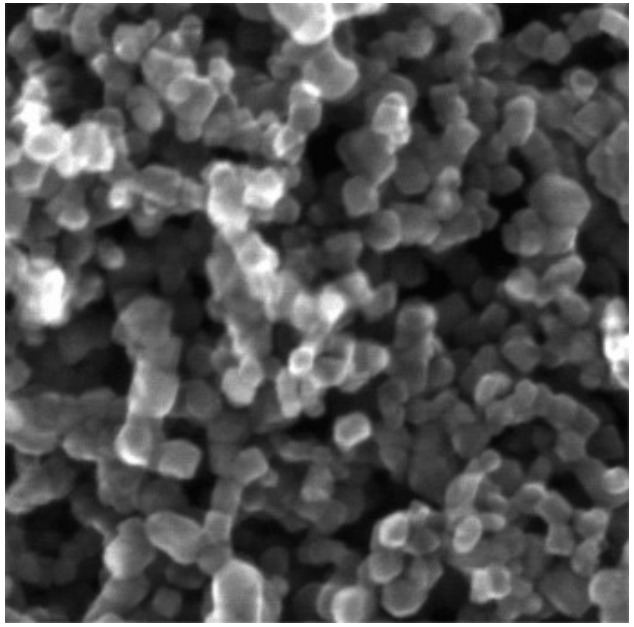
# Determination of the surface area by the BET method



# Structure

- Context
- Historical background
- Basic principles and mathematical ideas
- Measurement
- BET in modern research
- Conclusions

# Context

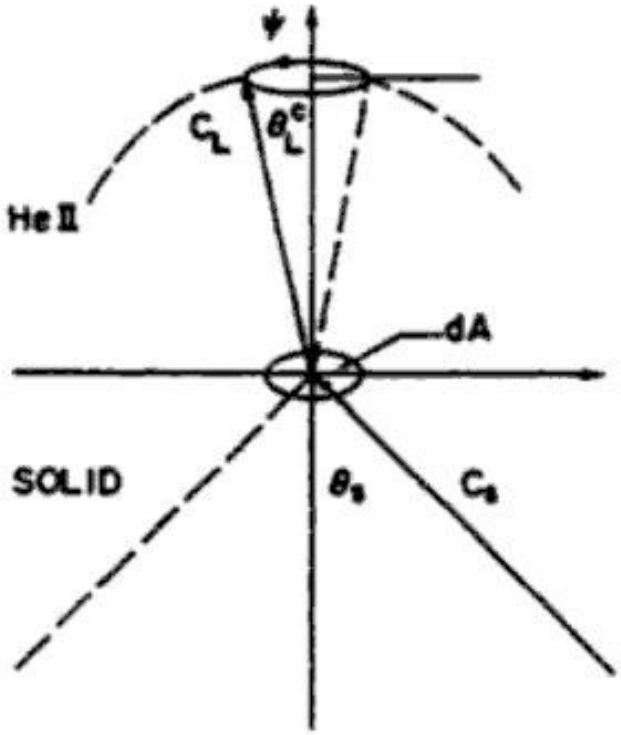
Heat exchange at the liquid (He) – solid (metal) interface

Acoustic mismatch causes weak coupling

$$\theta_L^C = \arcsin\left(\frac{c_L}{c_S}\right)$$

Ratio $c_l/c_s \approx 0.05 \rightarrow \theta \approx 3^\circ$

Photons that can cross the boundary: $1:10^5$



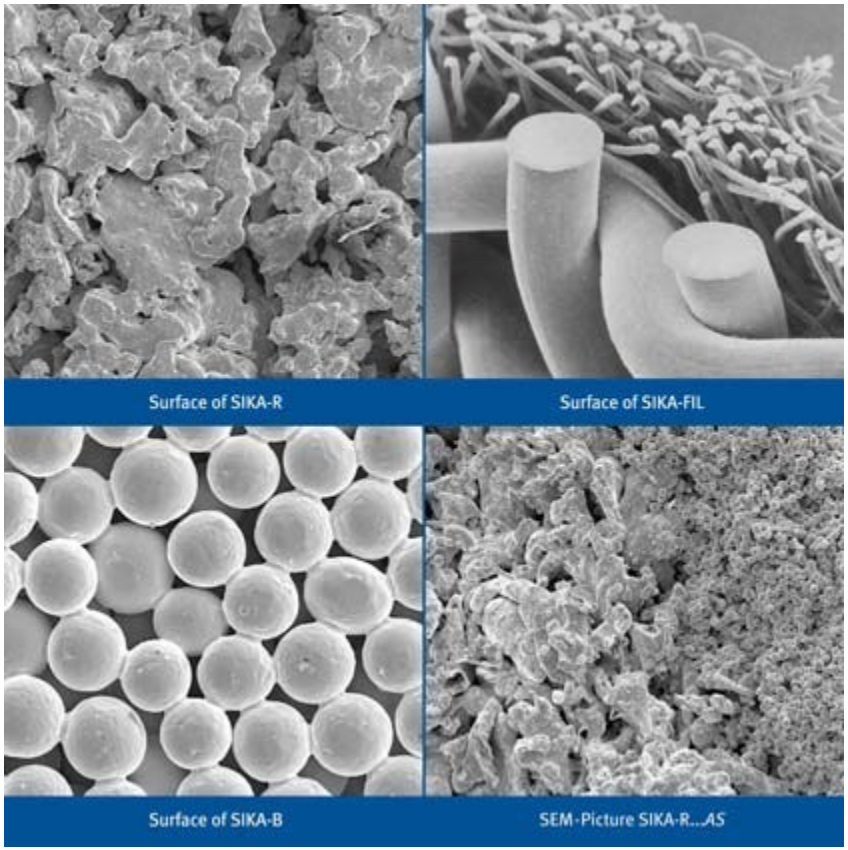

Kapitza resistance: $R_K = \frac{\Delta T}{\dot{Q}} = \frac{c}{AT^3}$

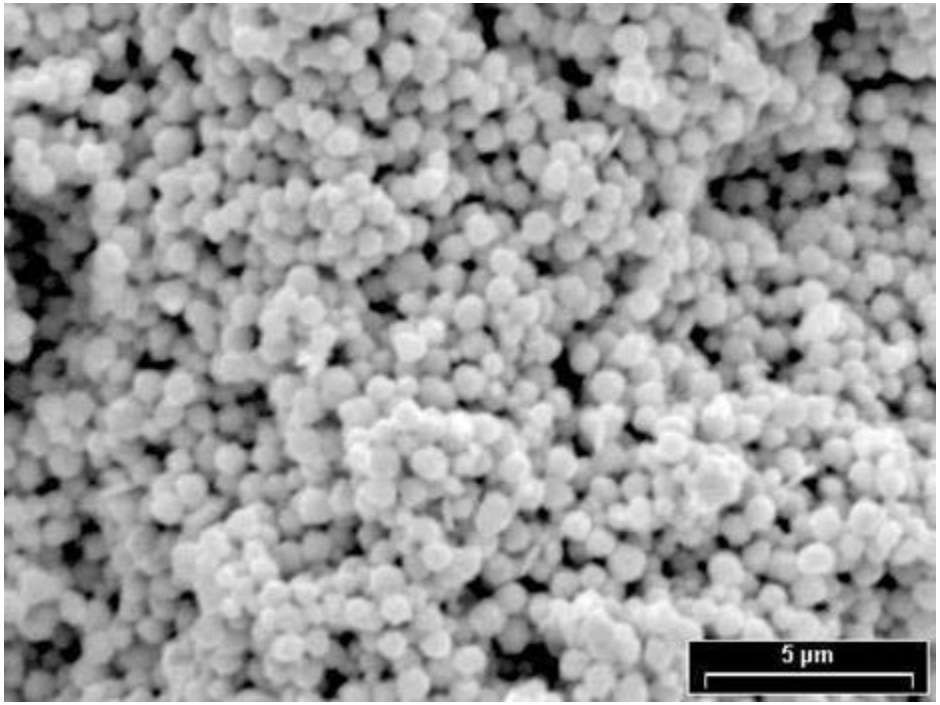
*I.M. Khalatnikov,* ***An introduction to the theory of Superfluidity****, 1965, Benjamin*

*S. W. Van Sciver,* ***Helium Cryogenics,*** *1986, Springer*

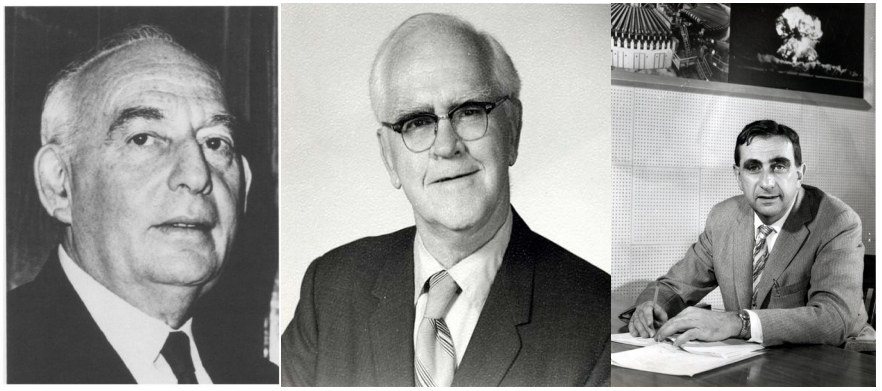
# Maximizing the surface

Sintering of silver powder



# Overview



Named after Stephen Brunauer, P.H. Emmet and Edward Teller

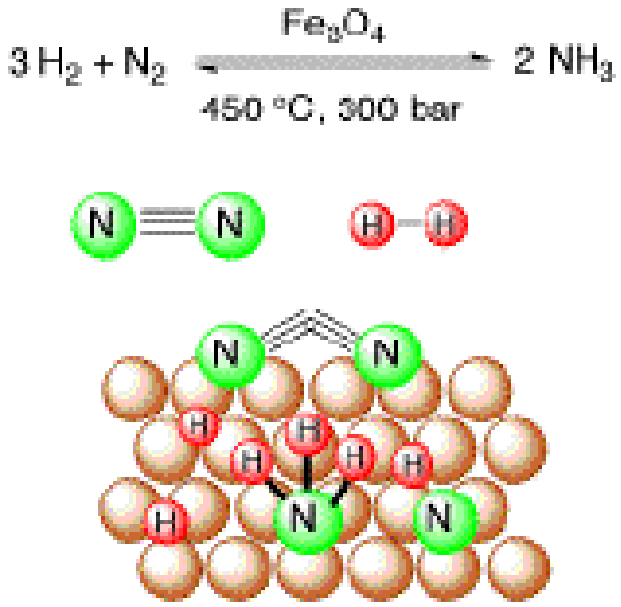
Developed in 1938

They were working on ammonia catalysts

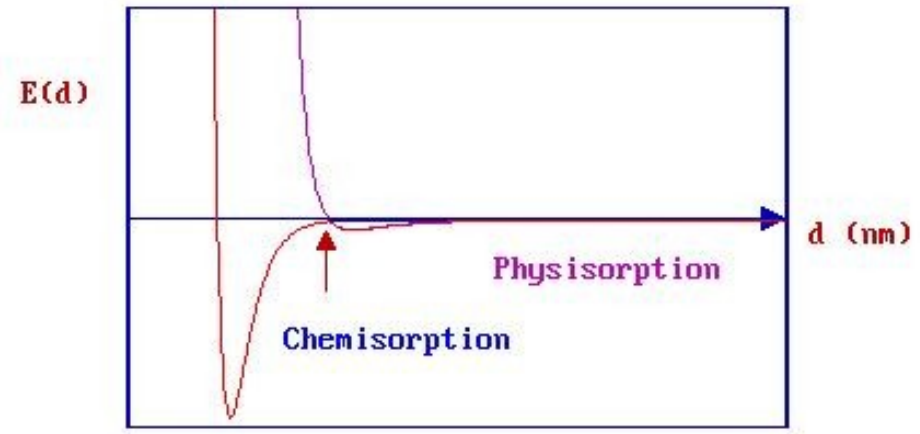
First method to measure the specific surface of finely divided and porous solids

# Applications

- Pharmaceuticals
- Catalysts
- Projectile propellants
- Medical implants
- Filters
- Cements
-
-

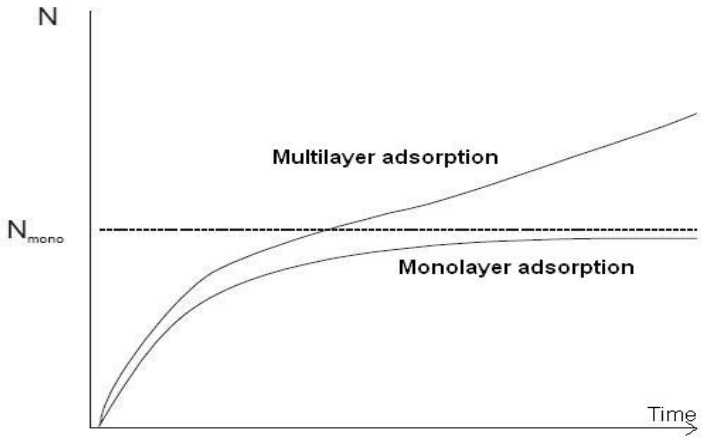


# Adsorption


Consequence of surface energy. The energy is minimized in the bulk when every atom/molecule is surrounded by neighbors.

# Adsorption



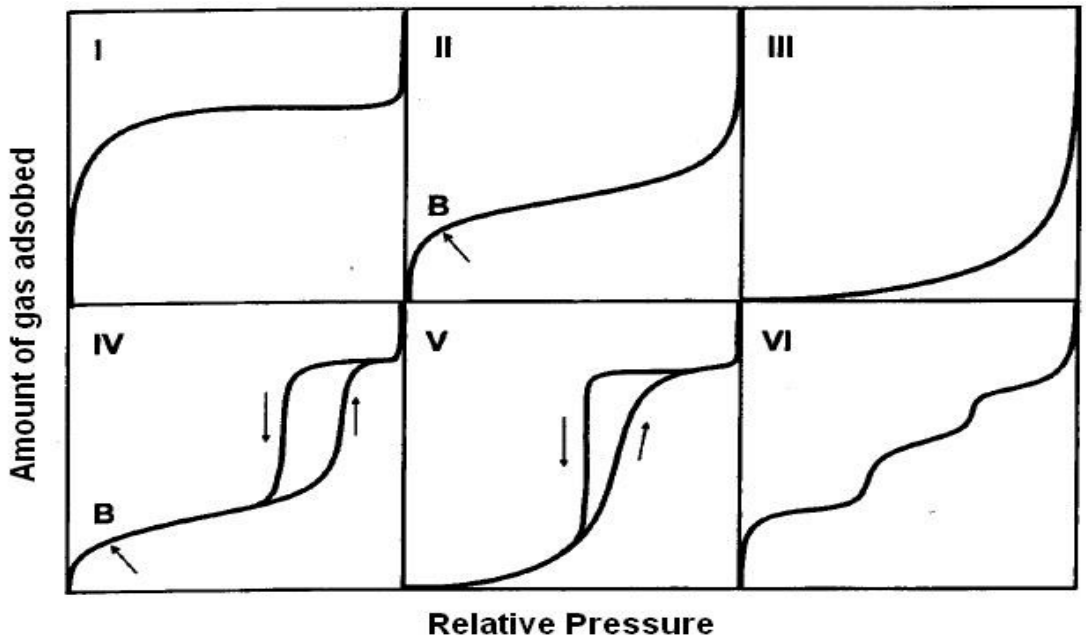

Physisorption, determined by:

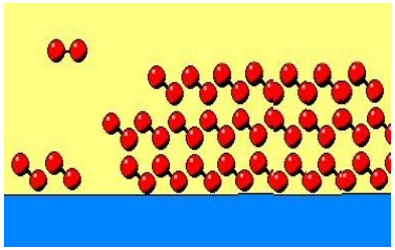
- Temperature
- Gas pressure
- Interaction between surface and gas (e.g vapor pressure)
- Surface area

Monolayer adsorption: Langmuir isotherm

Multilayer adsorption: BET theory

# Sorption-Isotherms



adsorbate

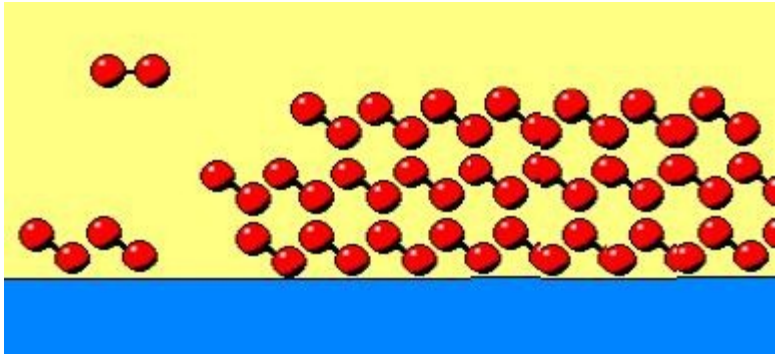
adsorbent

Classification after IUPAC 1984

Types II, IV and VI can be measured by BET method
(interaction adsorptiv-adsorbent > adsorptiv-adsorbate)

Types III, V have weak interactions between gas and adsorbent

# Assumptions




1. Homogeneous surface
2. No lateral interactions between molecules
3. Uppermost layer is in equilibrium with vapor phase
4. First layer: Heat of adsorption;
   Higher layers; Heat of condensation
5. At saturation pressure, the number of layers becomes infinite

# BET theory

- At equlilbrium:

$$a_i p s_{i-1} = b_i s_i e^{-\frac{E_i}{RT}}$$

- $s_i$ Surface area covered by i layers
- p Pressure
- $E_i$ Heat of Adsorption
- a, b Constants

- Total surface area of the sample A, the total volume adsorbed v and the volume of gas adsorbed when the entire surface is covered with:

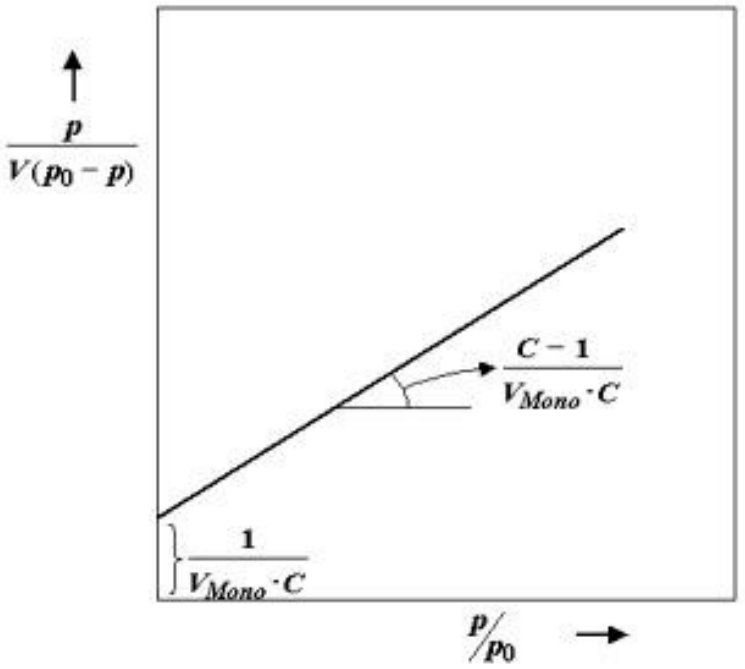
$$A = \sum_{i=0}^{\infty} s_i \qquad v = v_0 \sum_{i=0}^{\infty} i s_i \qquad v_m = v_0 A$$

Where $v_0$ is the volume of gas adsorbed on 1 $cm^2$ when it is covered by a complete unimolecular layer

# BET theory

From this, BET derived the BET equation:

$$v = \frac{v_m c p}{(p_0 - p)\{1 + (c-1)(p/p_0)\}}$$



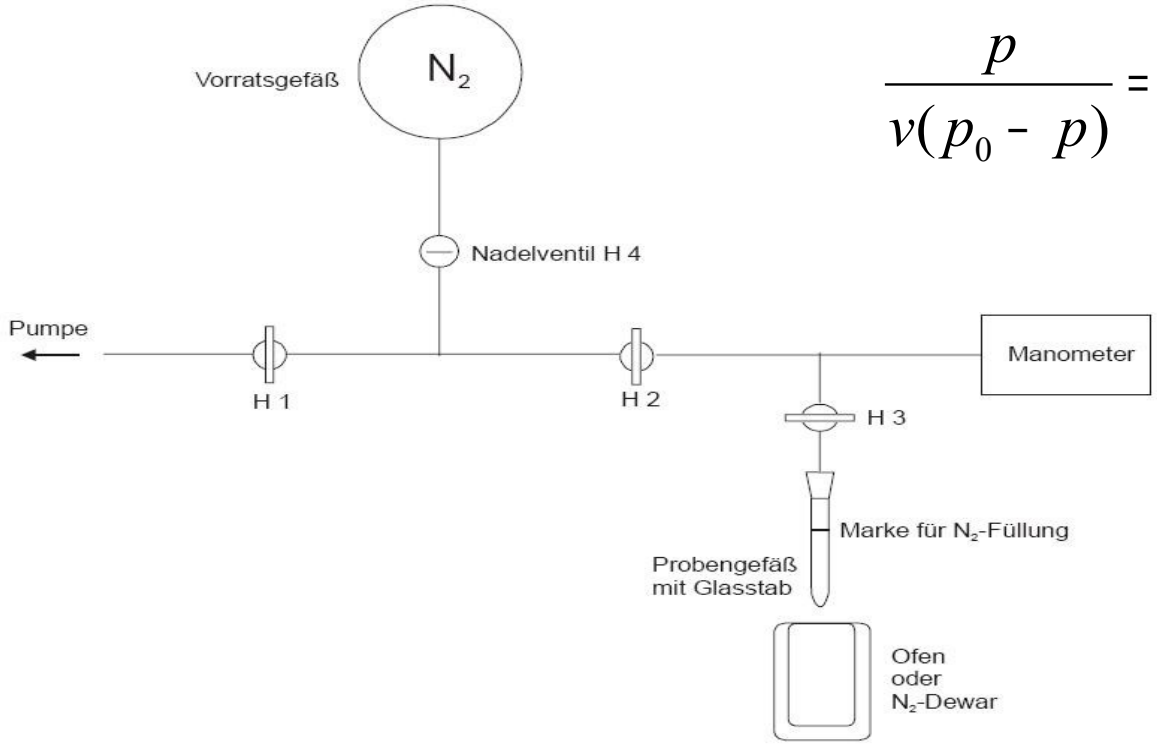

A more convenient form is the following:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_0}$$

$$c \approx e^{\frac{E_{ADS} - E_{COND}}{RT}} \qquad E_{ADS} >> E_{COND}$$

*S. Brunauer et. al. JACS, 60, 309-319 (1938)*

# Volumetric measurement




$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_0}$$

Measurement cycle to obtain equilibrium pressure and amount of gas adsorbed

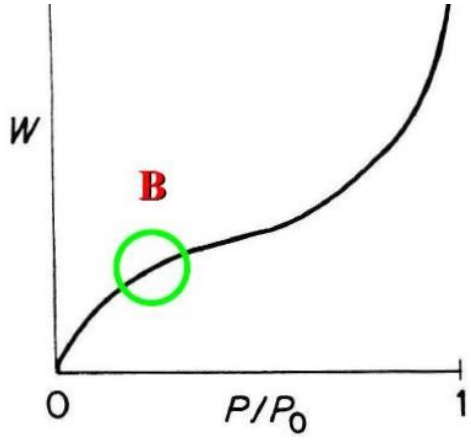
Gas: $N_2$ / $O_2$ / $CO_2$ / Krypton / He / methane

# Other methods

- Single point measurement

  ratio $p/p_0 \approx 0.03$

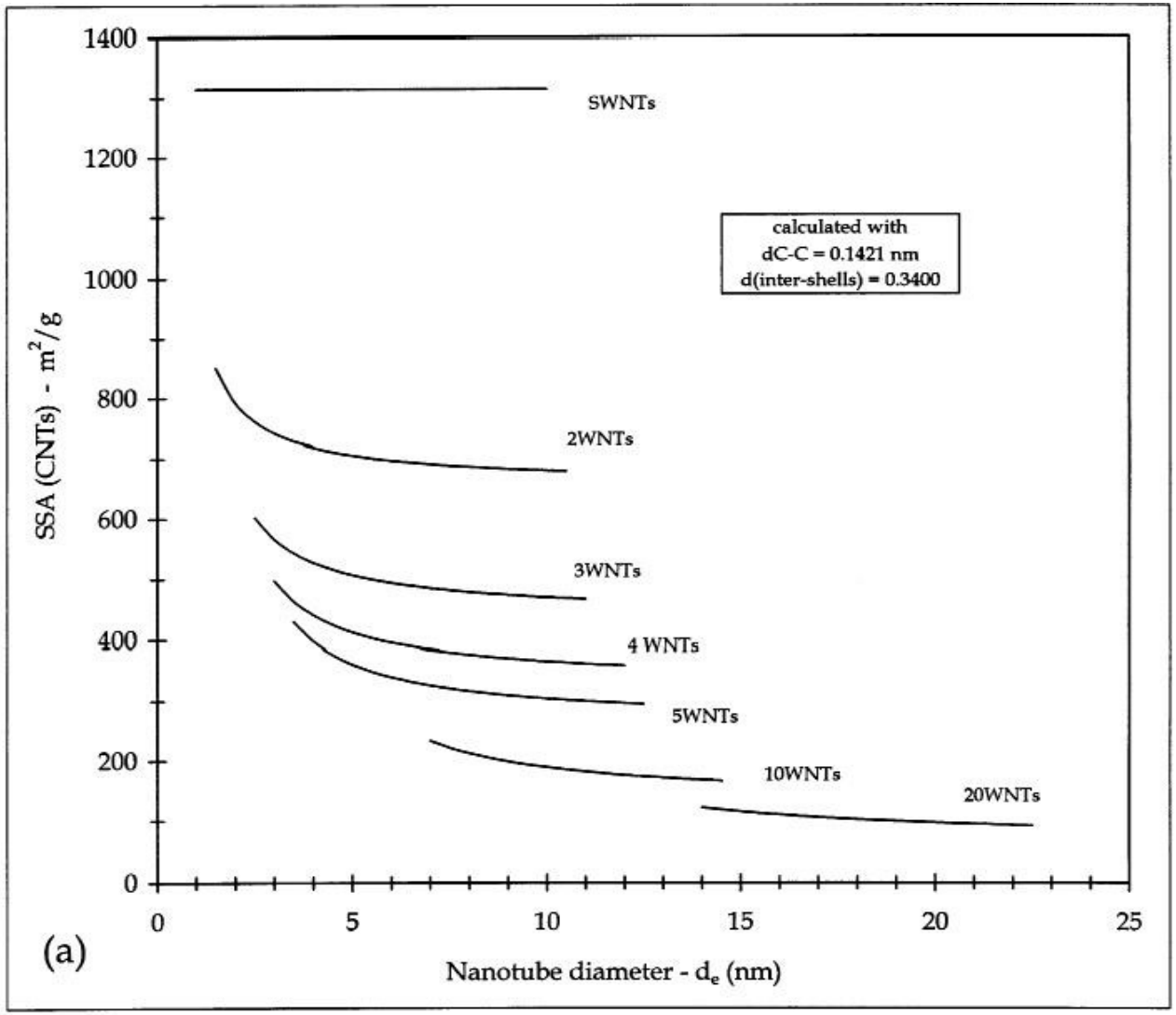
  Volume of gas adsorbed $\approx v_m$




- Flow deflection measurement

- Gravimetric measurement

# BET and CNT's




Peigney et al, *CARBON*, **39**, 507-514, (2001)

# BET and snow

- Snow can cover more than 50% of the surface of the northern hemisphere
- On snow surface chemical reactions can occur
  (e.g. $HNO_3 \rightarrow NO_x$)
- Understanding the mechanisms of reactions on snow surface, its size and the adsorption potential of trace gases on snow are important from an ecological point of view

L. Hanot et al., *Environ. Sci. Technol.*, **33**, 4250-4255, (1999)

http://lch.web.**psi**.ch/pdf/anrep03/17.pdf

# Summary

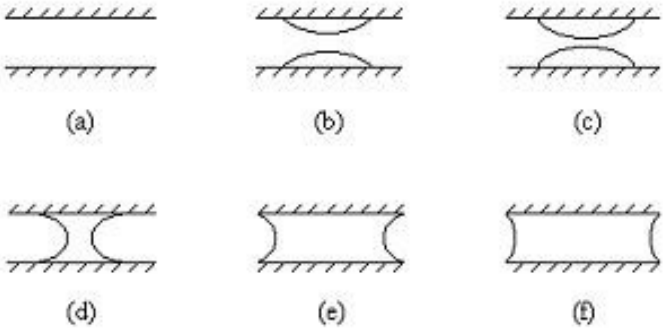
- The BET method is based on adsorption of gas on a surface
- The amount of gas adsorbed at a given pressure allows to determine the surface area
- It is a cheap, fast and reliable method
- It is very well understood and applicable in many fields

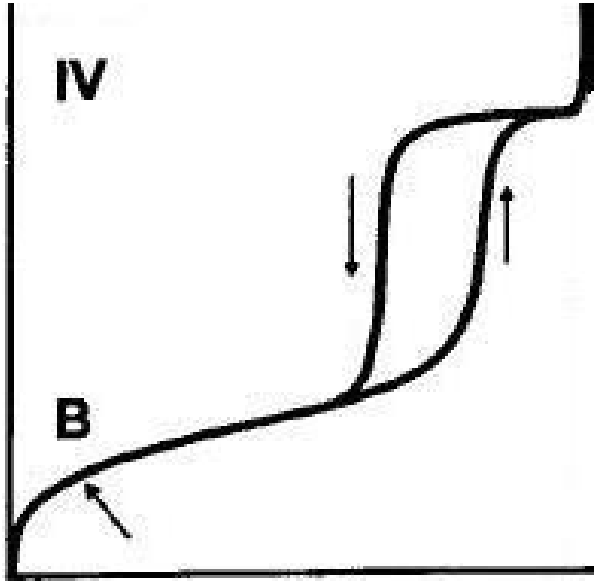
- Not applicable to all types of isotherms

Thank you for your attention!

# Porosity

- Pore volume
- Mean pore radius
- Distribution of radii




$$r_K = \frac{2\sigma V_m}{RT \ln \frac{p}{p_0}}$$

$r_k$ = pore radius

σ = surface tension

$V_m$ = molar volume of gas adsorbed in the pore