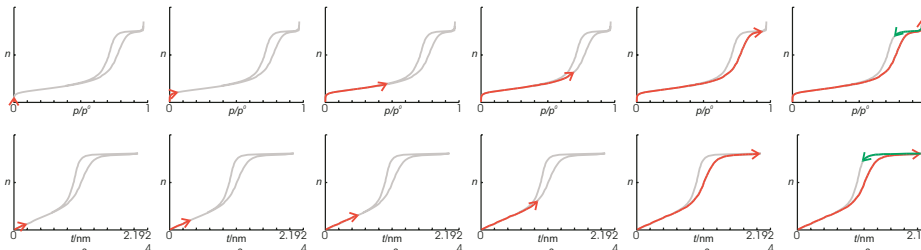
$$V_m = \frac{1}{\text{slope} + \text{intercept}} \quad A = \frac{LV_m}{V_{mol}} \rho_s$$



Adsorption isotherms can be classified in six types according to IUPAC [3,4]. The Type I is typical for microporous solids and chemisorption isotherms. Type II is shown by finely divided nonporous solids. Type III and Type V are typical of vapors, i.e. water on hydrophobic solids. Type IV and Type V feature an hysteresis loop generated by the capillary condensation in mesopores. The rare Type VI, the steps-like isotherm, is shown e.g. with nitrogen on special carbons.

Classification of pores according to their width  
 Micropores Less than 2 nm  
 Mesopores Between 2 nm and 50 nm  
 Macropores Larger than 50 nm

## Mesoporous Solid



At low relative pressures the surface of the pore walls adsorbs a multilayer of adsorbate. If the pressure is raised, droplets of adsorbate occur on optimal energetic points of the pore surface with curvatures according to the Kelvin equation. If the droplets touch each other, the pores will be filled with condensed adsorbate. This will evaporate during the desorption from pores showing core openings larger than the Kelvin radius. The adsorption branch is pore-dimension dependant, and the desorption branch is related to the pore openings.

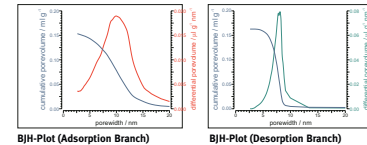
The Young-Laplace equation [1] describes the pressures at the interface of a liquid droplet and the gas phase above, using the surface tension:

$$p^* - p^0 = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

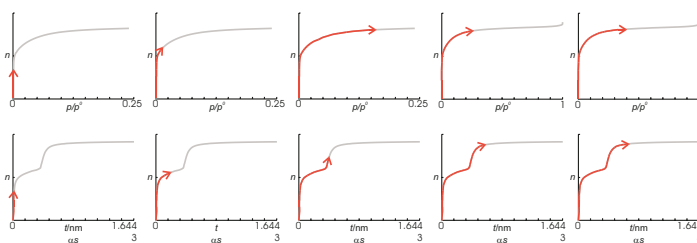
Considerations on the surface energy lead to the Kelvin equation, that put in relation the relative pressure and the curvature radius of the liquid meniscus:

$$\ln \frac{p^*}{p^0} = \frac{2\gamma V_m}{r_c p^0}$$

The Kelvin equation gives directly the core radius, considering that the wetting angle is equal to zero. Then, the pore radius is calculated taking into account the adsorbed film thickness on the pore walls and a cylindrical pore geometry [5].



## Microporous Solid



In micropores the potentials of both sides of the pore walls overlap, thus enhancing the adsorption potential [7]. The smaller the pore width the deeper the resulting potential becomes. This results in an enhanced adsorption energy, and adsorption takes place at very low pressures (see the right box figure). Micropores with the smaller width fill first, but adsorption on the surface of larger micropores occurs at the same time (secondary micropore filling).



Sorptomatic for gas adsorption  
 Thermo Electron Corporation, Milan Italy

## Symbols

as	ratio of volume adsorbed to volume adsorbed at $p/p^0=0.4$
A	surface area
$a_m$	area of one molecule of adsorbate ( $N_2: 16.2 \text{ \AA}^2$ )
d	diameter
e	potential energy
L	Avogadro's number ( $6.02210^{23} \text{ mol}^{-1}$ )
r	radius
V	volume
$p^0$	pressure
$p^*$	saturation vapour pressure
$V_m$	volume of one mole of an ideal gas (22.41 l/mol)
g	surface tension (dynes/cm)
G	Gibbs free energy
q	contact angle
n	amount of substance
$N_a$	number of molecules of adsorbate
$N_s$	number of molecules of adsorbent
s	thickness of adsorbate molecule
t	statistical thickness of adsorbed film
W	micropore volume

## Literature

- S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 2nd Ed. (1982)
- S. Brunauer, P.H. Emmet and E. Teller, J. Amer. Chem. Soc., 60, 309 (1938)
- S. Brunauer, L.S. Deming, W.S. Deming and E. Teller, J. Amer. Chem. Soc., 62, 1723 (1940)
- IUPAC Reporting physorption data for gas/solid systems, Pure Appl. Chem., 57, 603 (1985)
- E.P. Barrett, L.G. Joyner and P.P. Halenda, J. Amer. Chem. Soc. 73, 373 (1951)
- M.M. Dubinin, Quart. Rev. Chem. Soc. 9, 101 (1955)
- D.H. Everett and J.C. Powl, J. Chem. Soc., Faraday Trans. 1, 72, 619 (1976)
- G. Horvath and K. Kawazoe, J. Chem. Eng. Jap. 16, 6, 470 (1983)
- t-plot B.C. Lippens and J.H. de Boer, J. Catalysis 4, 319 (1965)
- $\alpha_s$ -plot K.S.W. Sing, Chem. & Ind. 1968, 1520

Strada Rivoltana, 20090 Rodano (MI), Italy  
 Tel. +390295059272 Fax +390295059309  
 www.thermo.com

## Nitrogen on Carbon

DP(NM)	$\theta$ LM(P/P)	P(TORR)	DG(KJ/MOL)
0.35	-19.488	2.6E-6	-12.5
0.4	-16.809	3.8E-5	-10.8
0.5	-12.167	3.9E-3	-7.79
0.6	-9.2192	7.5E-2	-5.9
0.7	-7.3229	0.5	-4.69
0.8	-6.0396	1.8	-3.86
1.0	-4.4245	9.1	-2.83
1.5	-2.6202	55	-1.68
2.0	-1.8524	119	-1.19

