Brunauer-Emmett-Teller (BET) surface area analysis

Introduction

❖ BET

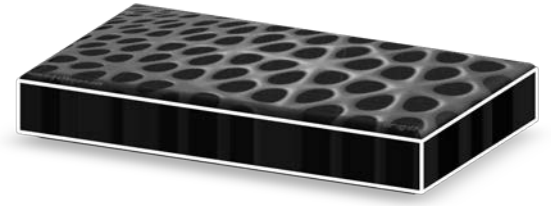
- Gas adsorption or Nitrogen adsorption
- Stephen **Brunauer**, Paul Hugh **Emmett**, and Edward **Teller**
- Directly measures surface area & pore size distribution
- BET theory deviates from **ideal** to **actual** analysis

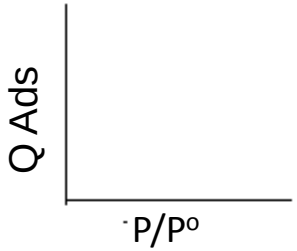
Basic Principle

Ideal } $PV = nRT$

Actual

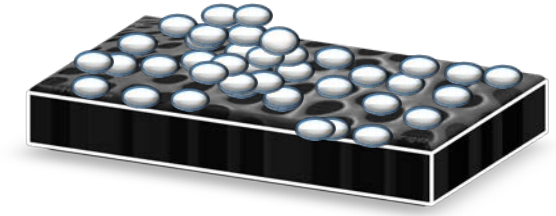
No gas molecules

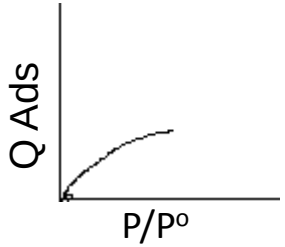




- Never start from no gas molecules

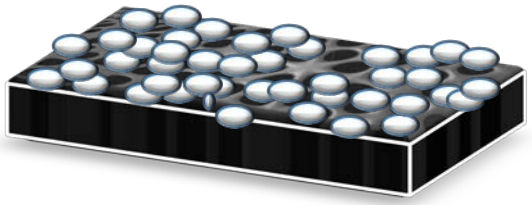
Nitrogen gas molecules

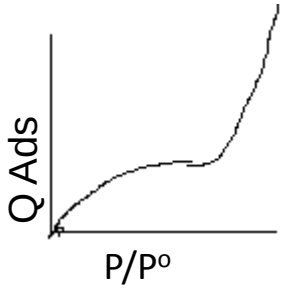




- Monolayer: Gas molecules clump together

Saturated Nitrogen gas molecules





- Multilayer: Gas molecules clump together
- Some pores are not filled

Basic Principle Cont.

❖ BET is an extension of **Langmuir model**

- Kinetic behavior of the adsorption process
- Rate of arrival of adsorption is equal to the rate of desorption
- Heat of adsorption was taken to be constant and unchanging with the degree of coverage, θ

Basic Principle Cont.

Assumptions

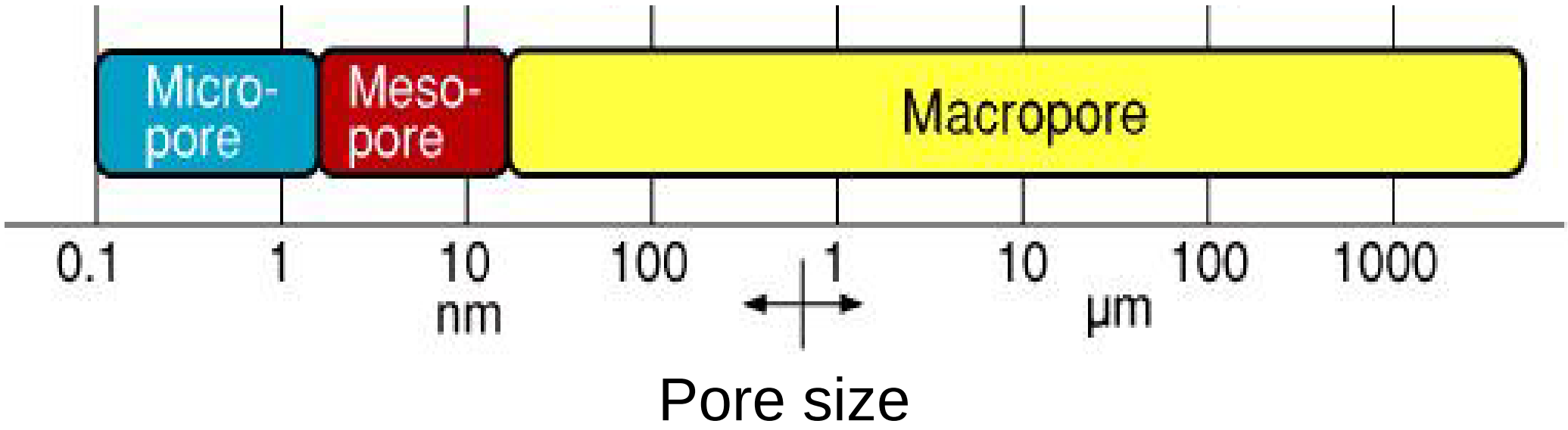
- Gas molecules behave ideally
- Only 1 monolayer forms
- All sites on the surface are equal
- No adsorbate-adsorbate interaction
- Adsorbate molecule is immobile

Basic Principle Cont.

- Homogeneous surface
- No lateral interactions between molecules
- Uppermost layer is in equilibrium with vapour phase
- First and Higher layer: Heat adsorption
- All surface sites have same adsorption energy for adsorbate
- Adsorption on the adsorbent occurs in infinite layers
- The theory can be applied to each layer

Basic Principle Cont.

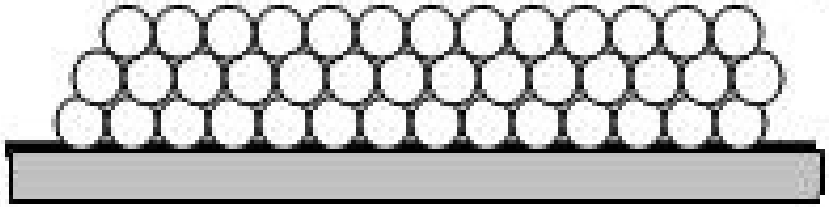
Pore classification



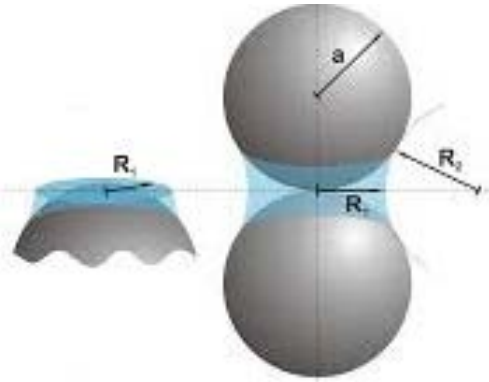
Basic Principle Cont.

Adsorption Mechanism

Monolayer



Multilayer



Capillary condensation

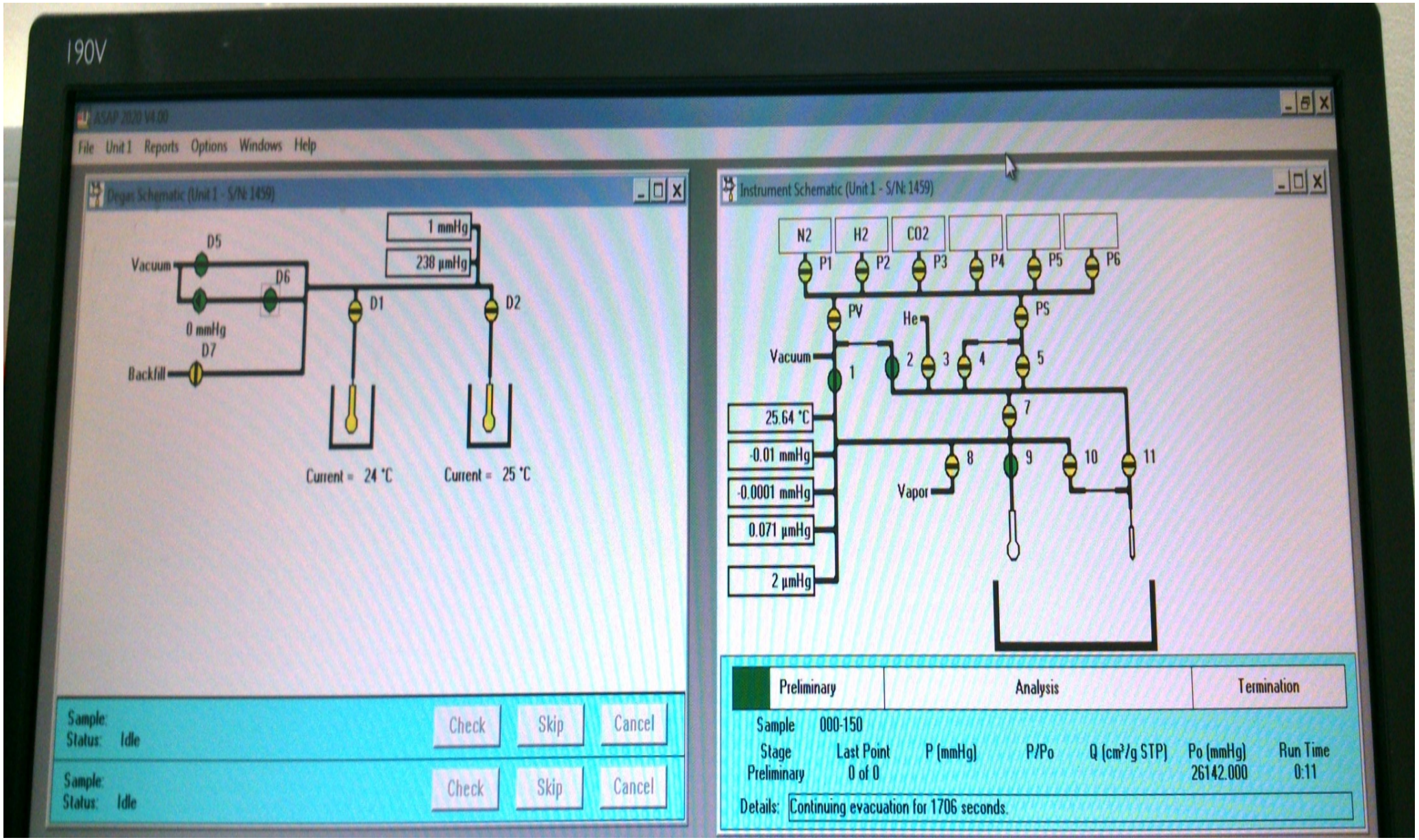
Sample preparation

- Weigh solid sample (200 ≈ 300 mg)

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

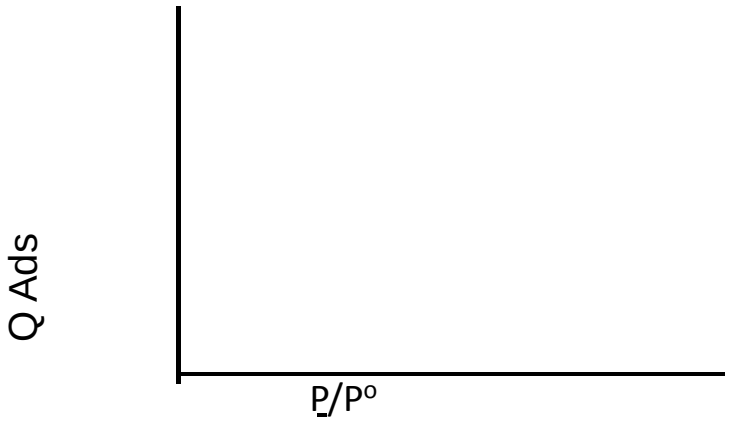
Instrument schematic

BET Equipment



Results

Presentation of data



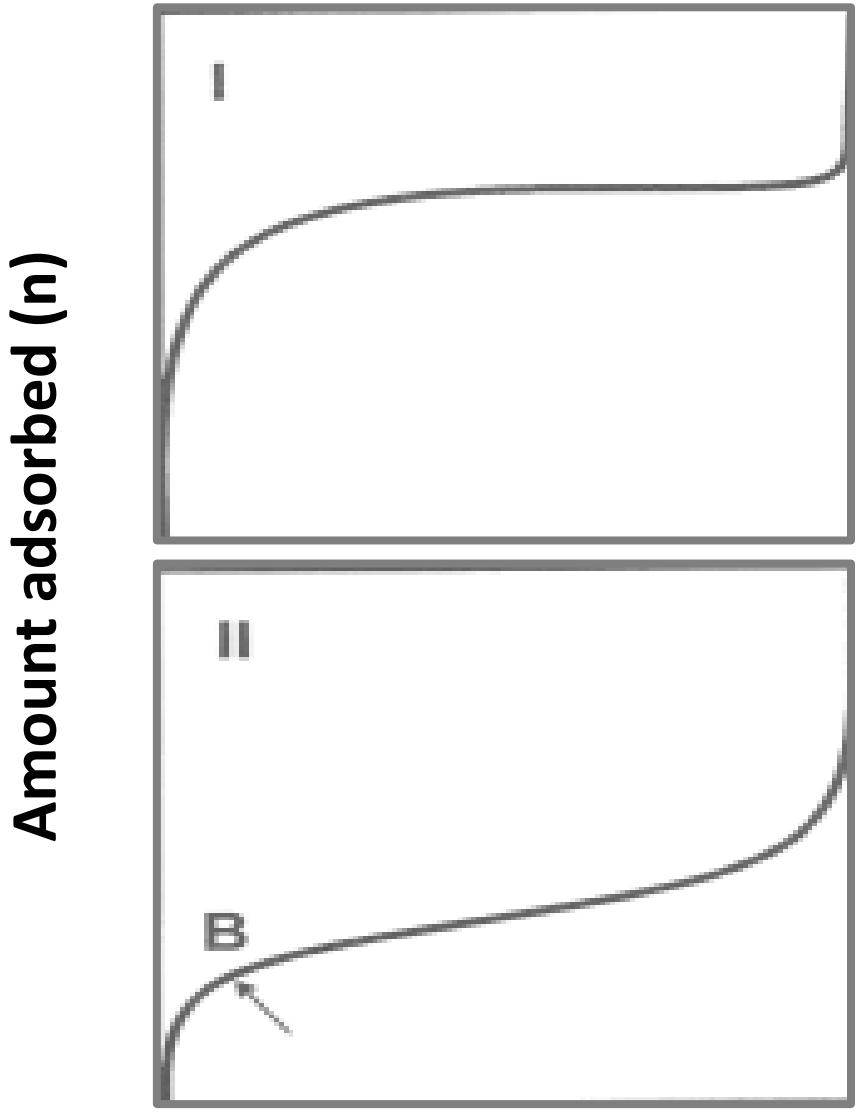
Graphically

Sample	Surface area (m^2/g)	Pore size (nm)
SiO_2	25.7	100
SiO_2/Al_2O_3	215.5	11

Tabulated

Results-Cont

❖6 types of adsorption isotherm



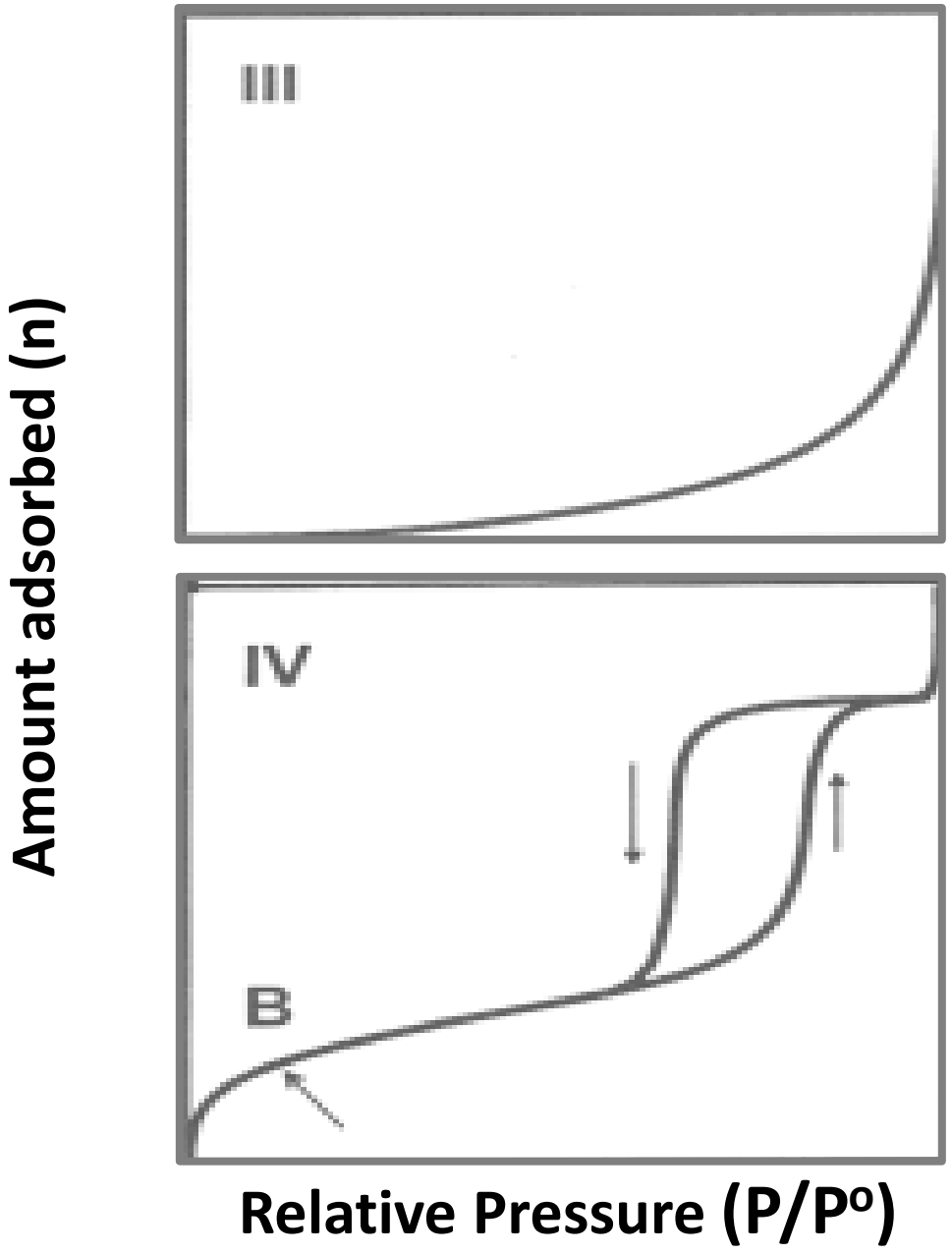
Type I

- Concave to P/P^o axis
- n^a approaches limiting value as $P/P^o \rightarrow 1$
- Microporous solids

Type II

- Unrestricted mono-multilayer adsorption
- B indicates complete monolayer coverage
- Non-porous or macroporous

Preliminary Results-Cont



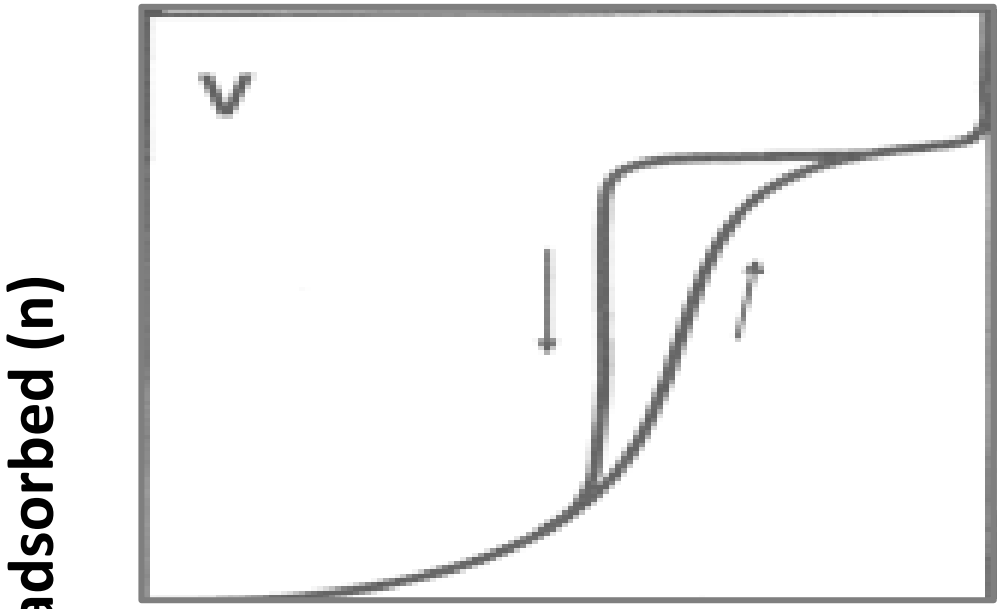
Type III

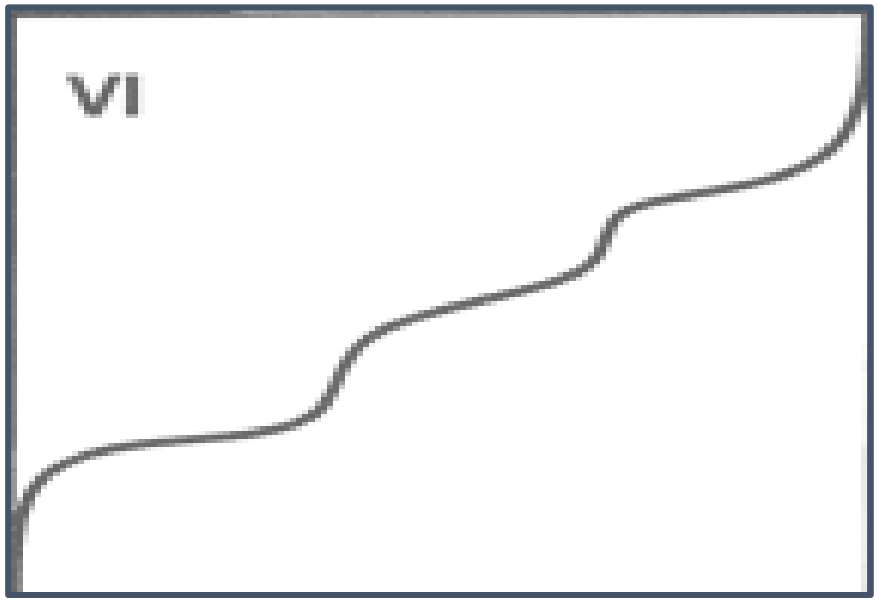
- Convex to P/P^o axis
- Not common
- Adsorbate-adsorbate interactions

Type IV

- Hysterisis loop
- Capillary condensation that occurs in a mesopores
- Limit uptake of high P/P^o
- Initial loop = mono-multilayer adsorption
- 2nd loop= desorption

Preliminary Results





Amount adsorbed (n)

Relative Pressure (P/P^o)

Type V

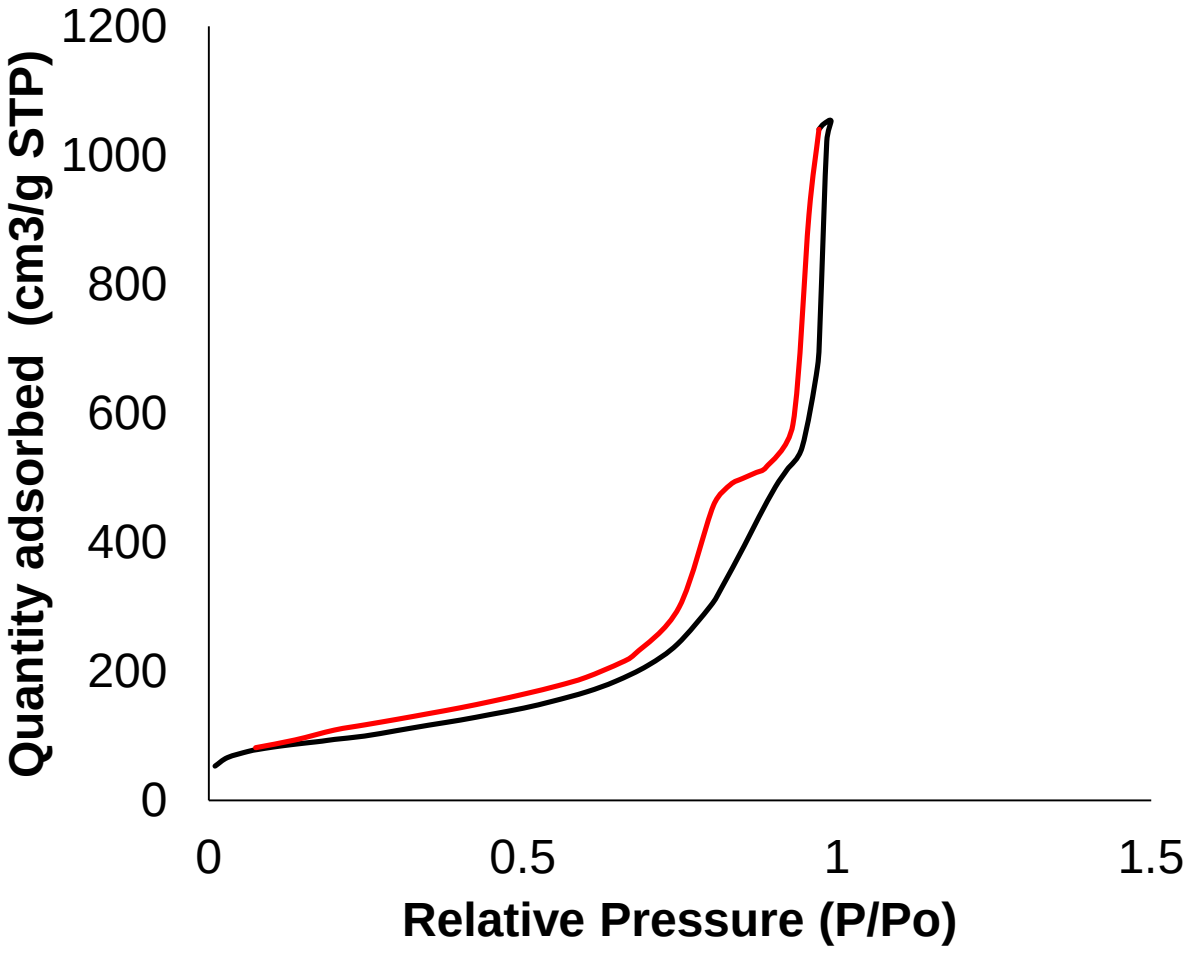
- Not common
- Weak adsorbate-adsorbate interactions
- Porous adsorbents

Type VI

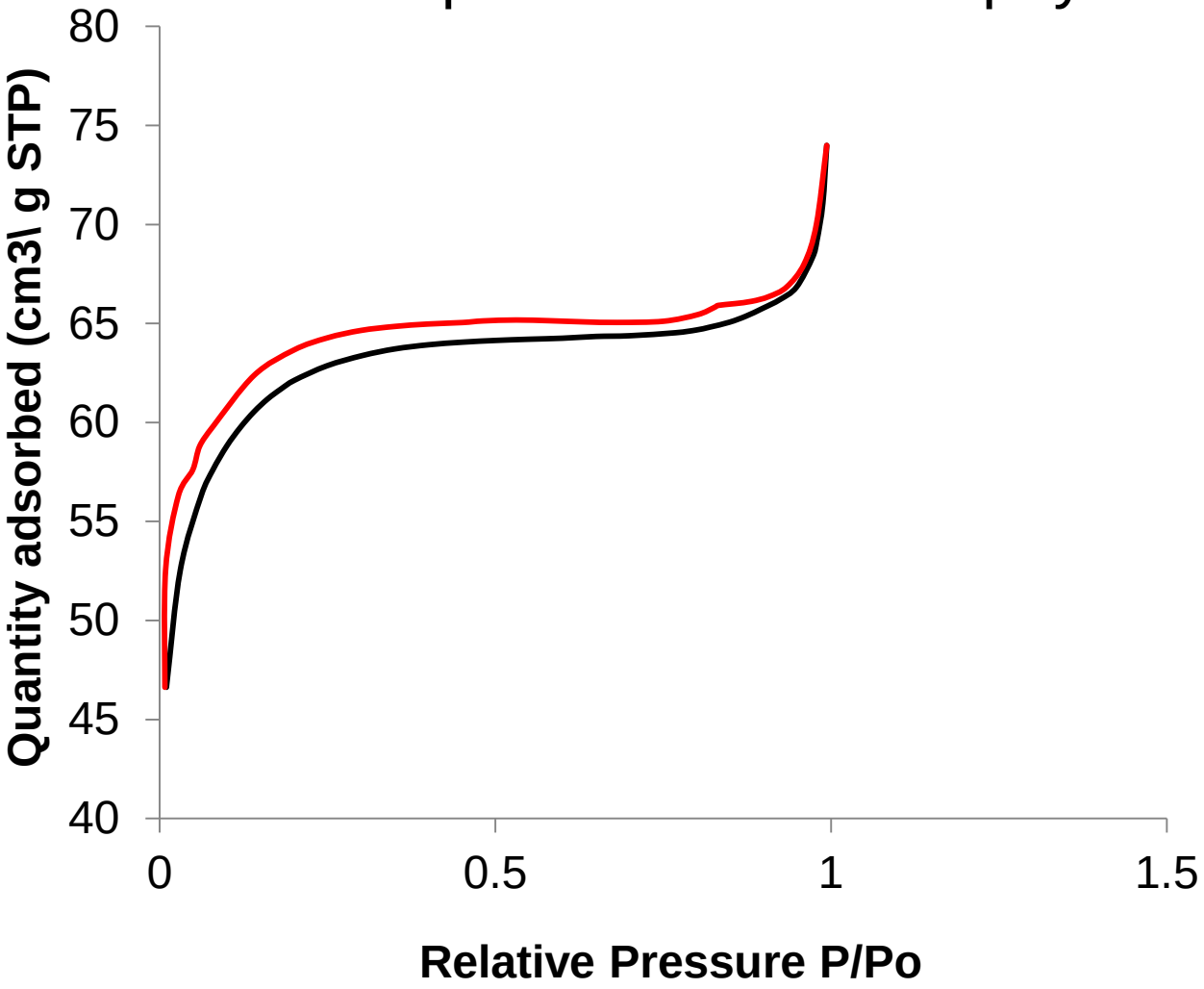
- Sharpness of peaks depends on the system and T
- Stepwise multilayer adsorption on a uniform non-porous surface

Application

PluS nanoparticles



PluS nanoparticles linked Porphyrin

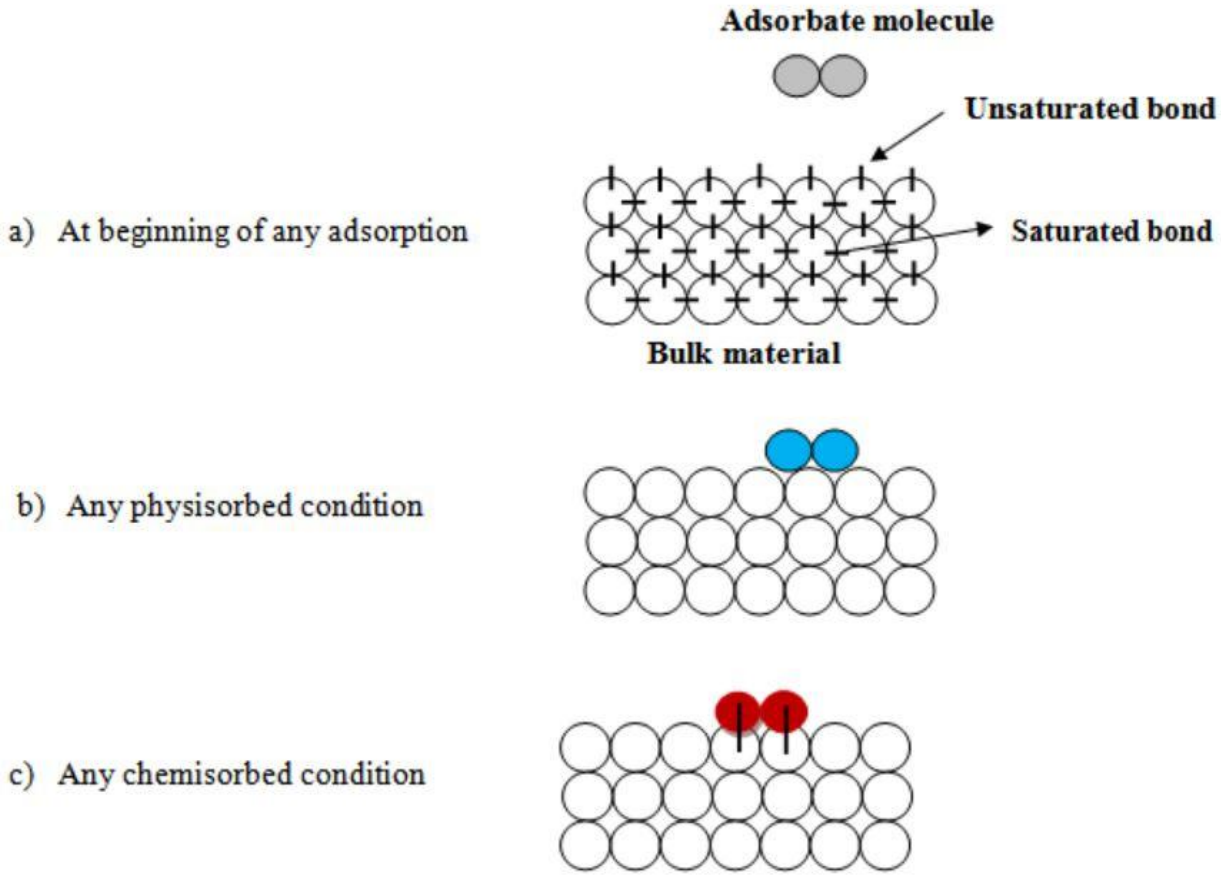


Application

Sample	Surface area (m^2/g)	Pore size (nm)
PluS NPs	330.0	18.9
PluS NPs-Porphyrins	192.5	2.4

Quantachrome Gas Adsorption Analyzer

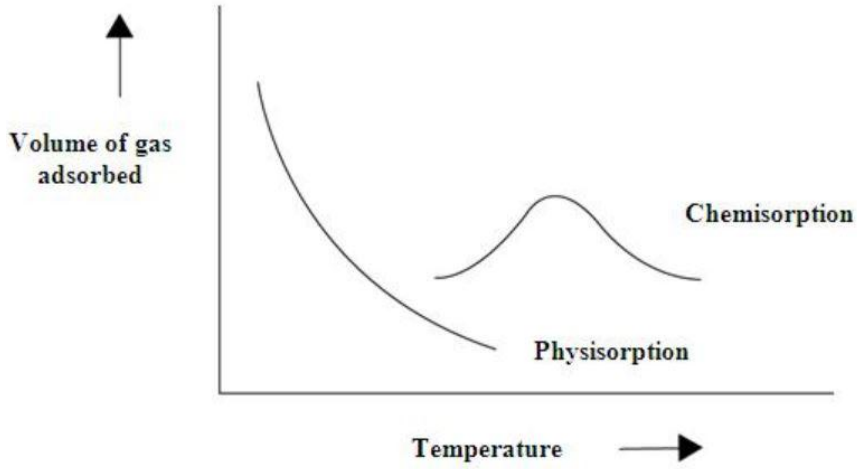
A distinctive characteristic of solid material is a distribution of weak surface energy sites. Gas or vapour molecules can become bound to these sites.



Quantity of molecules taken up by the surface depends on T, P, surface energy distribution and surface area

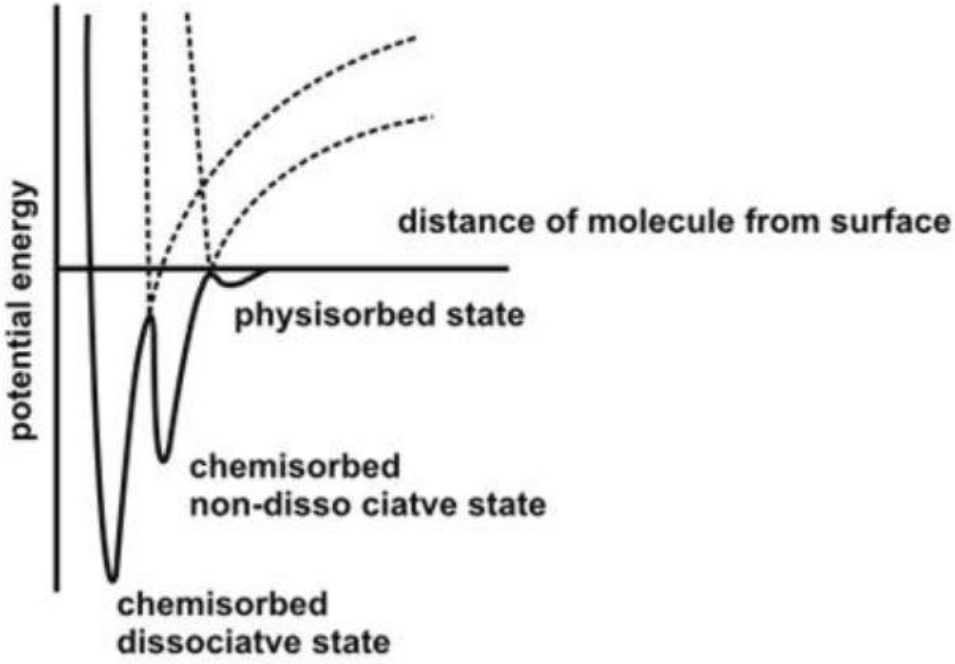
Adsorption/Desorption

- Adsorption is the sticking of gas molecules onto the surface of a solid… all available surfaces including that surface inside open pores.
- Increasing the pressure of gas over a solid causes increasing adsorption.
- Temperature dependent
- Desorption is the removal of gas molecules from the surface of a solid… all available surfaces including that surface inside open pores.
- Decreasing the pressure of gas over a solid causes increasing desorption.
- Done at same temperature as adsorption.



The Nature of Gas Sorption at a Surface

- **When the interaction between a surface and an adsorbate is relatively weak only physisorption takes place.**
- **However, surface atoms often possess electrons or electron pairs which are available for chemical bond formation.**
- **This irreversible adsorption, or chemisorption, is characterized by large interaction potentials which lead to high heats of adsorption. As is true for most chemical reactions, chemisorption is usually associated with an *activation energy*, which means that adsorbate molecules attracted to a surface must go through an energy barrier before they become strongly bonded to the surface.**



Physisorption vs Chemisorption

Property	Physisorption	Chemisorption
Forces	van der Waals	Chemical bonding
ΔH_{ads} (kJ mol^{-1})	< 40	50-200
E_a (kJ mol^{-1})	Rare	60–100
Isothermal Reversibility	Complete	Slow or none
Extent	Multilayers	Monolayer

Physisorption: Surface area and porosity are physical properties that impact the quality and character of solid phase materials, Pore size distribution, Pore Volume etc.

Chemisorption - measures the number of surface active sites which are used to promote a specified catalytic reaction. Critical parameters for chemisorption measurement are: the area of the active element, metal dispersion, surface acidity, exposed proportion of the active element.

Stage 1:

Isolated sites on the sample surface begin to adsorb gas molecules at low pressure.

Stage 2:

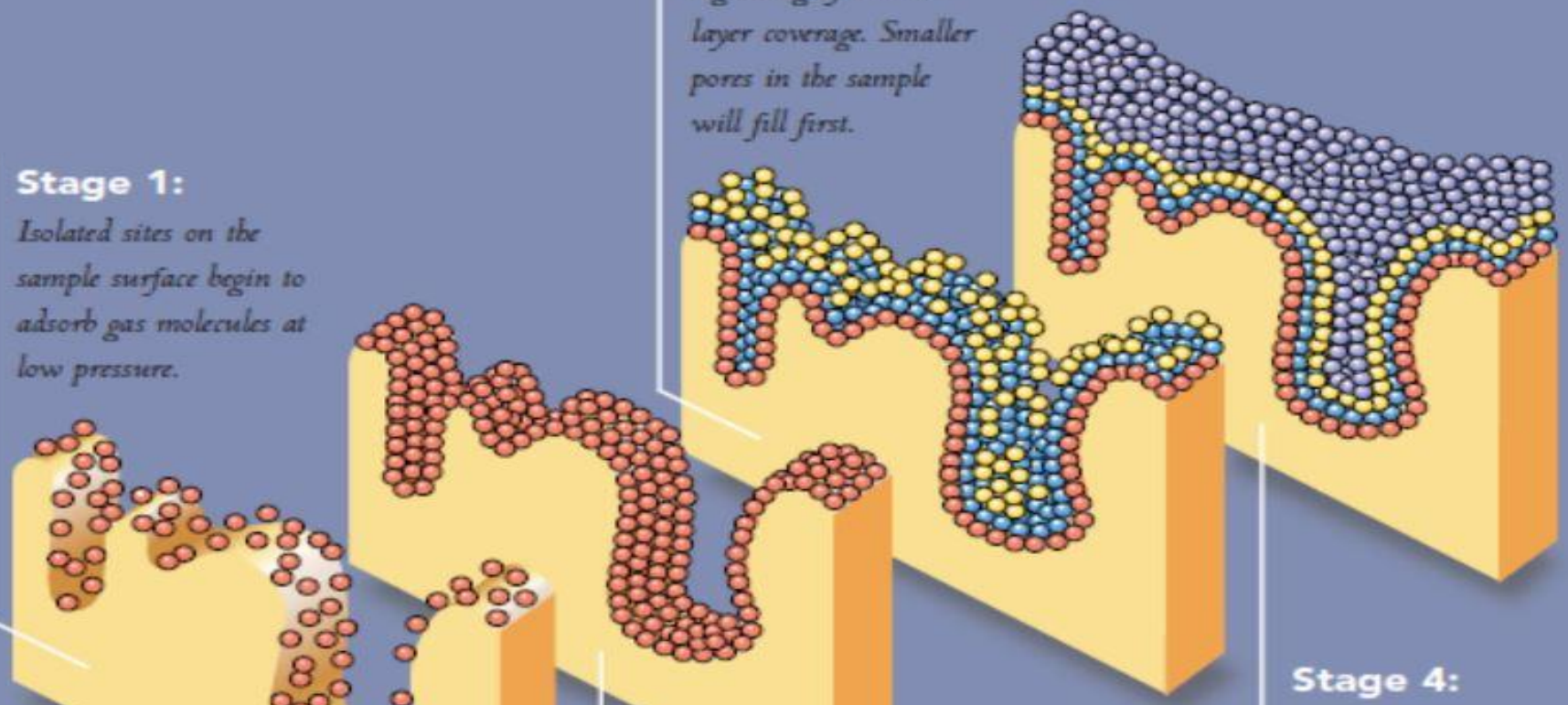
As gas pressure increases, coverage of gas molecules increases to form a monolayer (one molecule thick). BET equation is used to calculate the surface area.

Stage 3:

Further increasing gas pressure will cause the beginning of multi-layer coverage. Smaller pores in the sample will fill first.

Stage 4:

Still further increases in the gas pressure will cause complete coverage of the sample and fill all the pores. The BJH calculation can be used to determine pore diameter, volume and distribution.



Inert Gas Adsorption

- What can be measured using this technique?
  - Specific Surface Area
  - Pore Size Distribution
  - Heats of Adsorption
- Who would be interested in such results?
- Everyone who needs to understand how pore structure affects material performance.
  - **Surface Area**
    - affects dissolution rates.
    - affects electron/ion current density at electrode interface with electrolyte.
    - affects adsorption capacity.
    - represents surface free energy available for bonding in tabletting and sintering.
  - **Pore Size Distribution**

    -affects diffusion rates.

    -affects molecular sieving properties.

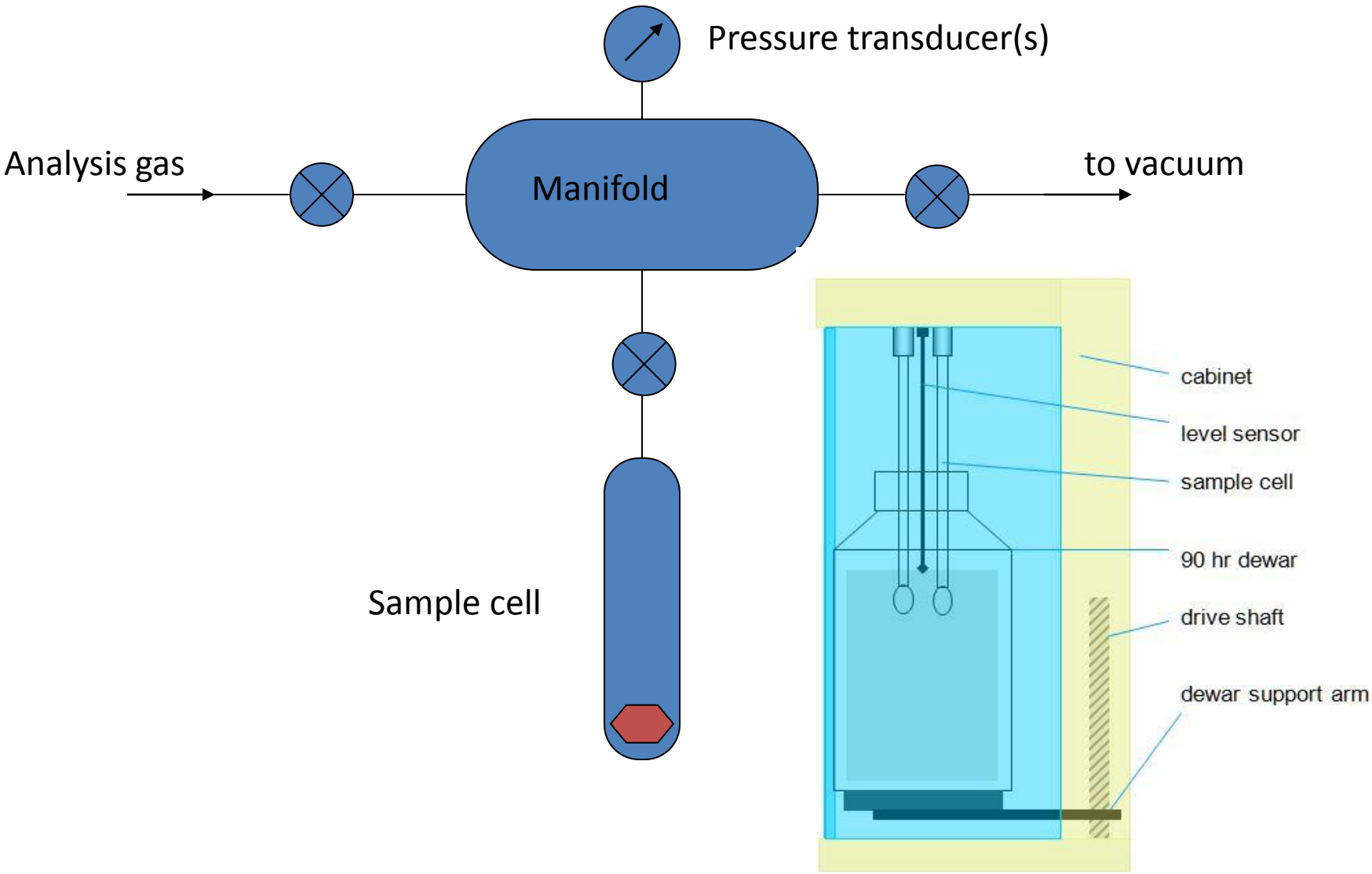
    - affects surface area per unit volume.

So, How Does It Work?

- **Basic Construction**
  - **Removable sample cell**
  - **Dosing manifold**
  - **Pressure transducers**
  - **Vacuum system**
  - **Analysis gas**
  - **Valves to move gas in and out of manifold and sample cell**
  - **Sample thermostat (dewar, furnace, cryostat)**

***** Before performing gas sorption expts, solid surfaces must be freed from contaminants like water and oils**

Basic Construction



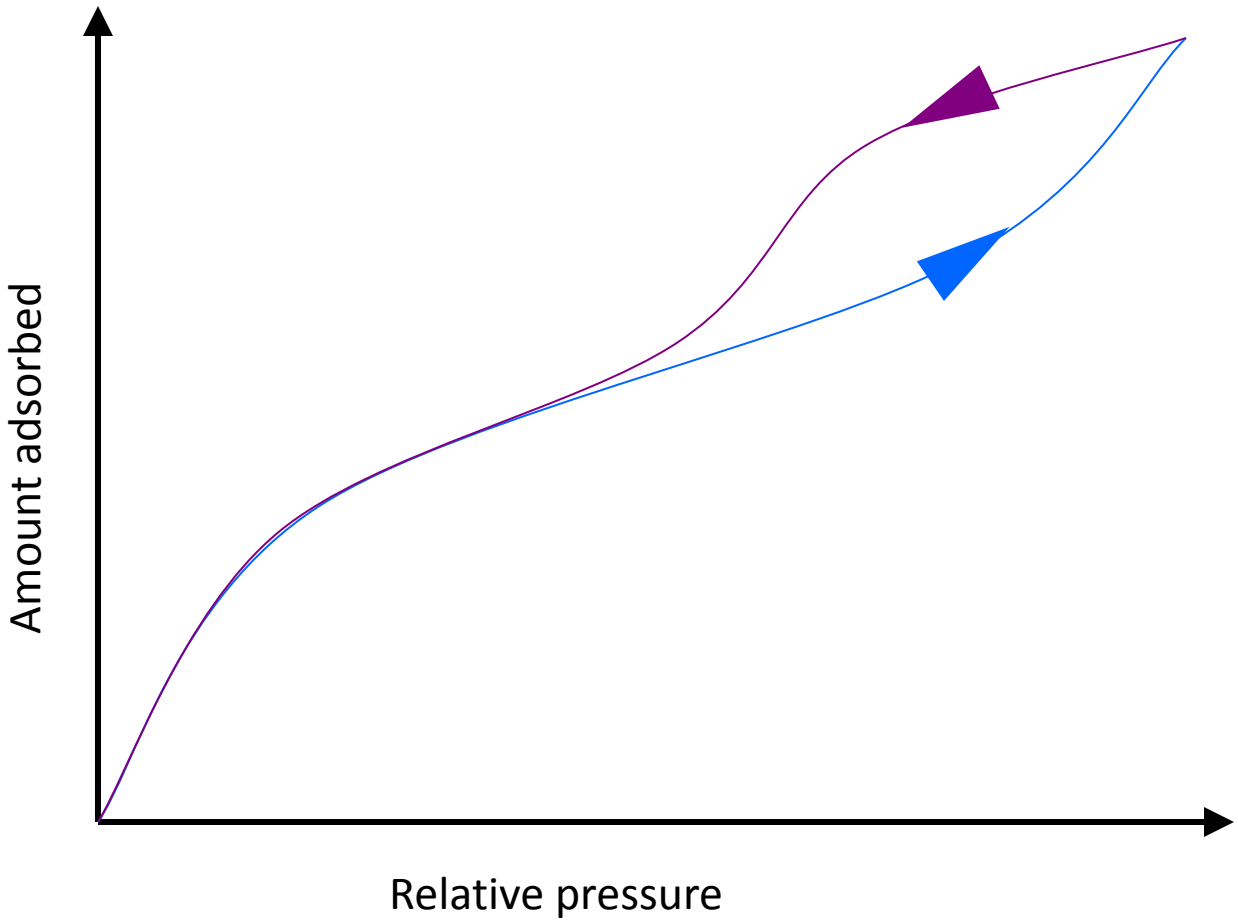
What is a Gas Sorption Analyzer?

- Does it actually measure surface area and pore size?

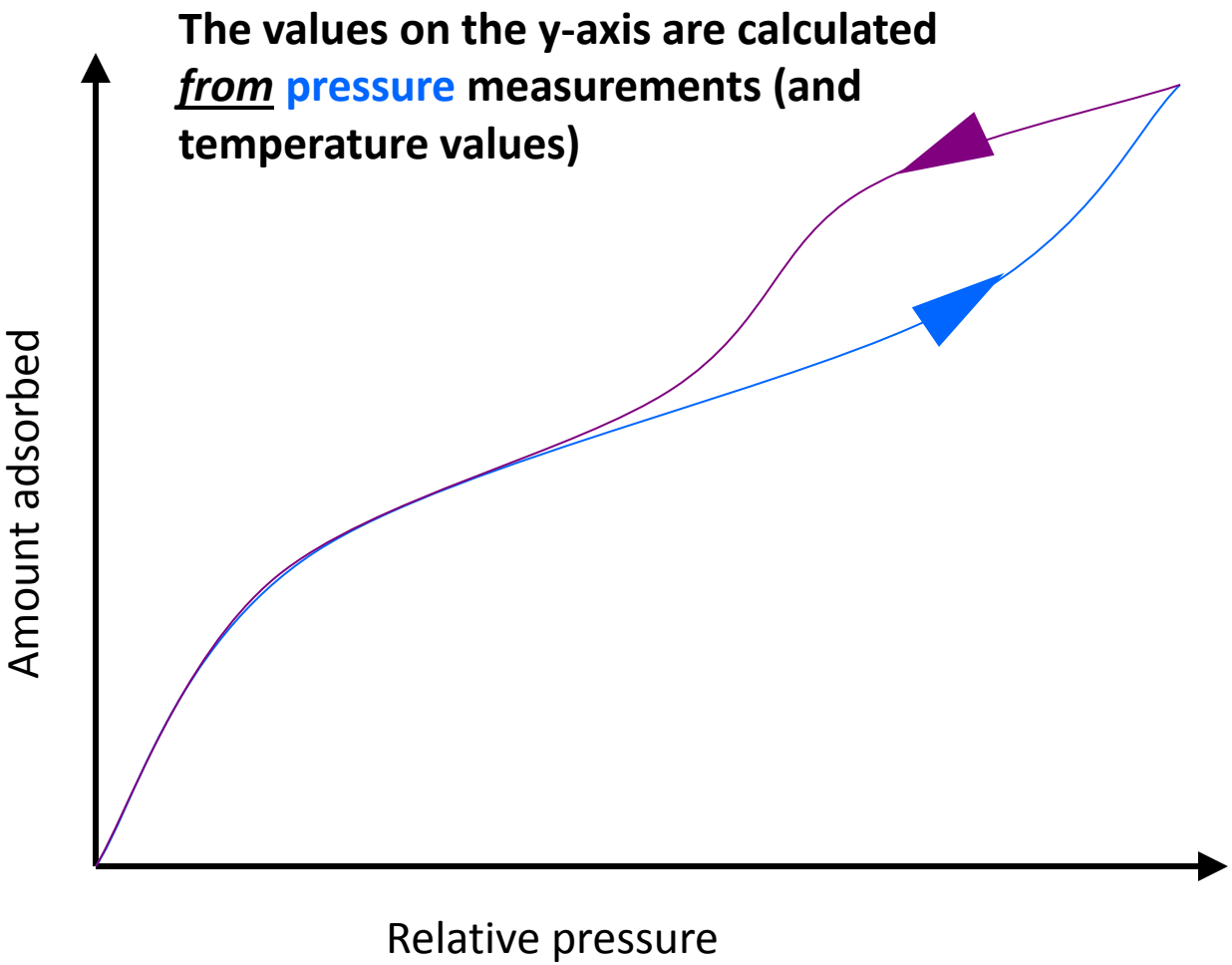
- NO!! It simply records various pressures of gas in the sample cell due to adsorption and desorption. *The instrument then calculates the amount (as STP volume) of gas adsorbed/desorbed. Surface area, pore size are calculated by PC software*
- Pressure measurements are critical!

What Is The Result?

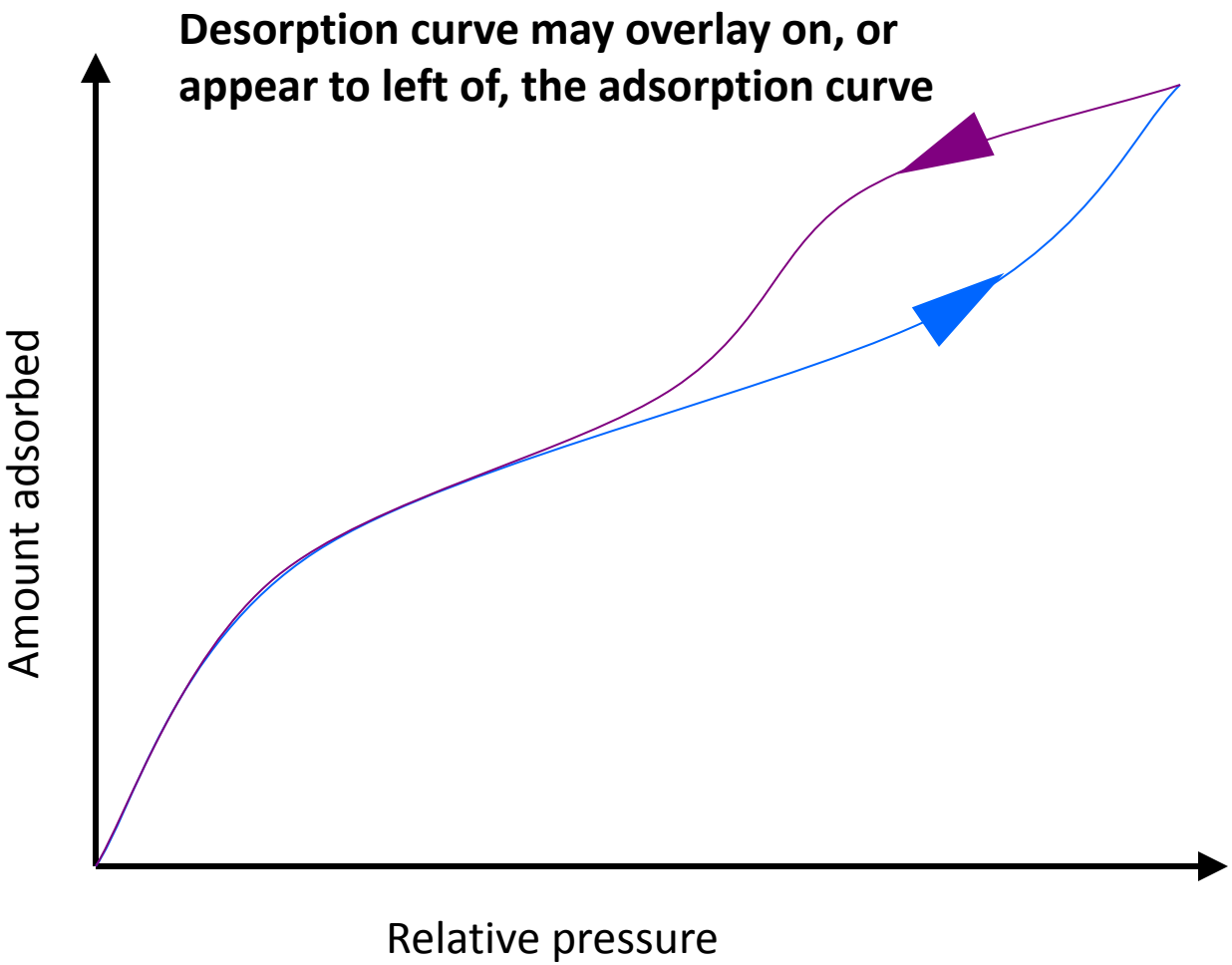
It's called an "isotherm"



What Is The Result?

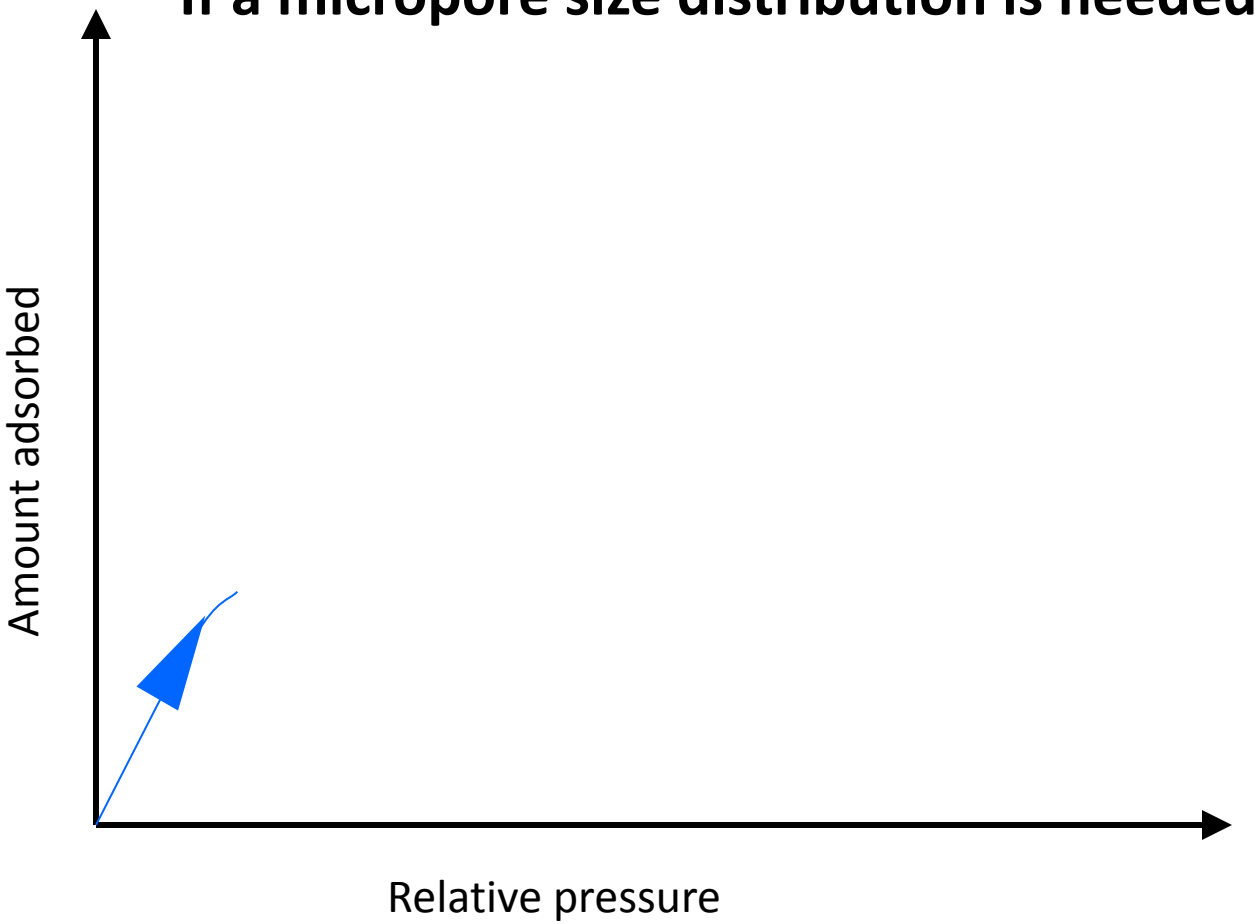


What Is The Result?



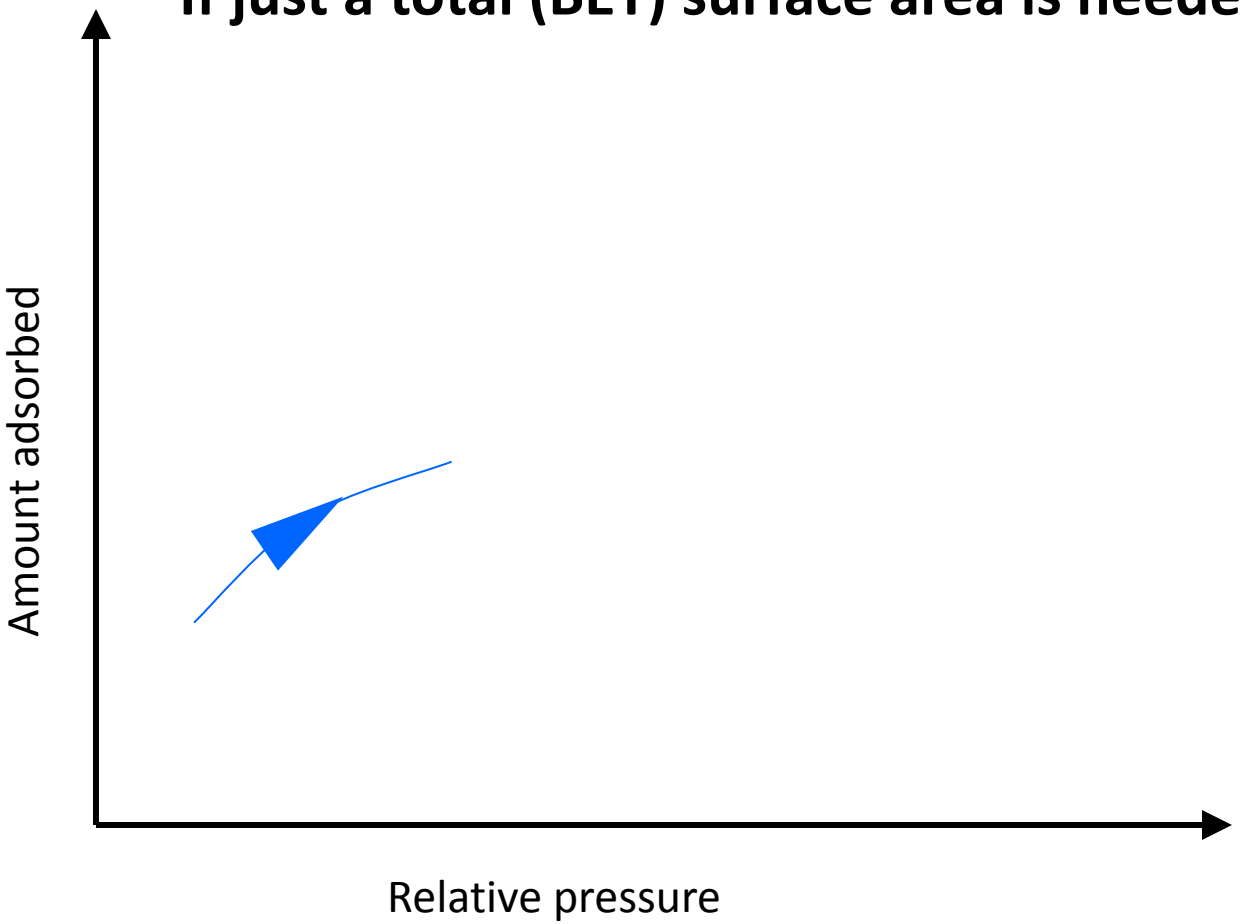
What To Analyze?

If a micropore size distribution is needed:



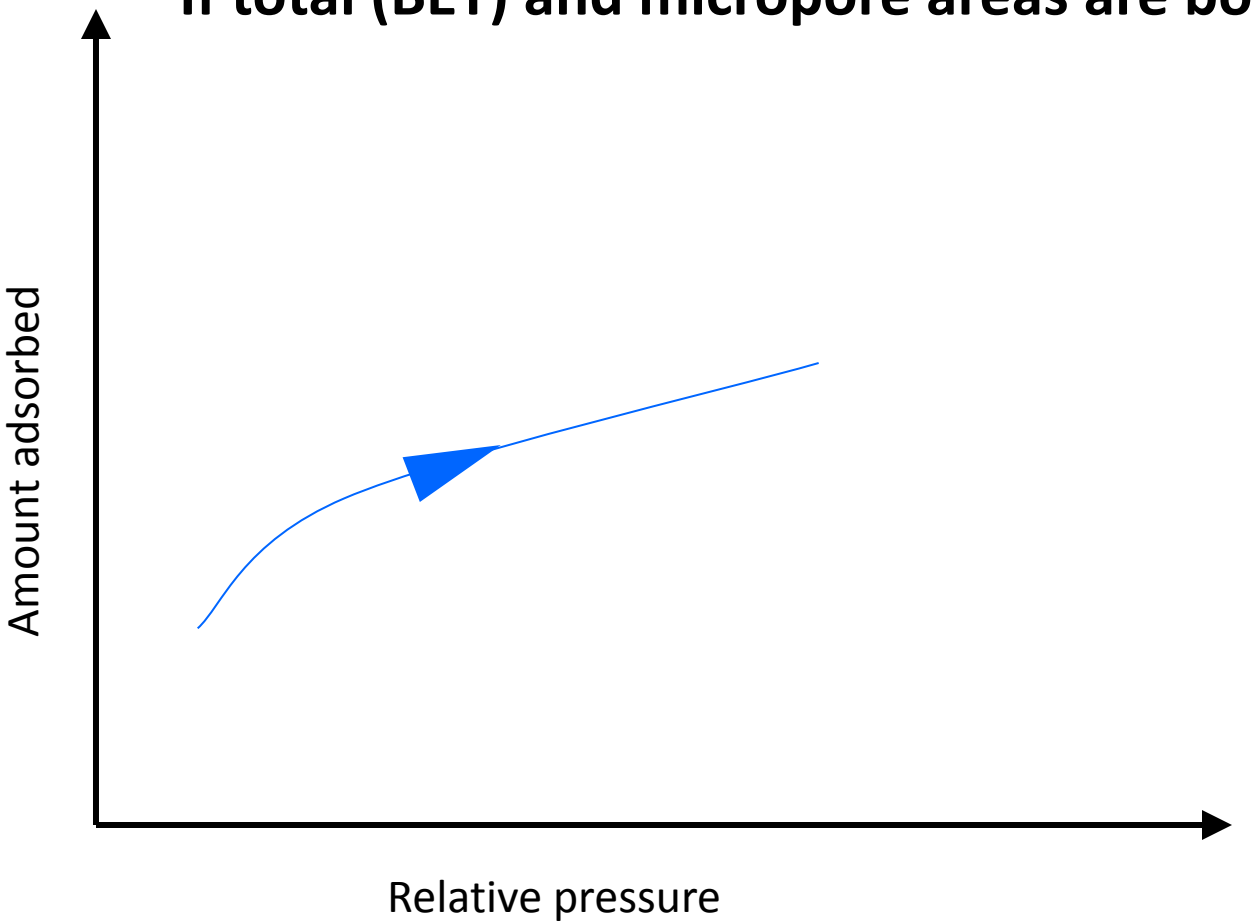
What To Analyze?

If just a total (BET) surface area is needed:



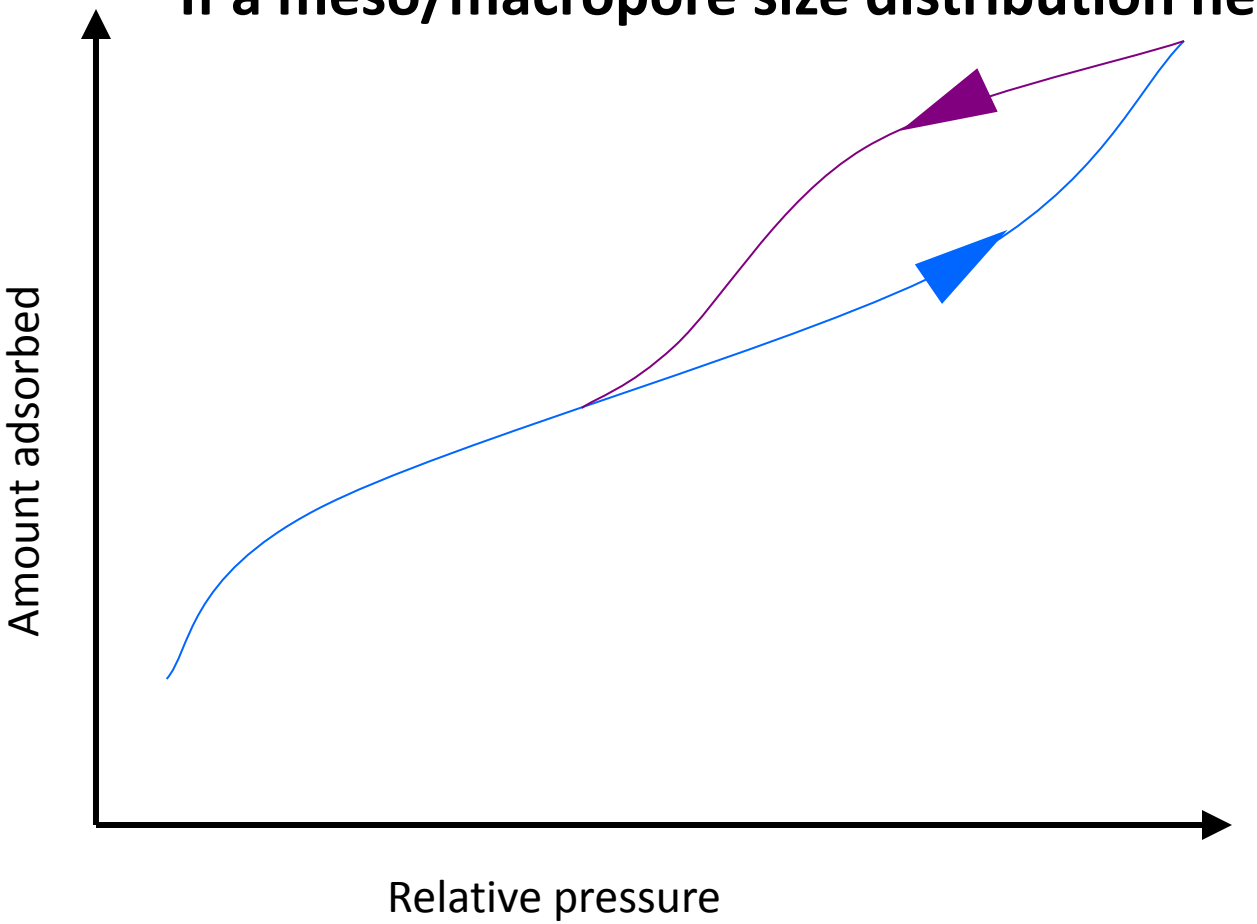
What To Analyze?

If total (BET) and micropore areas are both needed:



What To Analyze?

If a meso/macropore size distribution needed:

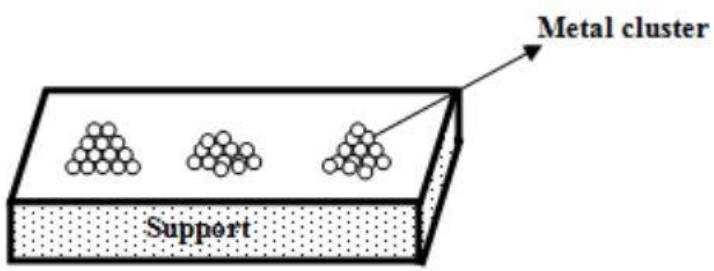


Reactive Gas Adsorption

- What can be measured using these techniques?
  - Amount of reactive sites on a surface
    - Active metal area
    - Dispersion
  - Heats of adsorption
  - Ease of reduction (TPR)
  - Ease of oxidation (TPO)
  - Bond strength (TPD)
  - Activation Energy

Active metal area/dispersion by	• **Chemisorption Methods**
	  • **Static**
	  • **Flow**

Reducibility by	• TPR (Temperature Programmed Reduction)
Oxidizibility by	• TPO (Temperature Programmed Oxidation)
Acid site strengths by	• TPD (Temperature Programmed Desorption)



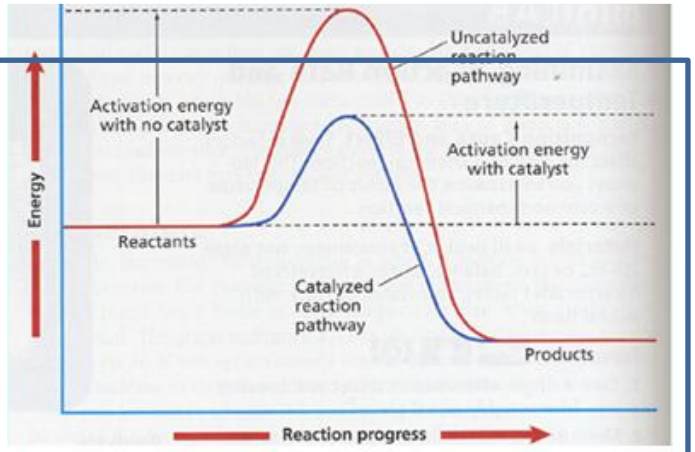
Dispersion is defined as the percentage of all metal atoms in the sample that are exposed.

Reactive Gas Adsorption

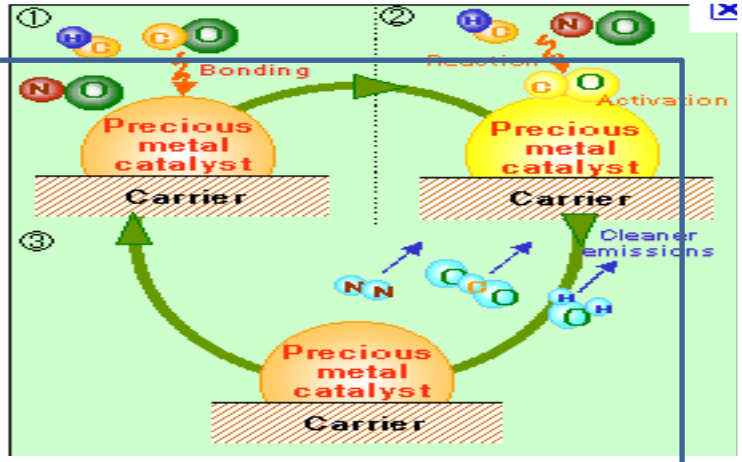
- Who would be interested in such results?
  - Catalyst researchers
    - Chemists
    - Chemical engineers
  - Catalyst manufacturers
  - Catalyst users
  - Catalyst regenerators

Idea : Catalysts utilize supports.

- **Typical Supports :**
  - **Silica/alumina**
  - **Clays**
  - **Zeolites**
  - **Carbon-graphite**
  - **Carbon black**
  - **Activated charcoal (carbon)**
  - **Titanium oxide**
- **Supports have**
  - **Ample Surface Area**
  - **Correct Pore Size**
  - **Proper Chemistry (E.g Alumina Acidic)**



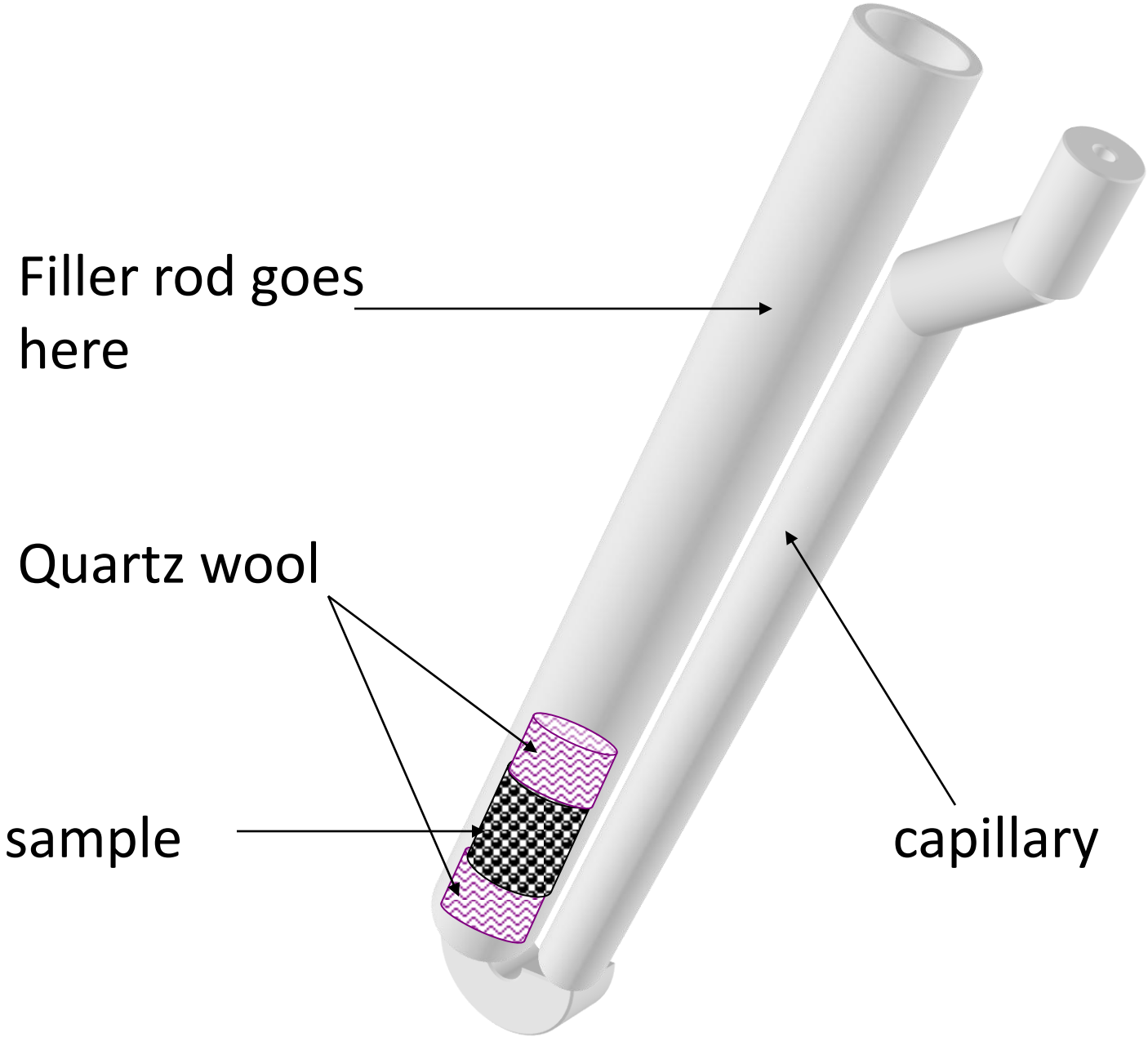
A catalyst acts by bringing reactants together to make a reaction more likely.



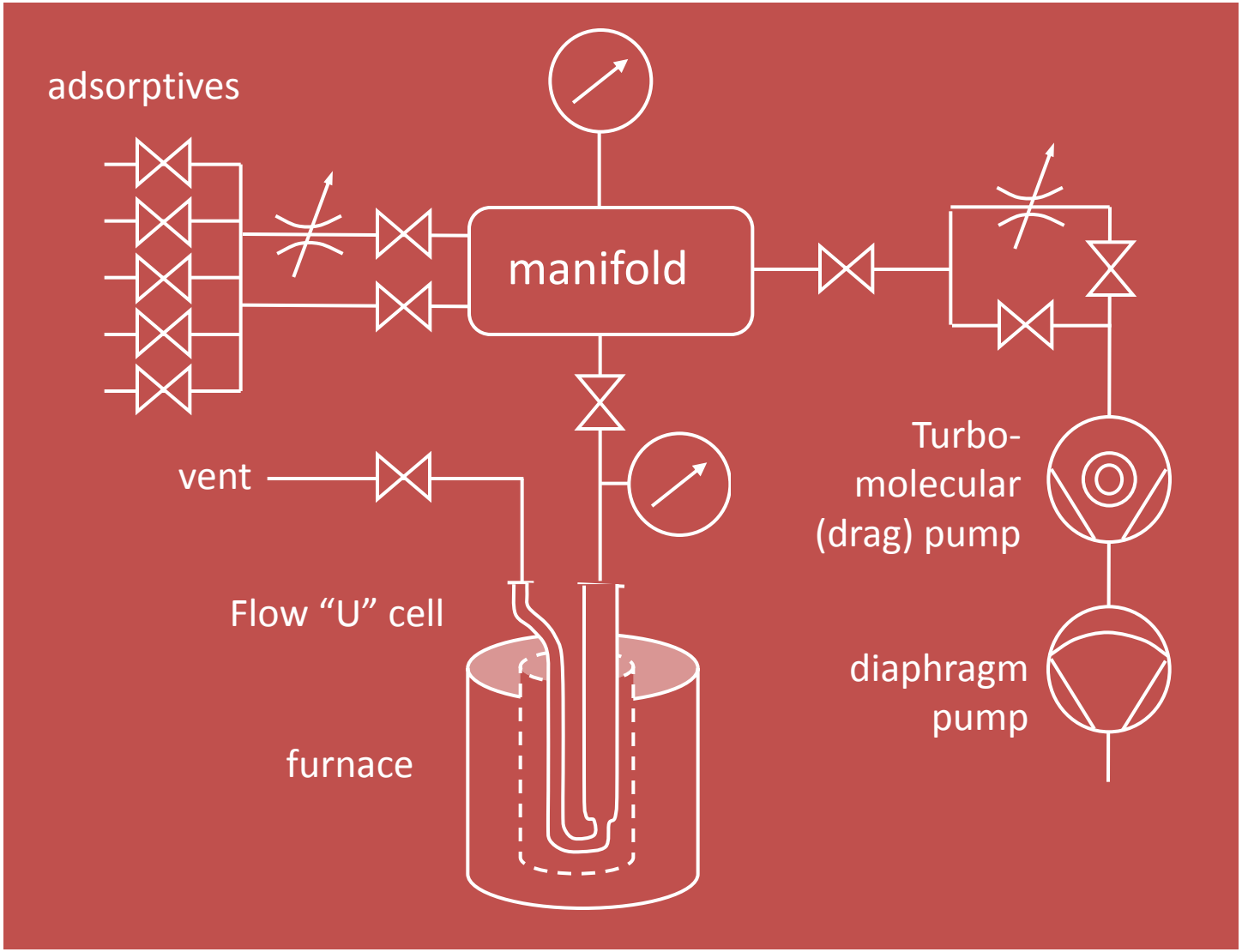
Reduces activation barriers, “holds” reactants in place.

Virtually all industrial chemical processes are facilitated / optimized with catalysts

Quartz Flow Cell



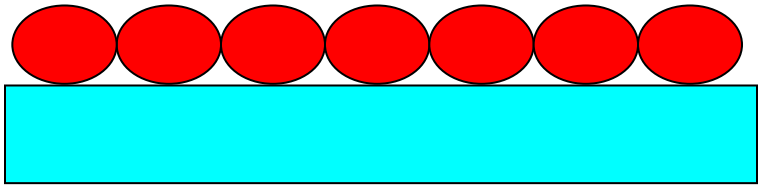
Chemisorption Setup

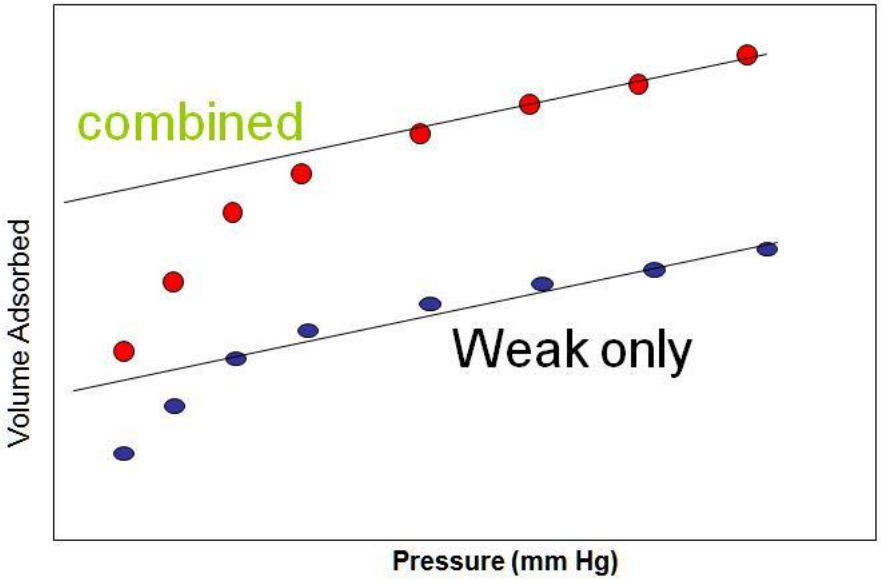


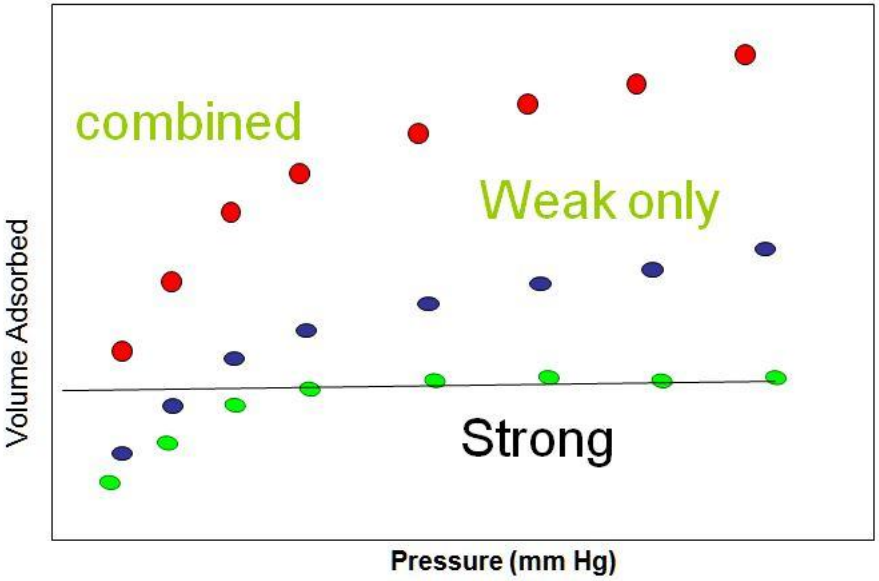
Principles of Calculation

Monolayer Volume, Vm

= volume of gas chemisorbed in a monomolecular layer





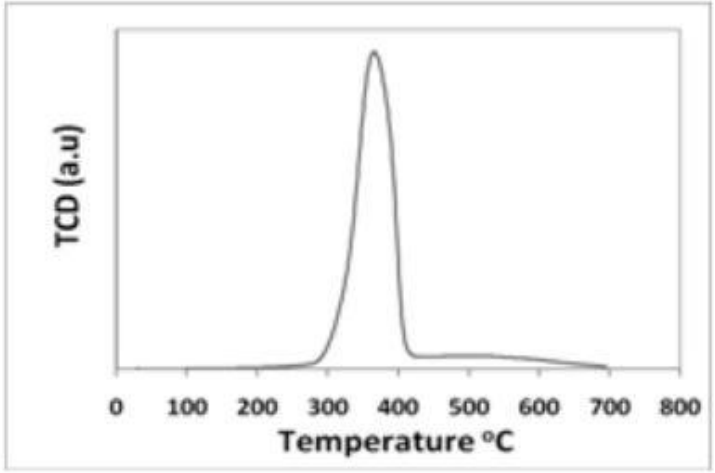


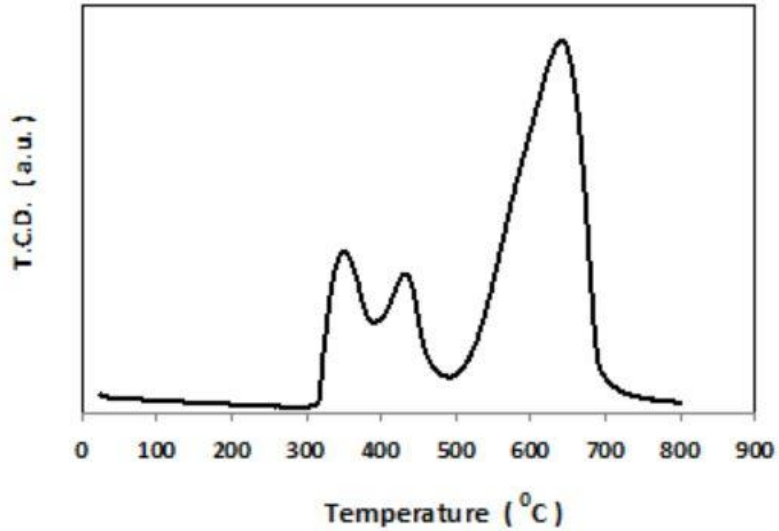
TPR measurements

Solid catalysts containing reducible metals are characterized using TPR. Following information can be gained from TPR curves:

1. Reduction peak temperature indicates the ease of reduction and degree of interaction between different species present in the catalyst sample. A higher reduction temperature indicates higher difficulty in reduction which can be attributed to the greater degree of interaction between the active metal and support.

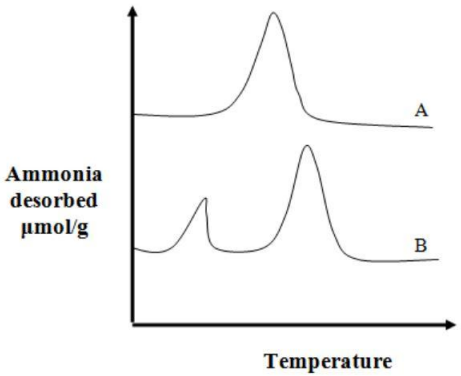
2. Multiple peaks indicate the presence of metal in different forms on the support having different level of interaction between species and support.





TPD measurements

a) Type and amount of different forms of adsorbed species which correspond to the presence of various peaks
b) Relative bond strength between the adsorbate and surface which corresponds to the various peaks at different temperature. Higher the desorption temperature stronger the bonds and site strength



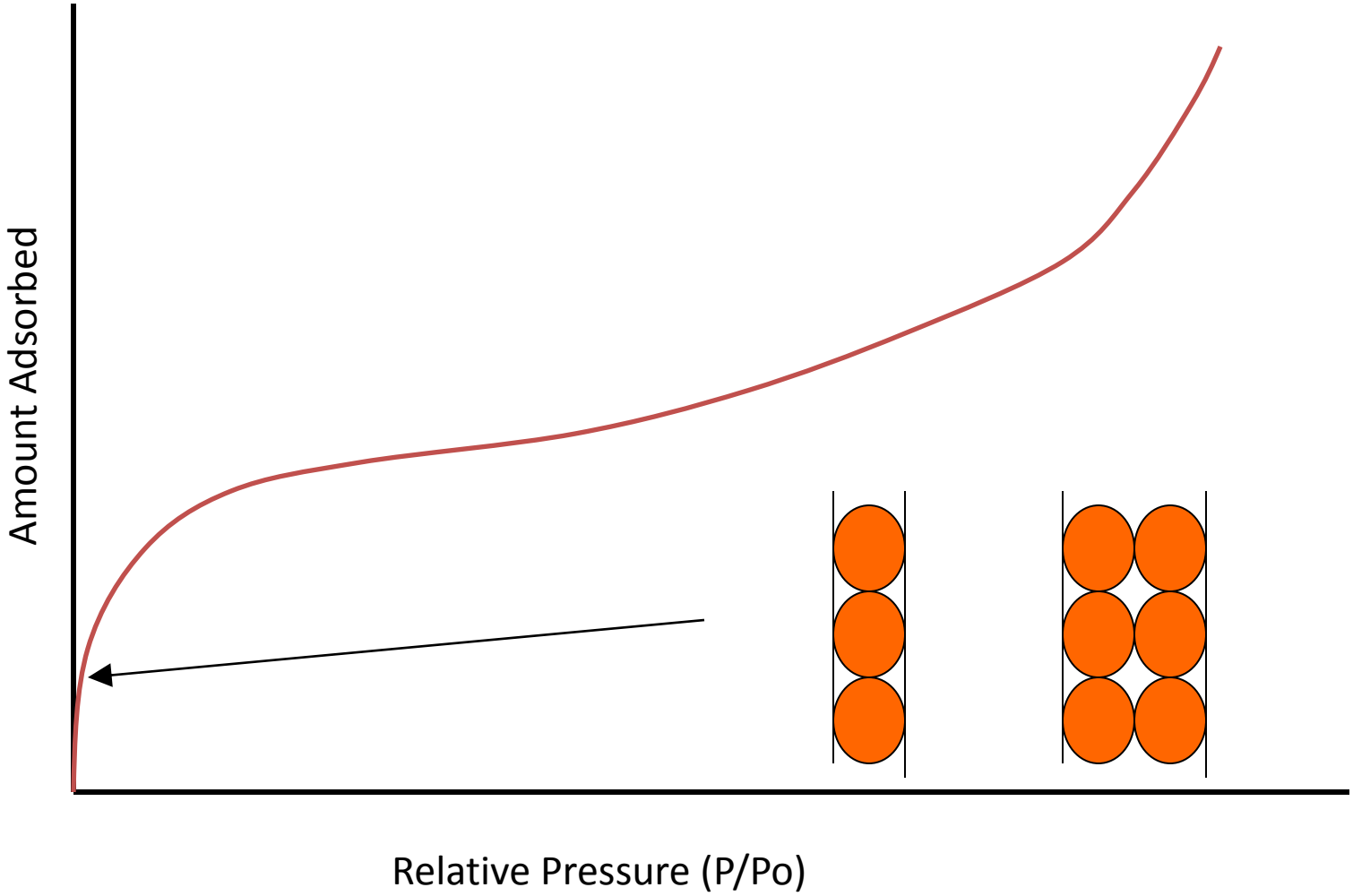
TPD is extensively used for
a) Study of acidic and basic sites on the surface
b) Study of gas adsorbed on surface
c) Study of organic compounds adsorbed on surface

For study of acidic and basic sites mainly two types of probe adsorbate molecules are used for TPD studies :
a) NH_3 desorption for determining acidic sites
b) CO_2 desorption for determining basic sites

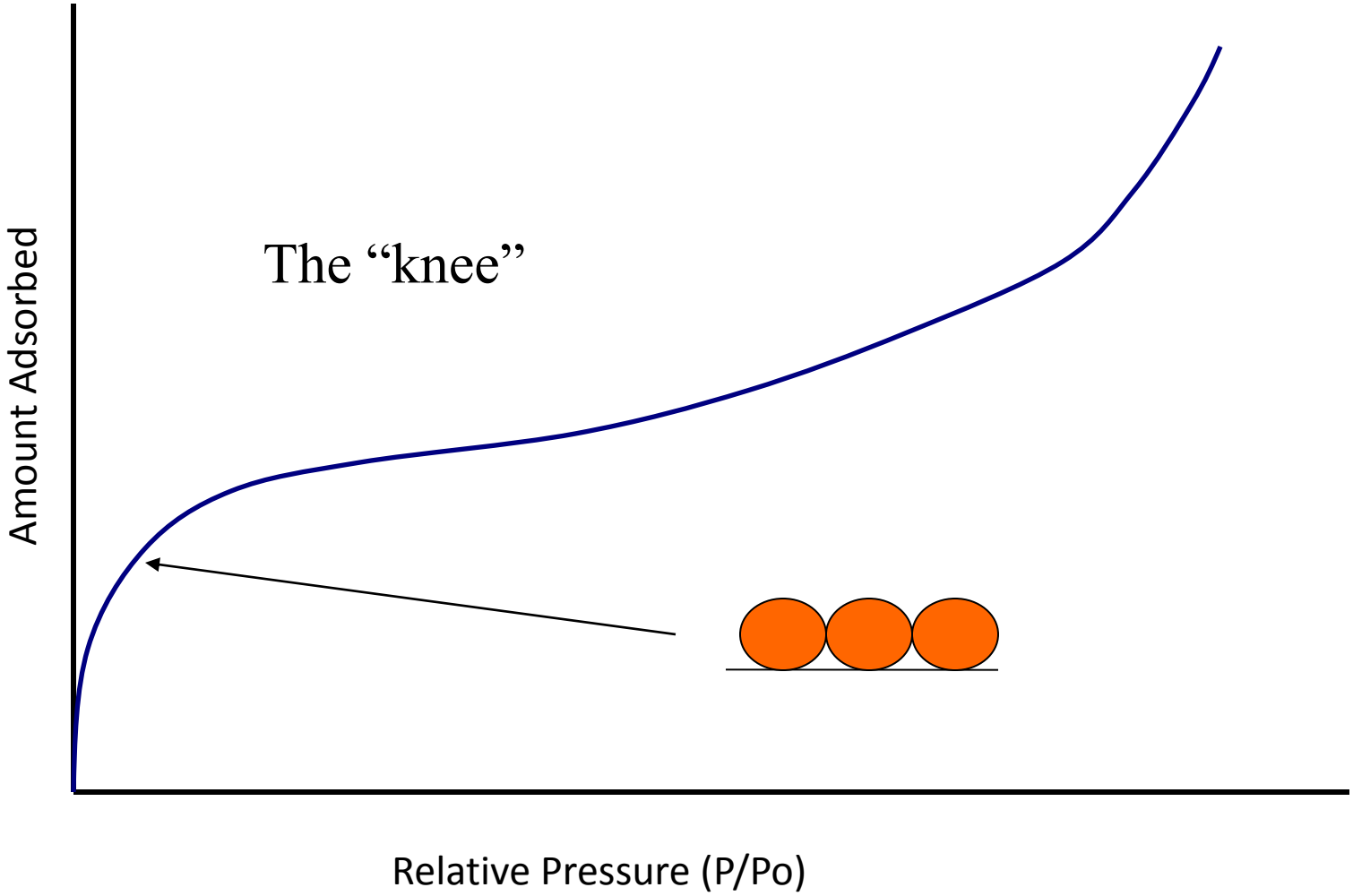
Since NH_3 is basic in nature it adsorbs on the acidic sites on the surface.
CO_2 is an acidic gas and can absorb on basic sites on catalysts surface.

Adsorption study of any gases such as CO, H_2, O_2, CH_4 on catalysts as required can easily be done using TPD. Total area under the curve gives capacity of adsorption and multiple peak positions gives the bond strength.

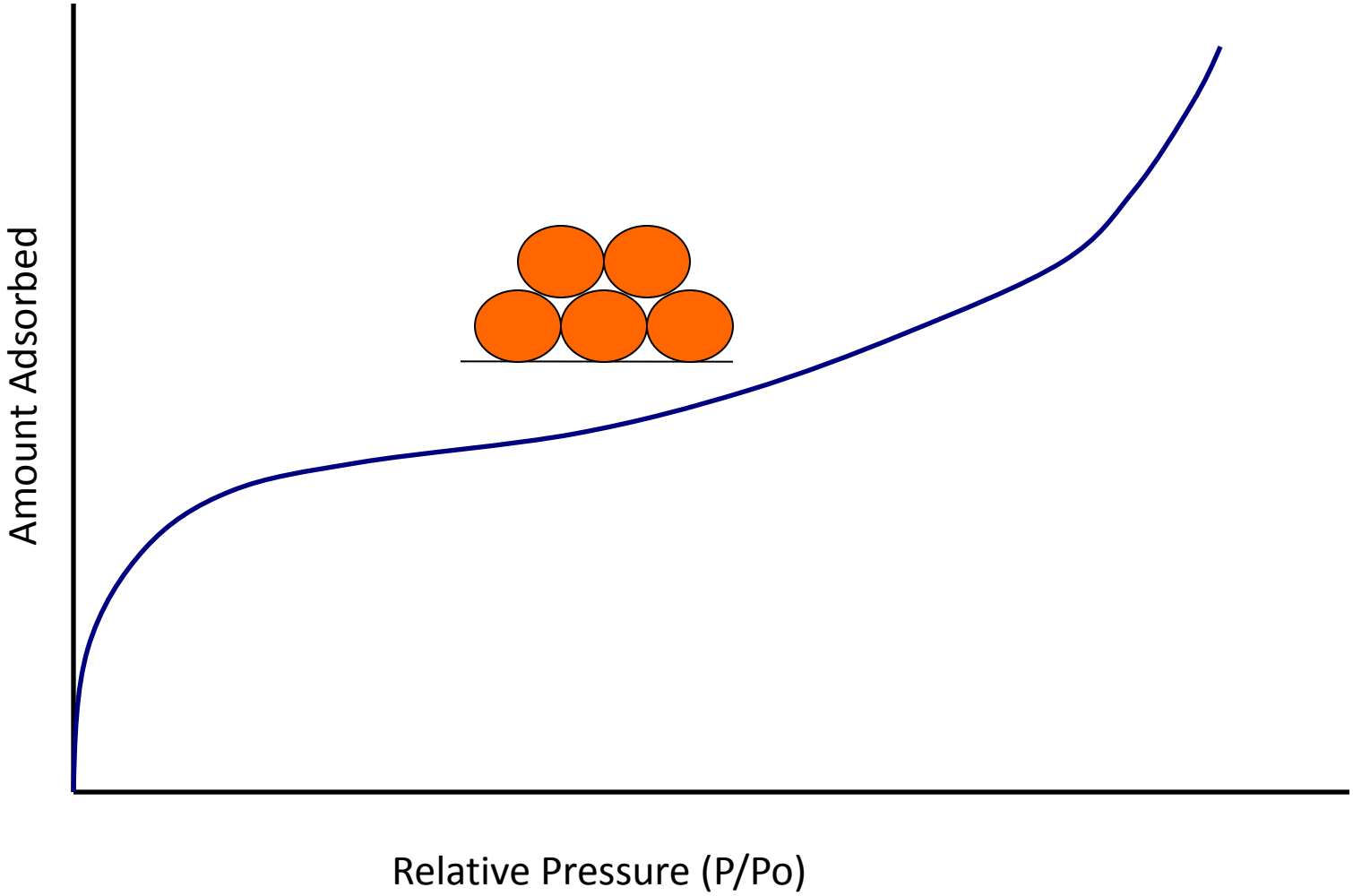
Very Low Pressure Behavior (micropore filling)



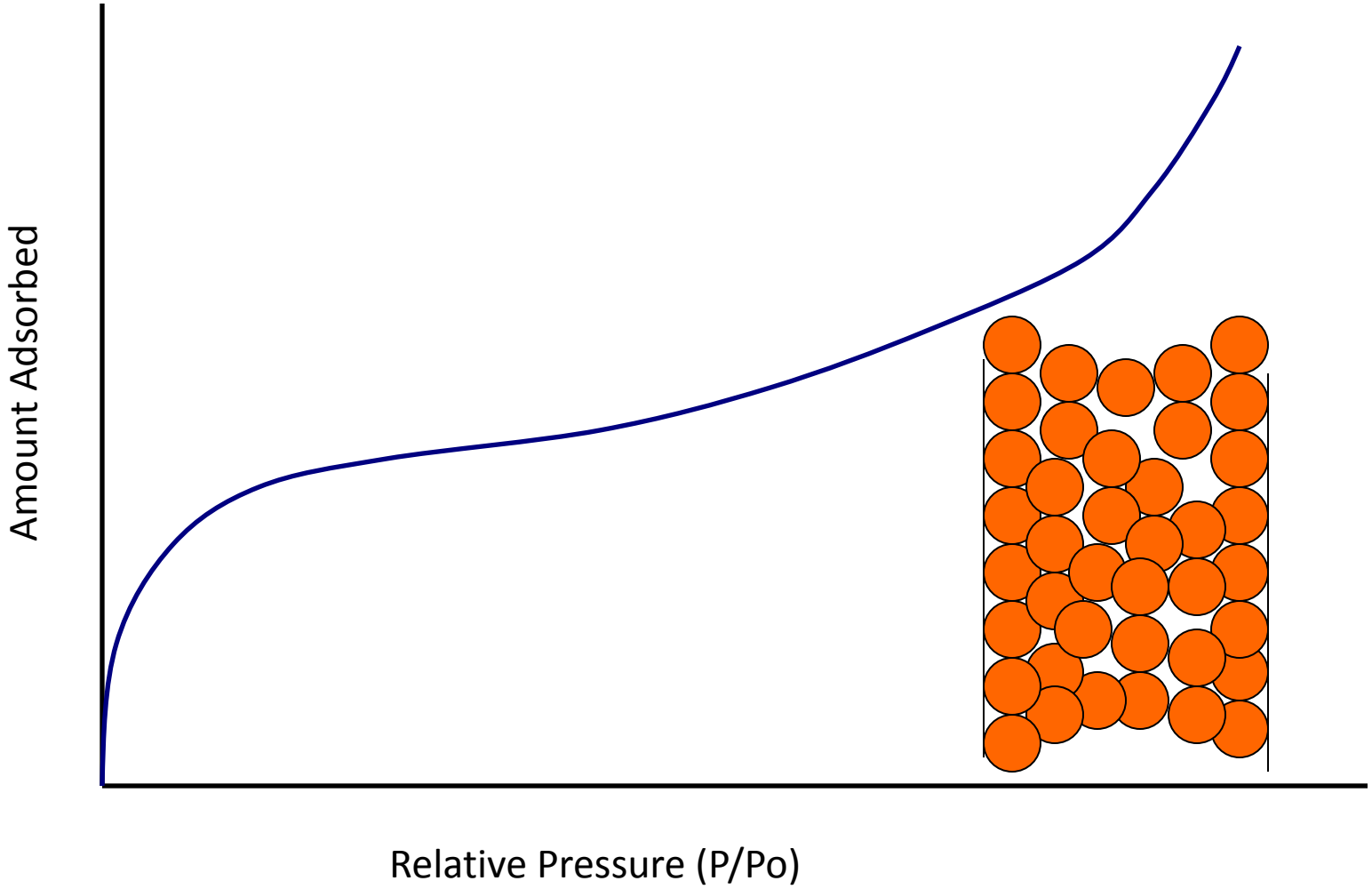
Low Pressure Behavior (monolayer)



Medium Pressure Behavior (multilayer)



High Pressure Behavior (capillary condensation)



Temperature Programmed Desorption

Temperature-Programmed Desorption (TPD) analyses determine the number, type, and strength of active sites available on the surface of a catalyst from measurements of the amounts of gas desorbed at various temperatures.

After the sample has been outgassed, reduced, or otherwise prepared, a steady stream of analysis gas flows through the sample bed and reacts with the active sites.

Programmed desorption begins by raising the temperature linearly with time while a steady stream of inert carrier gas flows through the sample.

At a certain temperature, the thermal energy overcomes the activation energy; therefore, the bond between the adsorbate and adsorbent breaks and the adsorbed species is liberated from the surface and swept away by the carrier gas.

If different active metals are present, the chemical bond between the adsorbed molecule and each metal type will likely be of different energy. Therefore the molecules adsorbed on each active metal will require a different thermal energy level to break the bond and desorb, resulting in distinct peaks on the plot of the TCD output signal vs. temperature.

presented

by

Neal Leddy

CMA Analytical Workshop

2012

SURFACE AREA AND POROSITY

centre for microscopy and analysis

Adsorption

- When a gas or vapour phase is brought into contact with a solid, part of it is taken up and remains on the outside attached to the surface.

- In physisorption (physical adsorption), there is a weak Van der Waals attraction between the adsorbate and the solid surface.

- Useful to characterise porous materials allowing for the determination of specific surface area, pore size distribution and pore volume.

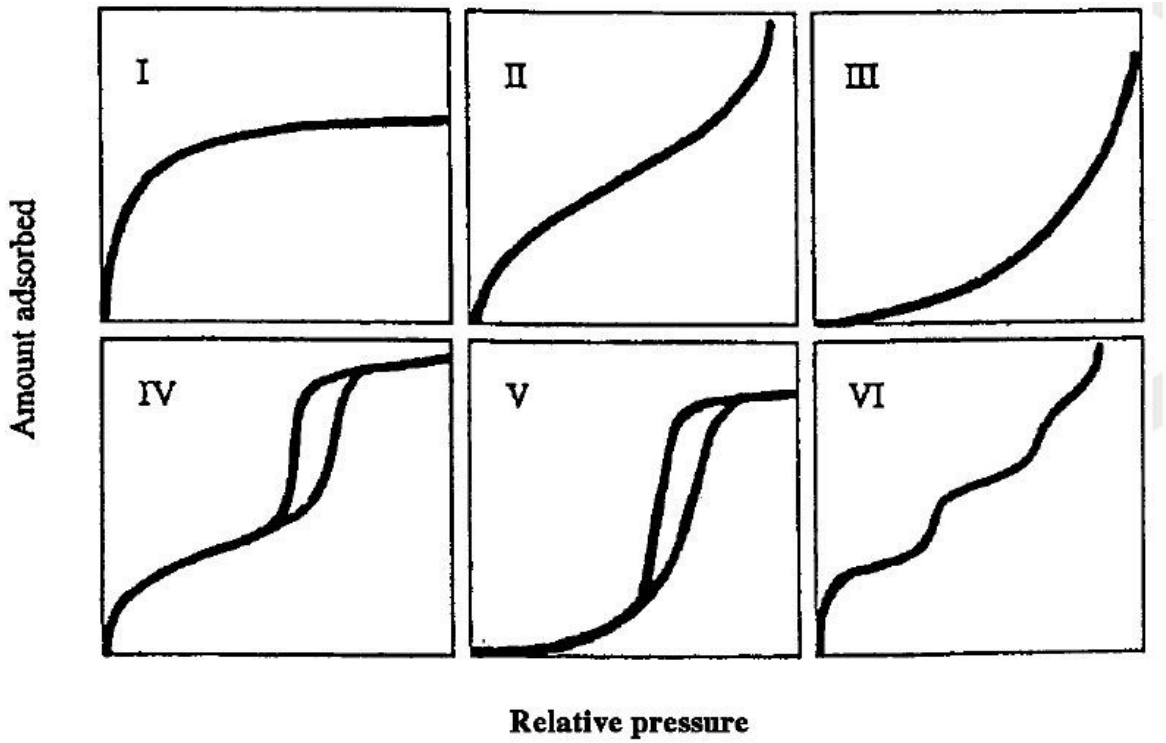
Characteristics of Physical Adsorption

- 1. Low heats of adsorption, no violent or disruptive structural changes.
- 2. Can involve multiple layers of adsorbate, thus allowing for pore measurements.
- 3. High temperatures tend to inhibit physical adsorption.
- 4. Adsorption equilibrium is achieved quickly since no activation energy is generally required.
- 5. Physical adsorption is fully reversible, allowing adsorbate to fully adsorb and desorb.

Adsorption Isotherms

- An Adsorption Isotherm is obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature (typically liquid N2, 77K). Conversely desorption Isotherms are achieved by measuring gas removed as pressure is reduced

lostherm types



described by Brunauer, Deming, Deming and Teller.

Type I

Pores are typically microporus with the exposed surface residing almost exclusively inside the microspores, which once filled with adsorbate, leave little or no external surface for further adsorption.

Type II

Most frequently found when adsorption occurs on nonporous powders or powders with diameters exceeding micropores.

Inflection point occurs near the completion of the first adsorbed monolayer

Type III

Characterised by heats of adsorption less than the adsorbate heat of liquification, adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface

Type IV

Occur on porous adsorbents with pores in the range of 1.5 – 100nm. At higher pressures the slope shows increased uptake of adsorbate as pores become filled, inflection point typically occurs near completion of the first monolayer

Type V

Are observed where there is small adsorbate-absorbent interaction potentials (similar to type III), and are also associated with pores in the 1.5 – 100nm range

Adsorbate

- The most common adsorbate used is Nitrogen, however, other adsorbates are used in some circumstances.

Gas	Temp (°C)	α factor x10^5 (1/mm Hg)	Cross Sectional Area (Å2/mol.)	Molecular weight (g/mol)
Ar	-195.8	11.4	14.2	39.948
	-183	3.94		
	-78	2.75		
CO_2	0	1.75	19.5	44.01
	25	1.55		
	-183	3.42		
CO	-195.8	6.58	16.3	28.01
N2	-183	3.78	16.2	28.0134
	-183	4.17		
O2	0	14.2		
C4H10	25	4.21	46.9	58.12
	-195.8	11.4		

BET

- Brunauer, Emmett and Teller (BET), most common method used to describe specific surface area:

  The BET equation –

$$\frac{1}{W\left(\left(P_0/P\right)-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right)$$

W= weight of gas adsorbed

P/P_0 =relative pressure

Wm = weight of adsorbate as monolayer

C = BET constant

BET equation requires a linear plot of $1/[W(P/P_0)-1]$ against P/P_0

- Slope (s) Intercept (i)

$$s = \frac{C-1}{W_m C} \qquad i = \frac{1}{W_m C}$$

$$W_m = \frac{1}{s+i}$$

- Wm (weight of monolayer)

- Total Surface area (S_t) can then be derived

$$S_t = \frac{W_m \; N \; A_{cs}}{M}$$

N = Avogadro's number (6.023×10^{23})

M = Molecular weight of Adsorbate

A_{cs} = Adsorbate cross sectional area (16.2Å^2 for Nitrogen)

- Specific Surface Area (S) is then determined by total Surface area by sample weight

$$S = S_t / w$$

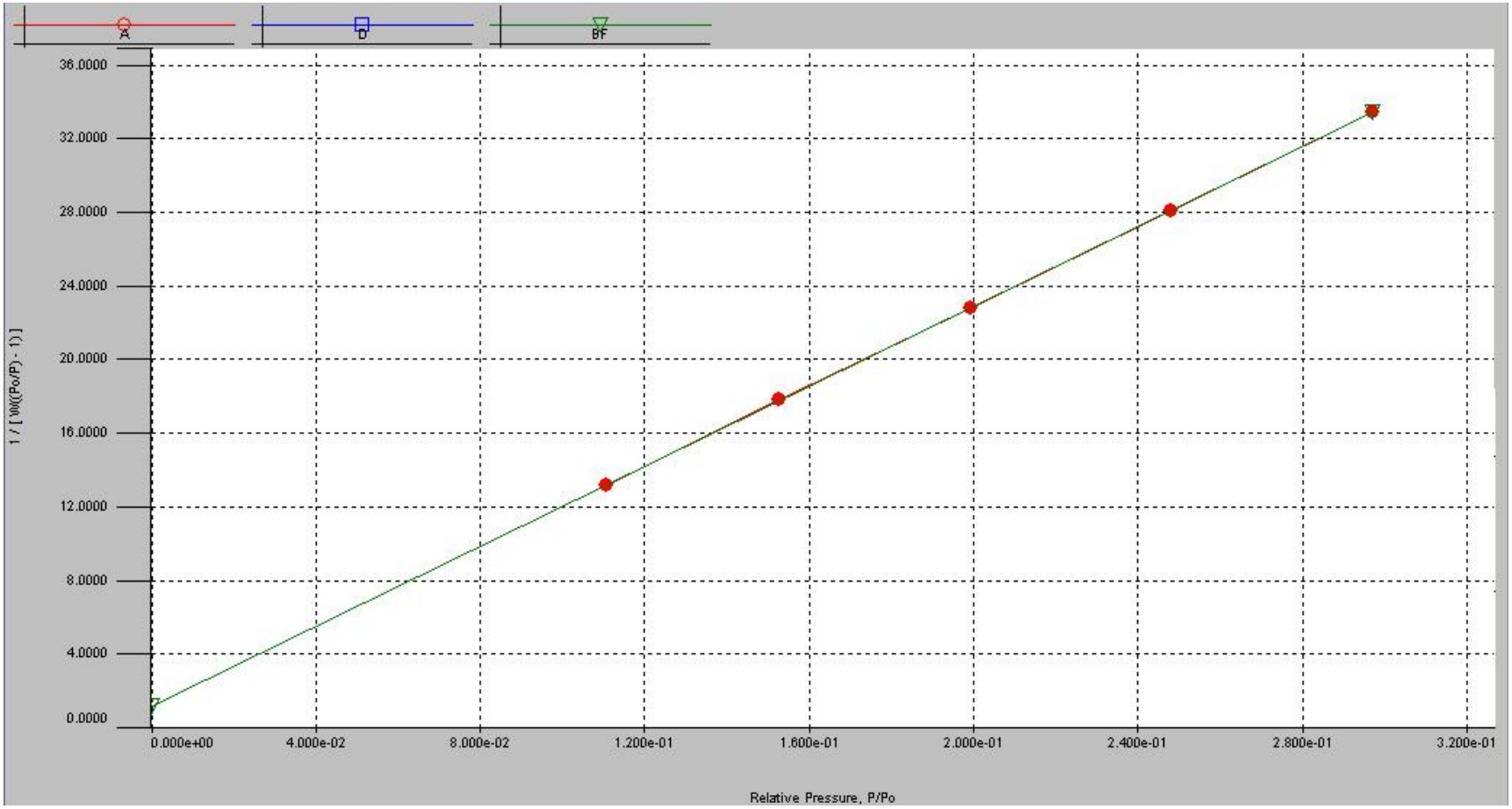
- Single point BET:

  Involves determining specific surface area using a single point on the isotherm

- Multipoint BET:

  Minimum of three data points.

Multipoint BET Plot



Relative Pressure P/Po	Volume @ STP cc/g	1/[W((Po/P)-1]
1.10536e-01	7.5355	1.3195e+1
1.53021e-01	8.1192	1.7804e+1
1.99422e-01	8.7403	2.2803e+1
2.48028e-01	9.4102	2.8045e+1
2.97227e-01	10.1099	3.3472e+1
Summary		
Slope = **108.451**		
Intercept = **1.195e+00**		
Correlation coefficient, r = **0.99999**		
C constant= **91.759**		
Surface Area = **31.762 m^2/g**		

C Constant

- Relative error between single and multipoint BET, (typically measured at P/P_0 of 0.3)

$$C = (s/i) + 1$$

Single/Multi point Comparison	
Constant	Relative error
1	0.70
10	0.19
50	0.04
100	0.02
1000	0.0002
Infinity	0

Langmuir

- The Langmuir equation describes Microporus material exhibiting Type I Isotherms.

- Assumes adsorption limited to one monolayer.

IUPAC classification on pores

- Macroporous >50nm
- Mesoporus 2-50nm
- Microporus <2nm

Porosity - pore volume

Total pore volume is derived from the amount of vapour adsorbed at a relative temperature close to unity (assuming pores are filled with liquid adsorbate).

V_{ads} = volume of gas adsorbed

V_{liq} = volume of liquid N_2 in pore

V_m = molar vol. of liquid adsorbc

P_a = ambient pressure

T = ambient temperature

$$V_{liq} = \frac{P_a \quad V_{ads} \; V_m}{R\,T}$$

Porosity - pore radius

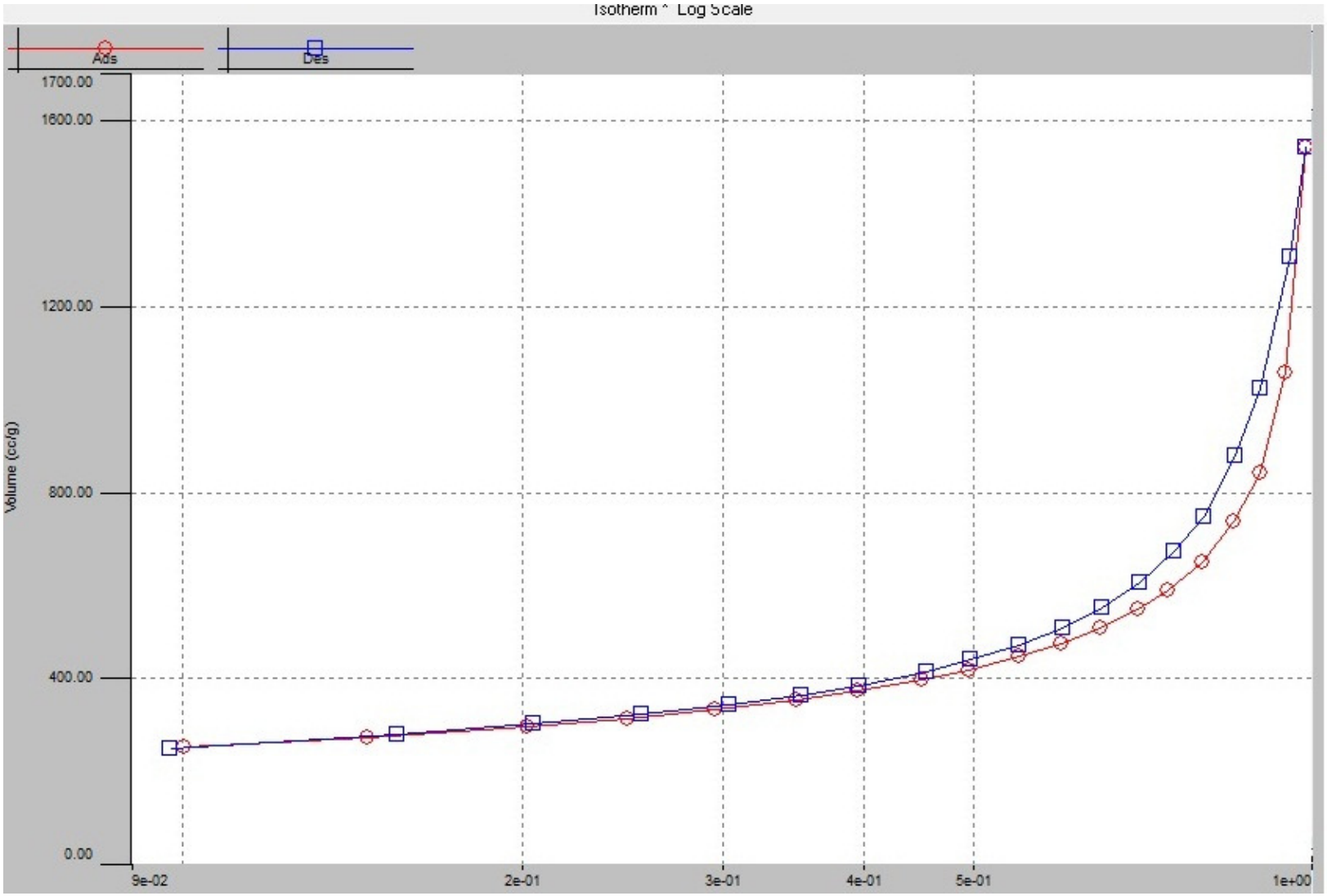
Average pore size is estimated from the pore volume.

Assuming cylindrical pore geometry (type A hysteresis) average pore radius (r_p) can be expressed as:

$$r_p = \frac{2V_{liq}}{S}$$

Other pore geometry models may require further information on the isotherm hysteresis before applying appropriate model.

Adsorption/Desorption Isotherm



Sample porosity data

- Pore Volume Data

Total pore volume for pores with Radius less than 15.93 Å at P/Po = 0.395090	5.787e-01 cc/g
BJH method cumulative adsorption pore volume	2.103e+00 cc/g
BJH method cumulative desorption pore volume	2.192e+00 cc/g
DH method cumulative adsorption pore volume	2.054e+00 cc/g
DH method cumulative desorption pore volume	2.146e+00 cc/g
HK method cumulative pore volume	4.257e-01 cc/g
SF method cumulative pore volume	4.358e-01 cc/g
NLDFT method cumulative pore volume	1.904e+00 cc/g

- Pore Size Data

Average pore Radius	3.505e+01 Å
BJH method adsorption pore Radius (Mode Dv(r))	1.698e+01 Å
BJH method desorption pore Radius (Mode Dv(r))	1.710e+01 Å
DH method adsorption pore Radius (Mode Dv(r))	1.698e+01 Å
DH method desorption pore Radius (Mode Dv(r))	1.710e+01 Å
HK method pore Radius (Mode)	1.838e+00 Å
SF method pore Radius (Mode)	2.261e+00 Å
NLDFT pore Radius (Mode)	2.376e+01 Å

Other Methods

- Barrett-Joyner-Halenda Method (BJH)
- Dollimore Heal Method (DH)
- Alpha S Method (αs)
- MP Method (MP)
- Dubinn-Radushkevic Method (DR)
- Dubinin-Astakhov Method (DA)
- Horvath-Kawazoe Method (HK)
- Saito-Foley Method (SF)
- Density Functional Theory Method (DFT)
- Frenkel-Halsey-Hill Method (FHH)
- Neimark-Kiselev Method (NK)

Degas

- Important step before measurement of surface area or pore size/volume

- Surfaces are 'cleaned' of water/organic vapours in two ways:-

    1. With heating under a vacuum

    2. Under a flow of dry, inert gas.

Analysis

- Adsorbate is introduced in to the manifold
- The valve to the sample cell is opened allowing the adsorbate to interact with the sample material.
- The pressure is repeatedly measured for the preset equilibration time, if the pressure drops dosing recurs and measurement proceeds until a stable reading is achieved.

Surface area and pore size determination

01. November 2013

A. Trunschke

Further reading

S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publisher, Dordrecht, 2004, Springer 2006.

R. Brdička, Grundlagen der physikalischen Chemie, Deutscher Verlag der Wissenschaften, Berlin 1982.
P.W. Atkins, J. de Paula, Physikalische Chemie, Wiley-VCH, Weinheim 2013.
G. Wedler, H.-J. Freund, Lehrbuch der Pysikalischen Chemie, Wiley-VCH, 2012.

F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), Handbook of Porous Solids, Vol. 1, Wiley-VCH, Weinheim 2002.

G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997.

Outline

1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

Outline

1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

Heterogeneous catalysis

1

- Heterogeneous catalysis happens at the interface between phases
- The number of active sites depends on the surface area

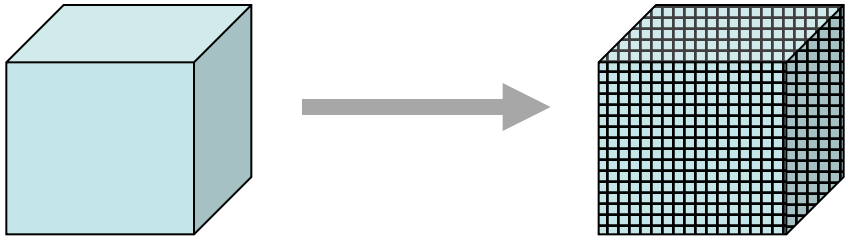
- Surface area is related to
  - Particle size
  - Particle morphology
  - Surface texturing
  - Porosity

- The accessibility of active sites requires pores that allow molecular transport
- Porosity: fraction of the total void volume with respect to the volume of the catalyst
- Texture:
  - pore size
  - pore size distribution
  - pore shape

Factors affecting surface area

1 particle of edge lenght = 1 m

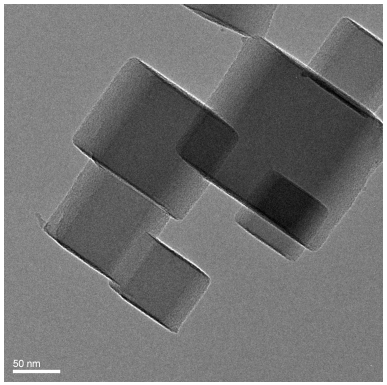
10^{18} particles of edge lenght = 10^{-6} m

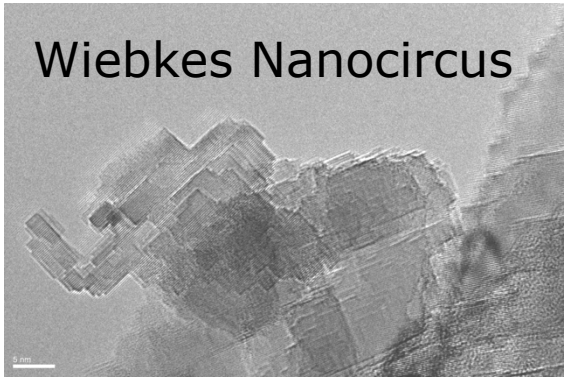


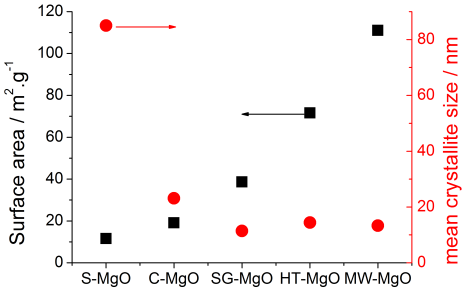
size

$S=6\ m^2$

$S_i=6x10^{-12}\ m^2$
$S_{total}=6x10^{6}\ m^2$



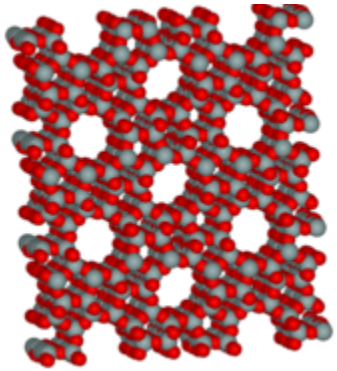




shape

$S=10\ m^2$ **MgO** $S=100\ m^2$

porosity



Numbers = orders of magnitude

$S=400\ m^2$ **Zeolite ZSM-5**

- Surface area from particle size distribution

  Dynamic light scattering

  Measures Brownian motion and relates this to the size of the particles by using a correlation function and the Stokes-Einstein equation

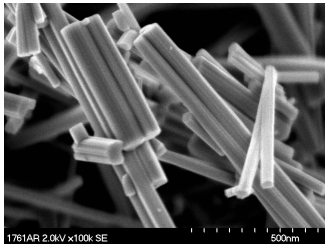
  Non-spherical particles will be measured as equivalent spheres

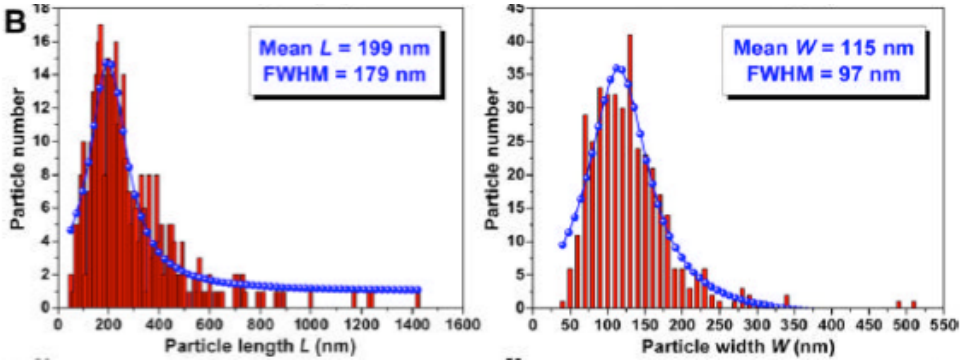
$$D_0 = \frac{kT}{6\pi\eta R}$$

D= Diffusion coefficient
k= Boltzmann constant
T= absolute temperature
η= dynamic viscosity of the solvent
R= radius of the particle

- Microscopy

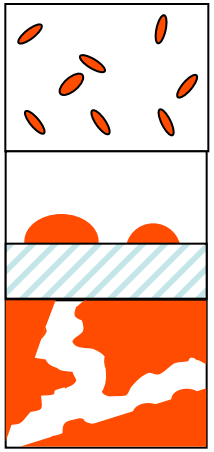
  Shape analysis





- Small angle X-ray scattering

  Scattering of X-rays by small domains of uniform matter (crystalline or amorphous), for which the electron density ρ^e is different from the continuous medium
  The central peak of scattered intensity gets broader as the domain size (particles, voids) decreases
  SAXS parameters (mean size / size distribution / specific surface area) are derived from analysis of the profile of the SAXS curve



- Mercury porosimetry

- Gas Adsorption

Surface area measurements

1

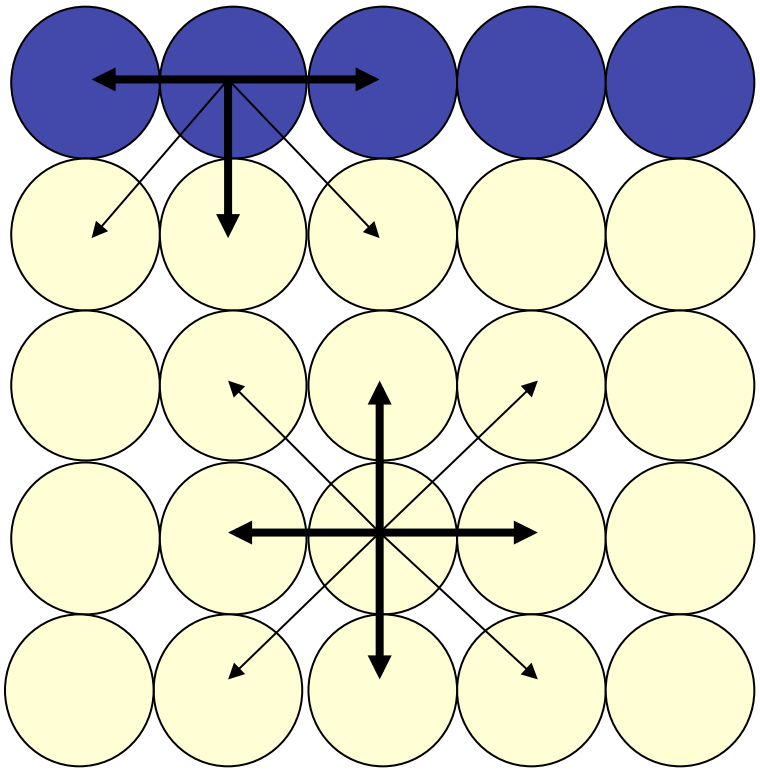
- Gas adsorption
  - Surface area
  - Pore volume
  - Texture
    - Pore size distribution
    - Pore geometry
    - Connectivity

Outline

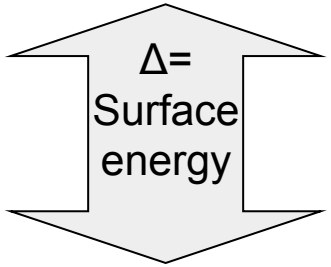
1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

Driving force of adsorption

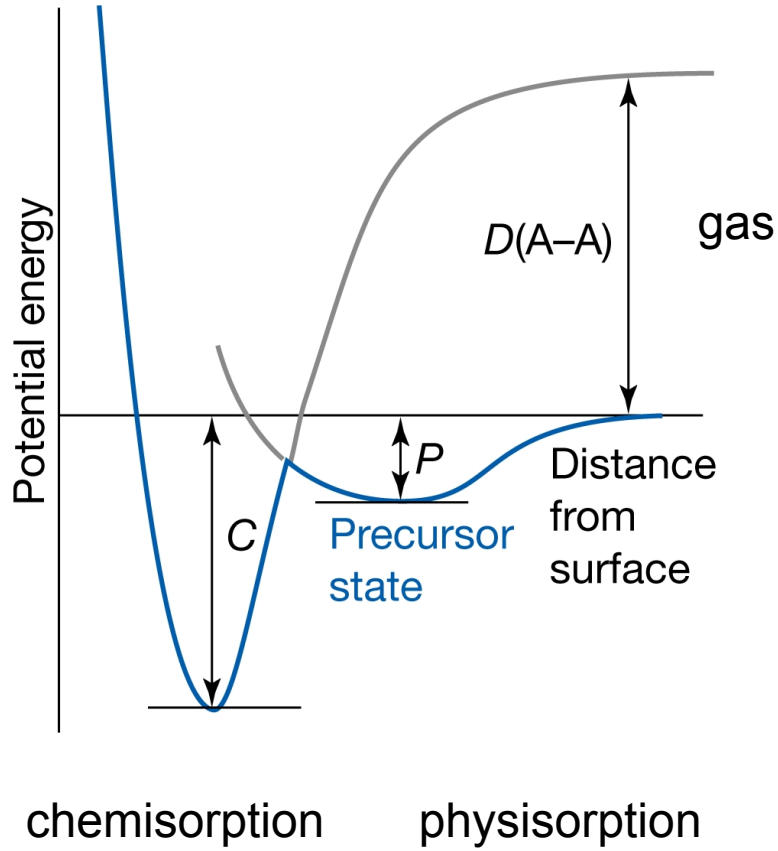
2



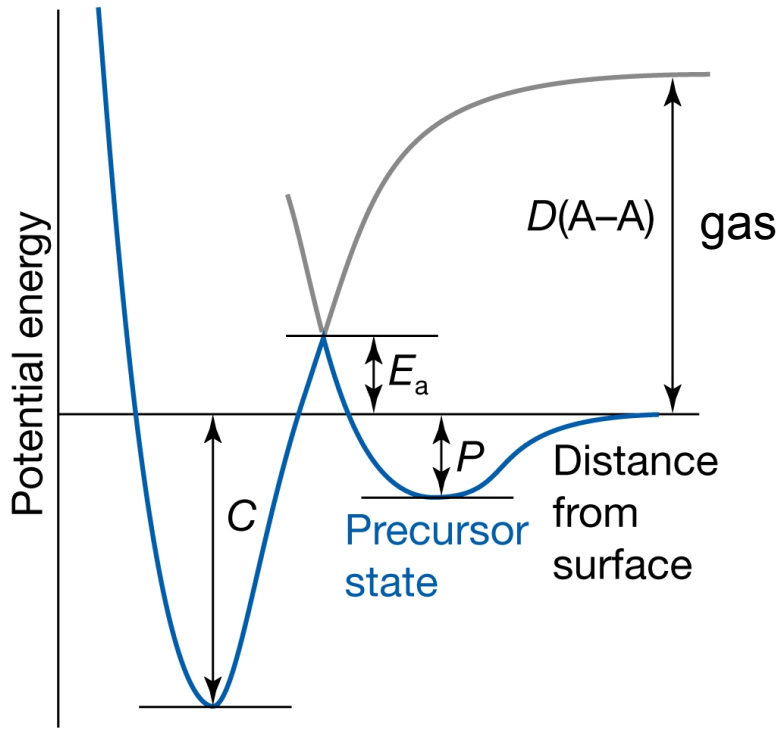
Surface atom – unbalanced forces



Bulk atom – balanced forces


Potential energy
D(A–A)
gas
P
C
Precursor state
Distance from surface
chemisorption
physisorption

activated chemisorption



chemisorption → Heterogeneous catalysis

physisorption → Surface area/pore size determination

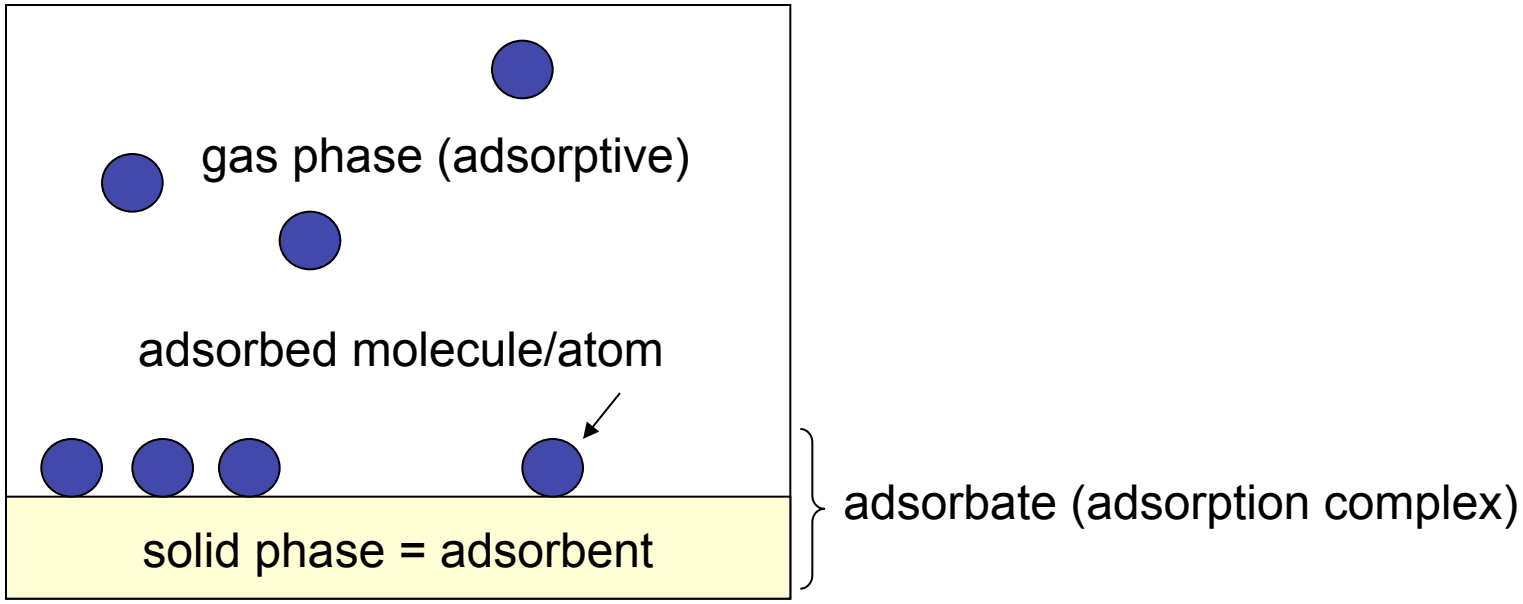
Van der Waal´s forces

1. Dispersion forces* (major part of the interaction potential)
   The electron motion in an atom or molecule leads to a rapidly oscillating dipole moment coupling of two neighboring moments into phase leads to a net attractive potential
2. Ion-dipole (ionic solid/polar gas molecule)
3. Ion-induced dipole (polar solid/polarizable gas molecule)
4. Dipole-dipole (polar solid/polar gas molecule)
5. Quadrupole interactions (symmetrical molecules e.g. $^{-}O\text{-}C^{++}\text{-}O^{-}$)

* F. London, Z. Phys. 63 (1930) 245.

Similar to forces that lead to liquifidation of vapors

	Physisorption	Chemisorption
Heat of adsorption	< 50 kJ mol^{-1}	> 500 kJ mol^{-1}
Coverage	Multilayer → Measurement of surface area	Monolayer or less, site restriction → Titration of active sites
Interaction	No structural changes, reversible	Disruption of chemical bonds may happen
Kinetics	Fast	Activation required
Pores	Pores may be filled → Pore volume measurements	-


gas phase (adsorptive)
adsorbed molecule/atom
solid phase = adsorbent
adsorbate (adsorption complex)

Relation between T, p, adsorbed amount (surface concentration)

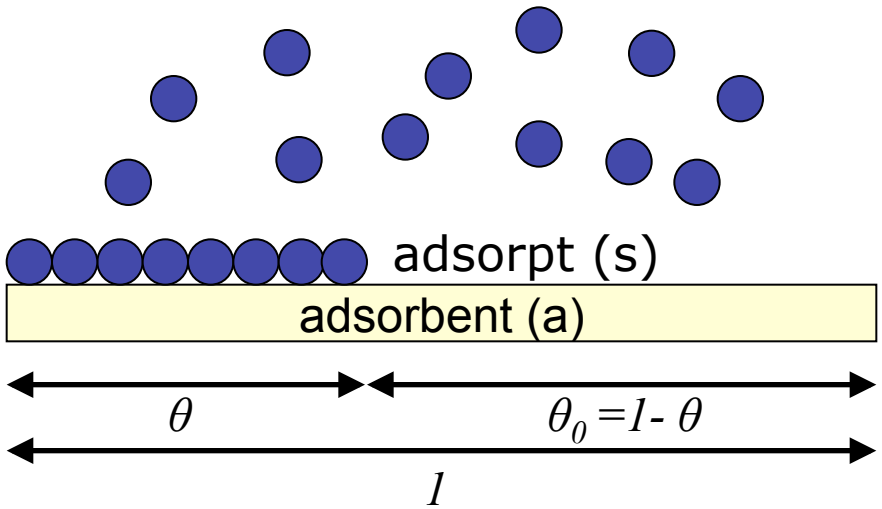
$\Gamma = n_s/s_a$

$\gamma = n_s/m_a$

$\Gamma = \gamma/S_{a,sp.}$

W_s

V_s



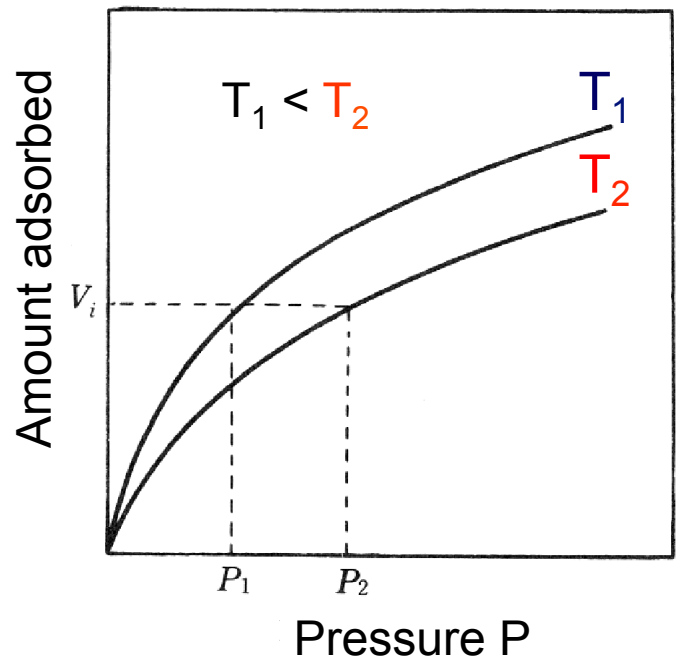
Fraction of occupied surface (coverage)

$\theta = \Gamma/\Gamma_m = \gamma/\gamma_m = N/N_m = W/W_m$

$\Gamma = f(p)$	<eq., T = const.>	adsorption isotherm
$\Gamma = f(T)$	<eq., p = const.>	adsorption isobar
$p = f(T)$	<eq., Γ = const.>	adsorption isostere

$$\Gamma = f(p)_T$$

Adsorption is favored at lower temperatures



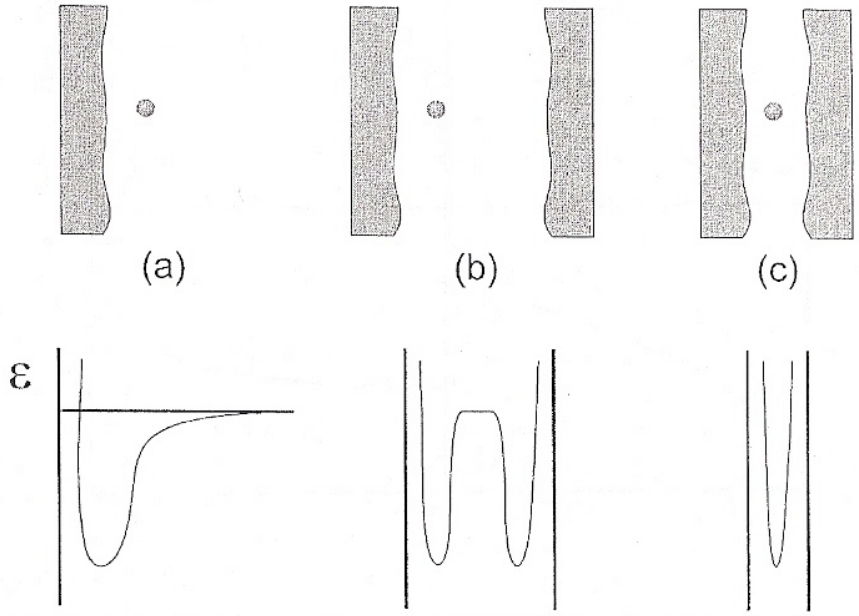
$$\Delta G = \Delta H - T\Delta S$$

Decrease in translation freedom by adsorption: $\Delta S<0$
Adsorption is a spontaneous process: $\Delta G<0$

↓

$\Delta H<0$ Exothermic process

Planar, nonporous, macropores | mesoporous | microporous



Schematic illustration of adsorption potential

$\Gamma = f(p)_T$

The shape of the isotherm of pure fluids depends on

- Interplay between the strength of fluid-wall and fluid-fluid interaction
- Pore space

Classification by the International Union of Pure and Applied Chemistry*

	Width* [nm]
Micropores	< 2
Mesopores	2 ~ 50
Macropores	> 50

- Ultramicropores below 0.7nm
- Supramicropores 0.7~2nm

Width*

- Diameter of a cylindrical pore
- Distance between opposite walls in case of slit pores

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

IUPAC classification of adsorption isotherms*

Adorption in micropores

Adsorption limited to a few molecular layers

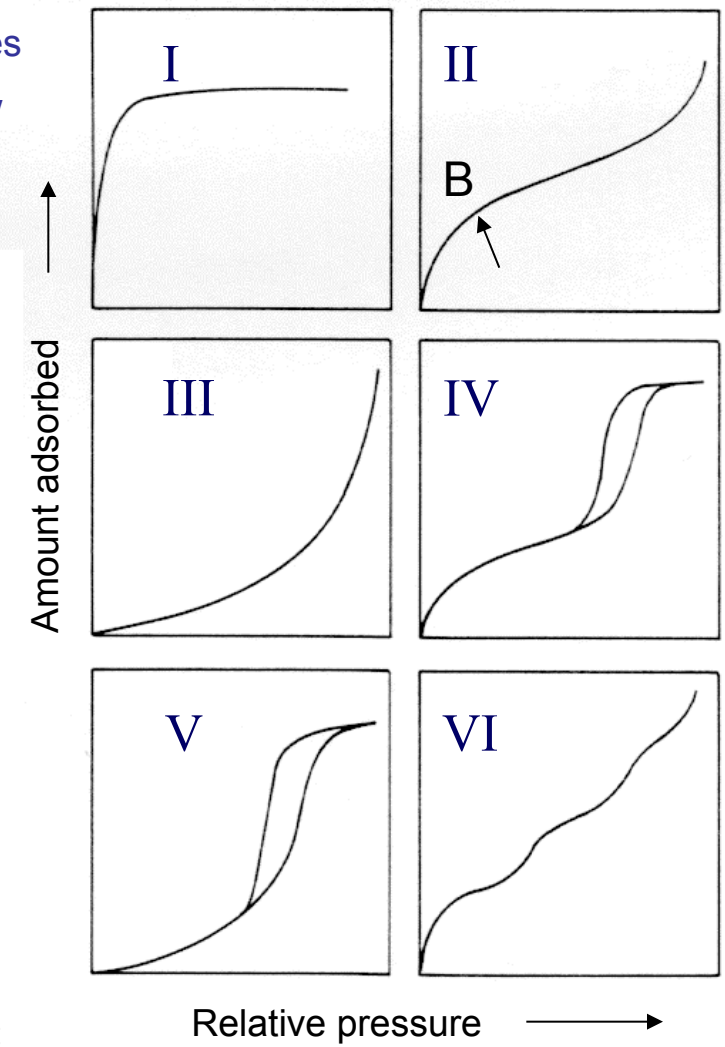
true chemisorption

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

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

Adsorption isotherm 2

- Mathematical description of the adsorption isotherms allows to determine surface area and pore data
- The models used for mathematical description are empirical models that fit more or less to experimental data
- The results are useful and required to interpret catalytic data
- Please consider in the discussion of your results that the surface area or the pore volume determined by using the various empirical models are approximated values

Outline

1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

$$S = A_x N_m$$

A_x cross-sectional area of the adsorbed molecule

- Nitrogen 0.162 nm^2
- Argon 0.166 nm^2
- Krypton 0.210 nm^2

N_m number of adsorbate molecules required to cover the solid with a single monolayer

Theories that give access to the monolayer capacity using the isotherm

- Langmuir
- BET

Description of Type I Isotherm

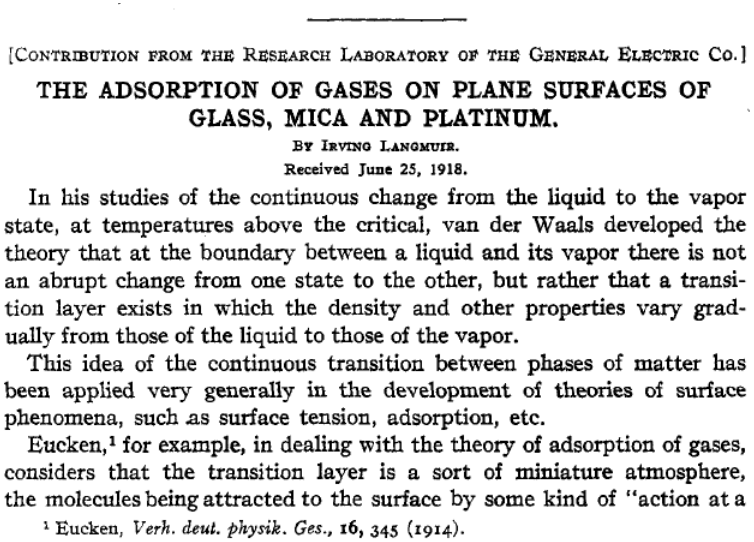
Assumptions

- Monolayer adsorption
- Energetically uniform surface
- No interactions between adsorbed species (heat of adsorption independent of coverage)

kinetic expression of the adsorption equilibrium

$$r_{ads} = r_{des}$$

$$dN_{ads} = dN_{des}$$



[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

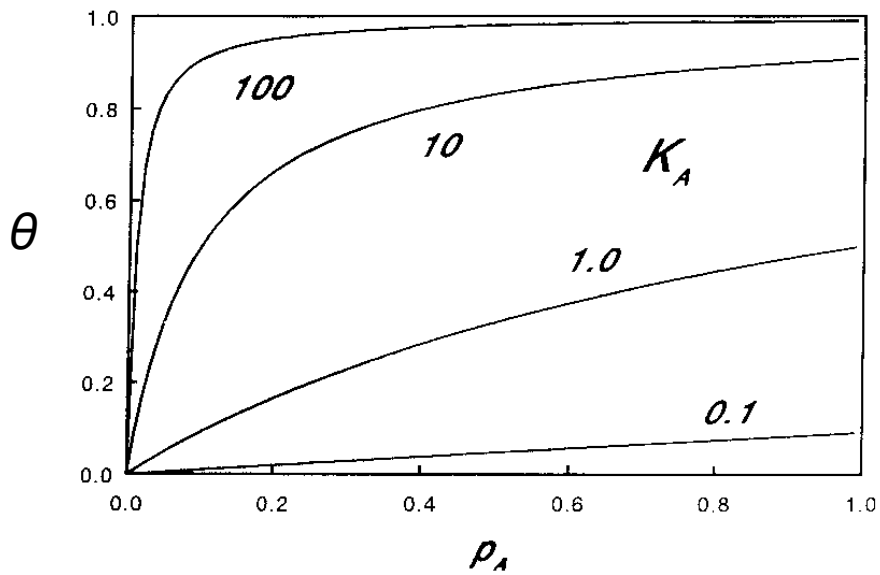
[1] Eucken, *Verh. deut. physik. Ges.*, **16**, 345 (1914).

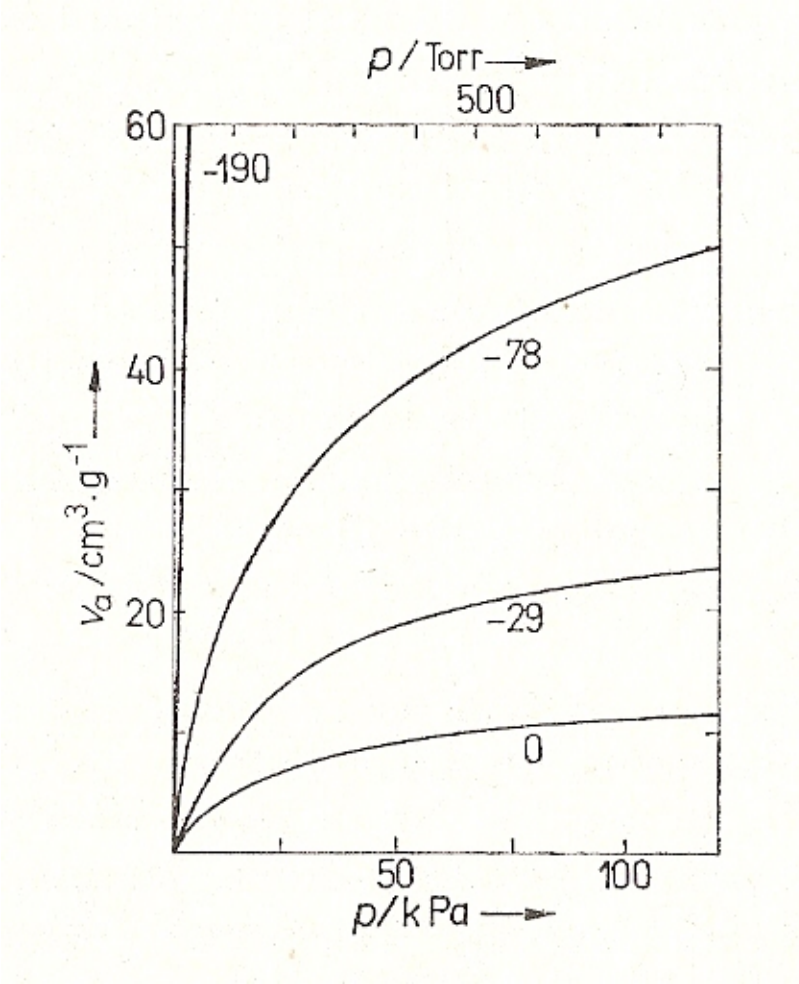
* I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361.

$$\frac{d\theta}{dt} = k_{ads} p N (1-\theta) = \frac{d\theta}{dt} = k_{des} N$$

$$\boxed{\theta = \frac{N}{N_m} = \frac{K\ p}{1+K\ p}}$$

$$K = \frac{k_{ads}}{k_{des}}$$





Adsorption of nitrogen on charcoal at different T

$$\theta = \frac{N}{N_m} = \frac{K\ p}{1 + K\ p}$$

Linear plot →

$$\frac{p}{N} = \frac{1}{KN_m} + \frac{p}{N_m}$$

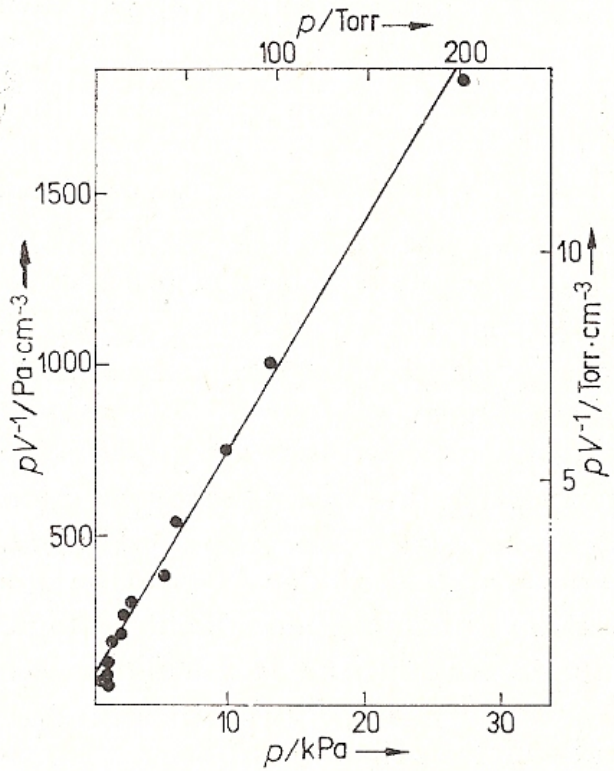
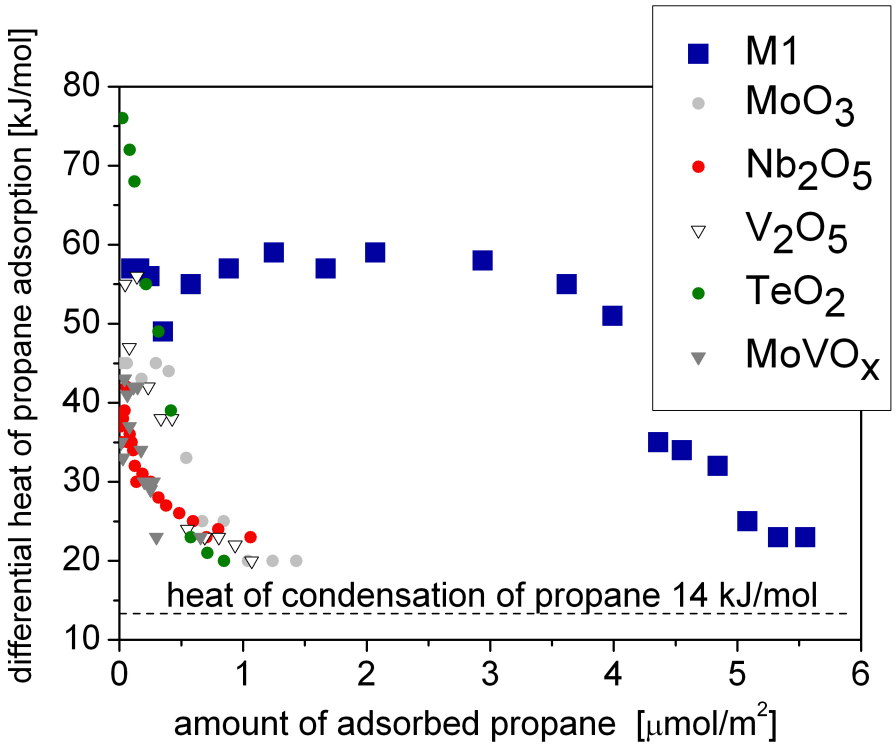


Abb. 6.47
Linearisierte Langmuirsche Adsorptionsisotherme für die Adsorption von Wasserstoff an Kupferpulver bei 25 °C

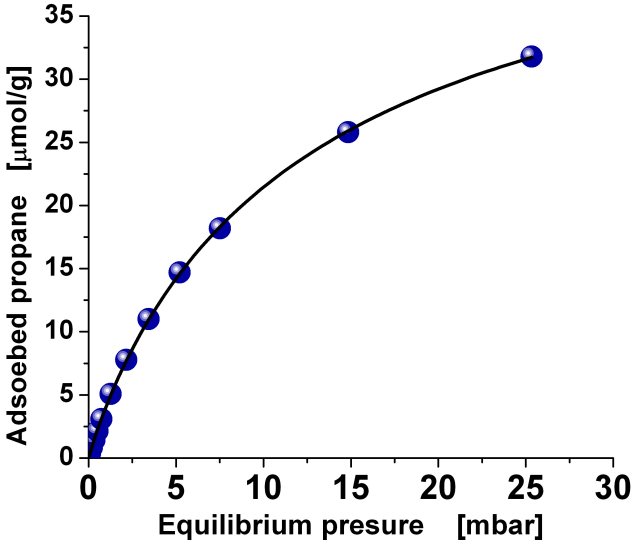
$$n = \frac{N}{N_A} = \frac{m_m}{M_{asdorptive}}$$

$$S = N_m A_x = \frac{m_m N_A A_x}{M_{asdorptive}}$$

M. Hävecker *et al.*, Journal of Catalysis 285 (2012) 48–60.



Adsoption isotherm of propane over M1 at T=313 K



Cross-sectional area of propane: 36 Å²

$K = 0.111(6)\ hPa^{-1}$

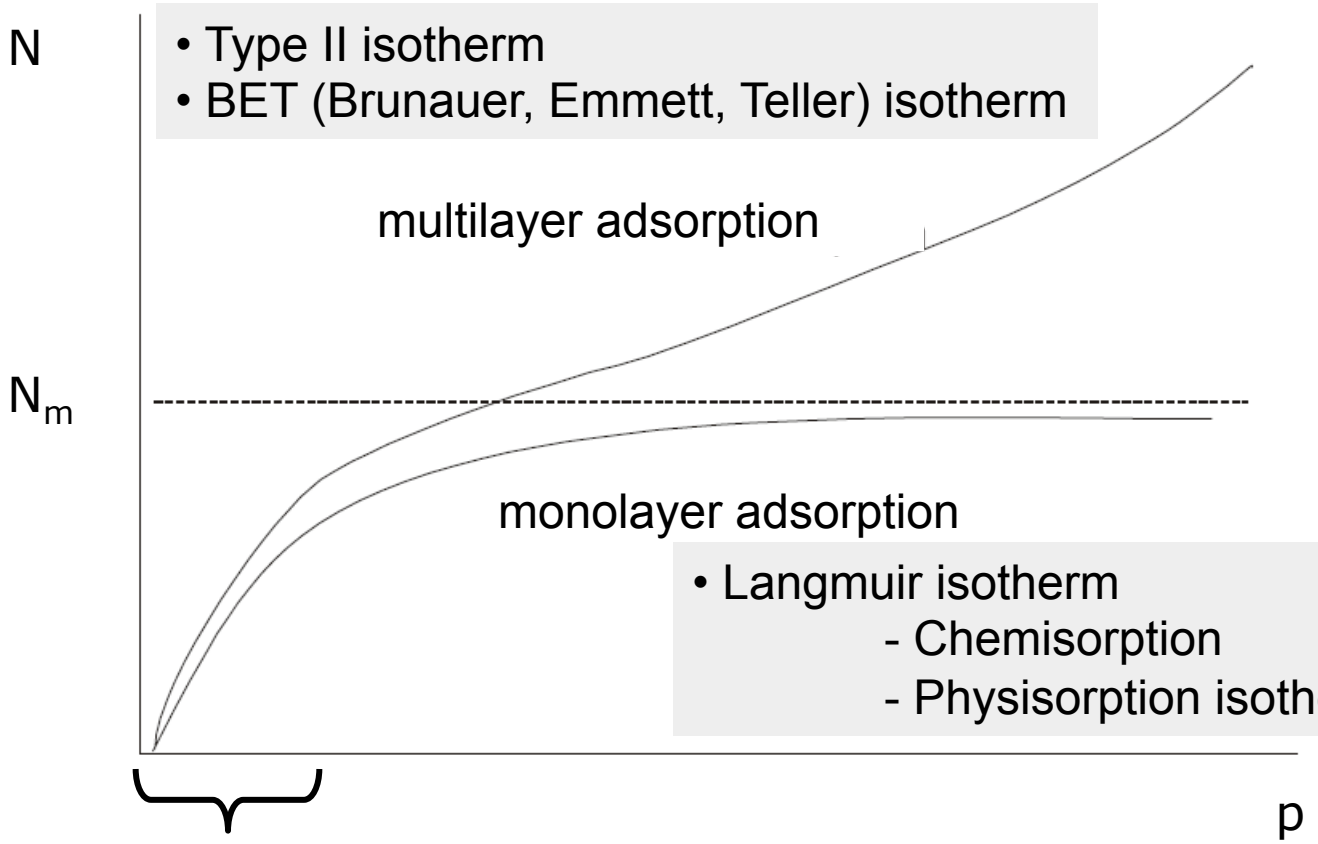
$N_m = 43\ \mu mol\ g^{-1}$

$S_{Langmuir} = 9.2\ m^2\ g^{-1}$

$S_{BET} = 8.8\ m^2\ g^{-1}$

A.L. McClellan, H.F. Harnsberger, J. Colloid Interface Sci. 23 (1967) 577.
S.J. Gregg, R. Stock, Trans. Faraday Soc. 53 (1957) 1355.

Other isotherms



- Type II isotherm
- BET (Brunauer, Emmett, Teller) isotherm

- Langmuir isotherm
  - Chemisorption
  - Physisorption isotherms of type I

- Freundlich isotherm
  (interaction of adsorbed molecules)
  $$\theta = c_1 p^{1/c2}$$
- Temkin isotherm
  (adsorption enthalpy is a function of the pressure)
  $$\theta = c_1 ln(c_2 p)$$

B. Frank *et al.*, ChemPhysChem 12 (2011) 2709 – 2713.

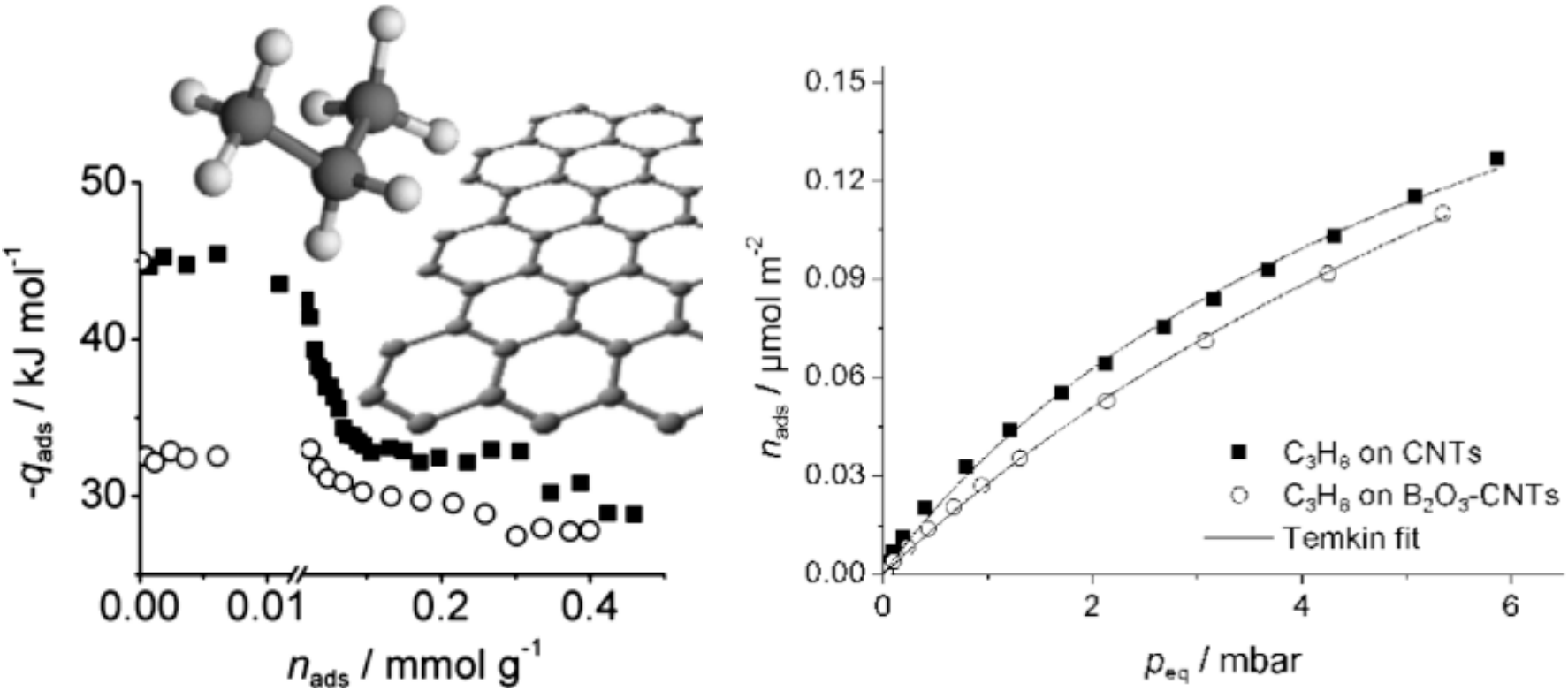


Figure 3. Isotherms of propane adsorption (313 K) on the oxygen surface groups of CNT and B_2O_3–CNT catalysts used in ODH of propane.

M. I. Temkin, Zhur. Fiz. Khim. 15 (1941) 296.

BET isotherm (Brunauer, Emmett, Teller)*

3

[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 ith 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 μ_i, it follows that

$$\mu_i = c_1 C^i \qquad (1)$$

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

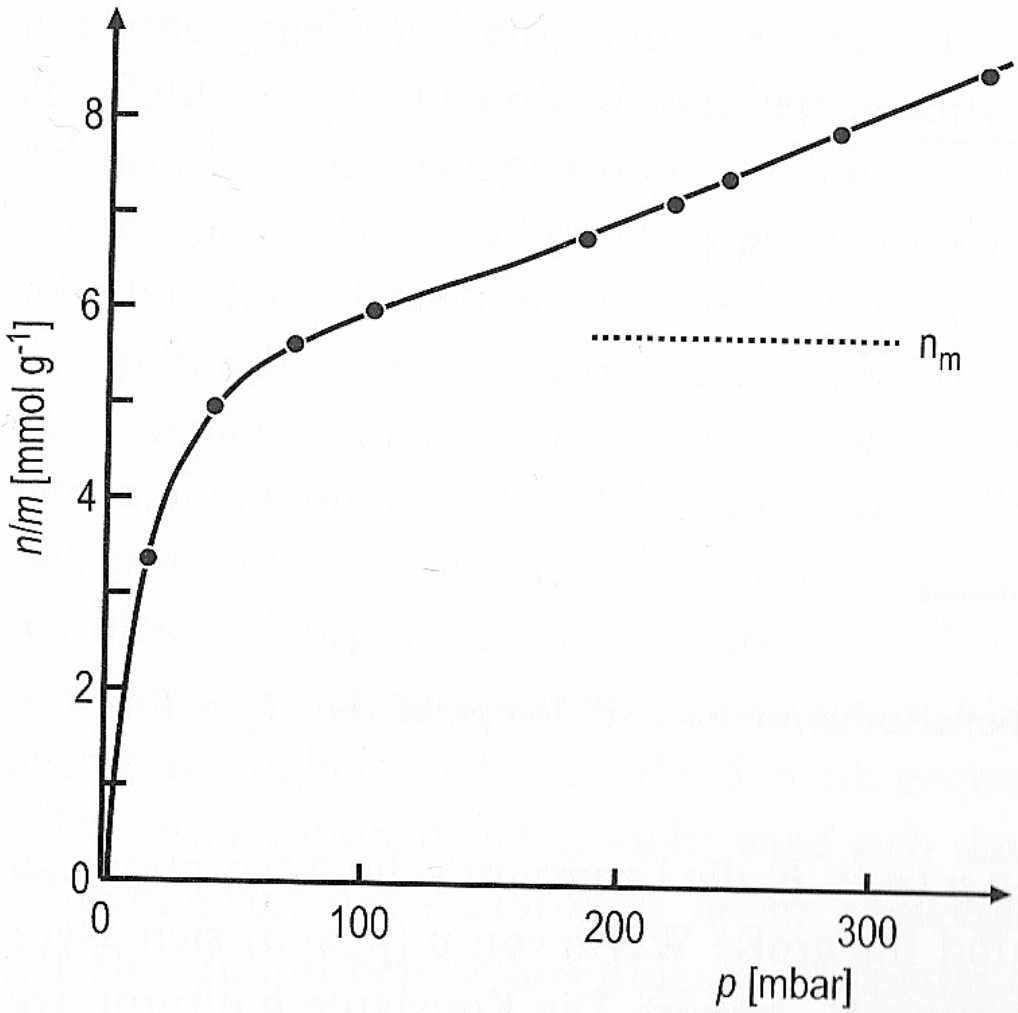
$$\phi_i = c_2 C^{2i} \qquad (2)$$

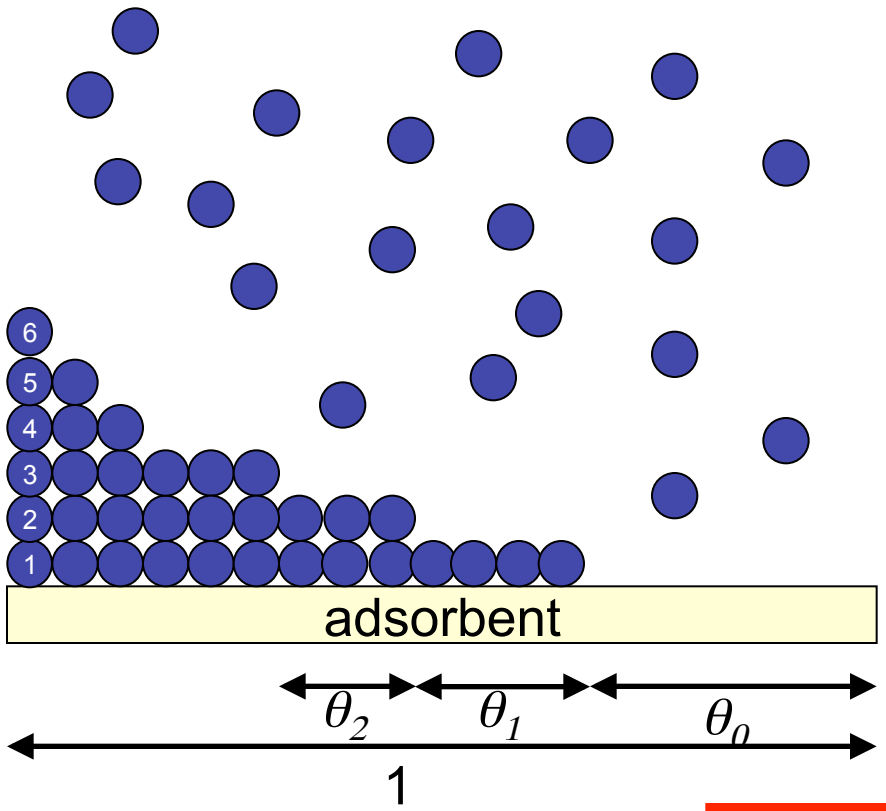
where c_2 is another constant. The equilibrium pressure of the nth layer (top layer), p_n, according to Boltzmann's law varies exponentially with the

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

Nitrogen adsorption on silica at 77 K

3





Description of all isotherm types

Assumptions

- Multilayer adsorption
- First layer: Langmuir adsorption
- Second and further layers: condensation of gas onto liquid
- Heat of adsorption:

  First layer > second layer = … = …= heat of condensation

$$\theta = \frac{N}{N_m} = \frac{C \cdot (p/p_0)}{(1 - p/p_0) \cdot [1 - p/p_0 + C(p/p_0)]}$$

p_0 …vapor pressure of liquid N_2

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

$$\frac{1}{W\left[p/p_0-1\right]}=\frac{1}{W_mC}+\frac{C-1}{W_mC}\left(\frac{p}{p_0}\right)$$

Relative pressures near completed monolayers
$0.05 < p/p_0 < 0.3$

W … mass of adsorbed N_2

$$W_m=\frac{1}{s+i}$$

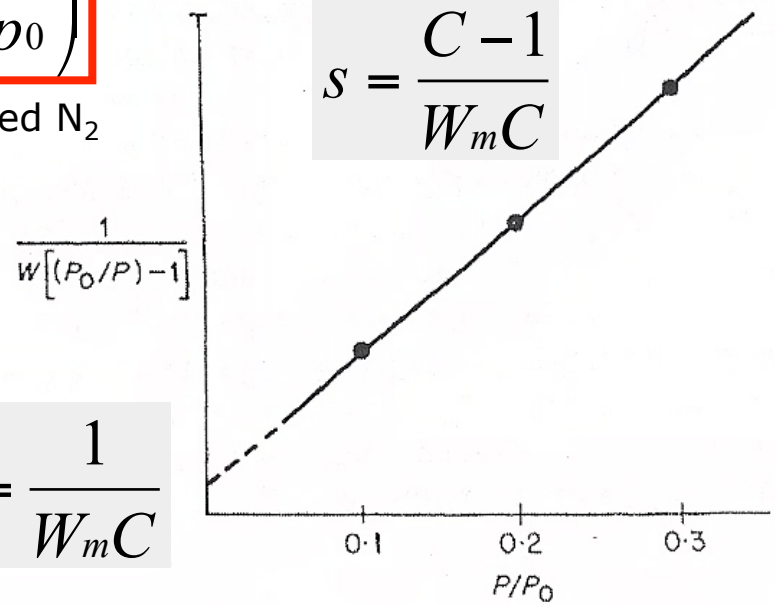
$$C=\frac{s}{i}+1$$

$$S=\frac{W_mN_AA_x}{M_{adsorptive}}$$

$$S_{sp.}=\frac{S}{m}$$

$$s=\frac{C-1}{W_mC}$$

$$i=\frac{1}{W_mC}$$



Single point BET
Assumption: For high values of C the intercept may be taken as zero

$$W_m=W\left(1-\frac{p}{p_0}\right)$$

$$S=W\left(1-\frac{p}{p_0}\right)\frac{N_A}{M_{adsorptive}}A_x$$

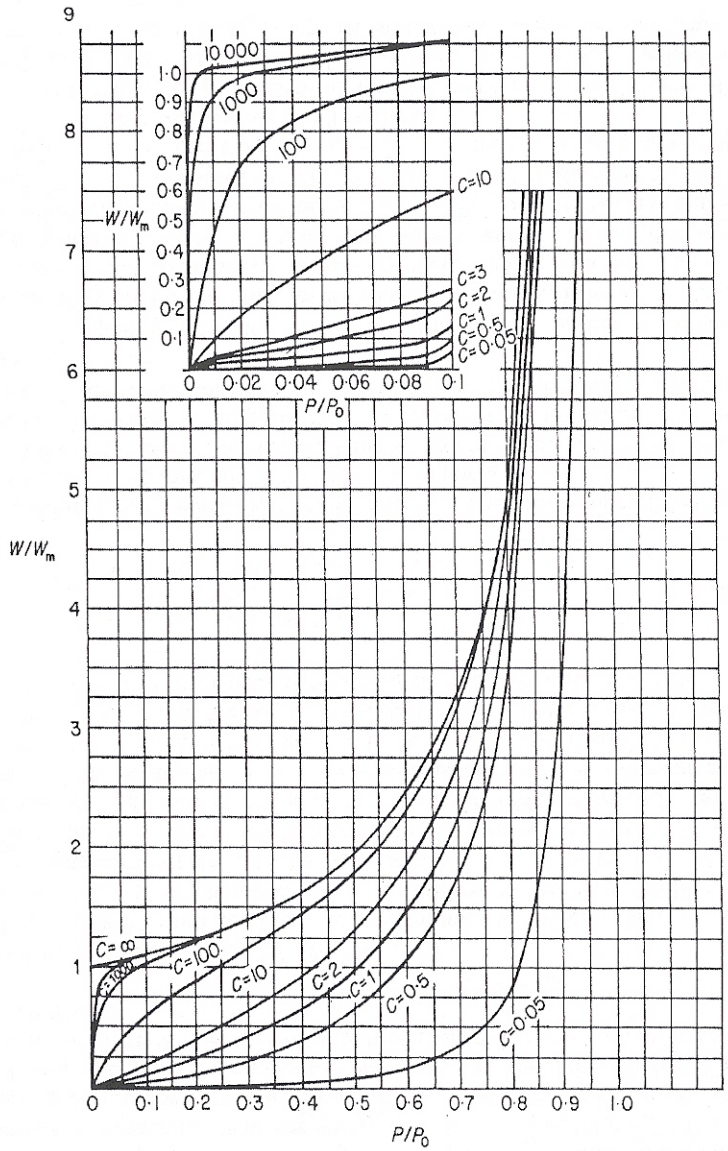


Figure 5.3 Isotherm shapes as a function of BET C values.

In the region of relative pressures near completed monolayers ($0.05<p/p_0<0.3$) experiment and theory agree well → powerful method of surface area determination

$$C=e^{(\Delta_{des}H-\Delta_{ev}H)/RT}$$

Table 5.3 Values of W/W_m and relative pressures for various values of C.

P/P_0	C = 0.05	C = 0.5	C = 1	C = 2	C = 3	C = 10	C = 100	C = 1000
0.02	0.001	0.010	0.020	0.040	0.059	0.173	0.685	0.973
0.05	0.003	0.027	0.052	0.100	0.143	0.362	0.884	1.030
0.10	0.006	0.058	0.111	0.202	0.278	0.585	1.020	1.100
0.20	0.015	0.139	0.250	0.417	0.536	0.893	1.200	1.250
0.30	0.030	0.253	0.429	0.660	0.804	1.160	1.400	1.430
0.40	0.054	0.417	0.667	0.952	1.110	1.450	1.640	1.660
0.50	0.095	0.667	1.000	1.330	1.500	1.820	1.980	2.000
0.60	0.172	1.060	1.490	1.870	2.040	2.340	2.480	2.500
0.70	0.345	1.790	2.330	2.740	2.910	3.190	3.320	3.330
0.80	0.833	3.330	4.000	4.440	4.620	4.880	4.990	5.000
0.90	3.330	8.330	9.090	9.520	9.680	9.900	9.990	10.000
0.94	7.350	14.700	15.700	16.200	16.300	16.600	16.700	16.700

Limitations

- BET theory ignores inhomogeneities of the surface and lateral adsorbate-adsorbate interactions

  High energy sites will be occupied at lower relative pressures

  Reason for the nonlinearity of BET plots at $p/p_0 < 0.05$

- Polarization forces would induce a higher heat of adsorption in the second layer than in the third and so forth

  Reason for the failure of the BET equation at $p/p_0 > 0.3$

- The BET equation is applicable for surface area analysis of nonporous materials

  Difficulties to separate mono-multilayer adsorption from pore filling

  Filling of ***micropores*** *is completed at $p/p_0 < 0.1$, however, linear BET plot are found at even lower relative pressures*

  → measured surface area reflects not a real internal surface, but a „characteristic" BET surface area

  For ***mesoporous materials*** *exhibiting pore diameters between* ***2 and 4 nm (MCM-41, MCM-48)*** *pore filling is observed at pressures close to mono-multilayer formation*

  → overestimation of monolayer capacity

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 ist 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.

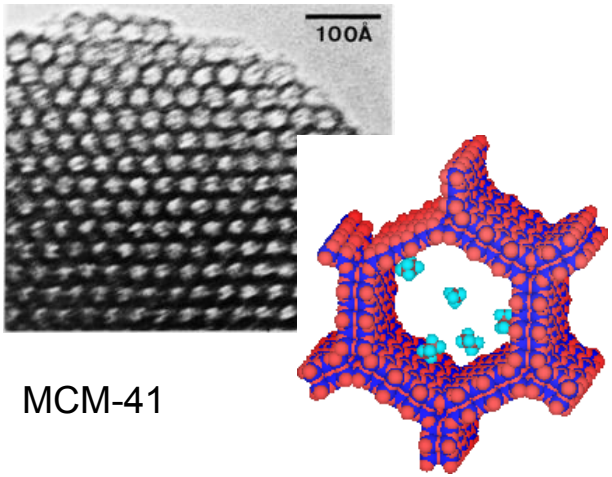
Outline

1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

Capillary condensation in mesopores (2 – 50 nm)

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

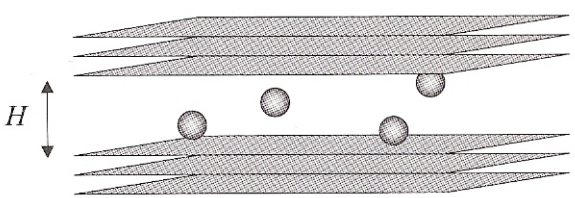
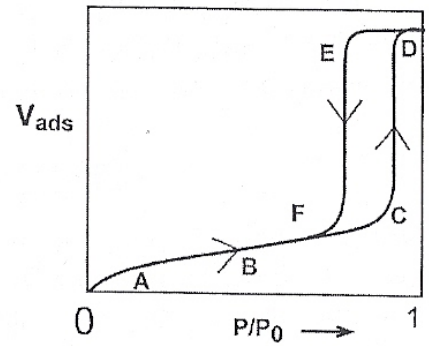
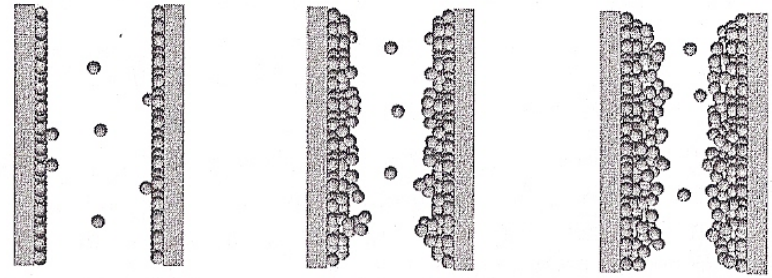


Fig. 3. The slit pore model. Each layer represents a graphene layer.





A Monolayer formation

B Multilayer adsorption

C Critical film thickness reached

D Capillary condensation

E Pore evaporation

F multilayer film

Classification* of the hysteresis loops

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

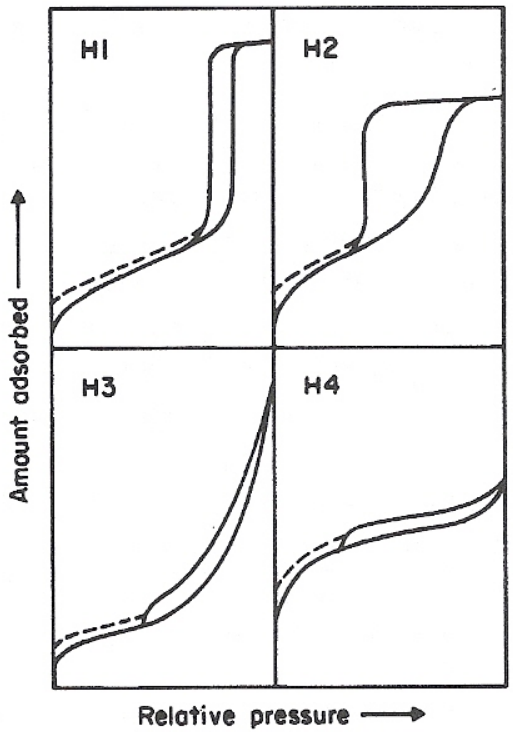


Fig. 3. Types of hysteresis loops

H1 well defined cylyndrical 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.

Kelvin equation

4

The relative pressure where the pore condensation occurs depends on the pore radius

The Kelvin equation provides a correlation between pore diameter and pore condesation pressure

Assumptions

- Pores of cylindrical shape
- No fluid-wall interactions

$$\ln \frac{p}{p_0} = \frac{-2\gamma V_l}{r_p R T}$$

γ surface tension of liquid nitrogen
V_l liquid molar volume
r_p pore radius
r_k critical radius
R universal gas constant
t statistical thickness

Consideration of fluid-wall interactions (modified Kelvin equation):

$$r_k = \frac{4.15}{\log(p_0/p)} \text{ Å}$$ (N_2, 77 K)

$$r_p = r_k + t$$

$$t = 3.54 \left[\frac{5}{\ln(p/p_0)} \right] \text{ Å}$$

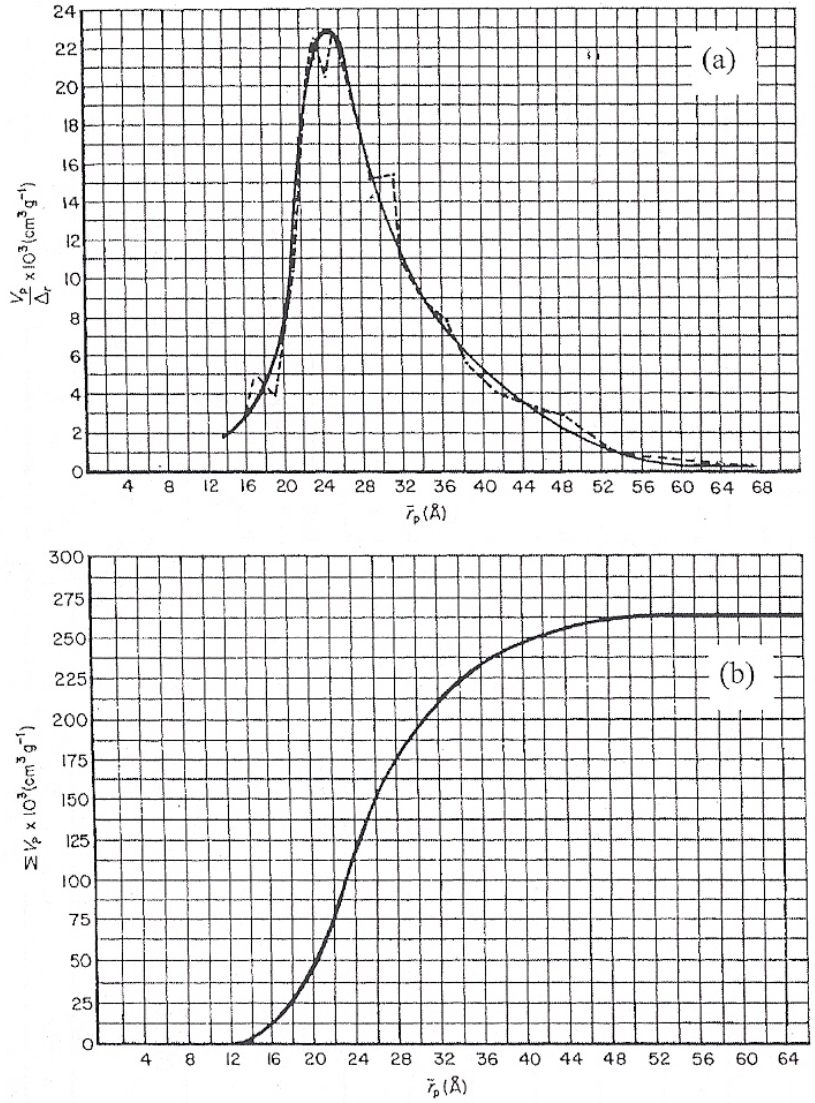


Figure 8.1 (a) Pore size distribution curve from table 8.1. Raw data: ---------; smoothed data ————; (b) Cumulative pore volume plot from table 8.1.

Why hysteresis? Which branch to use?

4

The shape of the isotherm does not depend only on the texture of the porous material, but also on the differences of the thermodynamic states between the confined fluid and the bulk fluid

H1 - independent cylindrical pores (MCM-41, SBA-15)

„Independent pore model“

- Pore condensation is associated with metastable states of the pore fluid in ordered materials
- The **desorption branch** of the hysteresis loop reflects the equilibrium phase transition
- Methods, which describe the equilibrium phase transition (**BJH**) have to be applied to the desorption branch
- (Applicable also to three-dimensional network of pores)

H2, H3 – disordered, connected pores

Origin of hysteresis not yet completely understood

- Pore blocking (inkbottle pores) associated with the desorption process
- Analysis of the **adsorption branch** (**NLDFT**-spinodal condensation method, Kelvin equation based approach calibrated for the adsorption branch)

Outline

1. Introduction
2. Adsorption
3. Surface area measurements – macroporous materials
4. Capillary condensation in mesopores
5. Adsorption in micropores

Micropores	Width* [nm]	Pore filling governed by
Supermicropores	0.7 ~ 2	Gas-solid interactions Cooperative mechanism
Ultramicropores	< 0.7	Bilayer thickness of the N_2 molecule! Gas-solid interaction

Micropore filling is a continuous process and different from pore condensation in mesopores

Adsorption potential theories (0.4 nm ~)

Classical methods based on macroscopic, thermodynamic assumptions

- Polanyi
- Dubinin (DR method)
- Stoeckli
- Horvath-Kawazoe

Density Functional Theory

Monto Carlo simulations

Empirical methods (0.7~2nm)

t-method

MP-method

α_s-method

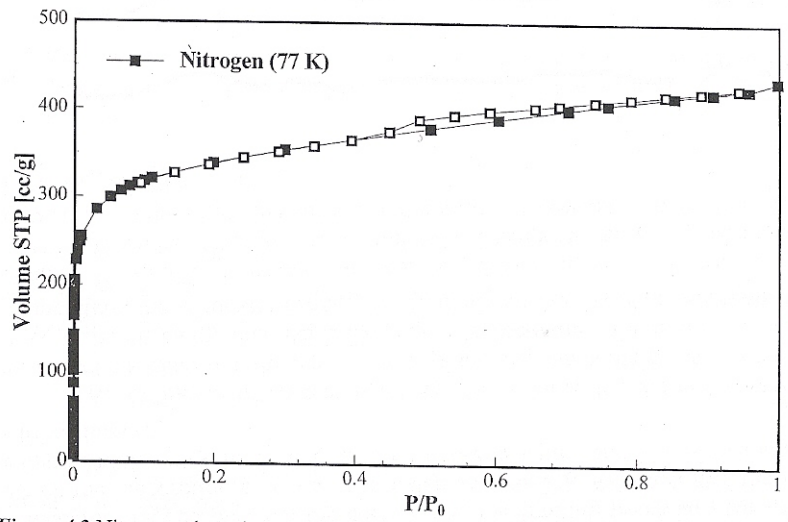


Figure 4.2 Nitrogen adsorption at 77.35 K on an active carbon sample, which contains, in addition to its microporosity, some mesoporosity indicated by the occurrence of hysteresis and the fact that the adsorption isotherm does not reveal a truly horizontal plateau at relative pressures > 0.1; the observed slope being associated with the filling of mesopores.

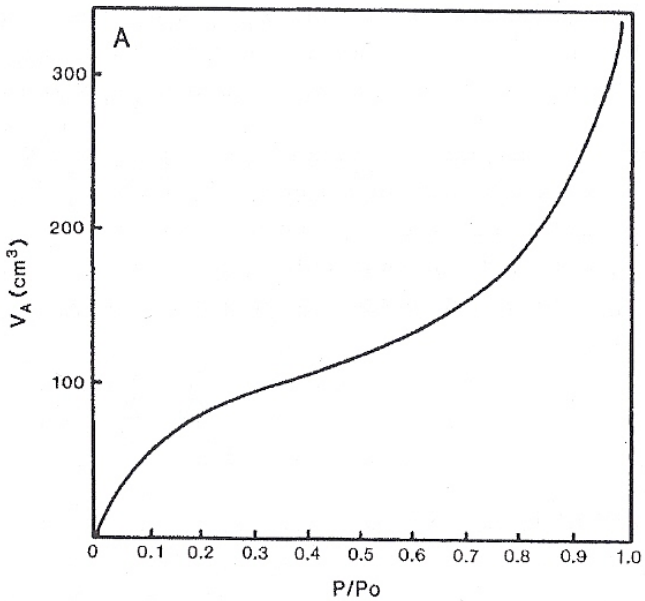
* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

Assumption

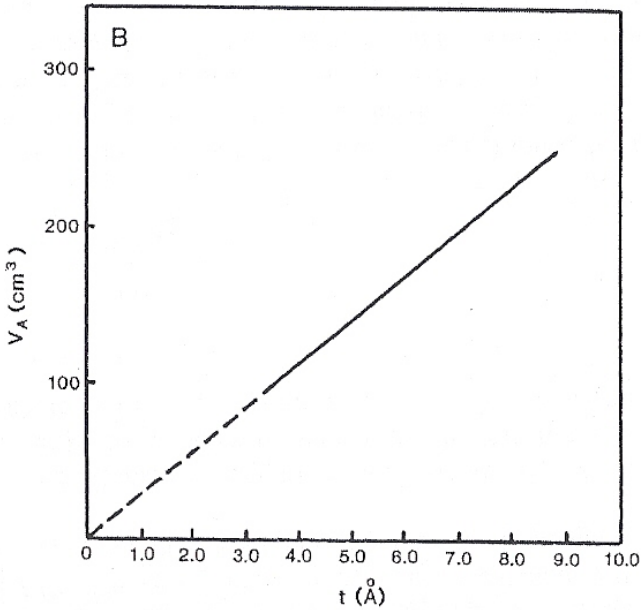
The thickness of the absorbed film on pore walls is uniform → statistical thickness *t*

$$t = 3.54 \frac{W_a}{W_m} \text{Å} = \frac{V_{liq}}{S} \times 10^4 \text{Å}$$ (N_2, 77 K)

It has been shown for type II isotherms that a plot of the volume adsorbed versus t gives a staight line throug the origin



V-t curve



In absence of micropores surface areas calculated from the slope comparable to BET values

Principle

- Comparing an isotherm of a microporous material with a standard type II isotherm of a nonporous absorbent with BET C constants similar to that of the microporous sample
- Plot of the reference isotherm as a t-curve: $V_{ads}=f(t)$
- The t values are in practice calculated with the help of thickness equations that desribe the particular standard reference curve

Siliceous materials

$$t = \left[\frac{13.99}{\log(p/p_0) + 0.034}\right]^{\frac{1}{2}} \text{Å}$$

J.H.De Boer *et al.,* J. Colloid Interface Sci. 21 (1966) 405.

C-like materials

$$t = 0.88(p/p_0)^2 + 6.45(p/p_0) + 2.98 \text{ Å}$$

ASTM standard D-6556-01

Intercept: Volume of micropores

$V_{micro} = i \times 0.001547\ cm^3$

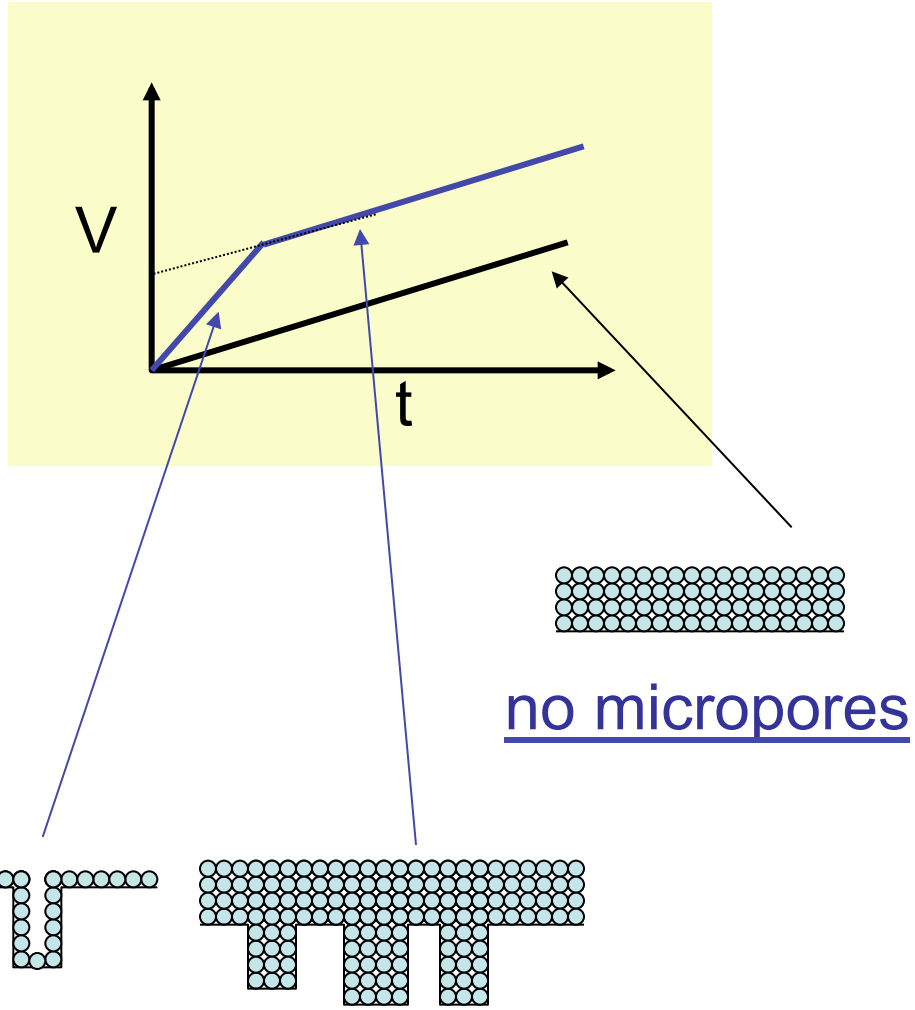
Slope: Surface area of micropores

$$t = \frac{V_{liq}}{S} \times 10^4\ \text{Å}$$

$S_t = s \times 15.47\ m^2/g$

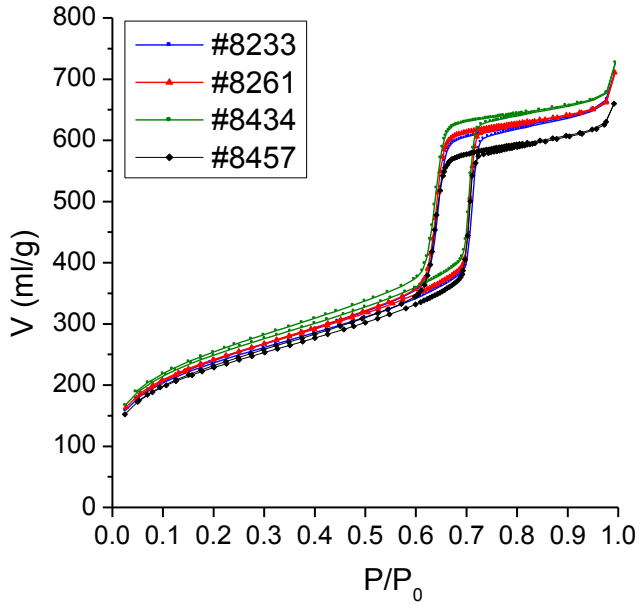
nonporous material: $S_t = S_{BET}$
microporous material: $S_t = S_{ext}$

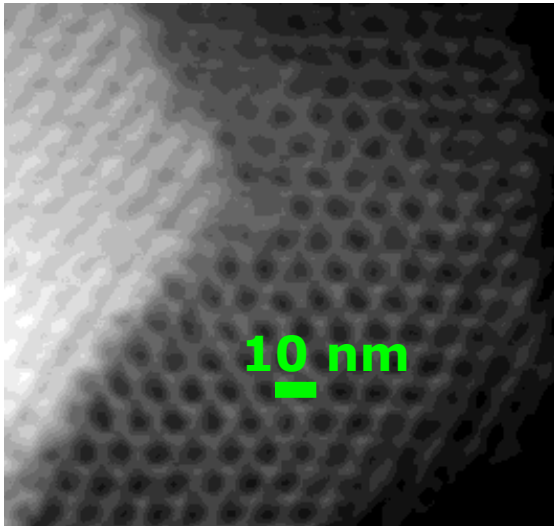
$S_{micro} = S_{BET} - S_{ext}$

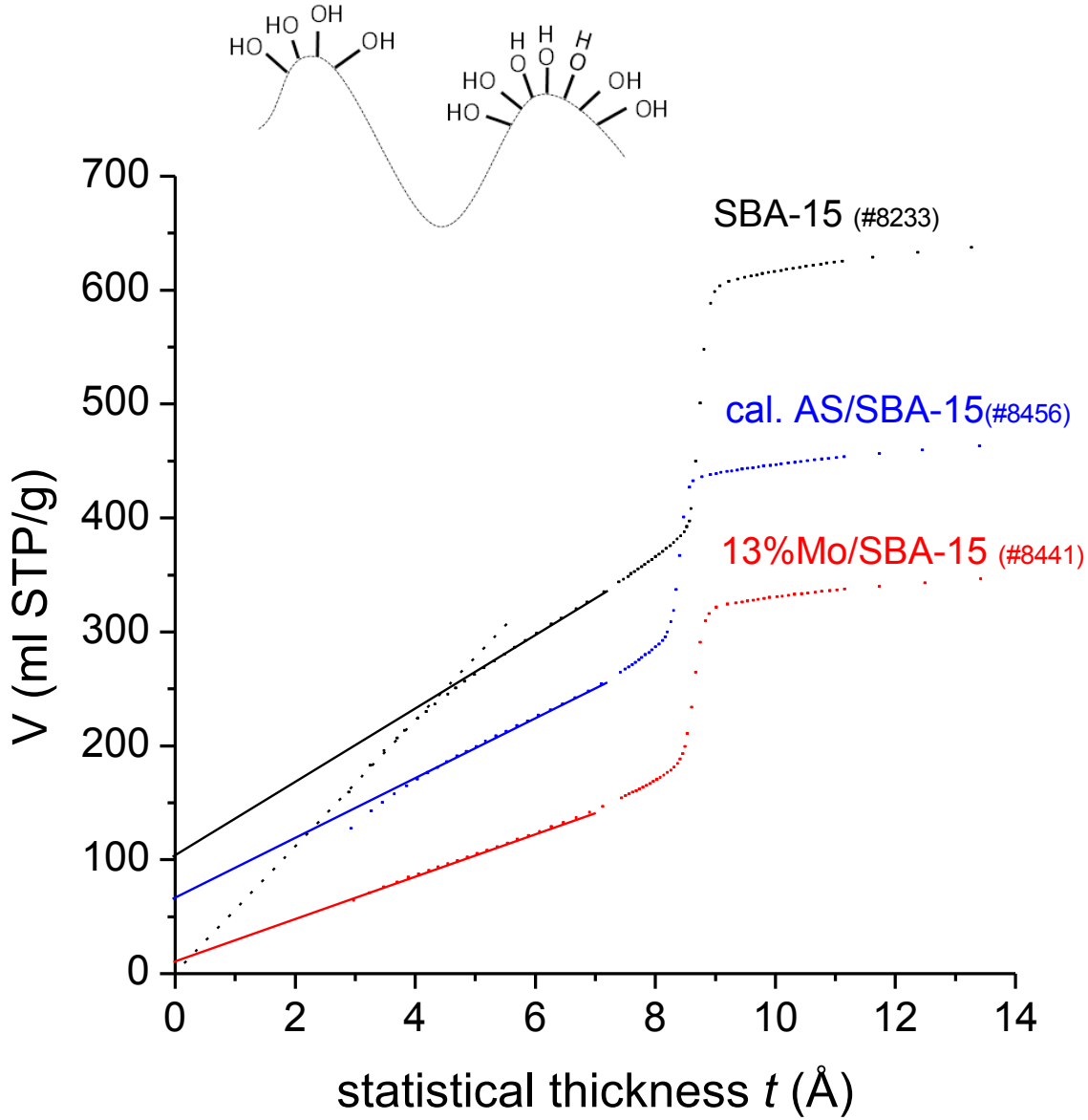


SBA-15: micropores and mesopores

5







Surface area and textural properties of modified SBA-15

5

Properties of MoO_x/SBA-15

Mo loading [a] (wt%)	Surface Mo density (nm^{-2}) Mo [b] (nm^{-2})	Isolated SiOH [c, d] (nm^{-2})	A_s (m^2/g)	A_μ [e] (m^2/g)	($\%$) [f]	V_p [g] (ml/g)	d_p [h] (nm)
0	0	1.6 [c]	859	261	36	1	7.5
2.1	0.21	1.1 [d]	637	164	31	0.79	7.1
5.1	0.58	0.88 [d]	554	127	28	0.71	7.1
6.6	0.85	0.68 [d]	490	135	28	0.61	7.1
9.7	1.09	0.39 [d]	556	96	21	0.78	7.2
13.3	2.51	0.07 [d]	332	36	13	0.55	7.4

[a] by XRF, [b] Mo loading (at%) divided by A_s, [c] by TG, [d] by IR at the dehydrated state using relative heights of the silanol peak at 3745cm^{-1}, [e] micropore (< ~0.9 nm of width) surface estimated by *t*-plot method, [f] A_μ divided by A_S, [g] at $P/P_0 = 0.95$, [g] at the dehydrated state; [h] estimated by NLDFT approach.

Experimental

Sample preparation:

1. Homogenization
2. Weighing
3. Outgassing adapted to the chemical nature of the sample in vacuum or under flow (repetitive cycling)

   Maximun residual pressure: 1 Pa (7.5×10^{-3} Torr)
   Micropore analysis: p<0.01 Pa

Pure & Appl. Chem., Vol. 57, No. 4, pp. 603–619, 1985.
Printed in Great Britain.
© 1985 IUPAC

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY INCLUDING CATALYSIS*

REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity

(Recommendations 1984)

Prepared for publication by the Subcommittee on Reporting Gas Adsorption Data Consisting of

K. S. W. SING (UK, Chairman); D. H. EVERETT (UK); R. A. W. HAUL (FRG); L. MOSCOU (Netherlands); R. A. PIEROTTI (USA); J. ROUQUÉROL (France); T. SIEMIENIEWSKA (Poland)

*Membership of the Commission during the period (1981–85) in which the report was prepared was as follows:

Chairman: 1981–83 J. Lyklema (Netherlands); 1983–85 K. S. W. Sing (UK); *Vice-Chairman*: 1981–85 J. Haber (Poland); *Secretary*: 1981–83 M. Kerker (USA); 1983–85 E. Wolfram (Hungary); *Members*: J. H. Block (FRG; Titular 1983–85, Associate 1981–83); N. V. Churaev (USSR; Associate 1981–85); D. H. Everett (UK; National Representative 1981–85); G. F. Froment (Belgium; National Representative 1981–85); P. C. Gravelle (France; Associate 1981–85); R. S. Hansen (USA; Titular 1981–83); R. A. W. Haul (FRG; National Representative 1981–83); J. W. Hightower (USA; Associate 1983–85); R. J. Hunter (Australia; Associate 1981–85); L. G. Ionescu (Brazil; National Representative 1983–85); A. S. Kertes (Israel; National Representative 1981–85); A. Kitahara (Japan; National Representative 1981–85); J. C. Kuriacose (India; National Representative 1983–85); J. Lyklema (Netherlands; National Representative 1983–85); A. Maroto (Argentina; Associate 1983–85, National Representative 1981–83); S. G. Mason (Canada; National Representative 1981–85); K. Meyer (GDR; National Representative 1981–85); P. Mukerjee (USA; Associate 1981–83); L. G. Nagy (Hungary; National Representative 1981–85); H. van Olphen (Netherlands; Associate 1981–83); J. A. Pajares (Spain; National Representative 1981–83); M. W. Roberts (UK; Titular 1981–83); J. Rouquérol (France; Associate 1983–85); K. S. W. Sing (UK; Associate 1981–83); P. Stenius (Sweden; Titular 1981–85, Associate 1981–83); M. S. Suwandi (Malaysia; National Representative 1983–85); L. Ter-Minassian-Saraga (France; Titular 1983–85, Associate 1981–83); A. Weiss (FRG; National Representative 1983–85); P. B. Wells (UK; Associate 1983–85); E. Wolfram (Hungary; Titular 1981–83).

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1985 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Experimental – Volumetric measurement

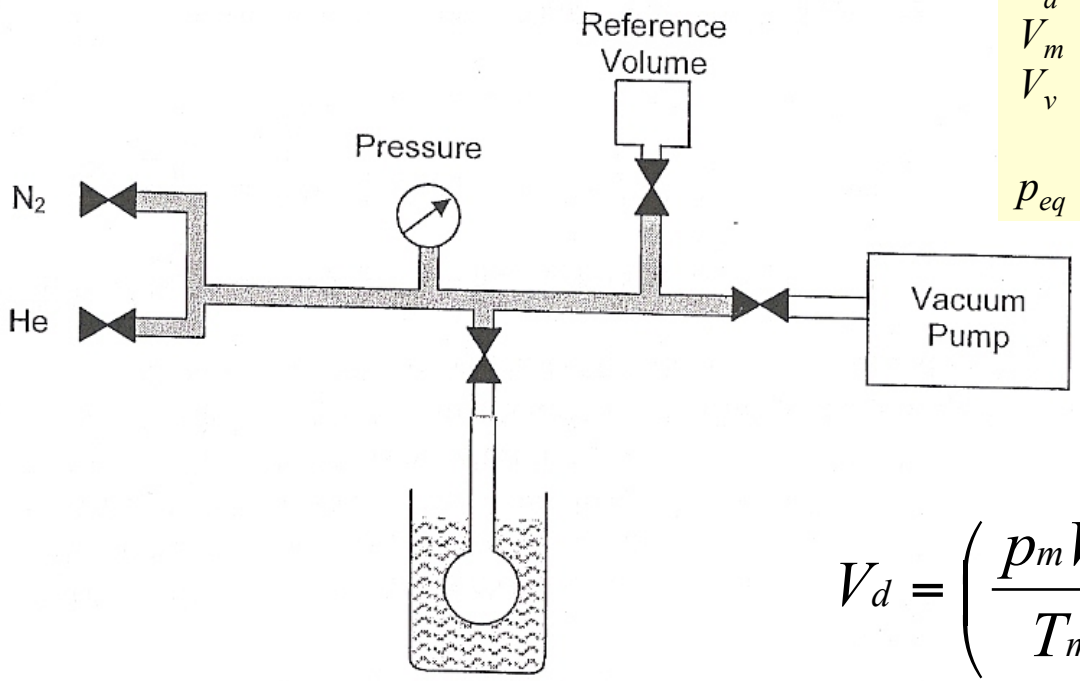


Figure 14.1b Simplified, modern static volumetric apparatus.

V_d volume of adsorptive dosed
V_m volume of manifold
V_v volume of the sample cell, which is not occupied by the adsorbent
p_{eq} equilibrium pressure after the dose

$$V_d = \left(\frac{p_m V_m}{T_m} - \frac{p_{eq} V_m}{T_{eq}} \right) \times \left(\frac{T_{Std}}{p_{Std}} \right)$$

$$V_s = V_d - \left(\frac{p V_{v77K}}{p_{Std}} \right)$$

$$T_{std} = 273.15\,\mathrm{K},\ p_{std} = 760\ \mathrm{torr}$$

$$V_{stp}[\mathrm{cm}^3] / 22414\,\mathrm{cm}^3 = n_s$$

Problems

Void volume determination

- He is not adsorbed
- He does not penetrate into regions inaccessible for the adsorptive (He removal procedure for micropore measurements!)

Corrections for non-ideality

Coolant level and temperature control

p_0 determination

Experimental

- p_0 is defined as the saturated equilibrium vapor pressure exhibited by the pure adsorptive contained in the sample cell when immersed in the coolant
- The saturation pressure increases exponentially with T
- Due to dissolved water vapor, oxygen or other gases the T is slightly elevated:

0.1-0.2 K ~ Δp = 10-20 torr

- BET plot not very sensitive to p_0
- Broad pressure range for micropore analysis:

$10^{-7} \leq p/p_0 \leq 1$

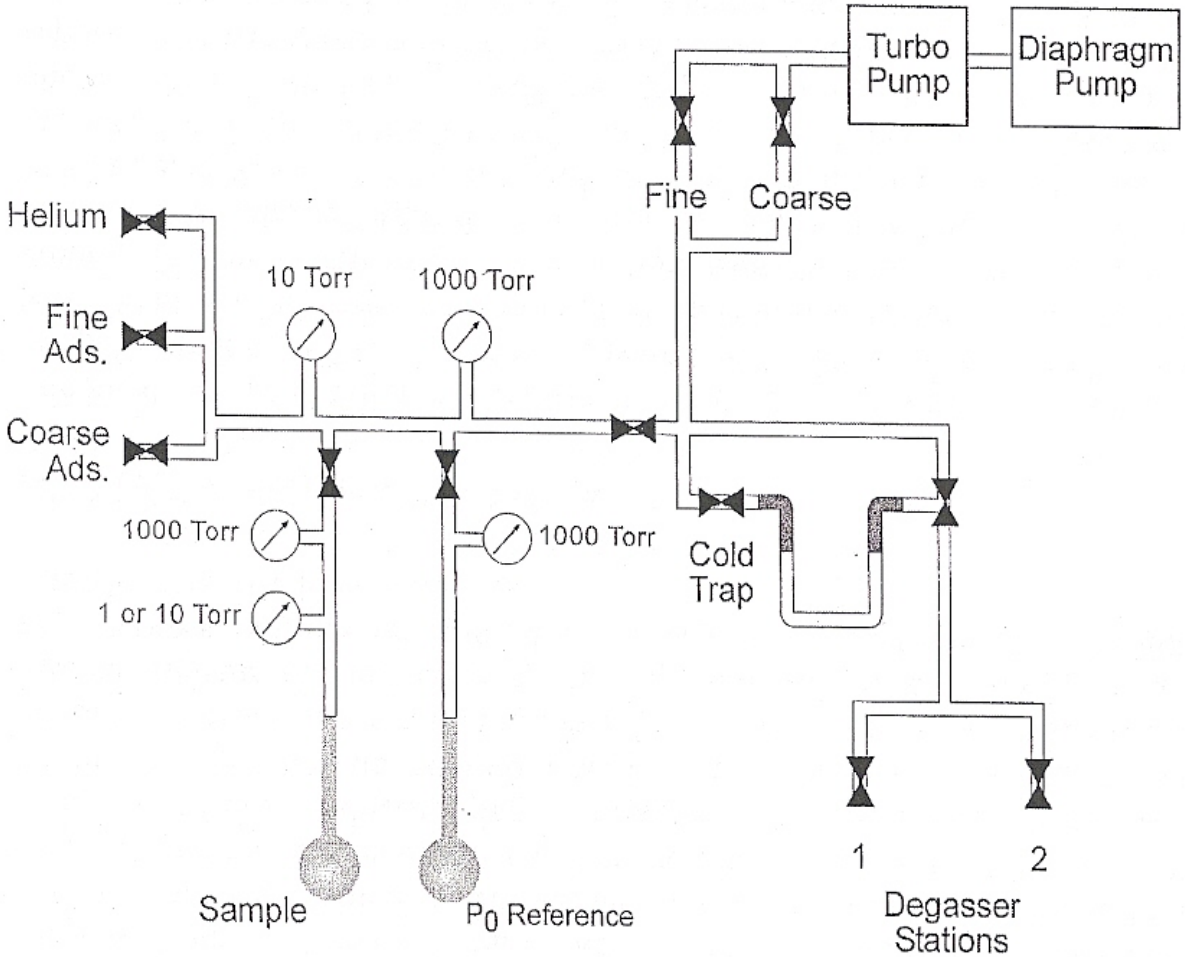


Figure. 14.3 Schematic representation of a high precision volumetric apparatus suitable for pore size analysis of micro- and mesoporous materials as well as for samples with low surface areas.

IUPAC Technical Report

Matthias Thommes*, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier, Francisco Rodriguez-Reinoso, Jean Rouquerol and Kenneth S. W. Sing

Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)

Abstract: Gas adsorption is an important tool for the characterisation of porous solids and fine powders. Major advances in recent years have made it necessary to update the 1985 IUPAC manual on Reporting Physisorption Data for Gas/Solid Systems. The aims of the present document are to clarify and standardise the presentation, nomenclature and methodology associated with the application of physisorption for surface area assessment and pore size analysis and to draw attention to remaining problems in the interpretation of physisorption data.

Keywords: IUPAC Physical and Biophysical Chemistry Division; nanostructured materials.

DOI 10.1515/pac-2014-1117
Received November 17, 2014; accepted April 30, 2015

CONTENTS

1. INTRODUCTION 1052
2. GENERAL DEFINITIONS AND TERMINOLOGY 1052
3. METHODOLOGY AND EXPERIMENTAL PROCEDURE 1055
3.1 The determination of physisorption isotherms 1055
3.2 Dead space (void volume) determination 1057
3.3 Outgassing the adsorbent 1057
4. EVALUATION OF ADSORPTION DATA 1058
4.1 Presentation of primary data 1058
4.2 Classification of physisorption isotherms 1058
4.3 Adsorption hysteresis 1059
4.3.1 Origin of hysteresis 1059
4.3.2 Types of hysteresis loops 1060

Article note: Sponsoring body: IUPAC Division of Physical and Biophysical Chemistry Division.

***Corresponding author: Matthias Thommes,** Applied Science Department, Quantachrome Instruments, 1900 Corporate Drive, Boynton Beach, FL, USA, e-mail: matthias.thommes@quantachrome.com
Katsumi Kaneko: Center for Energy and Environmental Science, Shinshu University, 4-17-1 Wakasato, Nagano-city, Japan
Alexander V. Neimark: Department of Chemical and Biochemical Engineering, Rutgers University, 98 Brett Road, Piscataway, New Brunswick, NJ, USA
James P. Olivier: Micromeritics Instrument Corp., 4356 Communications Drive, Norcross, USA
Francisco Rodriguez-Reinoso: Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, Alicante, Spain
Jean Rouquerol: Aix-Marseille Université, Laboratoire MADIREL, Centre de St Jérôme, Marseilles, France
Kenneth S. W. Sing: Brunel University, Uxbridge, London, UK

© 2015 IUPAC & De Gruyter

Unauthenticated
Download Date | 11/10/15 10:28 PM

5. ASSESSMENT OF SURFACE AREA 1061
5.1. Principles of the Brunauer–Emmett–Teller (BET) method 1061
5.1.1 The basic equation 1061
5.1.2 The derivation of n_m and a(BET) 1062
5.2 Standardisation of the BET method 1062
5.2.1. Choice of the adsorptive for BET area determination 1062
5.2.2. Application of the BET method to microporous materials 1063
6. ASSESSMENT OF MICROPOROSITY 1063
6.1. Choice of adsorptive 1063
6.2. Micropore volume 1064
6.3. Micropore size analysis 1065
7. ASSESSMENT OF MESOPOROSITY 1066
7.1. Pore volume 1066
7.2. Mesopore size analysis 1066
8. ASPECTS OF GAS ADSORPTION IN NON-RIGID MATERIALS 1067
9. GENERAL CONCLUSIONS AND RECOMMENDATIONS 1068
10. MEMBERSHIP OF SPONSORING BODIES 1068
11. REFERENCES 1069

1 Introduction

Gas adsorption is a well-established tool for the characterisation of the texture of porous solids and fine powders. In 1985 an IUPAC manual was issued on "Reporting Physisorption Data for Gas/Solid Systems", with special reference to the determination of surface area and porosity. The conclusions and recommendations in the 1985 document have been broadly accepted by the scientific and industrial community [1].

Over the past 30 years major advances have been made in the development of nanoporous materials with uniform, tailor-made pore structures (e.g., mesoporous molecular sieves, carbon nanotubes and nanohorns and materials with hierarchical pore structures). Their characterisation has required the development of high resolution experimental protocols for the adsorption of various subcritical fluids (e.g., nitrogen at $T = 77$ K, argon at 87 K, carbon dioxide at 273 K) and also organic vapours and supercritical gases. Furthermore, novel procedures based on density functional theory and molecular simulation (e.g., Monte–Carlo simulations) have been developed to allow a more accurate and comprehensive pore structural analysis to be obtained from high resolution physisorption data. It is evident that these new procedures, terms and concepts now necessitate an update and extension of the 1985 recommendations. Hence, this document is focused on the following objectives:

(i) to provide authoritative, up-to-date guidance on gas physisorption methodology;
(ii) to discuss the advantages and limitations of using physisorption techniques for studying solid surfaces and pore structures with particular reference to the assessment of surface area and pore size distribution.

The principal aim of this document is to clarify and standardise the presentation, nomenclature and methodology associated with the use of gas physisorption as an analytical tool and in different areas of pure and applied research.

2 General definitions and terminology

The definitions given here are in line with those put forward in the 1985 IUPAC Recommendation [1], while the symbols used are those given in the 2007 edition of the IUPAC manual "Quantities, Units and Symbols in

Unauthenticated
Download Date | 11/10/15 10:28 PM

Physical Chemistry". Where a *caveat* is added, it is intended to draw attention to a conceptual difficulty or to a particular aspect which requires further consideration.

In general, *adsorption* is defined as the enrichment of molecules, atoms or ions in the vicinity of an interface. In the case of gas/solid systems, adsorption takes place in the vicinity of the solid surface and outside the solid structure. The material in the adsorbed state is known as the *adsorbate*, while the *adsorptive* is the same component in the fluid phase. The *adsorption space* is the space occupied by the adsorbate. Adsorption can be physical (physisorption) or chemical (chemisorption). *Physisorption* is a general phenomenon: it occurs whenever an adsorbable gas (the adsorptive) is brought into contact with the surface of a solid (the *adsorbent*). The intermolecular forces involved are of the same kind as those responsible for the imperfection of real gases and the condensation of vapours. In addition to the attractive dispersion forces and the short range repulsive forces, specific molecular interactions (e.g., polarisation, field-dipole, field gradient-quadrupole) usually occur as a result of particular geometric and electronic properties of the adsorbent and adsorptive. In *chemisorption,* which is not dealt with in this document, the intermolecular forces involved lead to the formation of chemical bonds.

When the molecules of the adsorptive penetrate the surface layer and enter the structure of the bulk solid, the term *absorption* is used. It is sometimes difficult or impossible to distinguish between adsorption and absorption: it is then convenient to use the wider term *sorption* which embraces both phenomena, and to use the derived terms sorbent, sorbate and sorptive.

When the term adsorption is used to denote the onward process of adsorption, its counterpart is *desorption*, which denotes the converse process, in which the amount adsorbed progressively decreases. The terms adsorption and desorption are then used adjectivally to indicate the direction from which experimentally determined amounts adsorbed have been approached – by reference to the adsorption curve (or point), or to the desorption curve (or point). *Adsorption hysteresis* arises when the adsorption and desorption curves do not coincide.

The adsorption system is comprised of three zones: solid, gas and the adsorption space (e.g., the adsorbed layer) whose content is *the amount adsorbed* n^a. Evaluation of n^a is dependent on the volume, V^a, of the adsorption space, which is an unknown quantity in the absence of additional information. To address this issue, Gibbs proposed a model for assessing accurately an intermediate quantity called *the surface excess amount* n^σ. Adsorption is here assumed to be totally two-dimensional ($V^a = 0$) and to take place on an imaginary surface (Gibbs dividing surface, or GDS) which, in the case of gas adsorption, limits the volume V^g available for a homogeneous gas phase. Calculating the amount n^g in the gas phase in equilibrium with the adsorbent is then carried out by application of the appropriate gas laws. The difference between n (the total amount of adsorptive introduced in the system) and n^g is the *surface excess amount* n^σ.

Strictly speaking, the quantity experimentally determined by adsorption manometry or gravimetry is a surface excess amount n^σ. However, for the adsorption of vapours under 0.1 MPa, which is the main concern of this document, n^a and n^σ can be considered to be almost identical, provided the latter is calculated with a surface (the GDS) very close to the adsorbent surface. This requires an accurate determination of the void volume (gas adsorption manometry) or of the buoyancy (gas adsorption gravimetry) [see Section 3 and Ref. 2].

For gas adsorption measurements at higher pressures, the difference between n^a and n^σ cannot be ignored. Then, the experimental surface excess data can be converted into the corresponding amounts adsorbed, provided that the volumes of the adsorption space (V^a) and solid adsorbent (V^s) are known. In the simplest case, when the GDS exactly coincides with the actual adsorbing surface [2], the amount adsorbed n^a is given by

$$n^a = n^\sigma + c^g V^a \tag{1}$$

The relation, at constant temperature, between the amount adsorbed, n^a (or, alternatively, the surface excess amount n^σ), and the equilibrium pressure of the gas is known as the *adsorption isotherm*. The way the pressure is plotted depends on whether the adsorption is carried out at a temperature under or above the critical temperature of the adsorptive. At an adsorption temperature below the critical point, one usually adopts the *relative pressure* p/p°, where p is the equilibrium pressure and p° the saturation vapour pressure at

Unauthenticated
Download Date | 11/10/15 10:28 PM

the adsorption temperature. At an adsorption temperature above the critical one, where there is no condensation and no p° exists, one must necessarily use the equilibrium pressure p.

The surface of a solid can be considered and defined at different levels (*cf* Fig. 1). At the atomic scale, the *van der Waals surface* (Fig. 1, 1) is formed by the outer part of the van der Waals spheres of the surface atoms. The second surface, which is assessed by physisorption, does not coincide with the van der Waals surface. This surface is known in simulation studies as the *Connolly surface* (Fig. 1, 2) and is defined as the surface drawn by the bottom of a spherical probe molecule rolling over the van der Waals surface; this is the *probe-accessible surface*. The *r-distance surface* (Fig. 1, 3) is located at distance r from the Connolly surface.

In the case of porous adsorbents, the surface can be subdivided into an *external surface* and an *internal surface*, but with two different meanings: (i) in the general case, the external surface is defined as the surface outside the pores, while the internal surface is then the surface of all pore walls; and (ii) in the presence of microporosity it has become customary to define the external surface as the non-microporous surface. In practice, whatever definition is chosen, the method of assessment and the pore size and shape distribution must be taken into account. Because the accessibility of pores is dependent on the size and shape of the probe molecules, the recorded values of internal area and pore volume may depend on the dimensions of the adsorptive molecules (packing and molecular sieve effects). The *roughness* of a solid surface may be characterised by a *roughness factor*, *i.e.*, the ratio of the external surface to the chosen geometric surface. *Pore morphology* describes the geometrical shape and structure of the pores, including pore width and volume as well as the roughness of the pore walls. *Porosity* is defined as the ratio of the total pore volume to the volume of the particle or agglomerate.

In the context of physisorption, it is expedient to classify pores according to their size (IUPAC recommendation, 1985[1]):

(i) pores with widths exceeding about 50 nm are called *macropores*;
(ii) pores of widths between 2 nm and 50 nm are called *mesopores*;
(iii) pores with widths not exceeding about 2 nm are called *micropores*.

These limits, which were suggested by the analysis of nitrogen (77 K) adsorption-desorption isotherms are therefore to some extent arbitrary. Nevertheless, they are still useful and broadly accepted.

The term *nanopore* embraces the above three categories of pores, but with an upper limit ~ 100 nm.

The whole of the accessible volume present in micropores may be regarded as adsorption space. The process which then occurs is *micropore filling*, as distinct from the surface coverage which takes place on the walls of open macropores or mesopores. In the case of micropore filling, the interpretation of the adsorption isotherm only in terms of surface coverage is incorrect. Micropore filling may be regarded as a primary physisorption process (see Section 6). It is often useful to distinguish between the *narrow micropores* (also called *ultramicropores*) of approximate width < 0.7 nm and *wide micropores* (also called *supermicropores*).

Physisorption in mesopores takes place in three more or less distinct stages. In *monolayer adsorption* all the adsorbed molecules are in contact with the surface layer of the adsorbent. In *multilayer adsorption* the adsorption space accommodates more than one layer of molecules so that not all the adsorbed molecules are in direct contact with the adsorbent surface. In mesopores, multilayer adsorption is followed by pore condensation.

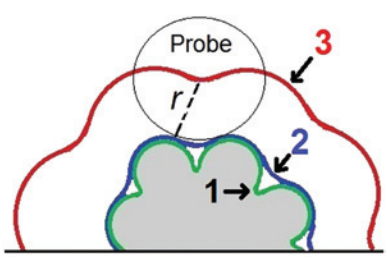


Fig. 1: Schematic representation of several possible surfaces of an adsorbent. 1: van der Waals; 2: Connolly, Probe-accessible; 3: Accessible, *r*-distance.

Unauthenticated
Download Date | 11/10/15 10:28 PM

Capillary (or pore) condensation is the phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure p less than the saturation pressure p° of the bulk liquid; i.e., capillary condensation reflects a vapour-liquid phase transition in a finite-volume system. The term capillary (or pore) condensation should not be used to describe micropore filling because it does not involve a vapour-liquid phase transition.

For physisorption, the *monolayer capacity* (n^a_m) is usually defined as the amount of adsorbate sufficient to cover the surface with a complete monolayer of molecules. In some cases this may be a close-packed array but in others the adsorbate may adopt a different structure. Quantities relating to monolayer capacity may be denoted by the subscript m. The surface coverage (θ) for both monolayer and multilayer adsorption is defined as the ratio of the amount of adsorbed substance to the monolayer capacity. The surface area (A_s) of the adsorbent may be calculated from the monolayer capacity, provided that the area (σ_m) effectively occupied by an adsorbed molecule in the complete monolayer is known. Thus,

$$A_s = n^a_m \cdot \mathrm{L} \cdot \sigma_m \tag{2}$$

where L is the Avogadro constant. The *specific surface area* (a_s) refers to unit mass of adsorbent:

$$a_s = A_s / m \tag{3}$$

The IUPAC manual of Quantities, Units and Symbols in Physical Chemistry [3] recommends the symbols A, A_s or S and a, a_s or s for area and specific area, respectively, but A_s and a_s are preferred to avoid confusion with Helmholtz energy A or entropy S.

Energetic data of physisorption can be assessed directly by adsorption calorimetry: the curve obtained of *differential energies of adsorption* $\Delta_{ads}\dot{u}$ or *differential enthalpies of adsorption*, $\Delta_{ads}\dot{h}$ (i.e., $\Delta_{ads}\dot{u} - \mathrm{R}T$ for an ideal gas) vs. amount adsorbed n^a allows one to study the energetics of surface coverage or micropore filling. The use of the term "*heat of adsorption*" is discouraged since it does not correspond to any well-defined thermodynamic change of state. The energetic data can also be assessed indirectly from adsorption isotherms obtained at different temperatures (i.e., the "isosteric" method, based on the use of the Clausius–Clapeyron equation) and this leads, for a given amount adsorbed, to the so-called "*isosteric heat*" q_{st} Strictly this quantity is more meaningful than a simple "heat", since it is equal, with opposite sign, to $\Delta_{ads}\dot{h}$. For this reason, the term "isosteric heat" is preferably replaced by the term *isosteric enthalpy of adsorption*. For both experimental and theoretical reasons, the calorimetric method is considered to be more reliable than the isosteric method, especially if one is studying micropore filling or the phase behaviour of the adsorbate.

3 Methodology and experimental procedure

3.1 The determination of physisorption isotherms

The various types of apparatus used for the determination of physisorption isotherms may be divided into two groups, depending on: (a) measurement of the amount of gas removed from the gas phase (i.e., manometric methods) and (b) direct measurement of the uptake of gas (i.e., gravimetric measurement of the change in mass of the adsorbent). In practice, static or dynamic techniques may be used in either case. As mentioned in Section 2, the surface excess amount is the quantity experimentally determined. For the adsorption of vapours below 100 kPa (1 bar) (e.g., N_2, Ar, Kr adsorption at cryogenic temperatures) the surface excess amount and the total amount adsorbed can be considered to be essentially identical (see Section 2).

A static manometric determination entails the measurement of changes of pressure of calibrated gas volumes: a known amount of pure gas is admitted to a confined, calibrated volume containing the adsorbent, which is maintained at constant temperature. As adsorption takes place, the pressure in the confined volume falls until equilibrium is established. The amount of gas adsorbed at the equilibrium pressure is given as the difference between the amount of gas admitted and the amount of gas required to fill the space around the

Unauthenticated
Download Date | 11/10/15 10:28 PM

adsorbent, i.e., the *dead space*. The adsorption isotherm is usually constructed point-by-point by admission of successive charges of gas to the adsorbent with the aid of a dosing technique and application of the appropriate gas laws. The volume of the dead space must, of course, be known accurately: it is obtained either by pre-calibration of the confined volume and subtracting the volume of the adsorbent (calculated from its density or by the admission of a gas which is adsorbed to a negligible extent). It is important to understand that the determination of the dead space usually accounts for the largest element of uncertainty in the total error inventory of the measured adsorbed amount.

A 'continuous' procedure can be used to construct the isotherm under quasi-equilibrium conditions: the pure adsorptive is admitted to (or removed from) the system at a slow and constant rate and a manometric or gravimetric technique used to follow the variation of the amount adsorbed with increase (or decrease) in pressure. In such measurements involving gas flow it is essential to confirm that the results are not affected by change in flow rate and to check the agreement with representative isotherms determined by a static method.

Two different carrier gas techniques may be employed to study the amount adsorbed. *Inverse gas chromatography*, which involves an elution phenomenon and the determination of a retention time, is mainly applied for studies in the low monolayer coverage (or micropore filling) region, although it has been used, apparently satisfactorily, up to monolayer coverage [2]. Adsorption/desorption under carrier gas (i.e., the Nelson and Eggertsen flow method [4]) also allows one to construct an adsorption/desorption isotherm, but this technique is frequently only applied for a single point surface area assessment. Both techniques require that the adsorption of the carrier gas be negligible.

Developments in vacuum microbalance techniques have maintained an interest in gravimetric methods for the determination of adsorption isotherms. With the aid of an adsorption balance the change in weight of the adsorbent may be followed directly during both the outgassing and adsorption/desorption stages. A gravimetric procedure is especially convenient for measurements with vapours (e.g., water vapour or some organic adsorptives) at temperatures not too far removed from ambient. At low temperatures (in particular at cryogenic temperatures), however, it can become difficult to control convection effects and to measure the exact temperature of the adsorbent.

The manometric method is generally considered the most suitable technique for undertaking physisorption measurements with nitrogen, argon, and krypton at cryogenic temperatures (i.e., 77 and 87 K, the boiling temperature of nitrogen and argon, respectively). In recent years, excellent commercial adsorption equipment has been developed and installed in almost every organisation concerned with the production and characterisation of nanoporous materials. Detailed descriptions of manometric methods (and the corresponding computational procedures) are not given here because they are available in recently published books and reviews.

Pore size analysis of nanoporous adsorbents over the complete micropore and mesopore range requires physisorption experiments which can span a broad spectrum of pressures (up to seven orders of magnitude) starting at ultralow pressures below 1 Pa (0.01 mbar). Hence, in order to study the adsorption of gases such as nitrogen and argon (at their boiling temperatures) within the relative pressure range $10^{-7} \leq p/p^0 \leq 1$ with sufficiently high accuracy, it is necessary to use special equipment, which ensures that the sample cell and the manifold can be evacuated to very low pressures with a highly efficient turbomolecular vacuum pumping system. Also, a combination of different pressure transducers, which cover various pressure ranges, is required. Another complication in the ultra-low pressure range is that for gas pressures below ca. 0.1 mbar (i.e., $p/p^0 < 10^{-4}$) for nitrogen and argon adsorption at 77 K and 87 K, respectively, pressure differences along the capillary of the sample bulb due to the Knudsen effect have to be taken into account. Hence, a thermal transpiration correction must be applied in order to obtain accurate data. Care must also be taken to properly select the equilibration conditions. Too short an equilibration time may lead to under-equilibrated data and isotherms shifted to too high relative pressures. Under-equilibration is often an issue in the very low relative pressure region of the isotherm, since equilibration in narrow micropores tends to be very slow. For highest accuracy the saturation pressure p° should be recorded for every datum point (by means of a dedicated saturation pressure transducer), this is most important for providing acceptable accuracy in the measurement

Unauthenticated
Download Date | 11/10/15 10:28 PM

of p/p^0 at high pressures, which is particularly important for evaluation of the size distribution of larger mesopores.

It is important to ensure that the purity of the adsorptive is not less than 99.999 %. In addition, the accuracy of the results depends on careful preparation and sampling of the adsorbent (see Section 3.3).

3.2 Dead space (void volume) determination

In the application of a manometric technique involving a dosing procedure it must be kept in mind that systematic errors in the measured doses of gas are cumulative and that the amount remaining unadsorbed in the dead space becomes increasingly important as the pressure increases. Hence, in order to correctly determine the amount adsorbed, an accurate knowledge of the dead space (i.e., the effective void volume) is crucial and can be determined before or after the measurement of the adsorption isotherm. The standard procedure uses a non-adsorbing gas such as helium to measure the dead space under the operational conditions. However, the use of helium for the dead space calibration may be problematic [2, 4, 5]. Recent investigations have confirmed that nanoporous solids with very narrow micropores may adsorb non-negligible amounts of helium at liquid nitrogen temperature (helium entrapment). If the entrapped helium is not removed prior to the analysis this can affect significantly the shape of the adsorption isotherm in the ultra-low pressure range [5]. Therefore, it is recommended that the sample should be outgassed after its exposure to helium, at least at room temperature, before continuing the manometric analysis.

It is advantageous to avoid the use of helium if the adsorbent consists of extremely narrow micropores, when in contrast to helium the entry of nitrogen or argon molecules is restricted, due to diffusion limitations. This situation arises with some zeolites and activated carbons. One way to avoid this problem is to determine the volume of the empty sample cell at ambient temperature using the adsorptive (e.g., nitrogen) followed by the measurement of a calibration curve (with the empty sample cell) performed under the same operational conditions as the adsorption measurements. This calibration curve essentially represents a multipoint dead space determination; the necessary correction for the sample volume can be made by means of the sample density (i.e., skeletal density).

3.3 Outgassing the adsorbent

Prior to the determination of an adsorption isotherm all of the physisorbed species should be removed from the surface of the adsorbent while avoiding irreversible changes of the surface or the solid structure. This may be achieved by outgassing, i.e., exposure of the surface to a high vacuum (for microporous materials, pressures <1 Pa are desirable) usually at elevated temperature. To obtain reproducible isotherms, it is necessary to control the outgassing conditions (the heating programme, the change in pressure over the adsorbent and the residual pressure) to within limits which depend on the nature of the adsorbent. With sensitive samples, a sample-controlled heating programme is recommended, which also reduces the risk of fine powder elutriation if the adsorbent is outgassed under high vacuum [2].

While outgassing under vacuum is the recommended method for microporous materials, it is sometimes expedient to achieve adequate cleanliness of the surface of non-microporous materials by flushing the adsorbent with an inert gas (which may be the adsorptive) at elevated temperature. To monitor the progress of outgassing, it is useful to follow the change in gas pressure by means of suitable vacuum gauges and, if the experimental technique permits, the change in weight of the adsorbent. Further information on the effect of outgassing may be obtained by the application of temperature programmed desorption in association with evolved gas analysis (e.g., using mass spectrometry). The conditions chosen for pretreatment of the adsorbent must be carefully controlled and recorded (i.e., the outgassing time and temperature and the residual pressure, or the conditions of flushing with adsorptive).

Unauthenticated
Download Date | 11/10/15 10:28 PM

4 Evaluation of adsorption data

4.1 Presentation of primary data

The quantity of gas adsorbed is measured in any convenient units, but for the presentation of the data, it is recommended that the amount adsorbed should be expressed in moles per gram of outgassed adsorbent. If possible, the composition of the adsorbent should be specified and its surface characterised. To facilitate the comparison of adsorption data, it is recommended that adsorption isotherms are displayed in graphical form with the amount adsorbed (preferably in $mol \cdot g^{-1}$) plotted against the equilibrium relative pressure (p/p^0), where p^0 is the saturation pressure of the pure adsorptive at the operational temperature, or against p, when the temperature is above the critical temperature of the adsorptive. If the adsorption measurements are made under conditions where the gas phase deviates appreciably from ideality (e.g., at high pressure), it is desirable that the isotherms should be presented in terms of gas fugacity rather than pressure.

4.2 Classification of physisorption isotherms

In the 1985 IUPAC recommendations physisorption isotherms were grouped into six types [1]. However, over the past 30 years various new characteristic types of isotherms have been identified and shown to be closely related to particular pore structures. Therefore, we now consider it expedient to refine the original IUPAC classifications of physisorption isotherms and associated hysteresis loops. The proposed updated classification of physisorption isotherms is shown in Fig. 2.

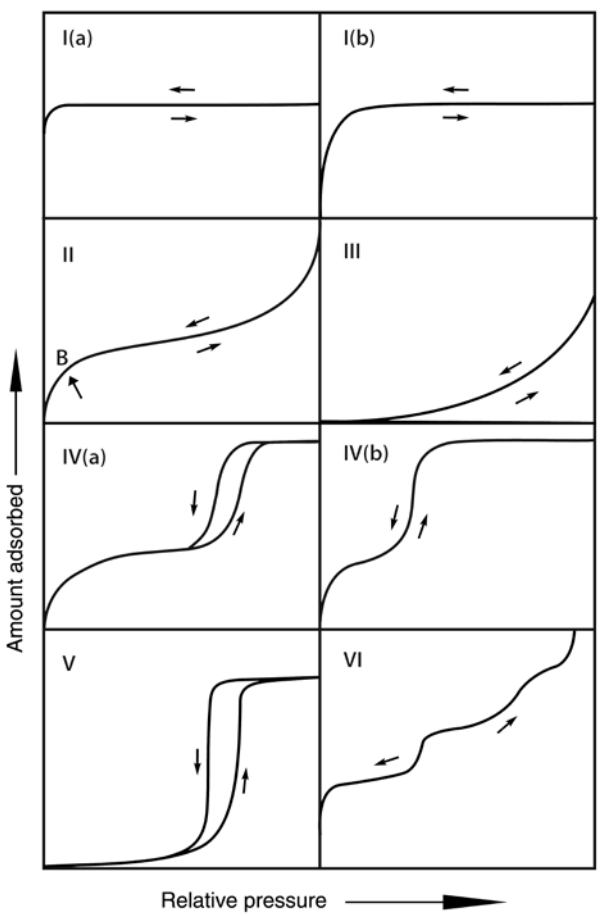


Fig. 2: Classification of physisorption isotherms.

Unauthenticated
Download Date | 11/10/15 10:28 PM

Reversible Type I isotherms are given by microporous solids having relatively small external surfaces (e.g., some activated carbons, molecular sieve zeolites and certain porous oxides). A Type I isotherm is concave to the p/p^0 axis and the amount adsorbed approaches a limiting value. This limiting uptake is governed by the accessible micropore volume rather than by the internal surface area. A steep uptake at very low p/p^0 is due to enhanced adsorbent-adsorptive interactions in narrow micropores (micropores of molecular dimensions), resulting in micropore filling at very low p/p^0. For nitrogen and argon adsorption at 77 K and 87 K, Type I(a) isotherms are given by microporous materials having mainly narrow micropores (of width < ~ 1 nm); Type I(b) isotherms are found with materials having pore size distributions over a broader range including wider micropores and possibly narrow mesopores (< ~ 2.5 nm).

Reversible Type II isotherms are given by the physisorption of most gases on nonporous or macroporous adsorbents. The shape is the result of unrestricted monolayer-multilayer adsorption up to high p/p^0. If the knee is sharp, Point B – the beginning of the middle almost linear section – usually corresponds to the completion of monolayer coverage. A more gradual curvature (i.e., a less distinctive Point B) is an indication of a significant amount of overlap of monolayer coverage and the onset of multilayer adsorption. The thickness of the adsorbed multilayer generally appears to increase without limit when $p/p^0 = 1$.

In the case of a Type III isotherm, there is no Point B and therefore no identifiable monolayer formation; the adsorbent-adsorbate interactions are now relatively weak and the adsorbed molecules are clustered around the most favorable sites on the surface of a nonporous or macroporous solid. In contrast to a Type II isotherm, the amount adsorbed remains finite at the saturation pressure (i.e., at $p/p^0 = 1$).

Type IV isotherms are given by mesoporous adsorbents (e.g., many oxide gels, industrial adsorbents and mesoporous molecular sieves). The adsorption behaviour in mesopores is determined by the adsorbent-adsorptive interactions and also by the interactions between the molecules in the condensed state. In this case, the initial monolayer-multilayer adsorption on the mesopore walls, which takes the same path as the corresponding part of a Type II isotherm, is followed by pore condensation. As already mentioned in Section 2, pore condensation is the phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure p less than the saturation pressure p^0 of the bulk liquid [6, 7]. A typical feature of Type IV isotherms is a final saturation plateau, of variable length (sometimes reduced to a mere inflexion point).

In the case of a Type IVa isotherm, capillary condensation is accompanied by hysteresis. This occurs when the pore width exceeds a certain critical width, which is dependent on the adsorption system and temperature (e.g., for nitrogen and argon adsorption in cylindrical pores at 77 K and 87 K, respectively, hysteresis starts to occur for pores wider than ~ 4 nm) [4, 6, 8]. With adsorbents having mesopores of smaller width, completely reversible Type IVb isotherms are observed. In principle, Type IVb isotherms are also given by conical and cylindrical mesopores that are closed at the tapered end.

In the low p/p^0 range, the Type V isotherm shape is very similar to that of Type III and this can be attributed to relatively weak adsorbent–adsorbate interactions. At higher p/p^0, molecular clustering is followed by pore filling. For instance, Type V isotherms are observed for water adsorption on hydrophobic microporous and mesoporous adsorbents.

The reversible stepwise Type VI isotherm is representative of layer-by-layer adsorption on a highly uniform nonporous surface. The step-height now represents the capacity for each adsorbed layer, while the sharpness of the step is dependent on the system and the temperature. Amongst the best examples of Type VI isotherms are those obtained with argon or krypton at low temperature on graphitised carbon blacks.

4.3 Adsorption hysteresis

4.3.1 Origin of hysteresis

Reproducible, permanent hysteresis loops, which are located in the multilayer range of physisorption isotherms, are generally associated with capillary condensation. This form of hysteresis can be attributed to

Unauthenticated
Download Date | 11/10/15 10:28 PM

adsorption metastability and/or network effects. In an open-ended pore (e.g., of cylindrical geometry), delayed condensation is the result of metastability of the adsorbed multilayer. It follows that in an assembly of such pores the adsorption branch of the hysteresis loop is not in thermodynamic equilibrium. Since evaporation does not involve nucleation, the desorption stage is equivalent to a reversible liquid–vapour transition. Therefore, if the pores are filled with liquid-like condensate, thermodynamic equilibration is established on the desorption branch [6–8].

In more complex pore structures, the desorption path is often dependent on network effects and various forms of pore blocking. These phenomena occur if wide pores have access to the external surface only through narrow necks (e.g., ink-bottle pore shape). The wide pores are filled as before and remain filled during desorption until the narrow necks empty at lower vapour pressures. In a pore network, the desorption vapour pressures are dependent on the size and spatial distribution of the necks. If the neck diameters are not too small, the network may empty at a relative pressure corresponding to a characteristic percolation threshold. Then, useful information concerning the neck size can be obtained from the desorption branch of the isotherm.

Theoretical and experimental studies have revealed [6–8] that if the neck diameter is smaller than a critical size (estimated to be ca. 5–6 nm for nitrogen at 77 K), the mechanism of desorption from the larger pores involves cavitation (i.e., the spontaneous nucleation and growth of gas bubbles in the metastable condensed fluid). Cavitation controlled evaporation has been found for instance with certain micro-mesoporous silicas, mesoporous zeolites, clays, and also some activated carbons. Contrary to the situation of pore blocking/percolation controlled evaporation no quantitative information about the neck size and neck size distribution can be obtained in the case of cavitation.

4.3.2 Types of hysteresis loops

Many different shapes of hysteresis loops have been reported, but the main types are shown in Fig. 3. Types H1, H2(a), H3 and H4 were identified in the original IUPAC classification of 1985, which is now extended in the light of more recent findings. Each of these six characteristic types is fairly closely related to particular features of the pore structure and underlying adsorption mechanism.

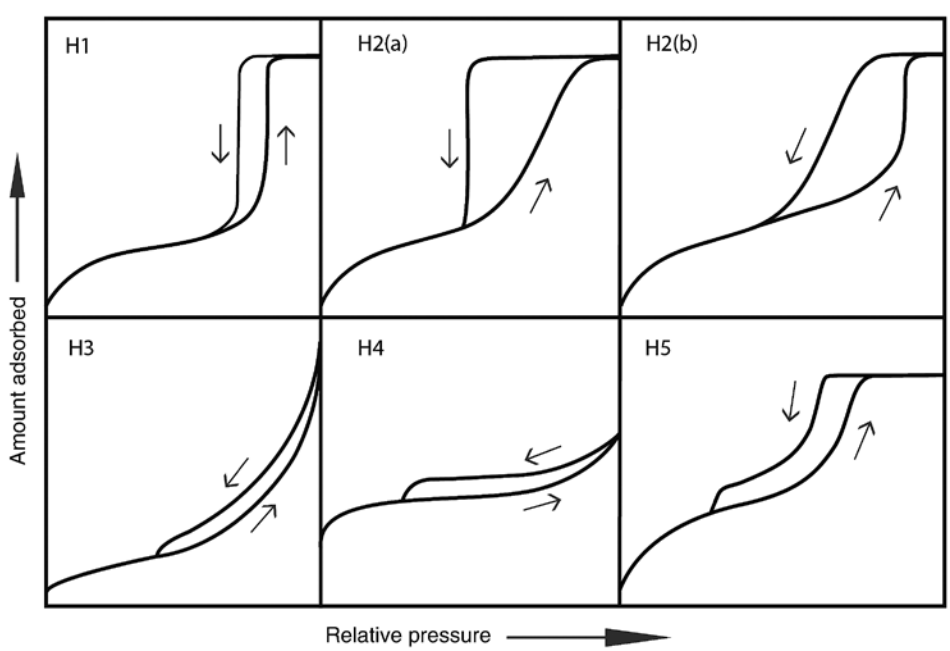


Fig. 3: Classification of hysteresis loops.

Unauthenticated
Download Date | 11/10/15 10:28 PM

The Type H1 loop is found in materials which exhibit a narrow range of uniform mesopores, as for instance in templated silicas (e.g., MCM-41, MCM-48, SBA-15), some controlled pore glasses and ordered, mesoporous carbons. Usually, network effects are minimal and the steep, narrow loop is a clear sign of delayed condensation on the adsorption branch. However, Type H1 hysteresis has also been found in networks of ink-bottle pores where the width of the neck size distribution is similar to the width of the pore/cavity size distribution (e.g., 3DOm carbons [6]).

Hysteresis loops of Type H2 are given by more complex pore structures in which network effects are important. The very steep desorption branch, which is a characteristic feature of H2(a) loops, can be attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation. H2(a) loops are for instance given by many silica gels, some porous glasses (e.g., vycor) as well as some ordered mesoporous materials (e.g., SBA-16 and KIT-5 silicas). The Type H2(b) loop is also associated with pore blocking, but the size distribution of neck widths is now much larger. Examples of this type of hysteresis loops have been observed with mesocellular silica foams and certain mesoporous ordered silicas after hydrothermal treatment.

There are two distinctive features of the Type H3 loop: (i) the adsorption branch resembles a Type II isotherm (ii) the lower limit of the desorption branch is normally located at the cavitation-induced p/p^0. Loops of this type are given by non-rigid aggregates of plate-like particles (e.g., certain clays) but also if the pore network consists of macropores which are not completely filled with pore condensate.

The H4 loop is somewhat similar, but the adsorption branch is now a composite of Types I and II, the more pronounced uptake at low p/p^0 being associated with the filling of micropores. H4 loops are often found with aggregated crystals of zeolites, some mesoporous zeolites, and micro-mesoporous carbons.

Although the Type H5 loop is unusual, it has a distinctive form associated with certain pore structures containing both open and partially blocked mesopores (e.g., plugged hexagonal templated silicas).

As already indicated, the common feature of H3, H4 and H5 loops is the sharp step-down of the desorption branch. Generally, this is located in a narrow range of p/p^0 for the particular adsorptive and temperature (e.g., at $p/p^0 \sim 0.4 - 0.5$ for nitrogen at temperatures of 77 K).

5 Assessment of surface area

5.1 Principles of the Brunauer–Emmett–Teller (BET) method

5.1.1 The basic equation

The Brunauer–Emmett–Teller method [2, 4] continues to be the most widely used procedure for evaluating the surface area of porous and finely-divided materials, in spite of the weakness of its theoretical foundations. Indeed, under certain carefully controlled conditions, the *BET-area* of a nonporous, macroporous or a mesoporous solid (i.e., giving a well-defined Type II or a Type IV(a) isotherm) can be regarded as the 'probe accessible area' (i.e., the effective area available for the adsorption of the specified adsorptive).

Two stages are involved in the application of the BET method. First, it is necessary to transform a physisorption isotherm into the 'BET plot' and from it derive a value of the BET monolayer capacity, n_m. In the second stage, the BET-area, a(BET), is calculated from n_m by adopting an appropriate value of the molecular cross-sectional area, σ.

It is customary to apply the BET equation in the linear form

$$\frac{p/p^\circ}{\boldsymbol{n}(1-p/p^\circ)} = \frac{1}{\boldsymbol{n}_m C} + \frac{C-1}{\boldsymbol{n}_m C}(p/p^\circ) \tag{4}$$

where $\boldsymbol{n}$ is the specific amount adsorbed at the relative pressure p/p° and $\boldsymbol{n}_m$ is the specific monolayer capacity.

Unauthenticated
Download Date | 11/10/15 10:28 PM

According to the BET theory, the parameter C is exponentially related to the energy of monolayer adsorption. It is now generally agreed that the value of C rather gives a useful indication of the shape of the isotherm in the BET range. Thus, if the value of C is at least ~ 80 the knee of the isotherm is sharp and Point B is fairly well defined (see Fig. 2). It was this characteristic point which was first identified by Brunauer and Emmett as the stage of monolayer completion and the beginning of multilayer adsorption. If C is low (< ~ 50) Point B cannot be identified as a single point on the isotherm. There is then an appreciable overlap of monolayer and multilayer adsorption and the precise interpretation of n_m is questionable. When C < 2, the isotherm is either Type III or Type V (see section V) and the BET method is not applicable. A high value of C (say, > ~ 150) is generally associated with either adsorption on high-energy surface sites or the filling of narrow micropores.

5.1.2 The derivation of n_m and a_s (BET)

A convenient way to derive $\boldsymbol{n_m}$ from the BET equation is to make use of the linear relation between $(p/p^\circ)/\boldsymbol{n}(1-p/p^\circ)$ and p/p° (i.e., 'the BET plot'). The range of linearity of the BET plot is always restricted to a limited part of the isotherm, often within the p/p° range of ~ 0.05–0.30 for Type II and Type IVa isotherms. However, in the case of Type IVb isotherms, caution is required since pore condensation may occur at quite low p/p^0. The linear BET range is shifted to lower relative pressures when the adsorption energy is high, especially if the surface is energetically homogeneous or crystalline (e.g., for the adsorption of nitrogen or argon on graphitised carbon or xenon on clean metal films).

A procedure which allows one to determine the linear BET range in an unambiguous way is described in Section 5.2.2, which is particularly useful if micropores are present, when the linear BET range is also located at lower relative pressures.

The second stage in the application of the BET method is the calculation of the BET-area from the monolayer capacity. This requires a knowledge of the average area, σ_m *(molecular cross-sectional area)*, occupied by the adsorbate molecule in the complete monolayer. Thus

$$a_s(\mathrm{BET}) = \boldsymbol{n}_m \cdot L \cdot \sigma_m / m \tag{5}$$

where a_s (BET) is the *BET specific area* of the adsorbent (of mass m).

5.2 Standardisation of the BET method

The calculated value of the BET area is dependent on (i) the adsorptive and operational temperature and (ii) the procedure used to locate the pressure range in applying the BET equation.

5.2.1 Choice of the adsorptive for BET area determination

Nitrogen (at its boiling temperature, 77 K) was traditionally the adsorptive generally used to obtain a(BET), with $\sigma_m(N_2)$ assumed to be 0.162 nm^2 (based on the assumption of a closed-packed monolayer). This is partly due to the fact that liquid nitrogen was readily available and also because nitrogen isotherms on many adsorbents were found to exhibit a well-defined Point B. However, it is now recognised that due to its quadrupole moment, the orientation of a nitrogen molecule is dependent on the surface chemistry of the adsorbent. This may lead to uncertainty in the value of $\sigma_m(N_2)$ – possibly ~ 20% for some surfaces [2].

Argon may seem to be an alternative adsorptive for surface area determination. Argon does not have a quadrupole moment and is less reactive than the diatomic nitrogen molecule. There are, however, several reasons why argon at 77 K is considered to be less reliable than nitrogen. At 77 K, argon is ca. 6.5 K below the bulk triple point temperature and hence the bulk reference state is in doubt. Furthermore, there is evidence that at 77 K, the structure of the argon monolayer is highly dependent on the surface chemistry of the adsorbent (e.g., giving rise to Type VI isotherms on highly uniform surfaces such as graphitised carbons).

Unauthenticated
Download Date | 11/10/15 10:28 PM

An alternative is argon adsorption at 87 K, i.e., at liquid argon temperature. Here, the problems encountered with argon at 77 K are not present. At 87 K, a cross-sectional area, σ_m(Ar), of 0.142 nm^2 is usually assumed. Because of the absence of a quadrupole moment and the higher temperature, σ_m(Ar) is less sensitive to differences in the structure of the adsorbent surface [2]. Furthermore, argon adsorption at 87 K offers advantages in particular for micropore analysis (see Section 6). Measurements at 87 K can be performed by using either liquid argon (instead of liquid nitrogen) or a cryostat (or cryocooler).

By using highly accurate manometric adsorption equipment, it is possible to assess surface areas as low as (~ 0.5–1) m^2 with nitrogen or argon as the adsorptive. In order to evaluate even lower surface areas, krypton adsorption at 77 K is generally the recommended adsorptive [4]. However, the behaviour of the krypton at 77 K is in some respect comparable to that of argon at 77 K: at this temperature krypton is well below (by *ca.* 38 K) its triple point and sublimates at *ca.* 0.22 kPa. The standard thermodynamic state of the adsorbed layer is therefore not well defined. For the BET analysis one usually assumes that the condensed adsorbate corresponds to a supercooled liquid (p° = 0.35 kPa). Due to the extremely low saturation pressure, the number of molecules in the free space of the sample cell is significantly reduced (to 1/300th) as compared to nitrogen or argon at their respective boiling temperatures: this leads to the high sensitivity of krypton adsorption at 77 K. However, evaluation of surface area is complicated by the difficulty in choosing the value of the cross-sectional area σ(Kr), which appears to vary from solid to solid (commonly used values for σ(Kr) range from ~ 0.17 to 0.23 nm^2). Since no generally valid recommendations can be made, it is essential to state the chosen values of p° and σ_m(Kr). In spite of that, krypton adsorption at 77 K is considered to be a very useful tool for routine work on materials with low-surface area.

5.2.2 Application of the BET method to microporous materials

As mentioned in Section 5.1, the BET method can be applied to many Type II and Type IV isotherms, but extreme caution is needed in the presence of micropores (i.e., with Type I isotherms and combinations of Types I and II or Types I and IV isotherms). It may be impossible to separate the processes of monolayer-multilayer adsorption and micropore filling. With microporous adsorbents, the linear range of the BET plot may be very difficult to locate. A useful procedure [9] allows one to overcome this difficulty and avoid any subjectivity in evaluating the BET monolayer capacity. This procedure is based on the following main criteria:

(a) the quantity C should be positive (i.e., a negative intercept on the ordinate of the BET plot is the first indication that one is outside the appropriate range);
(b) application of the BET equation should be restricted to the range where the term $n(1 - p/p^0)$ continuously increases with p/p^0;
(c) the p/p^0 value corresponding to n_m should be within the selected BET range.

It must be re-emphasised that this procedure should not be expected to confirm the validity of the BET monolayer capacity. Thus, the BET-area derived from a Type I isotherm must *not* be treated as a realistic probe accessible surface area. It represents an *apparent* surface area, which may be regarded as a useful adsorbent "fingerprint".

6 Assessment of microporosity

6.1 Choice of adsorptive

Physisorption filling of micropores always occurs at low relative pressures. The range of low pressure is dependent on the shape and dimensions of the micropores, the size of the adsorptive molecules and their interactions with the adsorbent and with each other. Adsorption in narrow micropores (i.e., the "ultramicropores"

Unauthenticated
Download Date | 11/10/15 10:28 PM

of width no more than two or three molecular diameters depending on pore geometry) involves some overlap of the adsorption forces and takes place at very low relative pressures. This process has been termed 'primary micropore filling', whereas wider micropores are filled by a secondary process over a wider range of higher relative pressure (e.g., $p/p^0 \approx 0.01$–0.15 for argon and nitrogen adsorption at 87 K and 77 K). Enhancement of the adsorbent-adsorbate interaction energy is now reduced and cooperative adsorbate–adsorbate interactions in the confined space become more important for the micropore filling process.

For many years, nitrogen adsorption at 77 K has been generally accepted as the standard method for both micropore and mesopore size analysis, but for several reasons it is now becoming evident that nitrogen is not an entirely satisfactory adsorptive for assessing the micropore size distribution. It is well known that the quadrupolar nature of the nitrogen molecule is largely responsible for the specific interaction with a variety of surface functional groups and exposed ions. This not only affects the orientation of the adsorbed nitrogen molecule on the adsorbent surface (as mentioned in Section 5.2.1), but it also strongly affects the micropore filling pressure. For example, with many zeolites and MOFs the initial stage of physisorption is shifted to extremely low relative pressures (to ~ 10^{-7}). The rate of diffusion is slow in this ultra-low pressure range, which makes it difficult to measure equilibrated adsorption isotherms. Additional problems are associated with pre-adsorbed N_2 molecules, which can block the entrances of narrow micropores, and specific interactions with surface functional groups so that the pore filling pressure is not clearly correlated with the pore size/structure. It follows that in order to measure an adsorption isotherm accurately careful consideration should be given to the choice of the adsorptive and the operational temperature.

In contrast to nitrogen, argon does not exhibit specific interactions with surface functional groups. However, as already indicated (Section 5.2.1), the interpretation of argon isotherms at liquid nitrogen temperature is not straightforward. At 87 K, this problem is avoided since argon fills narrow micropores at significantly higher relative pressures in comparison with nitrogen at 77 K [2, 4, 6]. This leads to accelerated equilibration and permits the measurement of high resolution adsorption isotherms. Hence, argon adsorption at 87 K allows a much more straightforward correlation to be obtained between the pore filling pressure and the confinement effect (depending on pore width and shape). This is particularly important for zeolitic materials, metal organic frameworks (MOFs) and some oxides and activated carbons [6].

Because of kinetic restrictions at cryogenic temperatures (87 K, 77 K) argon and nitrogen adsorption is of limited value for the characterisation of very narrow micropores. One way of addressing this problem is to use CO_2 (kinetic dimension 0.33 nm) as the adsorptive at 273 K. At 273 K, the saturation vapour pressure of CO_2 is very high (~ 3.5 MPa) and hence the pressures required for micropore size analysis are in the moderate range (~ 0.1 to–100) kPa. Because of these relatively high temperatures and pressures, diffusion is much faster and pores as small as 0.4 nm can be accessed. On the other hand, the easily measurable maximum relative pressure for measurements with CO_2 at 273 K is $p/p^0 \sim 3 \times 10^{-2}$ (corresponding to ambient pressure) and hence only pores < 1 nm can be explored.

Adsorption of CO_2 at 273 K has become an accepted method for studying carbonaceous materials with very narrow micropores and has been described in various textbooks and reviews [2, 4, 6]. However, CO_2 cannot be recommended for the pore size analysis of microporous solids with polar surface groups (e.g., oxides, zeolites, MOFs) since the quadrupole moment of CO_2 is even larger than that of N_2 which makes it difficult to correlate the CO_2 pore filling pressure with the pore size.

6.2 Micropore volume

If the physisorption isotherm is of Type I (see Fig.2), with a virtually horizontal plateau, the limiting uptake may be taken as a simple measure of the micropore capacity, n_p, with respect to the adsorption of the particular gas at the operational temperature. To convert n_p into the micropore volume V_P, it is usually assumed that the pores are filled with the condensed adsorptive in the normal liquid state. This assumption is known as the Gurvich rule [2, 4]. However, in practice, the plateau of the adsorption isotherm is rarely horizontal since most microporous adsorbents have appreciable external surface areas and many also have pores in

Unauthenticated
Download Date | 11/10/15 10:28 PM

the mesopore range. It follows that the Gurvich rule cannot always be applied in a straightforward way to determine the micropore volume.

A number of different methods have been proposed for the analysis of physisorption isotherms given by microporous solids. They can be divided into the older macroscopic procedures and those based on statistical mechanics (e.g., molecular simulation or density functional theory).

For routine analysis, the micropore volume is often assessed by application of a macroscopic procedure [2, 4]. One such approach involves the empirical comparison of an isotherm with an appropriate standard obtained on a non-porous reference material of similar chemical composition. In the t-method it is necessary to make use of a standard multilayer thickness curve, but this is dependent on the application of the BET method, which may not be strictly applicable (see Section 5). In order to overcome this problem the use of the α_s-plot method is preferred because it does not need the evaluation of monolayer capacity and is also more adaptable than the t-plot. In this method the standard isotherm is plotted in a reduced form $(n/n_x)_s$ versus the relative pressure p/p^0, where the normalising factor n_x is taken as the amount adsorbed at a preselected relative pressure (generally $p/p^0 = 0.4$). In order to construct the α_s-plot for a given adsorbent, the amount adsorbed n is plotted as a function of the reduced standard isotherm, $\alpha_s = (n/n_x)_s$. The micropore capacity is obtained by back extrapolation of a linear section of the α_s plot. A refinement of the α_s analysis makes use of high-resolution standard isotherm data at very low relative pressures [2, 4].

Another popular method for evaluation of the micropore volume is based on Dubinin's pore-volume-filling theory. In accordance with the Dubinin–Radushkevich (DR) equation, a plot of log n versus $\log^2(p^0/p)$ is linear provided the micropore size has a uniform Gaussian distribution and its extrapolation to the ordinate will give the micropore capacity. Although linear DR plots have been reported for the physisorption of various gases and vapours by microporous carbons, there are numerous examples of the linear region being apparently absent or restricted to a limited range of low relative pressures. The applicability of the DR method is then questionable [2, 4].

It must be kept in mind that these classical methods do not allow for the effect of micropore size and shape on molecular packing so that the adsorbate cannot always have bulk-liquid like properties. This problem has been addressed in methods based on molecular simulation (MC) and density functional theory (DFT), which are discussed in the next section.

6.3 Micropore size analysis

An empirical way of studying microporosity is by the application of a number of molecular probes of progressively increasing molecular diameter. The method is based on the measurement of both adsorption rates and capacities. A sharp adsorption cutoff might be expected to correspond to a given micropore size, but this does not take account of the complexity of most microporous materials. Although the results are often quite difficult to interpret, generally it is possible to obtain useful information about the effective range of window and/or pore entrance size.

Various semi-empirical methods include those proposed by Horvath and Kawazoe (the HK method), Saito and Foley and Cheng and Yang for the evaluation of the pore size distribution of slit, cylindrical and spherical pores, respectively [2, 4, 6]. Although these semi-empirical methods tend to underestimate the pore size, they may be in some cases useful for the comparison of microporous materials. Microscopic treatments such as density functional theory (DFT) and molecular simulation, which can describe the configuration of the adsorbed phase at the molecular level, are considered to be superior and to provide a more reliable approach to pore size analysis over the complete nanopore range [6, 8].

Thus, DFT and Monte Carlo simulation (MC) have been developed into powerful methods for the description of the adsorption and phase behaviour of fluids confined in well-defined pore structures [7, 8]. These procedures are based on the fundamental principles of statistical mechanics as applied to the molecular behaviour of confined fluids. They describe the distribution of adsorbed molecules in pores on a molecular level and thus provide detailed information about the local fluid structure near the adsorbent surface. The fluid–solid interaction potential is dependent on the pore model. Different pore shape models (e.g., slit,

Unauthenticated
Download Date | 11/10/15 10:28 PM

cylinder and spherical geometries and hybrid shapes) have been developed for various material classes such as carbons, silicas, zeolites.

Non-local-density functional theory (NLDFT) based methods for pore size/volume analysis of nanoporous materials are now available for many adsorption systems [4, 6, 8]. They are included in commercial software and are also featured in international standards (such as ISO 15901-3).

These methods allow one to calculate for a particular adsorptive/adsorbent pair a series of theoretical isotherms, $N(p/p^0,W)$, in pores of different widths for a given pore shape. The series of theoretical isotherms is called the kernel, which can be regarded as a theoretical reference for a given class of adsorbent/adsorptive system. The calculation of the pore size distribution function $f(W)$ is based on a solution of the general adsorption isotherm (GAI) equation, which correlates the experimental adsorption isotherm $N(p/p^0)$ with the kernel of the theoretical adsorption or desorption isotherms $N(p/p^0,W)$. For this purpose, the GAI equation is expressed in the form:

$$N(p/p^{o}) = \int_{W_{min}}^{W_{max}} N(p/p^{o}, W) f(W) dW \tag{6}$$

Although the solution of the GAI equation with respect to the pore size distribution function $f(W)$ is strictly an ill-posed numerical problem, it is now generally accepted that meaningful and stable solutions can be obtained by using regularisation algorithms [8].

Several approaches have been suggested to account for the heterogeneity of most adsorbents, which if not properly taken into account can lead to appreciable inaccuracy in the pore size analysis. Such methods include the development of complex 3D structural models of disordered porous solids by advanced molecular simulation techniques, but these are still too complex to be implemented for routine pore size analysis. The drawbacks of the conventional NLDFT model which assumes a smooth and homogenous carbon surface have been addressed by the introduction of two-dimensional DFT approaches [10]. Quenched solid density functional theory (QSDFT) is another approach to quantitatively allow for the effects of surface heterogeneity in a practical way [6, 8]. It has been demonstrated that taking into account surface heterogeneity significantly improves the reliability of the pore size analysis of heterogenous nanoporous carbons.

Finally, it must be stressed that the application of advanced methods based on DFT and molecular simulation can lead to reasonably accurate evaluation of the pore size distribution only if a given nanoporous system is compatible with the chosen DFT/MC kernel. If the chosen kernel is not consistent with the experimental adsorptive/adsorbent system, the derived pore size distribution may be significantly in error.

7 Assessment of mesoporosity

7.1 Pore volume

If a mesoporous adsorbent contains no macropores, its Type IV isotherm remains nearly horizontal over the upper range of p/p^0. The pore volume, V_p, is then derived from the amount of vapour adsorbed at a relative pressure close to unity (e.g., $p/p^0 = 0.95$), by assuming that the pores are filled with the adsorbate in the bulk liquid state, (i.e., by applying the Gurvich rule) [2, 4].

If macropores are present, the isotherm is no longer nearly horizontal near $p/p^0 = 1$ and the *total* pore volume cannot be evaluated from such a composite Type IV +Type II isotherm.

7.2 Mesopore size analysis

For many years mesopore size analysis was firmly based on the application of the Kelvin equation. Thus, the shift of the gas-liquid phase transition of a confined fluid from bulk coexistence, is expressed in terms of the

Unauthenticated
Download Date | 11/10/15 10:28 PM

surface tension γ of the bulk fluid and the molar liquid volume V_m. For cylindrical pores the modified Kelvin equation [2, 4] is:

$$\ln(p/p^0) = -2\gamma V_m / \mathrm{RT}(r_p - t_c) \tag{7}$$

where r_p is the pore radius and t_c the thickness of the adsorbed multilayer film, which is formed prior to pore condensation.

The many methods for mesopore size analysis, which make use of the modified Kelvin equation, include those proposed by Barrett, Joyner and Halenda (BJH) and Broeckhoff and de Boer [2, 4]. In order to account for the preadsorbed multilayer film, the Kelvin equation is combined with a standard isotherm (the *t*-curve), which is determined on certain well-defined nonporous solids. However, for the size analysis of narrow mesopores, the standard t-curve is not entirely satisfactory, because the curvature and enhanced surface forces are not properly taken into account. Similarly, the validity of the Kelvin equation is questionable as the mesopore width is reduced because macroscopic concepts can no longer be safely applied. This was clearly demonstrated with the aid of model mesoporous molecular sieves (e.g., M41S materials). Because of their high degree of order, the pore diameter of such model substances can be derived by independent methods (X-ray-diffraction, high-resolution transmission electron microscopy, etc.). It was shown [4, 6, 8] that the Kelvin equation based procedures, such as the BJH method, significantly underestimate the pore size for narrow mesopores (for pore diameter < ~ 10 nm the pore size will be underestimated by ~ 20–30 %).

The limitations of the Kelvin equation can be avoided by applying microscopic methods based on molecular simulation or DFT (e.g., NLDFT) which as discussed in detail in Section 6 yield the thermodynamics and density profiles of confined fluids and a description of the adsorbed phase on a molecular level. They capture the essential features of both micropore and mesopore filling and hysteresis [7, 8]. As a consequence they allow one to obtain a more reliable assessment of the pore size distribution over the complete range [6, 8]. Furthermore, one can obtain useful information from both the adsorption and desorption branches of the hysteresis loop. With certain ordered mesoporous materials, these methods are capable of quantitatively predicting the pore condensation and hysteresis behaviour by taking into account the underlying adsorption-desorption mechanisms including the delay in condensation due to metastability of the pore fluid [6, 8]. These advantages are crucial in the pore size analysis of materials which give rise to H2, H3, H4 and H5 hysteresis loops.

As indicated in Section 6, commercial DFT software is now available for various adsorbent systems and pore geometries (cylindrical, slit, spherical or hybrids). However, as already discussed, it is important to ensure that the chosen DFT and molecular simulation based methods are compatible with the experimental nanoporous system.

8 Aspects of gas adsorption in non-rigid materials

Physisorption isotherms are generally expected to be completely reversible in the monolayer, or micropore filling, range. In fact, for certain microporous systems (e.g., clays, coal, some activated carbons) *low pressure hysteresis* (LPH) may extend to the lowest attainable pressures [2]. Since such phenomena are sometimes difficult to reproduce, it might appear that low pressure hysteresis is an artefact simply due to faulty experimental technique. Of course, spurious data are obtained if insufficient time is allowed for the system to attain equilibrium. Another source of error is the presence of impurities either in the gas phase or on the surface. These complications must be avoided or removed before the evidence for reproducible and genuine LPH can be accepted. Genuine low pressure hysteresis is often associated with the expansion and contraction of adsorbents: the irreversible entry of the adsorbate molecules into pores of molecular dimensions can produce inelastic distortion of the adsorbent structure. A related effect, which has been termed “activated entry”, is the very slow diffusion of molecules through narrow pore entrances [2].

Unauthenticated
Download Date | 11/10/15 10:28 PM

Adsorption may also induce structural transformations of the adsorbent that affect the adsorption isotherm to a great extent. Well known are structural transformations in zeolites, like MFI ZSM-5, which are reflected in the appearance of low-pressure hysteresis loops below the range of pressures associated with capillary condensation. Structural transformations are observed in some metal-organic frameworks (MOFs) and their sorption behaviour is not easy to interpret [11, 12]. Application of standard methods for the assessment of surface area and pore size analysis may lead to meaningless BET surface areas and pore size distributions. Novel theoretical approaches based on realistic pore models, which allow one to take into account the non-rigid nature of the adsorbent into account, are needed. Some progress has been made during the last few years [12] but this area requires major attention in the future.

In addition to these irreversible changes, elastic deformation of the adsorbent commonly occurs in various systems, such as charcoal, activated carbon, porous glass, zeolites and silica gels. Elastic deformation is usually quite small (between ~ 0.1% and 1%); it does not affect significantly the sorption isotherm except for some polymers, aerogels and other materials of high porosity.

9 Conclusions and recommendations

Major advances in adsorption science over the past 30 years include: (i) Preparation of nanoporous materials with uniform pore structures, which are now used as model adsorbents; (ii) Introduction of high resolution adsorption techniques and reliable commercial instrumentation; and (iii) Application of density functional theory (DFT) and molecular simulation.

The original IUPAC classifications of physisorption isotherms and hysteresis loops have been extended and refined to include new characteristic types, which are associated with certain well-defined adsorption systems.

Caution is required in applying the Brunauer–Emmett–Teller (BET) method for the assessment of surface area. Use of a recommended procedure (see Section 5.2.2) improves the reproducibility of the method, when micropores are present, but one then obtains an apparent surface area (i.e., "BET area") which serves as a useful "fingerprint" of the adsorbent.

The choice of adsorptive is crucial in the characterisation of porous materials. Nitrogen at 77 K has been widely used, but the interpretation of the isotherm data is not always straightforward. For various reasons, argon adsorption at 87 K is considered to be more reliable and is now recommended – particularly for micropore size analysis.

It is now evident that pore size analysis of narrow mesopores cannot be reliably achieved by the application of procedures based on the Kelvin equation, such as the Barrett–Joyner–Halenda (BJH) method. This traditional approach may still be useful, however, for routine work (e.g., industrial process control).

Density functional theory (DFT) based computational procedures are included in commercially available software and provide a reasonably reliable assessment of the nanopore size distribution (i.e., for both mesopores and micropores), provided that the given nanopore structure is compatible with the chosen DFT kernel.

The characterisation of poorly ordered nanoporous and non-rigid adsorbents (e.g., certain MOFs) represents a major challenge. More work is also required on the development of new certified reference materials and improved procedures for routine data analysis.

10 Membership of sponsoring bodies

President: Roberto Marquardt; **Vice President:** Angela Wilson; **Secretary:** Assaf Friedler; **Past President:** Kaoru Yamanouchi; **Titular Members:** Kristin Bartik, Andrea Russell, Jürgen Stohner, Yun Hin Taufiq-Yap, Frank van Veggel; **Associate Members:** Kankan Bhattacharyya, Attila Császár, Joaquim Luís de Faria, Vadim

Unauthenticated
Download Date | 11/10/15 10:28 PM

Yu. Kukushkin, Álvaro Mombrú Rodríguez, Xin Sheng Zhao; **National Representatives:** Md. Abu bin Hasan Susan, Jiří Cejka, Horácio Corti, Supa Hannongbua, Sung-Jin Kim, Eduard Klein, Marc Koper, Michal Korenko, Kari Laasonen, James Mdoe, Vladislav Tomišić.

This manuscript (PAC-REP-14-11-17) was prepared in the framework of IUPAC project 2010-009-1-100.

References

[1] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pieroti, J. Rouquerol, T. Siemieniewska. *Pure Appl. Chem.* **57**, (1985).
[2] J. Rouquerol, F. Rouquerol, K. S. W. Sing, P. Llewellyn, G. Maurin. *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*, Academic Press (2014).
[3] E. R. Cohen, T. Cvitas, J. G. Frey, B. Holmström, K. Kuchitsu, R. Marquardt, I. Mills, F. Pavese, M. Quack, J. Stohner, H. L. Strauss, M. Takami, A. J. Thor. *Quantities, Units and Symbols in Physical Chemistry*, 3rd ed., RSC Publishing, Cambridge, UK (2007).
[4] S. Lowell, J. Shields, M. A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area. *Porosity and Density*, Springer, 2004.
[5] J. Silvestre-Albero, A. M. Silvestre-Albero, P. L. Llewellyn, F. Rodriguez-Reinoso. *J. Phys. Chem. C* **117**, 16885 (2013).
[6] M. Thommes, K. A. Cychosz. *Adsorption* **20**, 233 (2014).
[7] P. A Monson. *Microporous Mesoporous Mater*. **160**, 47 (2012).
[8] J. Landers, G. Y. Gor, A. V Neimark. *Colloid. Surfaces A: Physicochem. Eng. Aspects* **437**, 3 (2013).
[9] J. Rouquerol, P. Llewellyn, F. Rouquerol. *Stud. Surf. Sci. Catal.* **160**, 49 (2007).
[10] J. Jagiello, J. P. Olivier. *J. Phys. Chem. C* **113**, 19382 (2009).
[11] K. Kaneko, T. Itoh, T. Fujimori. *Chem Lett*. **41**, 466 (2012).
[12] A. V. Neimark, F. Coudert, A. Boutin, A. Fuchs. *JPC Lett.* **1**, 445 (2010).

Note: Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC or De Gruyter permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, the name De Gruyter, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organisation and De Gruyter.

Unauthenticated
Download Date | 11/10/15 10:28 PM