# BET
# Surface Area Measurement and Porosity

# IUPAC Classification on pores

**Micropores**

**Mesopores**

**Macropores**

**Zeolite, Activated carbon, Metal organic framework**

**Mesoporous silica, Activated carbon**

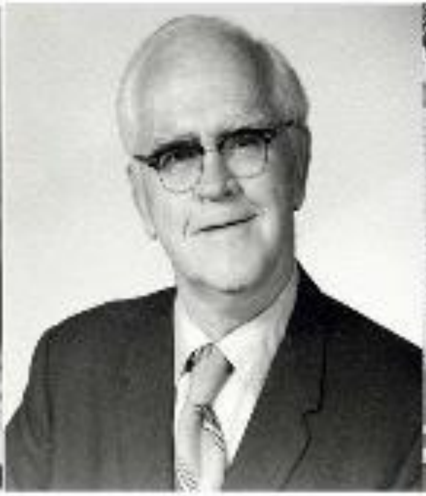
**Sintered metals and ceramics**

**2 nm**

**50 nm**

# BET Theory and how its used to calculate surface area of porous solids

Stephen Brunauer

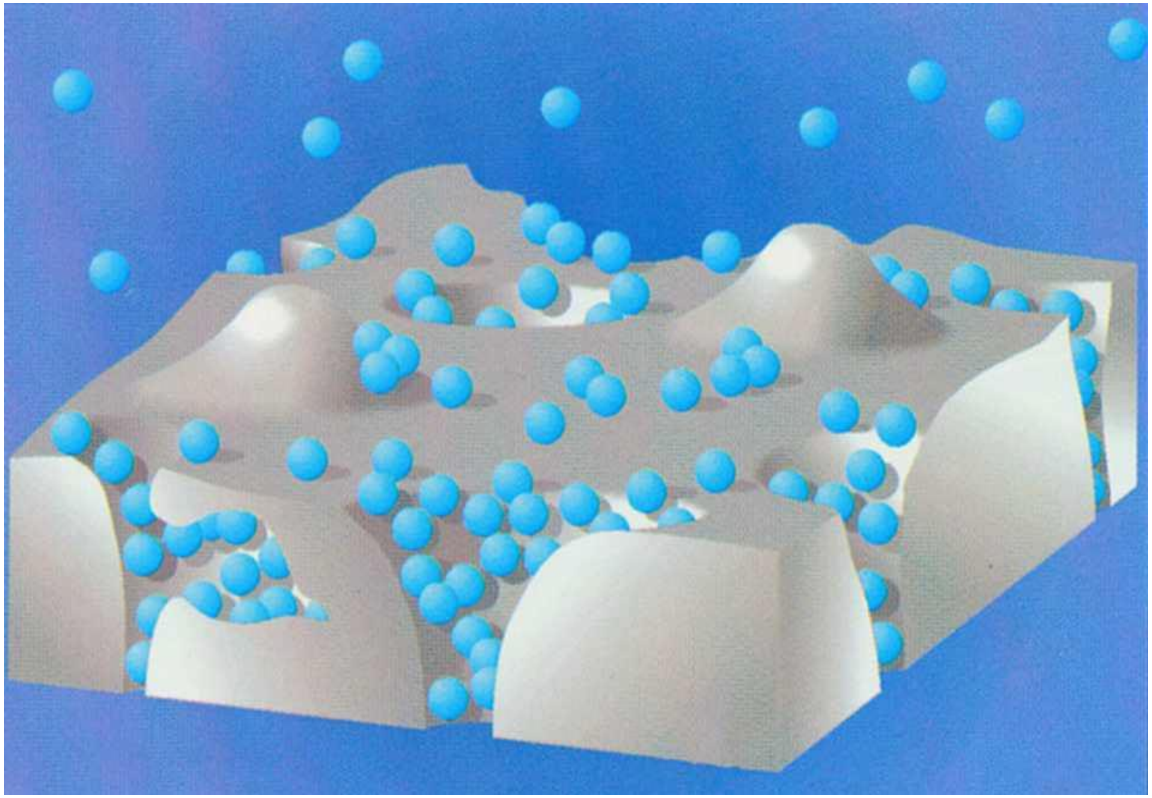


Paul Emmett

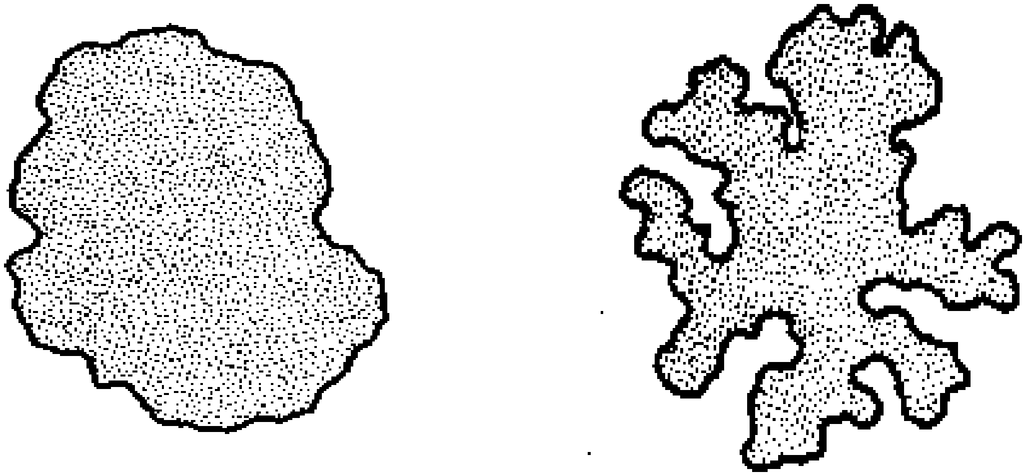
Edward Teller

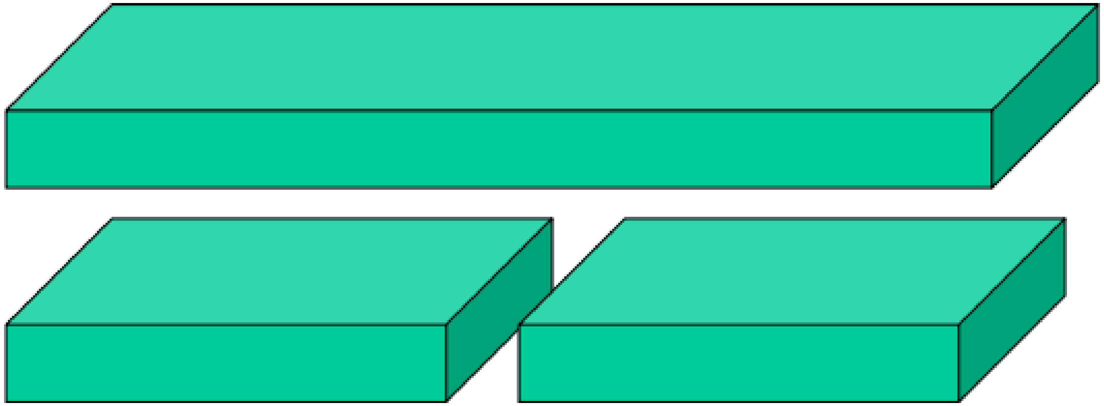
**Directly measures surface area & pore size distribution from physisorption of gas onto the sample**

# BET Theory seeks to explain the physical adsorption of gas molecules onto solid surfaces



# Particles of similar size can vary drastically in surface area

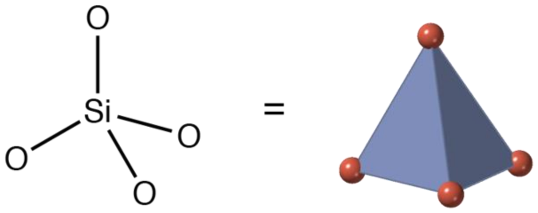




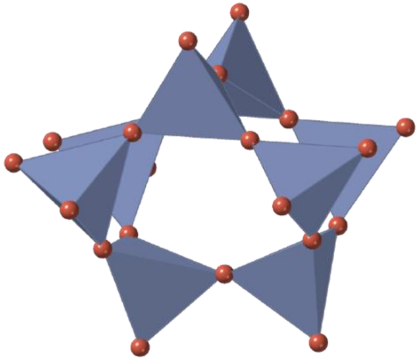
**Constant volume**

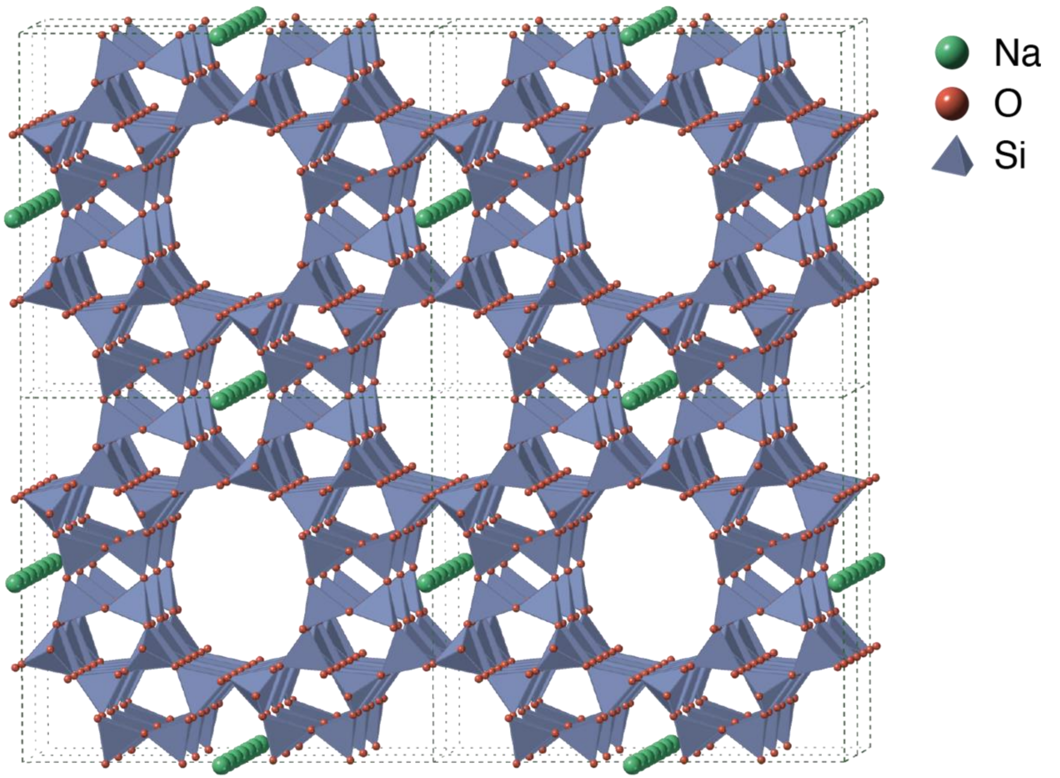
**Smaller size -- greater surface area**

$SiO_4$ tetrahedron



secondary building unit (cage)



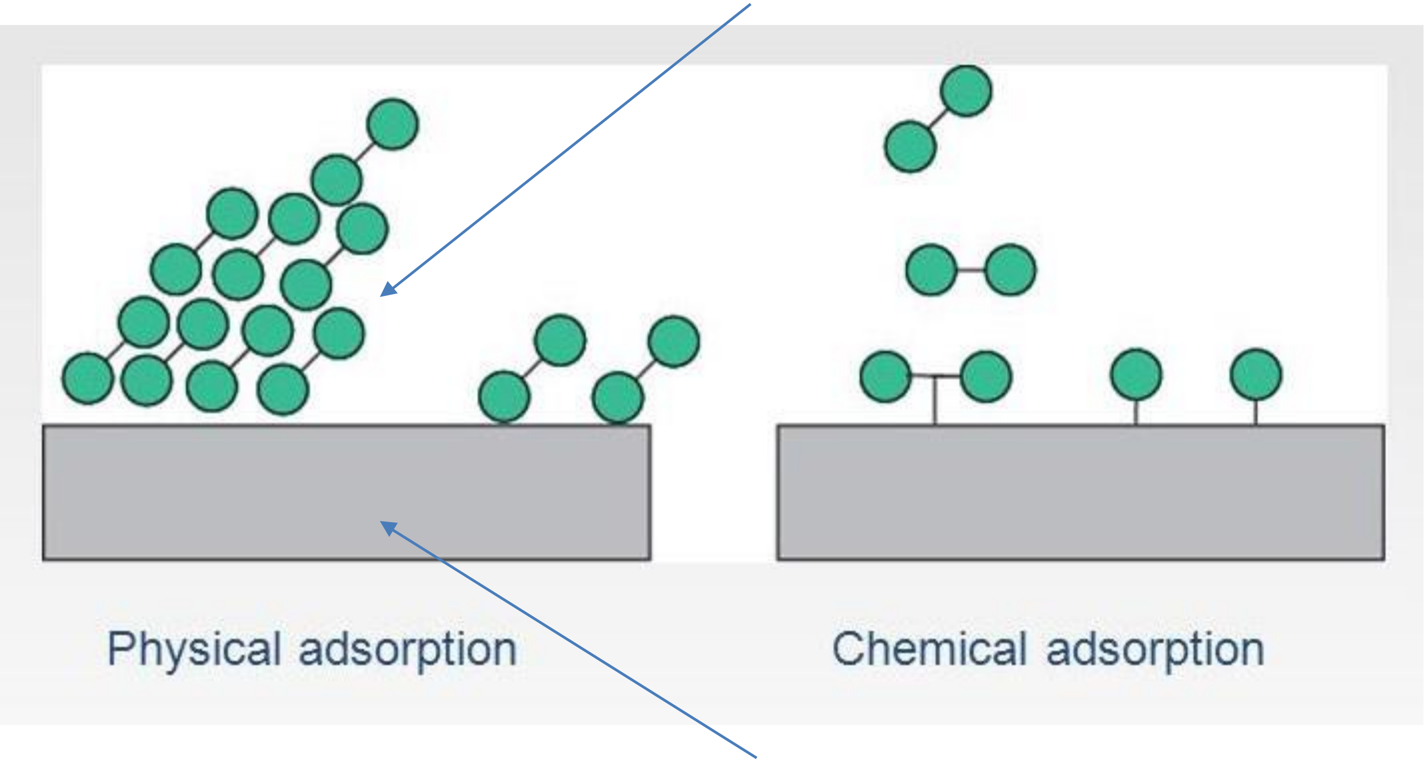


Mordenite (MOR framework)

There are many materials (for example zeolites, MOF, COF) which are porous, and pores have a significant role in their characteristic functioning.

Physical adsorption occurs due to Van der Waals forces when at low temperatures and without chemical reactions

Adsorbate



Adsorbent

# Langmuir Model of Adsorption

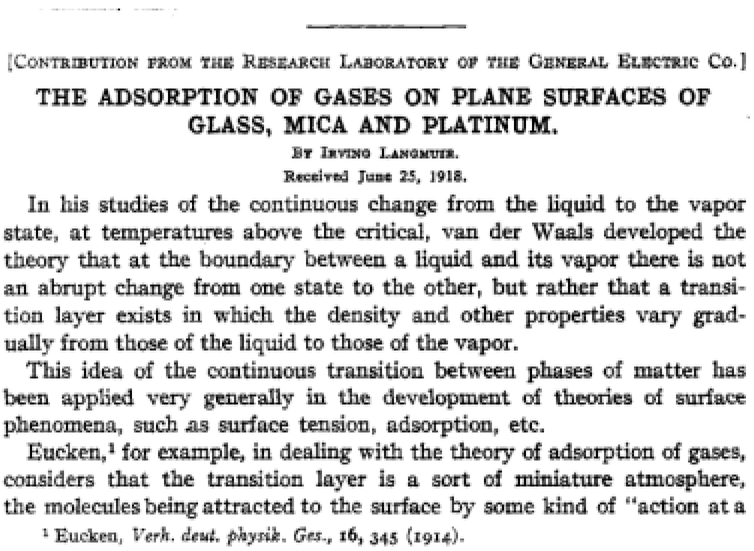
Gas molecules behave ideally

Only 1 monolayer forms

All sites on the surface are equal

No adsorbate-adsorbate interaction

Adsorbate molecule is immobile



[Contribution from the Research Laboratory of the General Electric Co.]

THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM.

By Irving Langmuir.

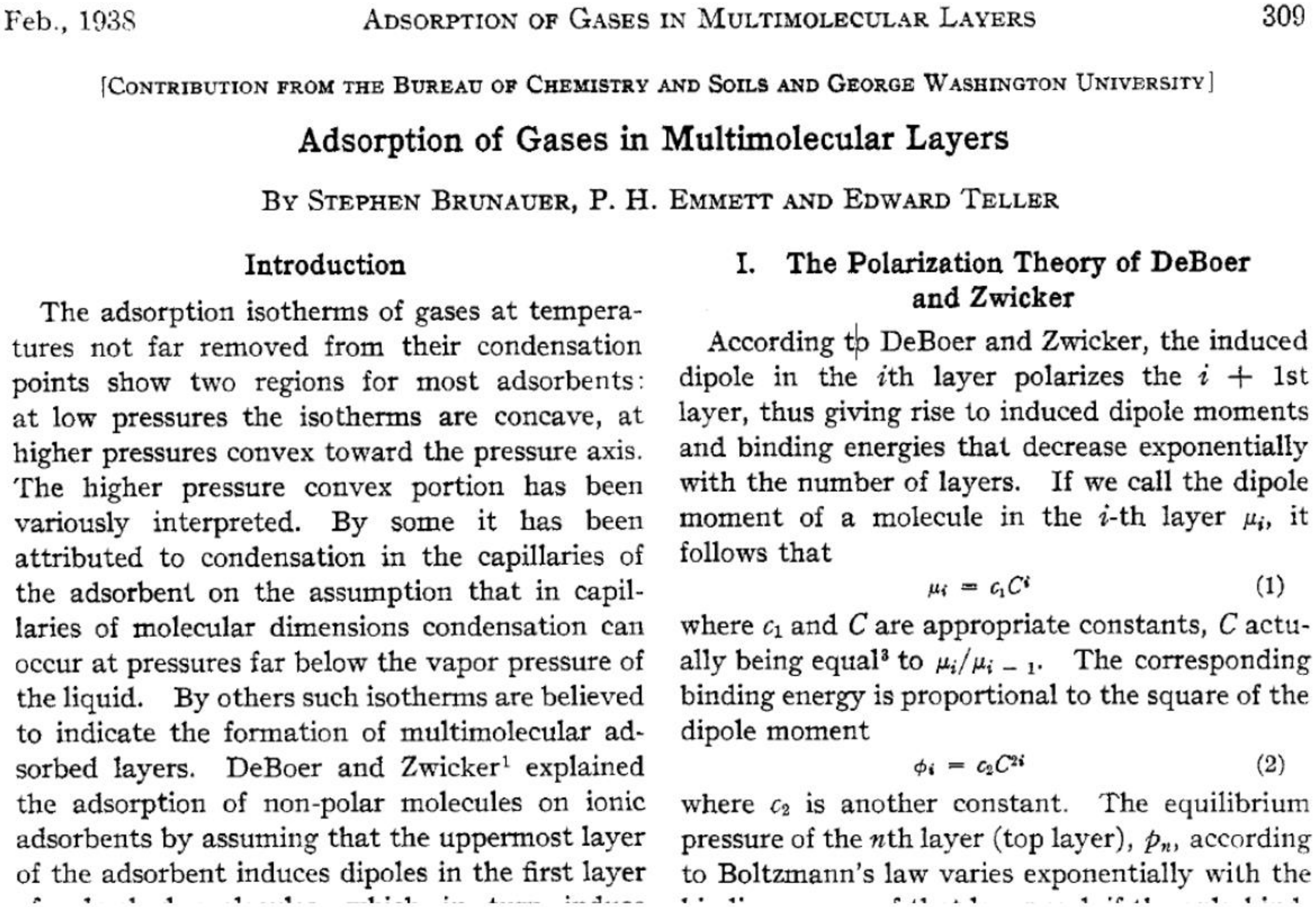
Received June 25, 1918.

In his studies of the continuous change from the liquid to the vapor state, at temperatures above the critical, van der Waals developed the theory that at the boundary between a liquid and its vapor there is not an abrupt change from one state to the other, but rather that a transition layer exists in which the density and other properties vary gradually from those of the liquid to those of the vapor.

This idea of the continuous transition between phases of matter has been applied very generally in the development of theories of surface phenomena, such as surface tension, adsorption, etc.

Eucken,[1] for example, in dealing with the theory of adsorption of gases, considers that the transition layer is a sort of miniature atmosphere, the molecules being attracted to the surface by some kind of "action at a

[1] Eucken, *Verh. deut. physik. Ges.*, **16**, 345 (1914).



[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS AND GEORGE WASHINGTON UNIVERSITY]

# Adsorption of Gases in Multimolecular Layers

BY STEPHEN BRUNAUER, P. H. EMMETT AND EDWARD TELLER

## Introduction

The adsorption isotherms of gases at temperatures not far removed from their condensation points show two regions for most adsorbents: at low pressures the isotherms are concave, at higher pressures convex toward the pressure axis. The higher pressure convex portion has been variously interpreted. By some it has been attributed to condensation in the capillaries of the adsorbent on the assumption that in capillaries of molecular dimensions condensation can occur at pressures far below the vapor pressure of the liquid. By others such isotherms are believed to indicate the formation of multimolecular adsorbed layers. DeBoer and Zwicker[1] explained the adsorption of non-polar molecules on ionic adsorbents by assuming that the uppermost layer of the adsorbent induces dipoles in the first layer

## I. The Polarization Theory of DeBoer and Zwicker

According to DeBoer and Zwicker, the induced dipole in the $i$th layer polarizes the $i + 1$st layer, thus giving rise to induced dipole moments and binding energies that decrease exponentially with the number of layers. If we call the dipole moment of a molecule in the $i$-th layer $\mu_i$, it follows that

$$\mu_i = c_1 C^i \tag{1}$$

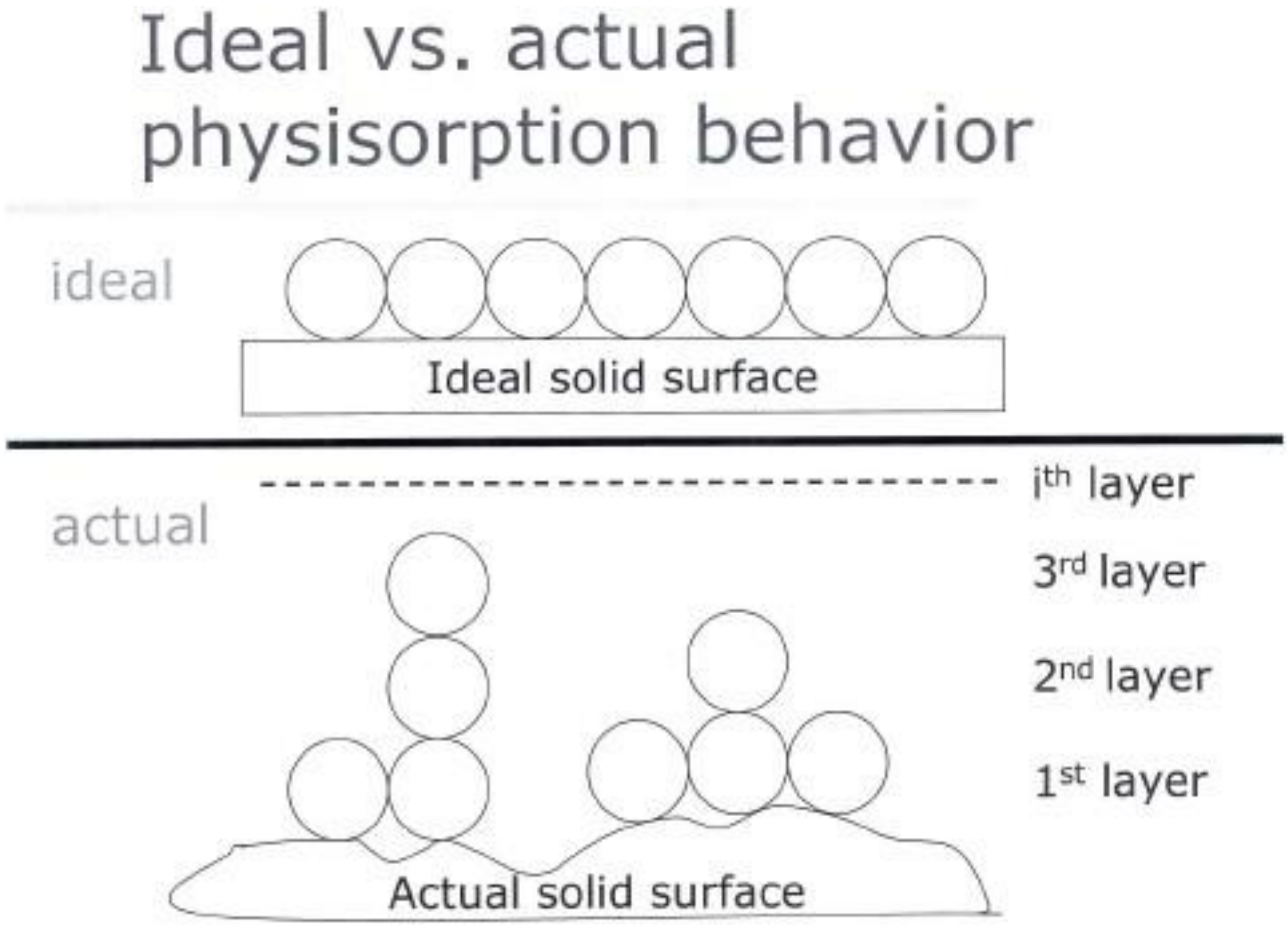
where $c_1$ and $C$ are appropriate constants, $C$ actually being equal[3] to $\mu_i/\mu_{i-1}$. The corresponding binding energy is proportional to the square of the dipole moment

$$\phi_i = c_2 C^{2i} \tag{2}$$

where $c_2$ is another constant. The equilibrium pressure of the $n$th layer (top layer), $p_n$, according to Boltzmann's law varies exponentially with the

* S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

# BET Theory extends the Langmuir theory from monolayer adsorption to multilayer adsorption



# Sample preparation

- Weigh solid sample (200 ≈ 300 mg)

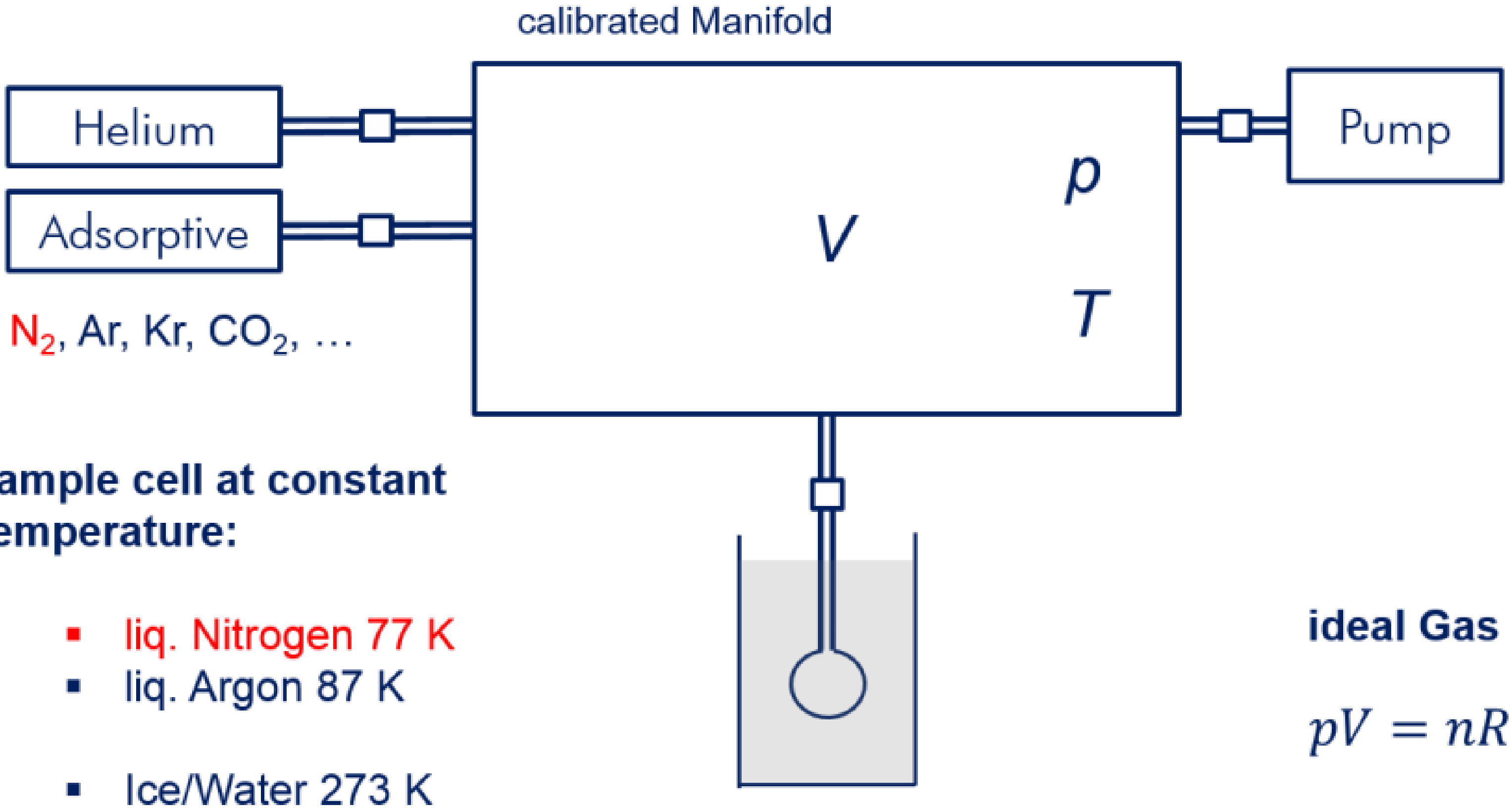
- The sample is purified by degassing
  - Temperature
  - Time
  - Vacuum conditions

# BET Instrument

Quantachrome Autosorb iQ

BELSORP-maxII (BELSORP – series) from Microtrac BEL Corp

Anton Paar Nova 600 BET



$N_2$, Ar, Kr, $CO_2$, …

**Sample cell at constant Temperature:**

- liq. Nitrogen 77 K
- liq. Argon 87 K

- Ice/Water 273 K
- Acetone/Dry Ice 196 K

- Circulating bath
- CryoSync: 82 K – 100 K

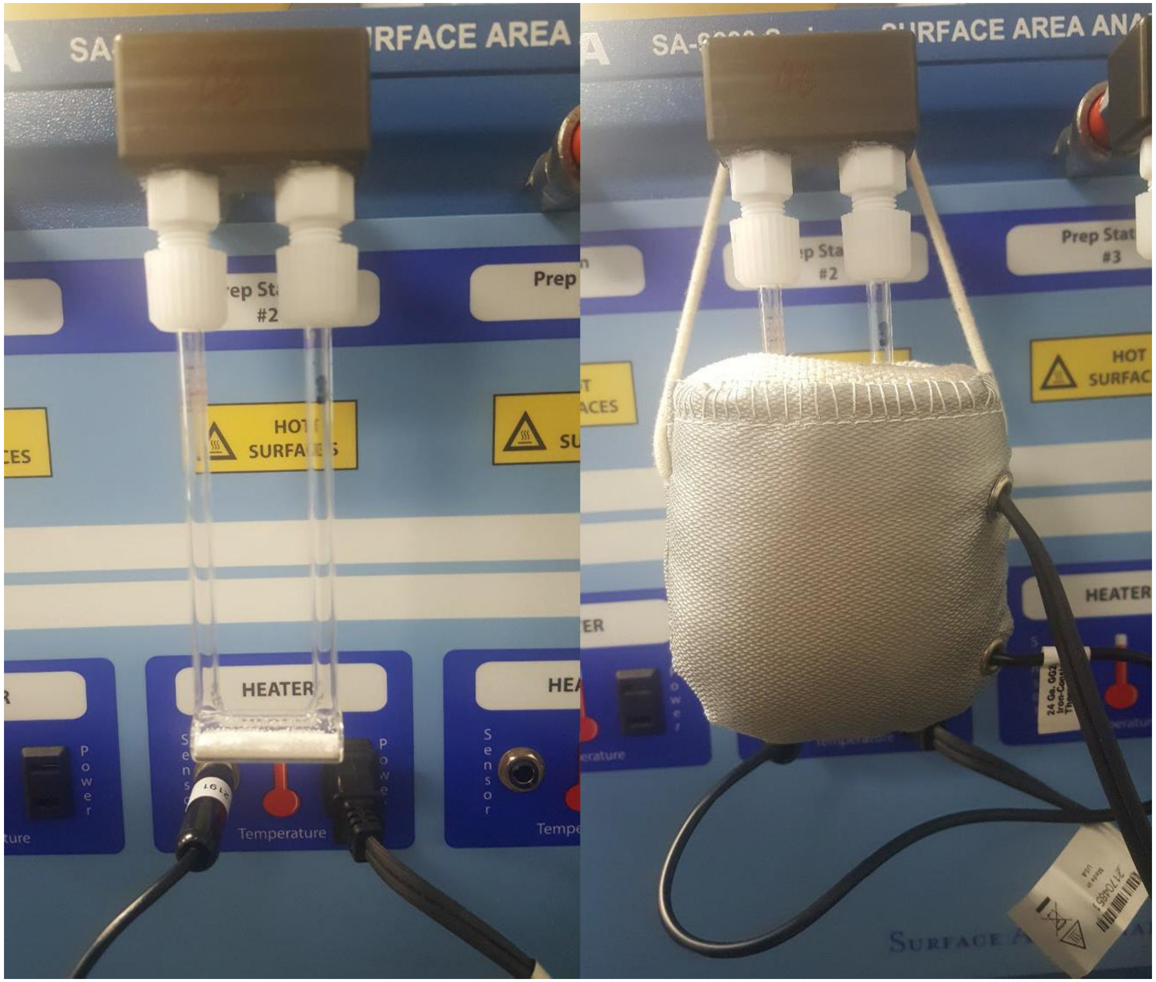
**ideal Gas**

$$pV = nRT$$

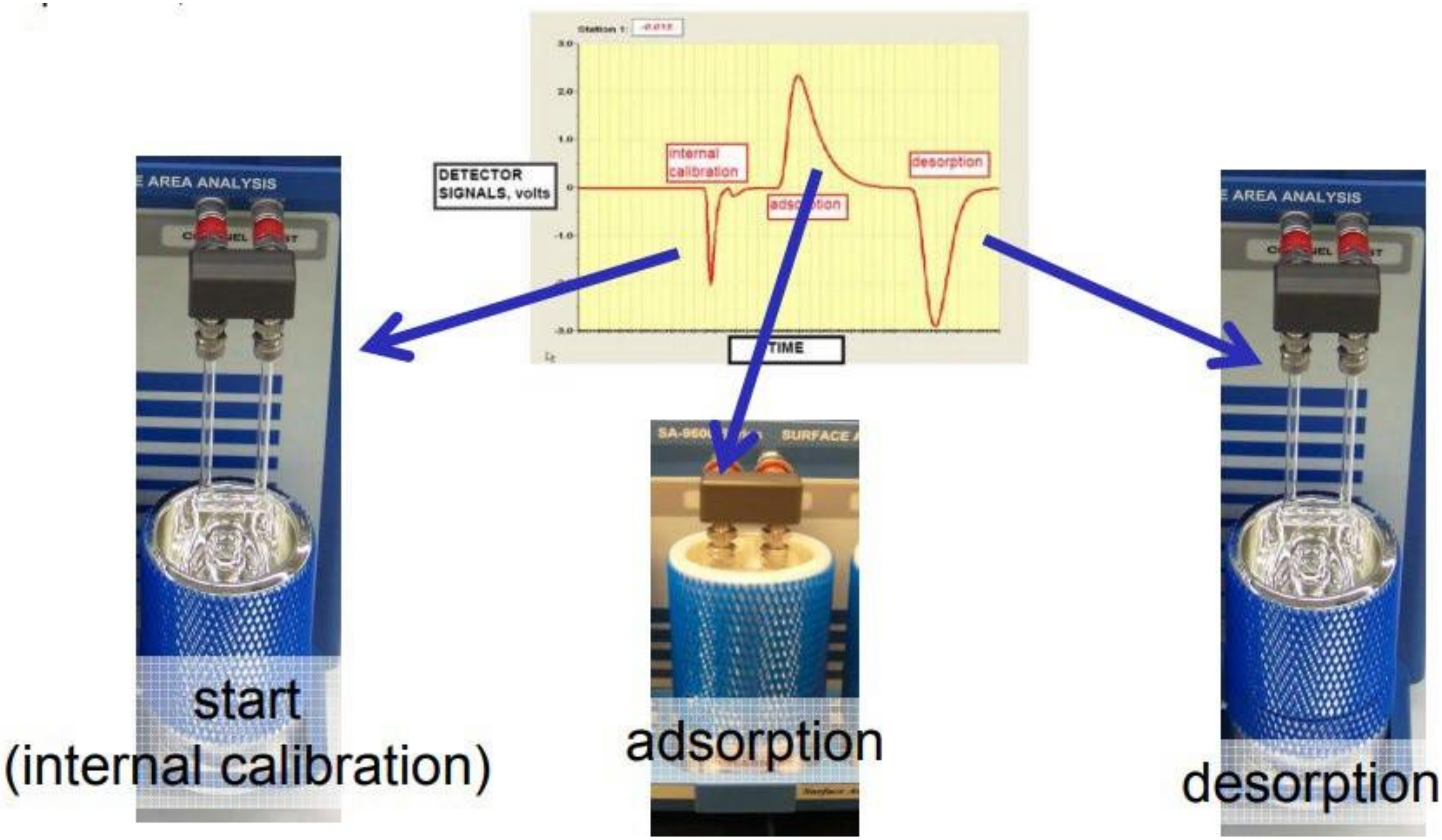
Pressure ***p*** and temperature ***T*** are measured.
The calibrated volume ***V*** is constant.

The gas adsorbed can be determined by the pressure drop (volumetric), the weight gain of the powder (gravimetric) or change in thermal conductivity through the gas (dynamic flow).

# Have to insert sample into cell and degas sample to remove excess moisture on surface



# BET measurement includes calibration of 1 $cm^3$ of nitrogen, adsorption, and desorption

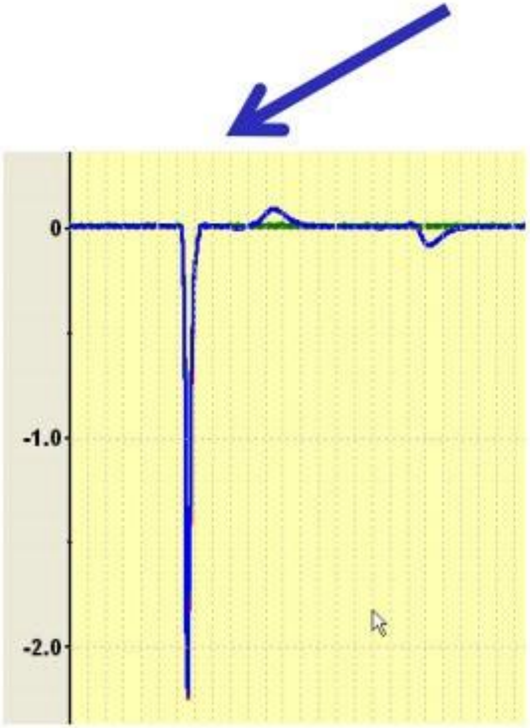


start
(internal calibration)

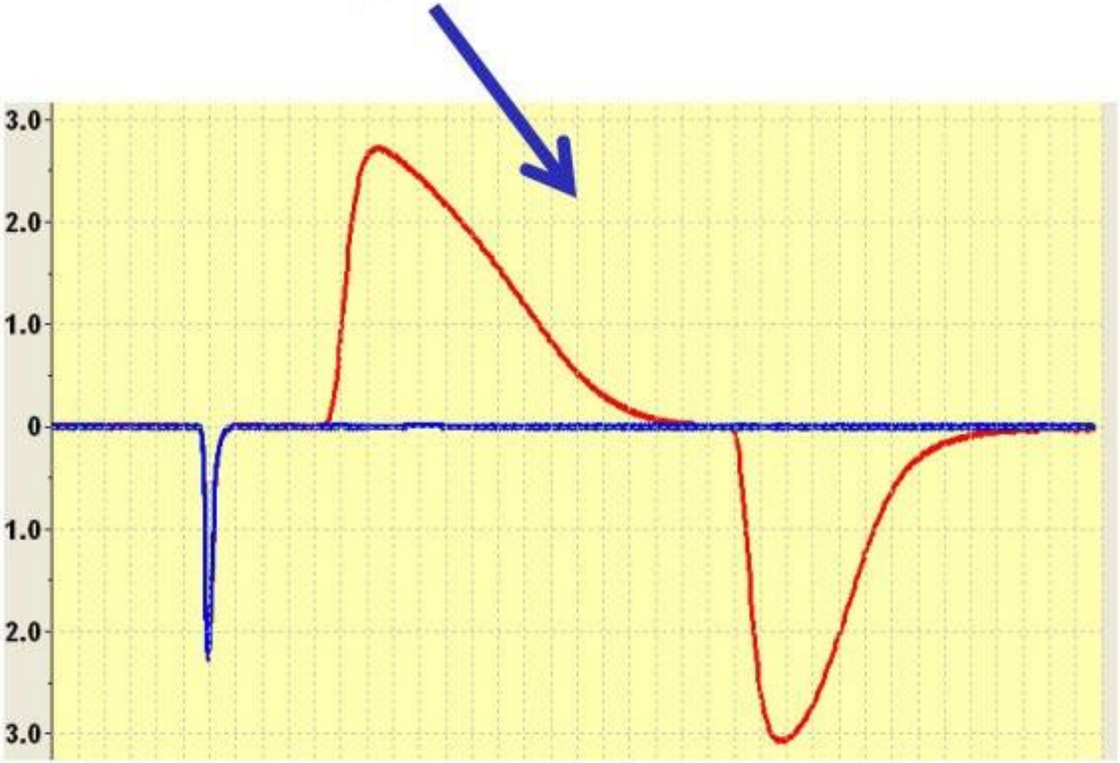
adsorption

desorption

# Large surface area samples will adsorb and desorb more nitrogen

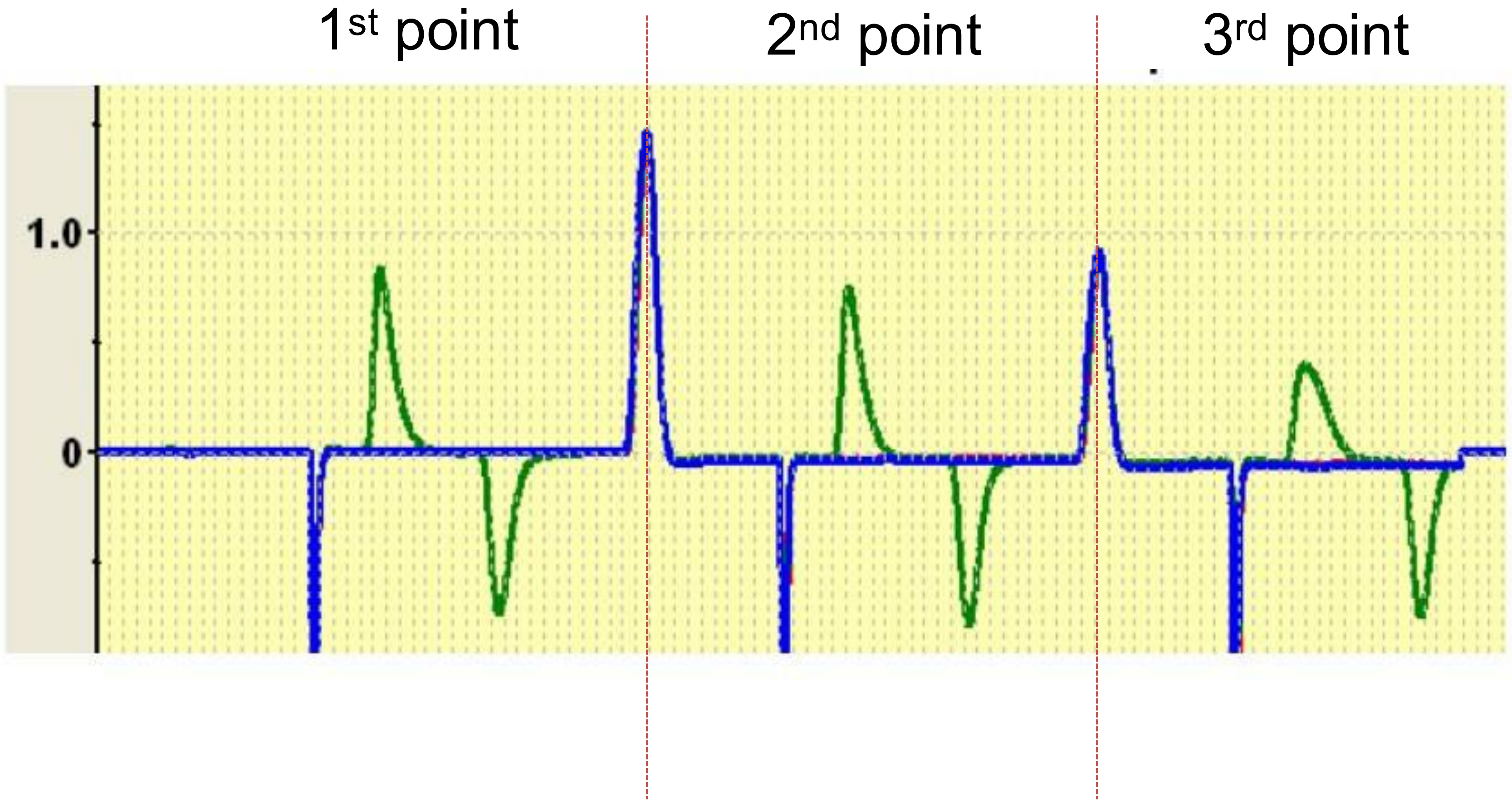


Small surface area

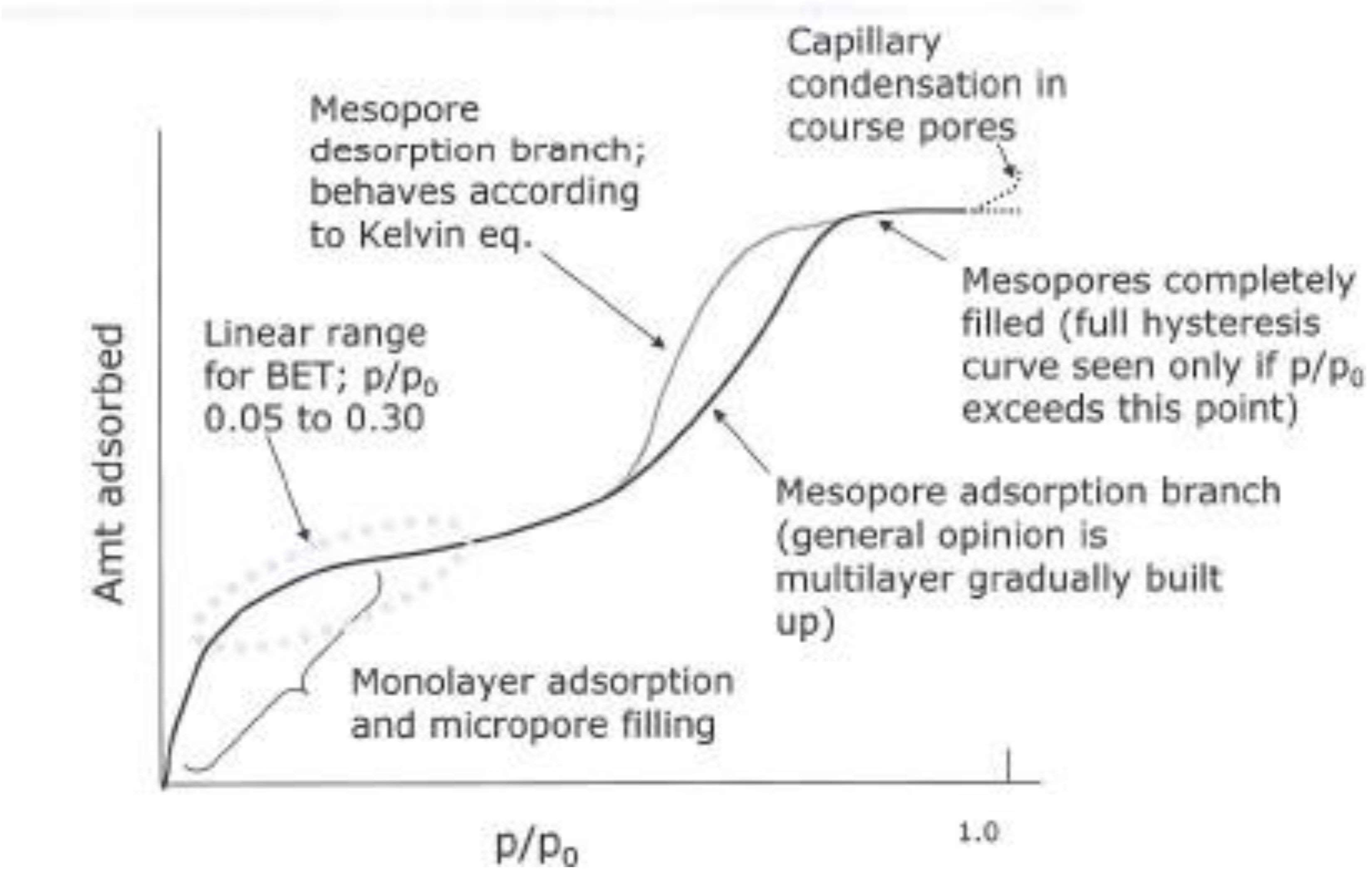


Large surface area

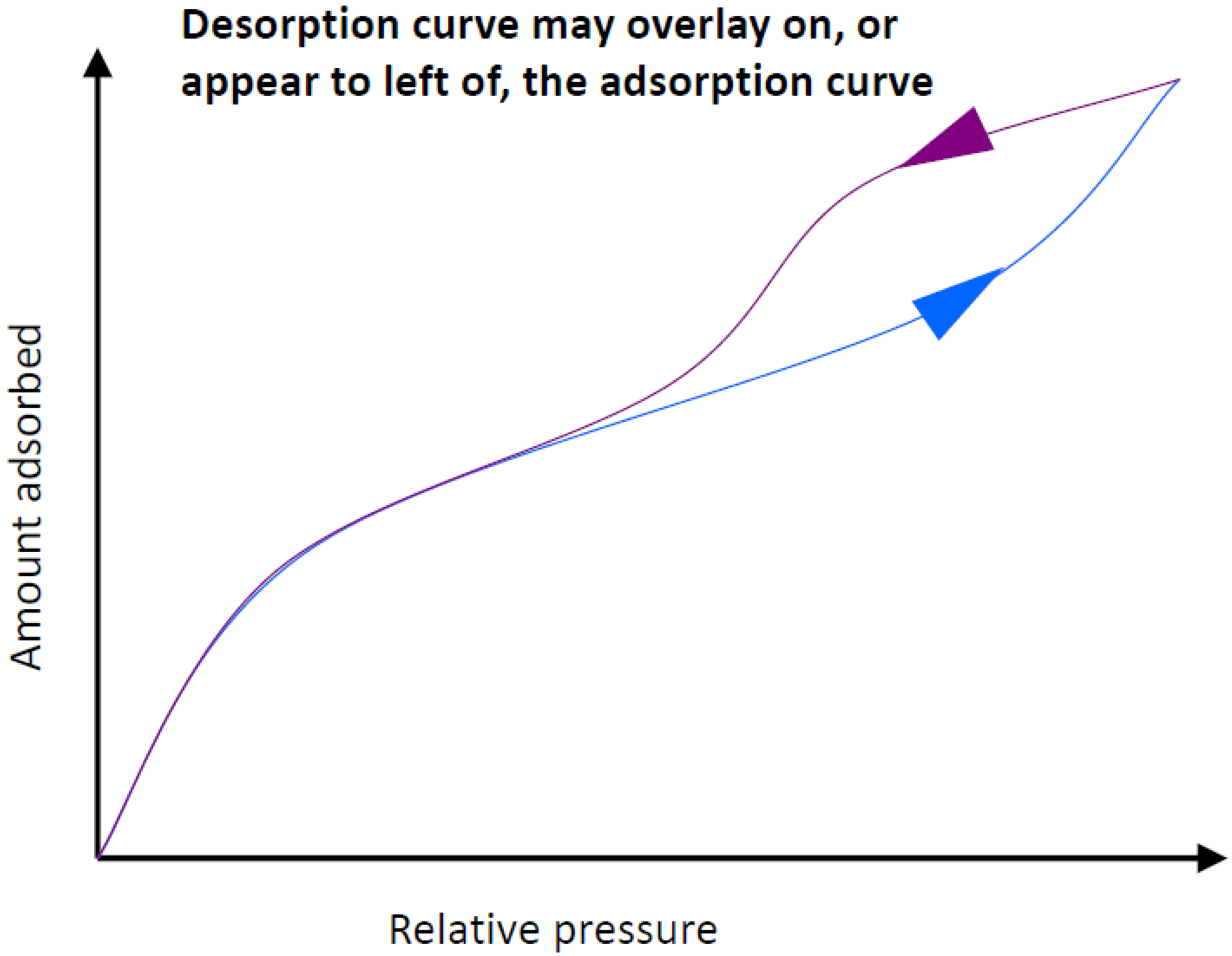
# BET multipoint measurement example

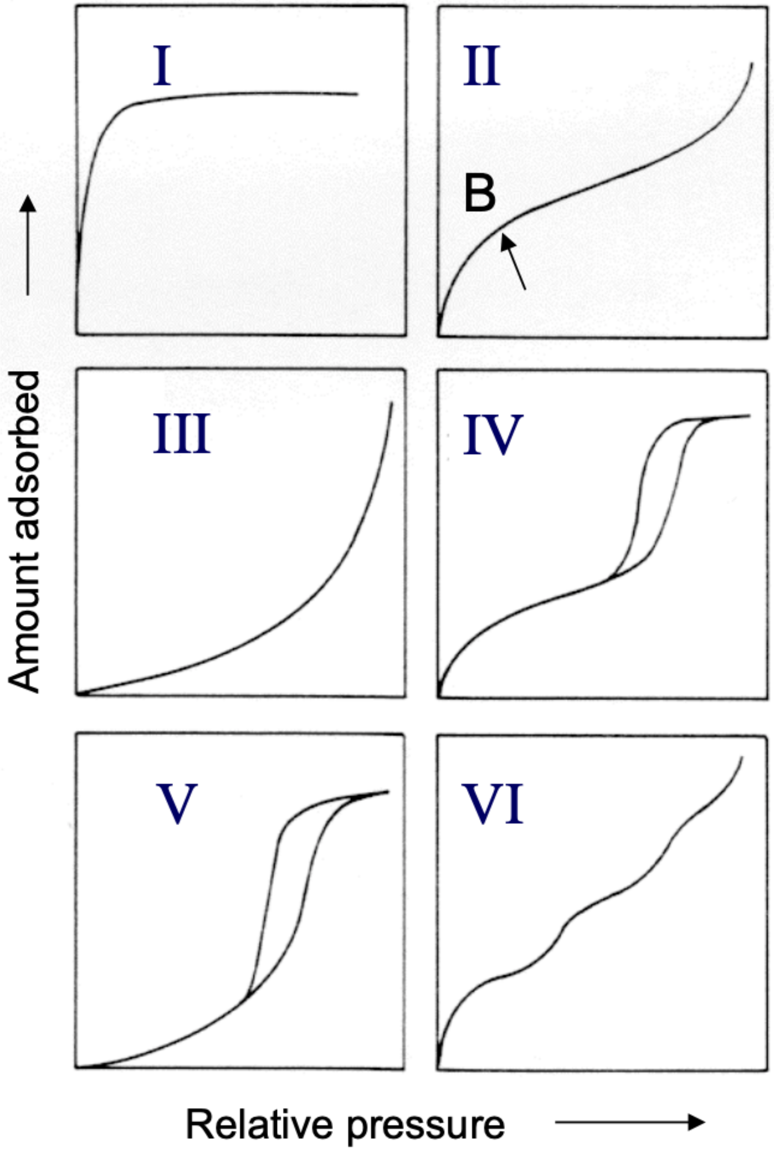


# Can only assume linear relationship for adsorption isotherms in the range of $0.05 < p/p_0 < 0.30$



# Isotherm


Desorption curve may overlay on, or appear to left of, the adsorption curve



Adorption in micropores

Adsorption limited to a few molecular layers

true chemisorption

Zeolites, active carbon

Weak adsorbtive-adsorbent interactions

Nitrogen on polyethylene

Weak interactions and capillary condensation

Unrestricted monolayer-multilayer adsorption

Nonporous or macroporous adsorbent

B monolayer coverage complete

Monolayer-multilayer adsorption and capillary condensation

Complete pore filling

Stepwise multilayer adsorption on a nonporous non-uniform surface

Ar or Kr on graphitized carbon

# We use the BET equation to determine the monolayer absorbed gas volume ($v_m$)

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

$v$ = adsorbed gas quantity

$p_0$ = saturation pressure of adsorbate

$p$ = equilibrium pressure of adsorbate

$c$ = BET constant = $\exp\left(\frac{E_1 - E_L}{RT}\right)$

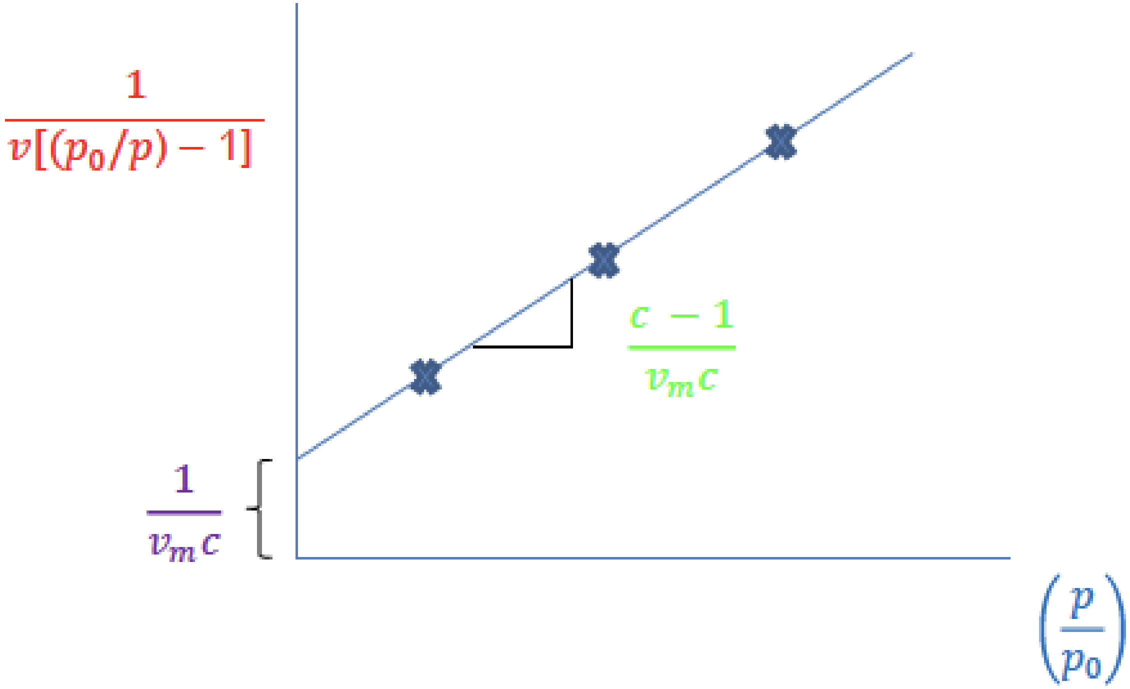
$E_1$ = heat of adsorption for the first layer

$E_L$ = heat of vaporization

# BET equation can be plotted to determine monolayer adsorbed gas quantity and the BET constant

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

$$y = mx + b$$



# Take numerical values for slope and intercept to solve for $v_m$ and c

$$slope = \frac{c-1}{v_m c}$$

$$\text{intercept} = \frac{1}{v_m c}$$

$$v_m = \frac{1}{slope + intercept}$$

$$c = 1 + \frac{slope}{intercept}$$

# From the monolayer absorbed gas volume ($v_m$), we can determine total and specific surface area

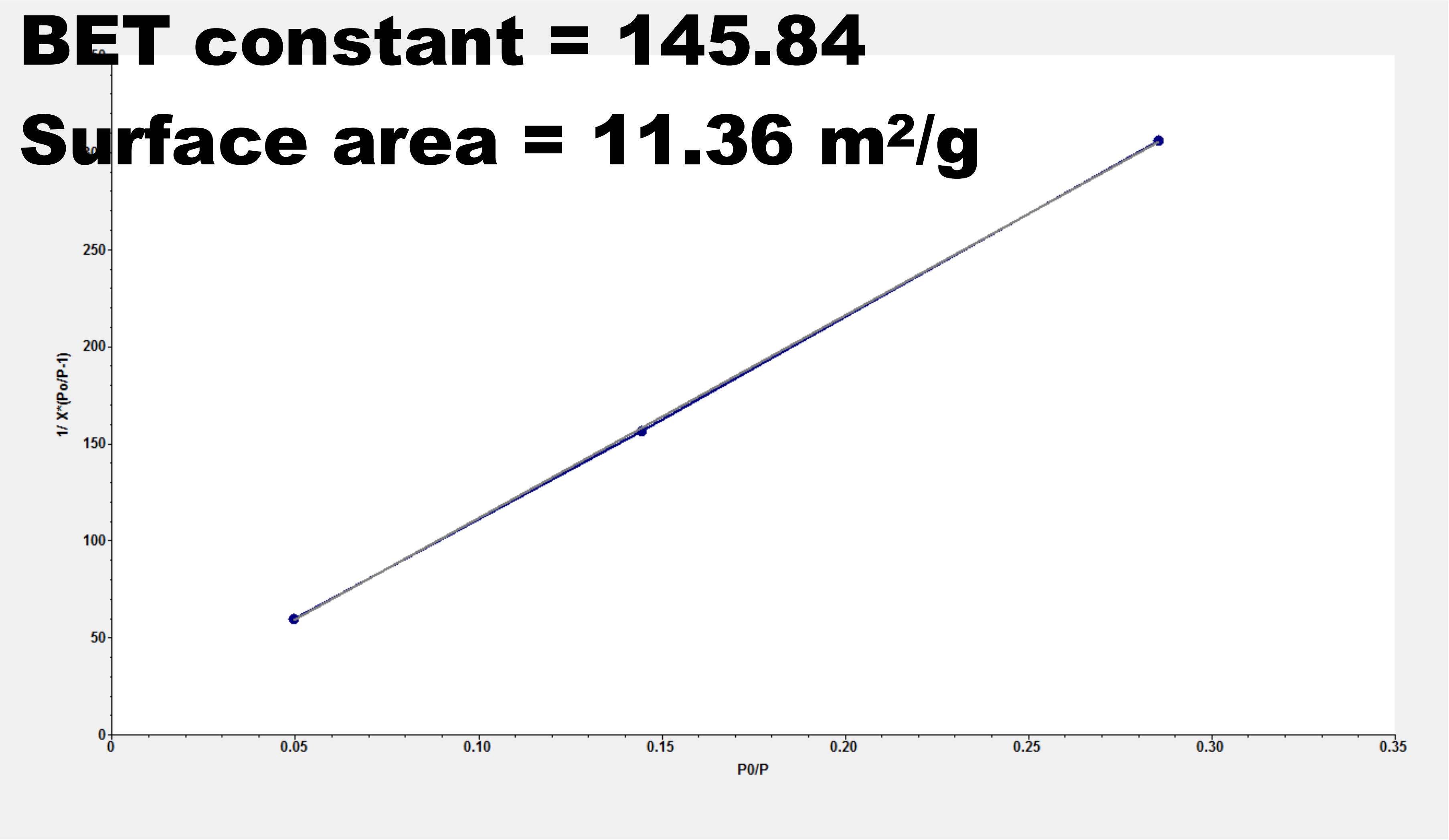
$$S_t = \frac{v_m N s}{V}$$

$S_t$ = total surface area of sample material
$v_m$= monolayer absorbed gas volume
$N$ = Avogadro's number = 6.02 x $10^{23}$ molecules/mol
$s$ = cross-sectional area of adsorbed gas molecule
$V$ = molar volume of adsorbed gas

$$S_{BET} = \frac{S_t}{a} \text{ [=] m}^2\text{/g}$$

$S_{BET}$ = specific surface area
$a$ = mass of sample

# Plot at least 3 points to obtain multi-point plot, solve for BET constant (c) and $V_m$ (monolayer volume)



**BET constant = 145.84**

**Surface area = 11.36 m²/g**

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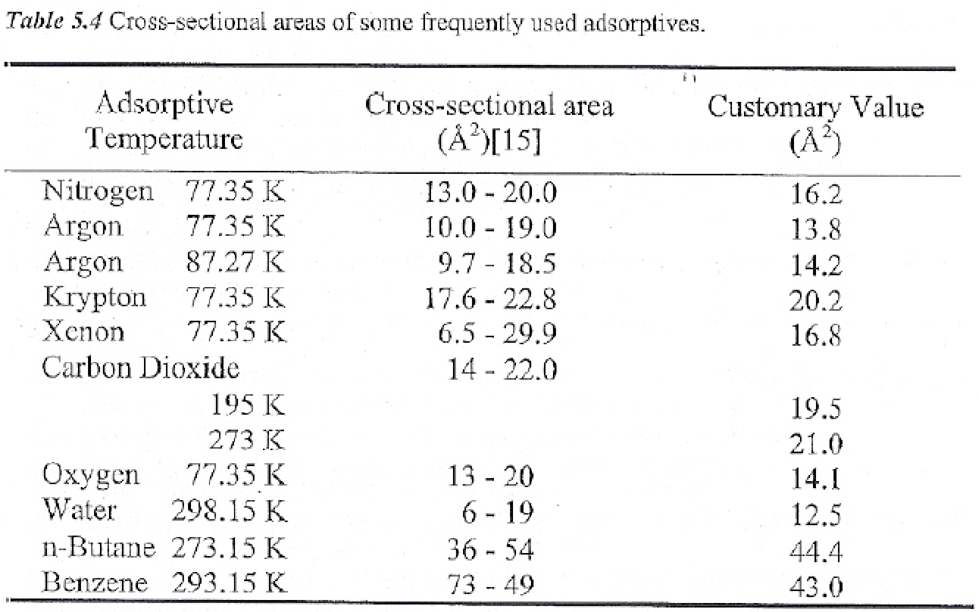


*Table 5.4* Cross-sectional areas of some frequently used adsorptives.

| Adsorptive | Temperature | Cross-sectional area ($Å^2$)[15] | Customary Value ($Å^2$) |
|---|---|---|---|
| Nitrogen | 77.35 K | 13.0 - 20.0 | 16.2 |
| Argon | 77.35 K | 10.0 - 19.0 | 13.8 |
| Argon | 87.27 K | 9.7 - 18.5 | 14.2 |
| Krypton | 77.35 K | 17.6 - 22.8 | 20.2 |
| Xenon | 77.35 K | 6.5 - 29.9 | 16.8 |
| Carbon Dioxide | | 14 - 22.0 | |
| | 195 K | | 19.5 |
| | 273 K | | 21.0 |
| Oxygen | 77.35 K | 13 - 20 | 14.1 |
| Water | 298.15 K | 6 - 19 | 12.5 |
| n-Butane | 273.15 K | 36 - 54 | 44.4 |
| Benzene | 293.15 K | 73 - 49 | 43.0 |

Krypton established for low surface area measurements (0.5-0.05 $m^2$) due to its low saturation pressure at 77K

***Nitrogen as the standard adsorptive***

For most of the adsorbents the C constant lies in the range from about 50 to 300 (no weak interaction, no chemisorption)

Its permanent quadrupole moment is responsible for the formation of well-defined monolayers on most of the surfaces

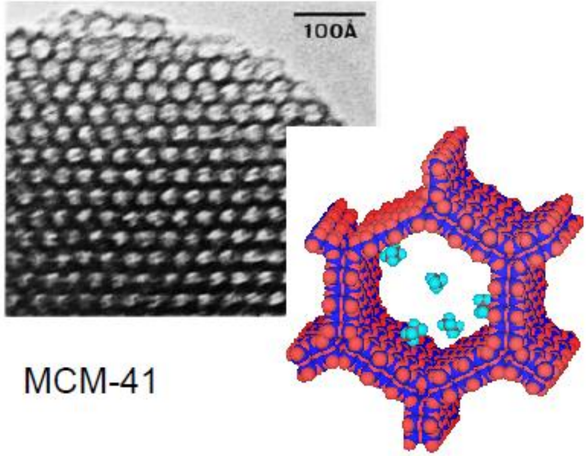
Overestimation of surface areas of hydroxylated silica surfaces by 20% due to specific interactions with the polar surface groups (use 13.5 $Å^2$)

* Literatur IUPAC.

# Capillary condensation in mesopores

Capillary condensation

Phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure $p$ less than saturation pressure $p_0$ of the bulk liquid



MCM-41

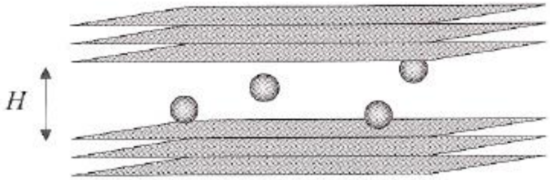
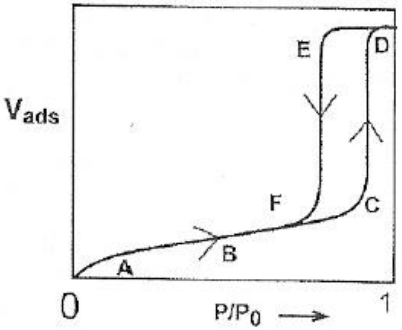
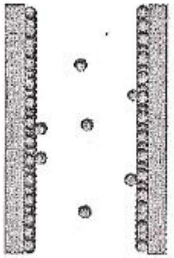
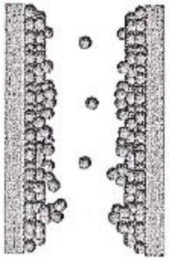


Fig. 3. The slit pore model. Each layer represents a graphene layer.

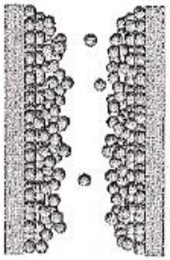




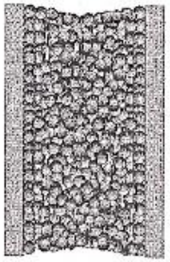
A Monolayer formation



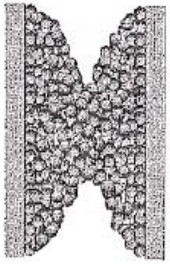
B Multilayer adsorption



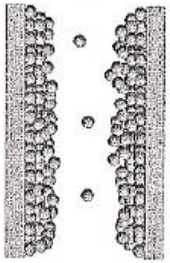
C Critical film thickness reached



D Capillary condensation



E Pore evaporation



F multilayer film

# Classification of the Hysteresis Loop in Type IV Isotherm

The wider the pore size distribution the less sharper is the pore condensation step

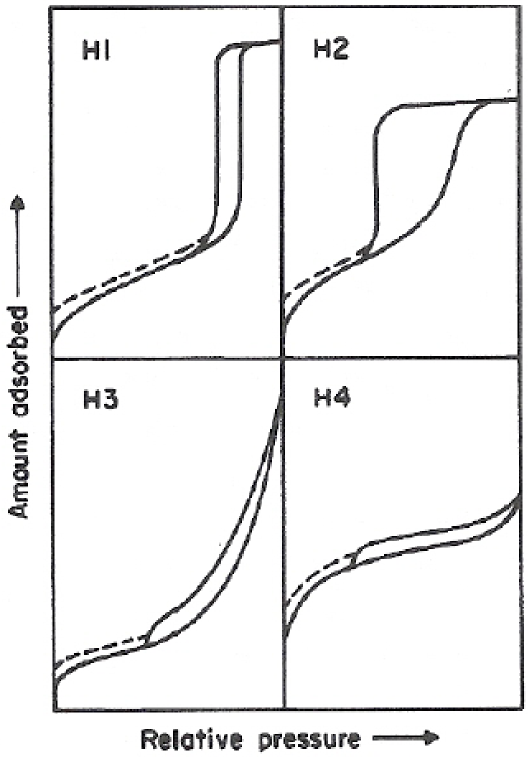


Fig. 3. Types of hysteresis loops

H1 well defined cylindrical pore channels

H2 disordered pores
(pore blocking, percolation phenomena)

H3 non-rigid aggregates of plate-like particles
(slit-shaped pores)

H4 narrow slit pores including pores in the
micropore region

***Low pressure hysteresis***
***no accurate pore size analysis possible!***

- Changes in the volume of the adsorbent
  - Swelling of non-rigid pores
- Irreversible uptake of molecules in the pores
- Chemisorption

* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.