Determination of the surface area by the BET method
Structure

• Context
• Historical background
• Basic principles and mathematical ideas
• Measurement
• BET in modern research
• Conclusions
Heat exchange at the liquid (He) – solid (metal) interface

Acoustic mismatch causes weak coupling

\[ \theta^C_L = \arcsin\left(\frac{c_L}{c_s}\right) \]

Ratio \(c_L/c_s \approx 0.05 \rightarrow \theta \approx 3^\circ\)

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

Kapitza resistance:

\[ R_K = \frac{\Delta T}{Q} = \frac{c}{AT^3} \]

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

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

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
5. At saturation pressure, the number of layers becomes infinite
BET theory

• At equilibrium:

\[ a_i ps_{i-1} = b_i s_i e^{\frac{-E_i}{RT}} \]

- \( s_i \) 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:

\[ A = \sum_{i=0}^{\infty} s_i \quad v = v_0 \sum_{i=0}^{\infty} is_i \quad v_m = v_0 A \]

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:

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

\[ c \approx e^{\frac{E_{ADS} - E_{COND}}{RT}} \quad E_{ADS} >> E_{COND} \]

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

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 \( \frac{p}{p_0} \approx 0.03 \)
  Volume of gas adsorbed \( \approx v_m \)

• Flow deflection measurement

• Gravimetric measurement
BET and CNT's

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. \( \text{HNO}_3 \rightarrow \text{NO}_x \))
- 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

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
- $\sigma =$ surface tension
- $V_m =$ molar volume of gas adsorbed in the pore