Ceramic Processing
3 Powder Characterization

Characteristics & Properties of Ceramics

❑Characteristics of a material

"parameters that specify the chemical and physical aspects of its composition and structure" (Reed (1995), p. 69)

- Composition
- Structure

❑Properties of a material

"its response to changes in the physical or chemical environment." (Reed (1995), p. 69)

- Thermal
- Mechanical
- Chemical
- Electrical
- …

Powder Characterization

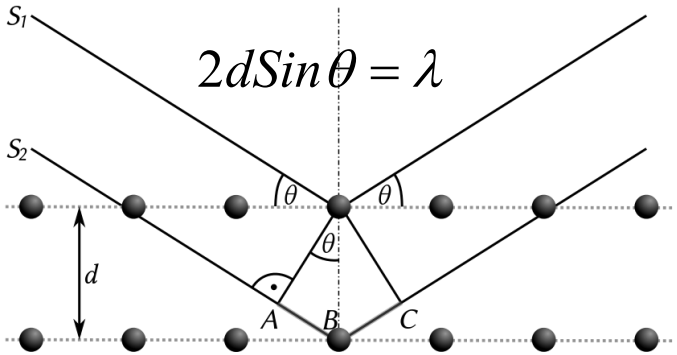
- **Powder characteristics critical to**
  - Starting material quality control
  - Microstructural control of processed ceramic body
- **Powder characterization reveal information about**
  - Chemical composition
    - Phase composition: e.g., Al_2O_3 vs. SiO_2
    - Major and impurity elements and content
    - Other impurities: e.g., adsorbed water content
    - …
  - Structure
    - Primary particle size, shape, and size distribution
    - Secondary particle size and shape
    - Packing density
    - Porosity
    - Specific surface area
    - …

Chemical Composition Analysis

- **Impurity elements and/or impurity phase always exist**
- **Common techniques**
  - X-ray diffraction
  - Optical atomic spectroscopy
    - atomic absorption, emission and fluorescence
  - X-ray fluorescence spectroscopy (XRF)
  - Additional (surface) chemical analysis techniques
    - XPS
    - AES
    - EDX
    - SIMS
  - Mass spectrometry (MS) and gas chromatography (GC)
  - Titration
  - Electrochemical methods
  - Nuclear and radioisotope analysis
  - …

Phase Analysis via X-ray Diffraction (XRD)

- **X-ray diffracts in crystal lattice leading to certain unique pattern**
- **For crystal structure/phase analysis**
- **Other considerations:**
  - Solid samples: powders or bulk
  - Simple, fast operation
  - Detection limit: ~2% by weight (synchrotron X-ray even better)
  - Comprehensive standard database available (ICDD-JCPDS)
  - Quantitative analysis possible (e.g., via use of standards & calibration curves or Rietveld analysis)
  - Cannot detect atom concentration easily
  - Not sensitive to amorphous phases



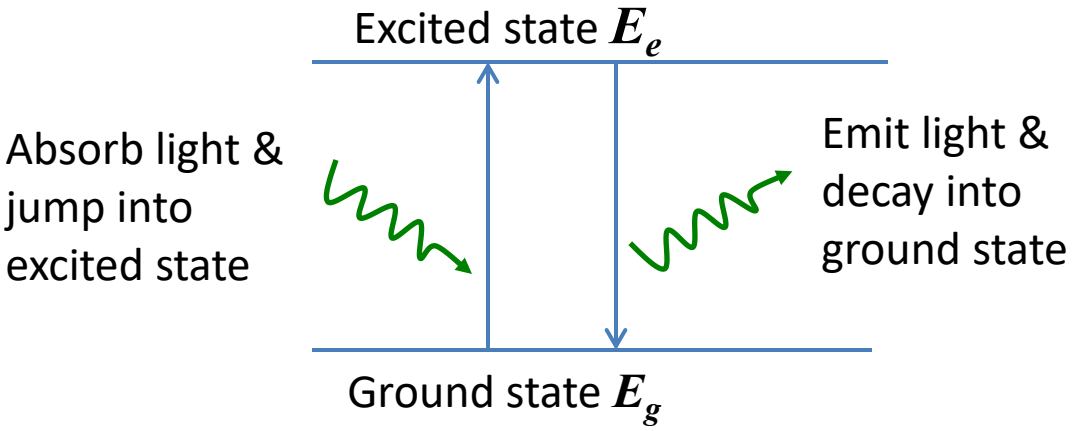
https://commons.wikimedia.org/wiki/File:Bragg_XRD.svg

Elemental Analysis via Optical Atomic Spectroscopy (1)

- **Atoms transition between ground and excited states accompanied by light absorption or emission**

  Characteristic frequency

$$\nu = \frac{E_e - E_g}{h}$$



Absorbed/emitted light frequency are often atoms specific

For a known standard with atom concentration C_s, the measured intensity is I_s

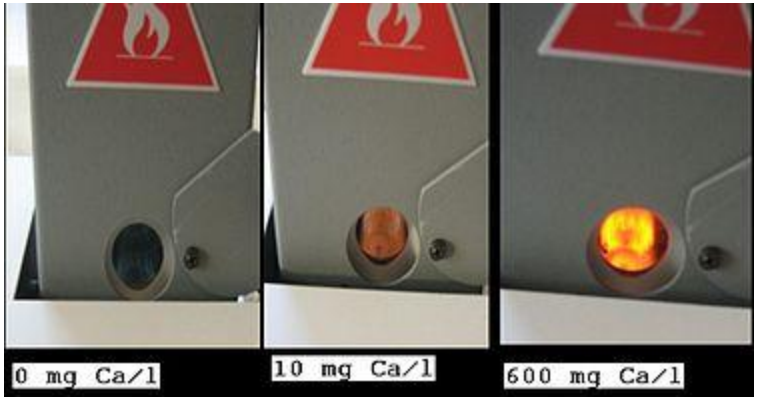
Then for unknown sample, atom concentration C_u and the measured intensity I_u satisfy

$$\frac{C_u}{I_u} = \frac{C_s}{I_s} \quad \text{or} \quad C_u = C_s \frac{I_u}{I_s}$$

Elemental Analysis via Optical Atomic Spectroscopy (2)

- **OAS for elemental analysis**
- **Common procedure:**
  - Dissolute the substance into liquid
  - Atomization
    - Flame: Temperature of 2300-2700 °C
      Droplets→Nanoparticle→Vapor→Atoms
    - Inductively coupled plasma (ICP)
  - Atoms absorption spectroscopy (AAS)
    - Shine light and measure spectroscopy (e.g., Flame AAS)
  - Atoms Emission Spectroscopy (AES)
    - Emit light and measure spectroscopy (e.g., ICP-AES)
- **Other considerations**
  - Sample: liquid solution or solid to be dissolved
  - Detection limit: sub-ppm by weight

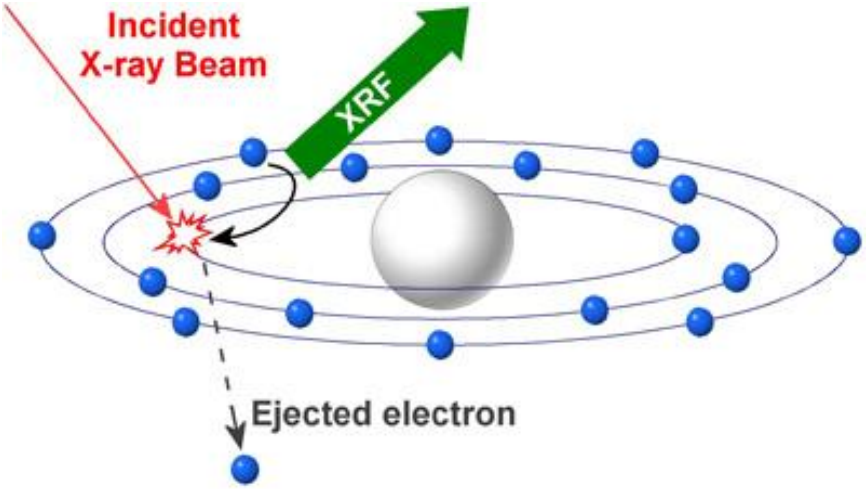
https://en.wikipedia.org/wiki/Atomic_absorption_spectroscopy



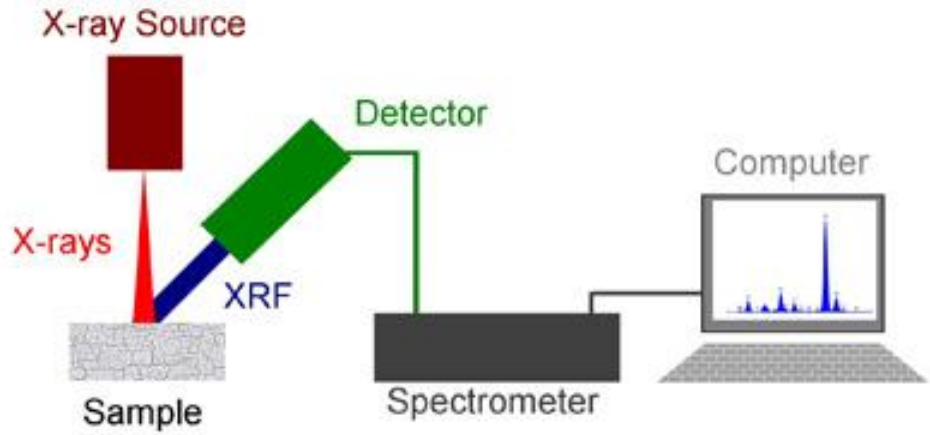
https://en.wikipedia.org/wiki/Atomic_emission_spectroscopy

Elemental Analysis via X-ray Fluorescence Spectroscopy (XRF)

- **When high energy X-ray shines onto sample, it knocks out inner layer electrons, which, upon relaxation, will emit X-ray with lower energy than incident X-ray (termed fluorescent radiation) and it is analyzed due to atom specificity for such effect**
- **Other considerations**
  - Solid bulk sample usually
  - Detection limit: >10 ppm by weight



http://www.horiba.com/us/en/scientific/products/x-ray-fluorescence-analysis/tutorial/x-ray-fluorescence-the-basic-process/



http://www.horiba.com/us/en/scientific/products/x-ray-fluorescence-analysis/tutorial/xrf-spectroscopy/

Other (Surface) Elemental Analysis Techniques

- Primarily used for surface elemental analysis

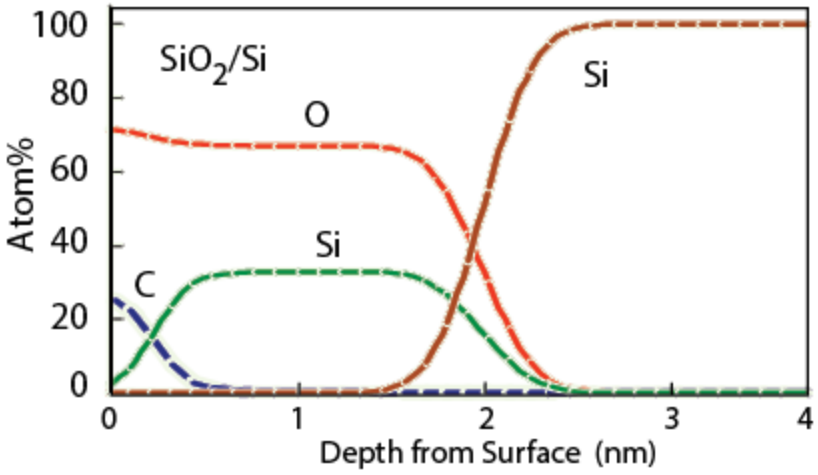
	Auger Electron Spectroscopy (AES)	X-ray Photoelectron Spectroscopy (XPS or ESCA)	Secondary Ion Mass Spectroscopy (SIMS)
Incident particle	Electrons (1-20 keV)	X-ray (often 1254 or 1487 eV)	Ions (He^+, Ne^+, Ar^+ at 100 eV – 30 keV)
Emitted particle	Auger electron	Photoelectrons	Sputtered ions
Element range	>Li	>Li	>H
Sensitivity	10^{-3} (0.1%)	10^{-3} (0.1%)	10^{-6}-10^{-9} (ppm-ppb)
Depth of analysis	2 nm	2 nm	1 nm
Lateral resolution	>20 nm	>150 um	50 nm-10 mm

After Table 3.8 of Rahaman (2003), p. 170

Depth Profiling for Composition Analysis

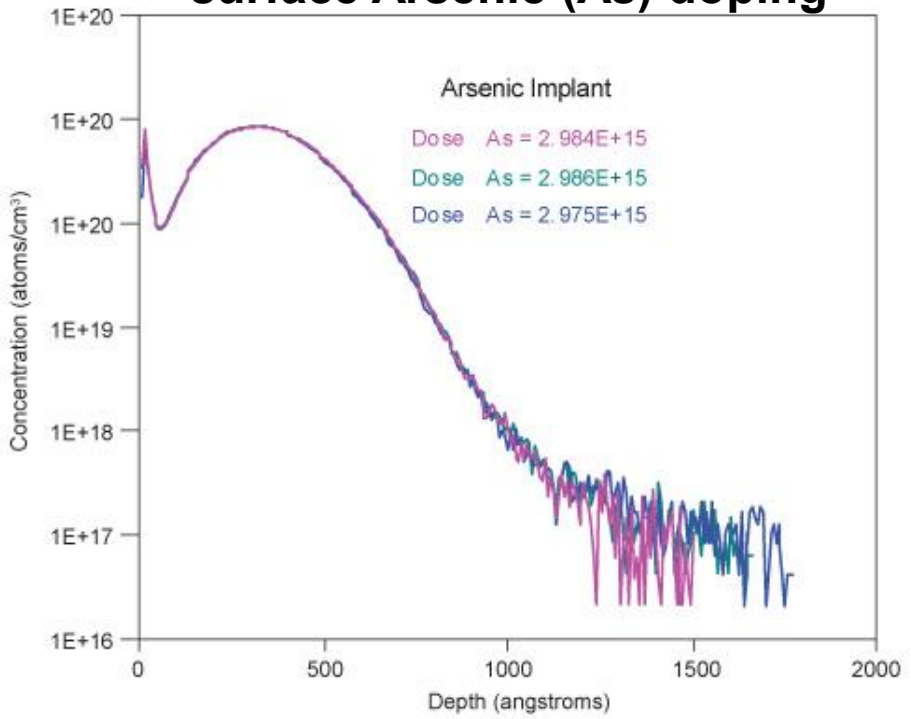
- When coupled with depth profiling (e.g., via sputtering), surface composition characterization techniques could provide bulk (still near surface) elemental composition information

XPS depth profiling of Si surface with thin SiO_2 layer



http://www.nanolabtechnologies.com/esca-xps

SIMS depth profiling of Si with surface Arsenic (As) doping

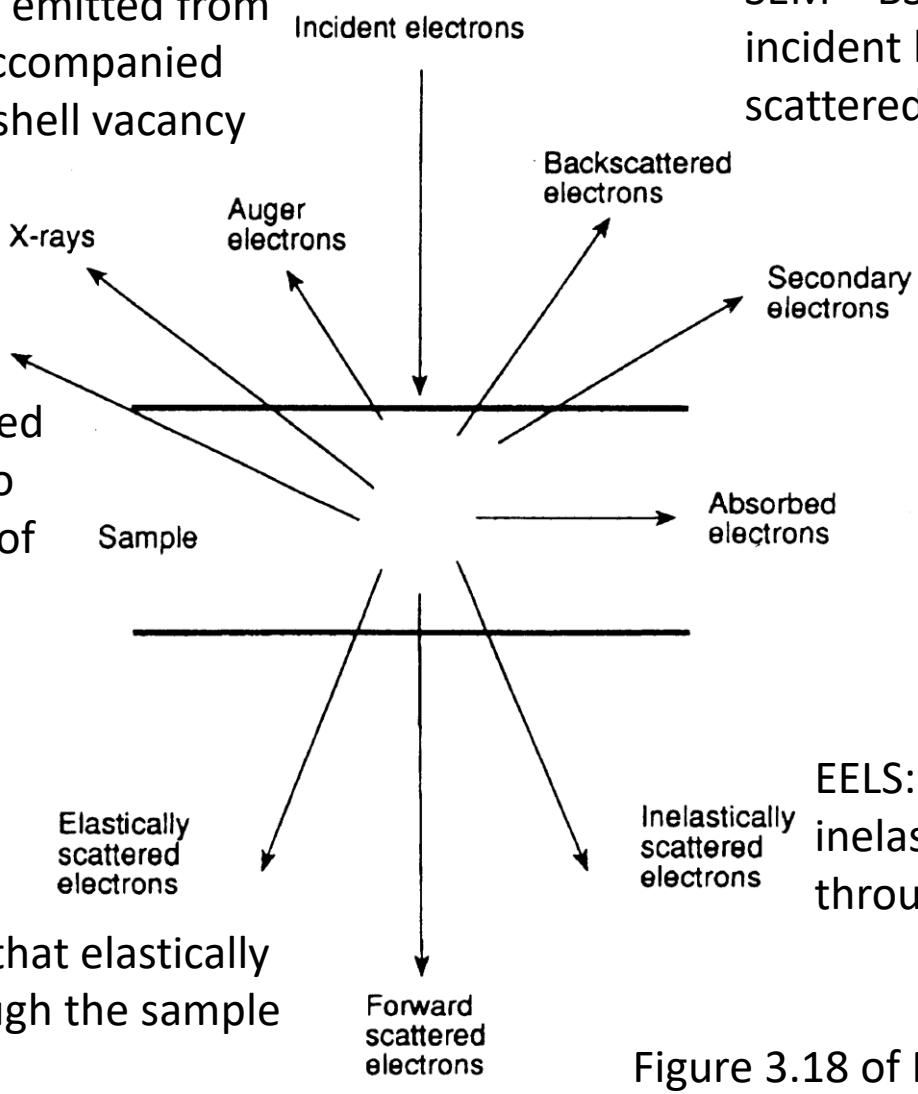


http://www.eag.com/mc/depth-profiling.html

Electron Related Characterization Techniques

AES: electrons that is emitted from sample that is also accompanied by filling of an inner shell vacancy from the same atom

SEM – BS mode: electrons from incident beam that is elastically scattered backward



SEM - SE mode: electrons from sample that is directly knocked out (or ionized) by incident radiation (e.g., electron or photon)

EDX: X-ray that is emitted from sample that is also accompanied by filling of an inner shell vacancy from the same atom

EELS: electrons that is inelastically scattered through the sample

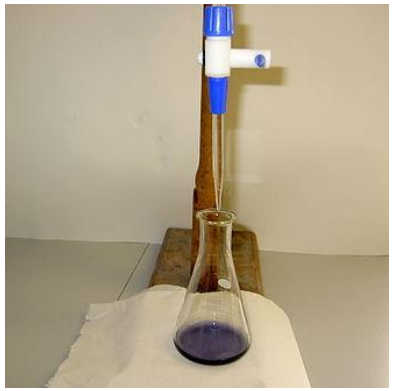
TEM: electron that elastically scattered through the sample

Figure 3.18 of Rahaman (2003), p. 166

Other Chemical Composition Analysis Methods

- **Mass spectrometry (MS)**
  - Atomization then analysis via MS (e.g., via ICP-MS)
- **Infrared absorption (IR) or thermal conductivity detector (TCD)**
  - Vaporization (e.g., via combustion) then analysis via IR or TCD
  - Often for **C, S, N, O, H** analysis, but NOT for trace element analysis
  - Examples:
    - LECO carbon and sulfur analysis via combustion
    - LECO nitrogen, oxygen, and hydrogen analysis via fusion
- **Thermal gravimetric analysis (TGA)**
  - Determine moisture or other adsorbed species content
- **Other**
  - Titration
  - Electrochemical

http://sirius.mtm.kuleuven.be/Research/Equipment/fiches/simultaneous-DSC-and-TGA.html



https://en.wikipedia.org/wiki/Titration

Primary Particles

❑Definition

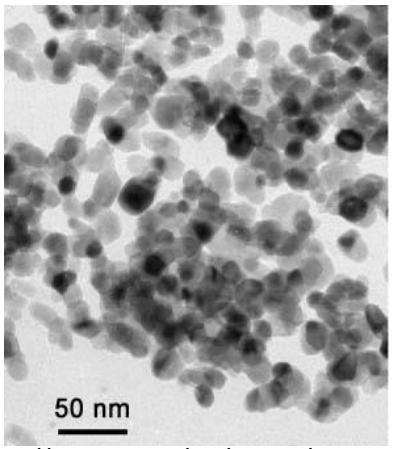
"Smallest unit in the powder with a clearly defined surface" (Rahaman (2003), p. 127)

Sometimes also referred to as "ultimate" particles

❑Features

- Cannot be broken down into smaller particles by simple (weak) agitation (e.g., via ultrasound)
- Can be a single crystal, or polycrystalline particle, or a glass
- If pores present, must be isolated from each other

YSZ nano powder



http://ssnano.com/inc/sdetail/yttria_stabilized_zirconium_oxide_nanoparticles/325

Agglomerates

❑Definition

"a cluster of primary particles held together by surface forces, by liquid, or by a solid bridge" (Rahaman (2003), p. 127)

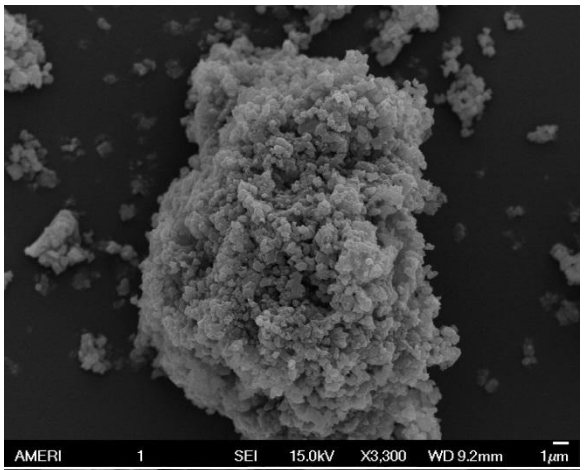
❑Features

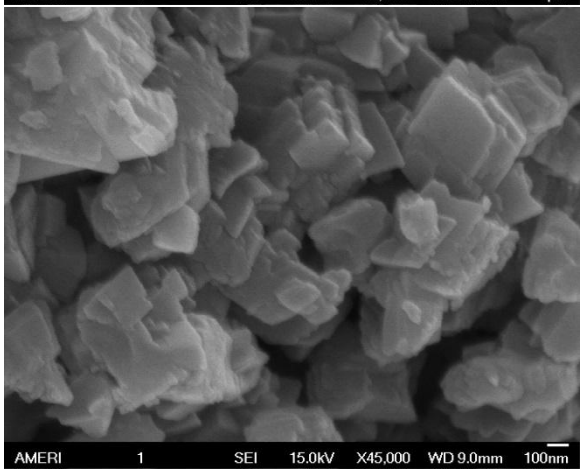
- Generally have **interconnected pores**

❑Classification

- Soft agglomerates
  - Primary particles hold together by weak surface forces
  - Can be broken down by weak agitation (e.g., sonication in liquid suspension)
- Hard agglomerates/also called **Aggregates**
  - Primary particles hold together by chemical bonding such as solid bridges
  - Can only be broken down/separated by energetic processes such as mechanical milling

B_6O agglomerates
by Paniz Foroughi

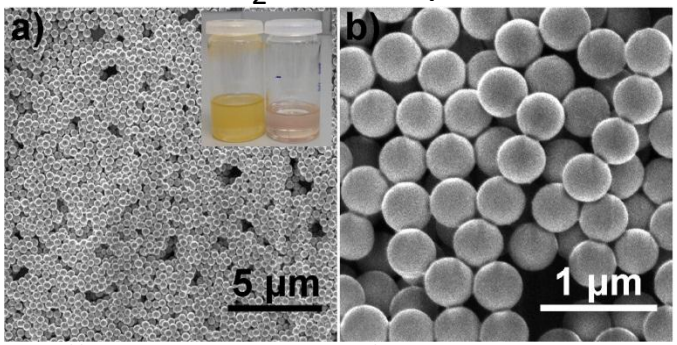




Colloids, Granules, Gravels, & Flocs

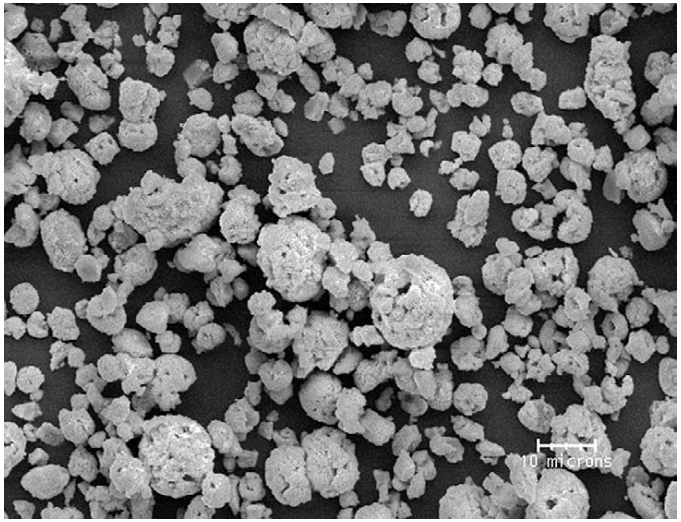
- **Colloids**
  - Finely divided phase with particle size in the range of 1-1000 nm (often in a liquid)
- **Granules**
  - Large particles with size of ~100-1000 μm, OR
  - Large, soft agglomerates formed purposefully by addition of granulating agents to improve flowability of powder during filling and compaction in pressing
- **Gravels**
  - Very coarse particles (~10 mm or larger)
- **Flocs (or Floccules or Coagules)**
  - Clusters of particles in liquid suspension, in which particles held together weakly by electrostatic force or by organic polymers

Colloidal SiO_2 and suspension



http://free-stock-illustration.com/colloidal+silica+suspension

Spray dried YSZ granules



2014 Oerlikon Metco

Summary of Structures in Powders

❑Particles

- General description of things that move separately without distinguishing between primary particles and agglomerates

❑Glossaries

Primary particles

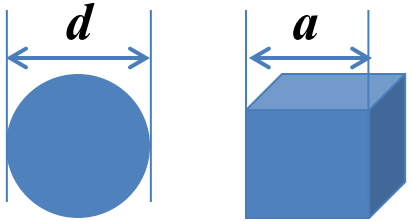
Soft agglomerates

Hard agglomerates or Aggregates

Particle Size

❑ **Equi-dimensional particle (e.g., sphere or cube)**

Use its characteristic size (diameter or cube edge length) to represent the size



❑ **Irregularly-shaped particles**

Definition of size depends on the way it is measured, for example

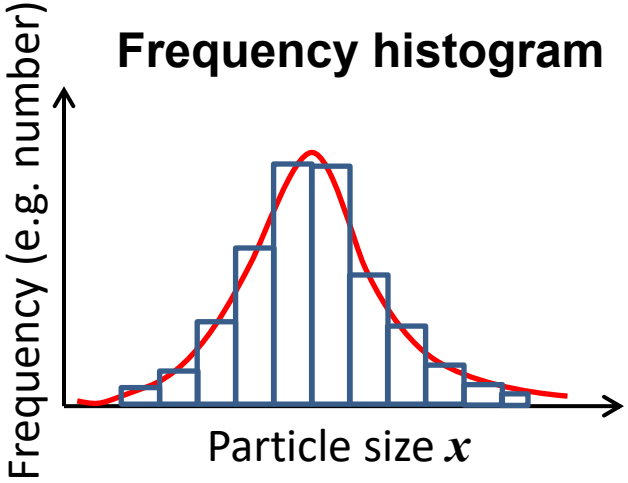
- Volume diameter d_V – diameter of sphere having the same volume
- Surface diameter d_S – diameter of sphere having the same surface area
- Stokes diameter d_{STK} – diameter of sphere having the same sedimentation rate
- Sieve diameter d_A – Width of the minimum square aperture through which the particle will pass
- …

See Rahaman (2003), p. 130-131 for more information

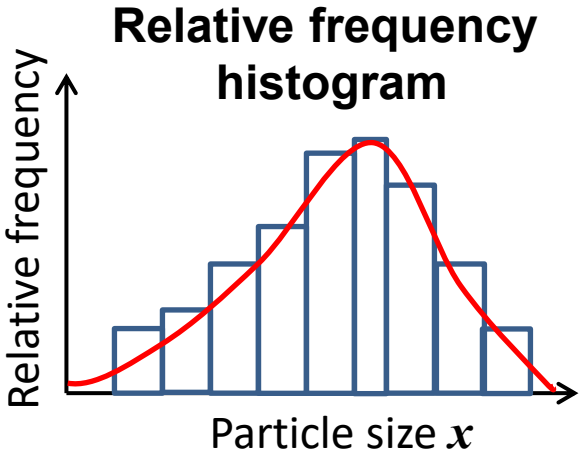
Particle Size Distribution (PSD)

- **Real powders have a range of sizes – particle size distribution (PSD), presented in different forms:**

Frequency histogram

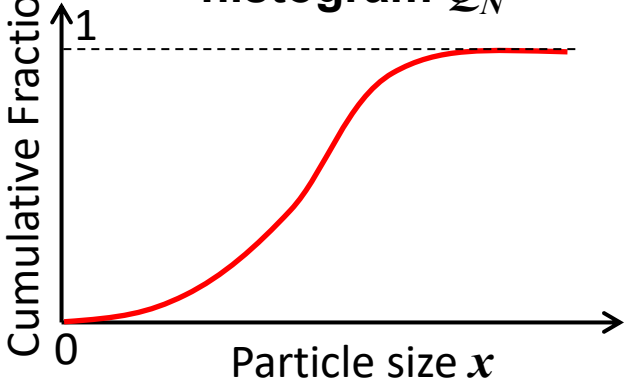


Relative frequency histogram

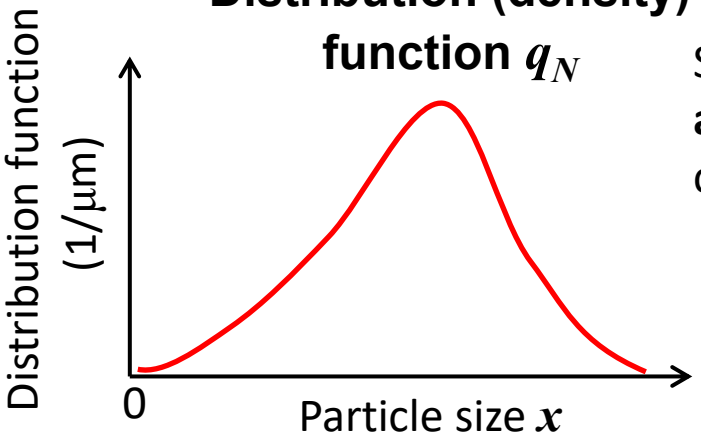


Sum of **total bar height** = 1

Cumulative frequency histogram Q_N



Distribution (density) function q_N



Sum of **total area** under curve = 1

$$q_N = \frac{dQ_N}{d_x}$$

Mathematic Description of PSD

❑Normal distribution

$$q_N(x) = \frac{1}{s\sqrt{2\pi}} \exp\left[-\frac{(x-\bar{x})^2}{2s^2} \right]$$

- Limitation
  - Finite fraction with negative size (impractical)
  - No upper size limit

❑Lognormal distribution

$$q_N(\ln x) = \frac{1}{s\sqrt{2\pi}} \exp\left[-\frac{(\ln x-\bar{x})^2}{2s^2} \right]$$

- Limitation
  - Still no upper size limit

❑Other distribution

- Empirical distributions

Characteristic Sizes for PSD

❑Mean or Average

- Arithmetic mean

$$\bar{x}_N = \frac{\sum_i^N x_i}{N} \quad \text{or} \quad \bar{x}_N = \frac{\sum_i^n n_i x_i}{\sum_i^n n_i}$$

- Volume weighed-average

$$\bar{x}_V = \frac{\sum_i^n V_i x_i}{\sum_i^n V_i} = \frac{\sum_i^n n_i x_i^4}{\sum_i^n n_i x_i^3}$$

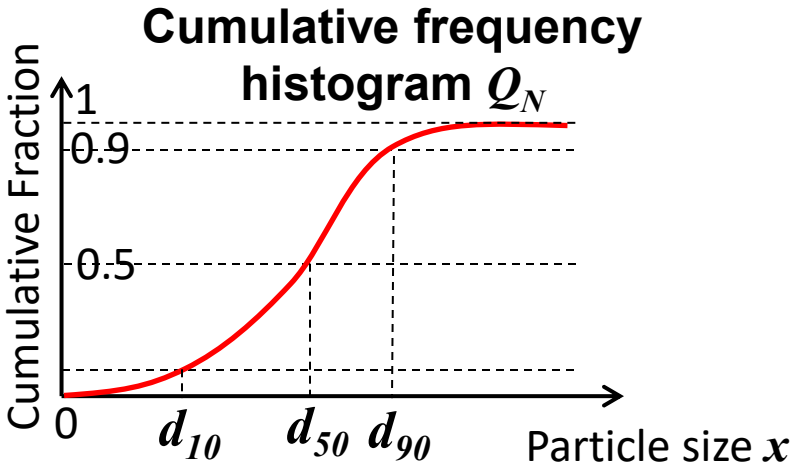
❑Median

- From distribution function d_{50}

❑Other

- d_{10} and d_{90}
- Standard deviation

$$s = \left[\frac{\sum_i^n n_i (x_i - \bar{x})^2}{\sum_i^n n_i} \right]^{1/2}$$

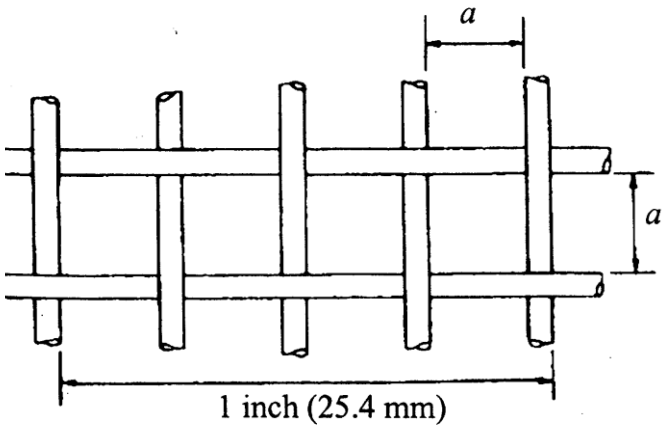


PSD via Sieving (1)

- **Particles classified by ability/inability to pass through sieves with different opening sizes**
- **Factors**
  - Wire diameter w
  - Opening width a
  - Mesh number M - number of wires/opening per linear length, mostly in inch
  - Opening area A – fraction area that is not blocked by wires

http://www.formtest.de/en/laborgeraete/gesteinspruefung/bestimmung-der-korngroessenverteilung-nach-en-933-2.php

http://www.hmk-test.com/particle-size-distribution-sieve-analysis/



$$M = \frac{1}{a + w}$$

$$A = \frac{a^2}{(a + w)^2}$$

PSD via Sieving (2)

❑Features

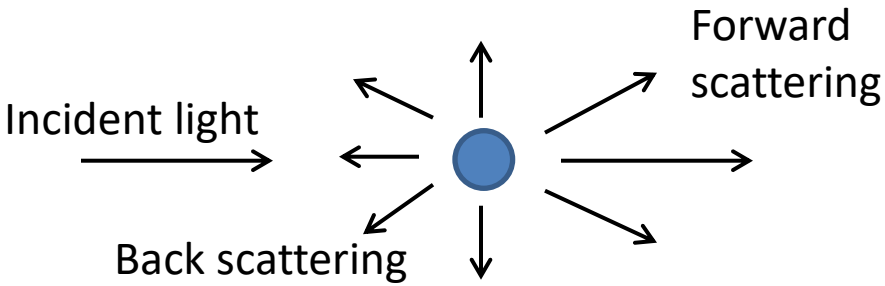
- Used for sizing relatively coarse powders
- Not effective for powders with size less than ~1 μm due to severe agglomeration and clogging of sieve
- Dry sieving most cases
- Time consuming, but used in traditional ceramics industry for raw materials specification

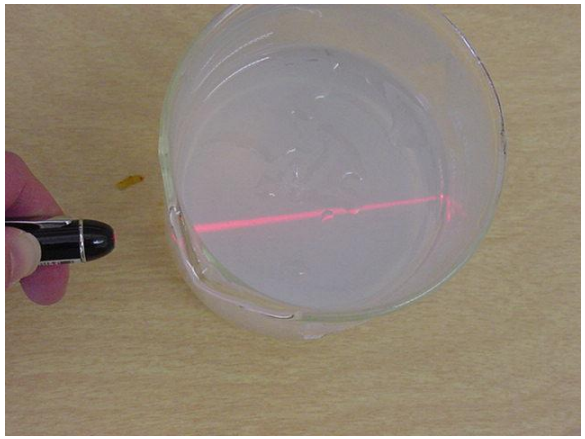
❑Examples for selected sieves

US sieve number M	Sieve opening size a (μm)	Wire diameter w (μm)	Fractional opening area A
25	710	310	48%
45	355	211	39%
80	180	140	32%
170	90	61	36%
325	44	35	31%

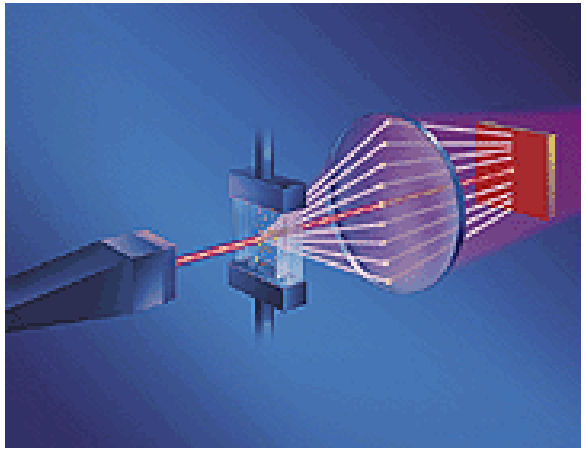
PSD via Light Scattering

- **Light passes through particles in liquid or gas leading to scattering**
  - $d << \lambda$ Rayleigh scattering
  - $d \sim \lambda$ Mie scattering
  - $d >> \lambda$ Faunhofer diffraction





https://pk014.k12.sd.us/10th%20Chemistry/chapter%20one/notes%20elements,%20compounds%20mixtures/light_colloid.jpg



http://www.particletesting.com/Services-Provided/Particle-Size-and-Shape.aspx

- **Measurement of scattered light intensity at different angles (for Mie/Frauhofer) and at different time (for Brownian motion/ Rayleigh) gives size information**
- **Widely used: 5 nm – 1000 μm**
- **Automatic analysis**

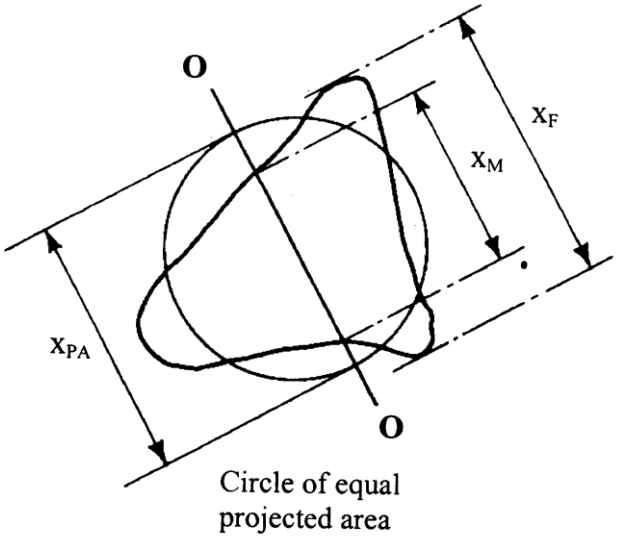
PSD via Microscopy & Image Analysis

❑Microscopy

- Optical microscopy: > ~1 μm particles
- Scanning electron microscopy (SEM): > ~10 nm particles
- Transmission electron microscopy (TEM): > ~1 nm particles

❑Image analysis

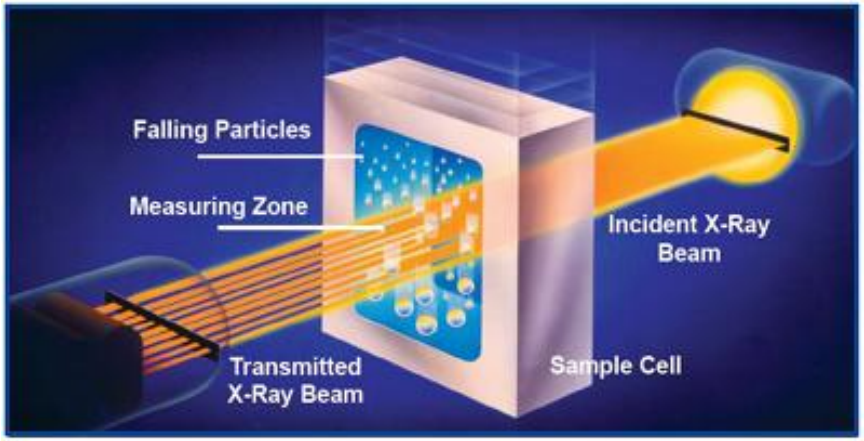
- Need measurements on numerous (>>100) particles
- Different ways of defining size



Other PSD Analysis Methods

❑(X-ray) Sedimentation

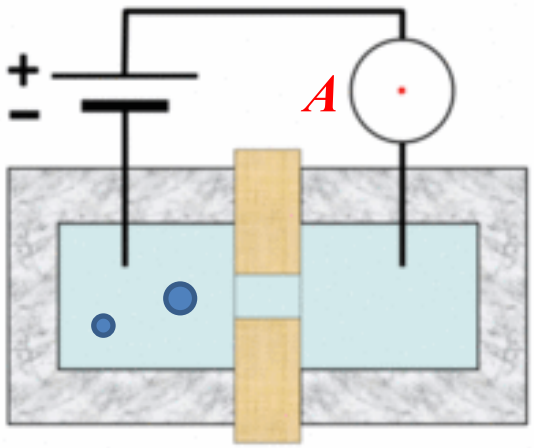
- Particles of different sizes fall in liquid with different terminal velocity
- Measure change of particle concentration (as determined from X-ray intensity) with time to determine the PSD
- ~0.1 - 100 μm



http://www.particletesting.com/Services-Provided/Particle-Size-and-Shape.aspx

❑Electrical sensing zone (Coulter counter)

- As particles pass through the small opening, electrical resistance (current) will change, depending on particle size, which yield PSD information
- ~0.5 - 500 μm



https://en.wikipedia.org/wiki/Coulter_counter

Surface Area and Porosity for Powders

- **Powders may contain significant surface area and porosity, which are important to other behaviors in powder and subsequent processing**

- **Specific surface area (SSA)**

  Total surface area per unit weight of solids, often in units of m^2/g

- **Pores**
  - Micropores: pore size <2 nm
  - Mesopores: pore size 2-50 nm

  } Catalysis, filtration, adsorption

  - Macropores: pore size > 50 nm

Measurement of Surface Area & Porosity

- **Specific surface area (SSA)**

  Total surface area per unit weight of powder sample

- **Relative porosity**

  Relative volume percentage of agglomerates that are occupied by pores

- **Pore size distribution**

  Size distribution of pores

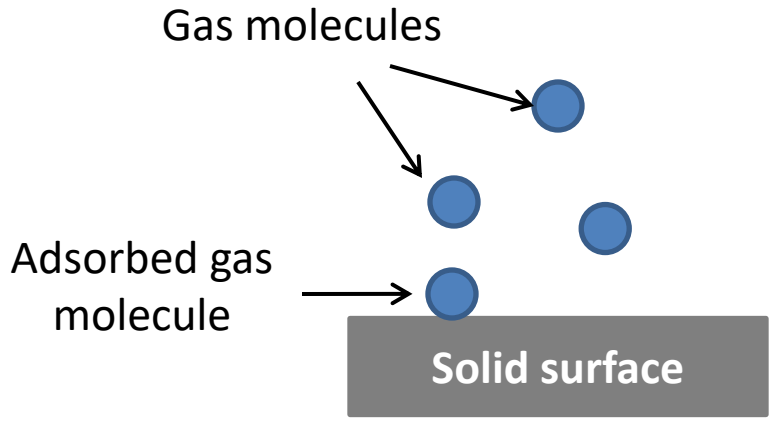
- **Measurements for <u>closed pores</u>**
  - Archemedis methods
  - Image analysis

- **Measurement for <u>open pores</u>**
  - Gas adsorption/Capillary condensation: often used for micro and mesopore range (<50 nm)
  - Mercury (intrusion) porosimitry
  - Image analysis

Specific Surface Area & Porosity Analysis via Gas Adsorption

❑Gas adsorption

Condensation of gases (adsorbate) on the free surface of the solid (adsorbent)



❑Types of gas adsorption

- **Physical adsorption (Physisorption)**

  Adsorption caused by physical forces between solid and the gas molecules, which does NOT involve change in electronic structures

  - Weak adsorption - relatively easy to separate via mild heating and/or vacuum
  - Examples:
    - N_2 or other inert gas adsorption on many solids
- **Chemical adsorption (Chemisorption)**

  Adsorbed gas form strong chemical bonds with the surface

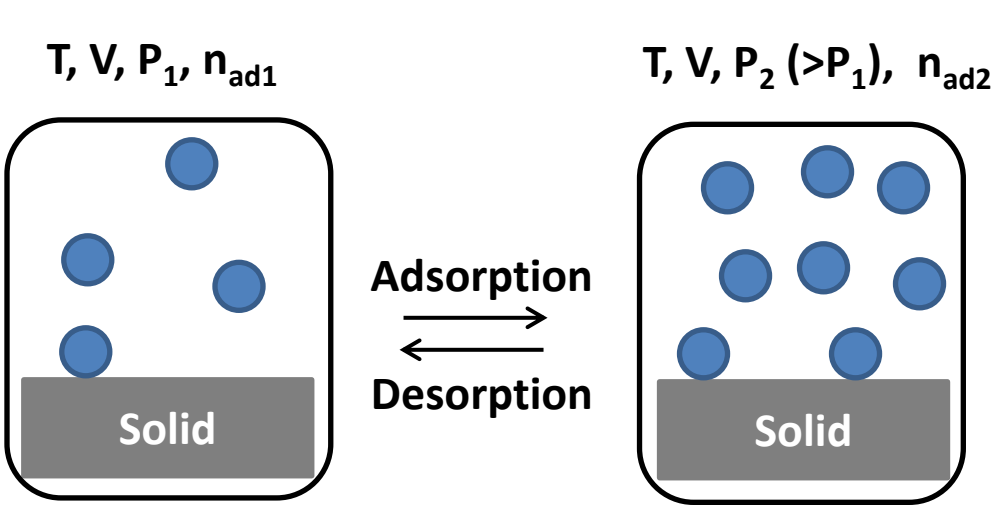
  - Strong adsorption – hard to separate unless extreme heating or other chemical agents
  - Examples
    - Sulfur adsorption on metals or oxides
    - O_2 adsorption on metals

Gas Adsorption Isotherm

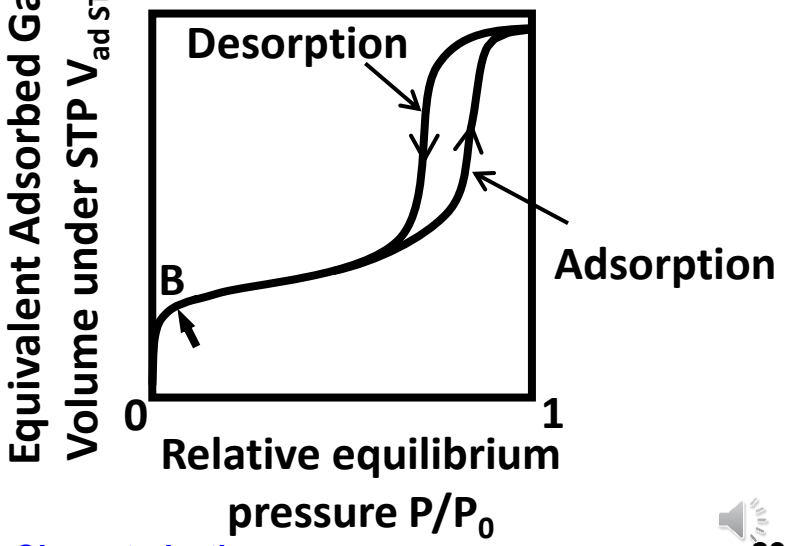
❑Physical Adsorption

When a gas is in contact with degassed solid with relatively clean surface, the equilibrium pressure and the amount of gas adsorbed on solid surface satisfy certain relationship.

The measured total amount of gas adsorbed (often presented in terms of the equivalent volume under standard temperature and pressure STP of 0 ^{o}C, P_0=10^5 Pa) under different relative equilibrium pressure (P/P_0) at a fixed temperature gives the so-called **adsorption (or desorption) isotherm** (Rahaman (2003))



$$n_{ad} = f(P)_{T,gas,solid}$$



Measurement of Gas Adsorption Isotherm

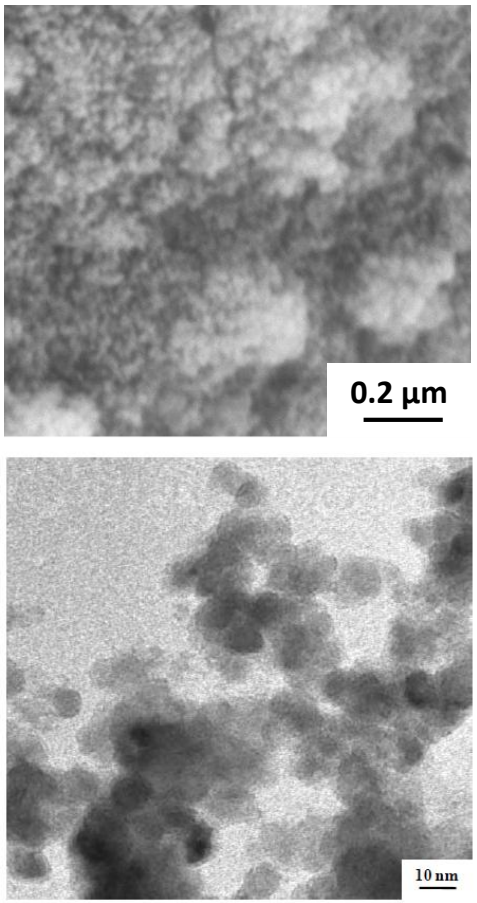
❑Measurement Procedure

1. Degassing – remove adsorbed species (H_2O) etc. from solid surface by heating (~200-400 ^oC) in vacuum
2. Cool to liquid N_2 temperature in vacuum and continue degass until certain level of vacuum achieved
3. Measure the amount of gas (typically N_2) required to reach a pre-set (relative) equilibrium pressure $\boldsymbol{P_i/P_0}$ at liquid N_2 temperature
   A. Add gas to reach pre-set pressure
   B. Pressure in the closed system drops due to gas adsorb onto the surface/condense into pores
   C. Repeat from step A until pressure stabilizes
4. Repeat step 3 at another pre-set equilibrium pressure

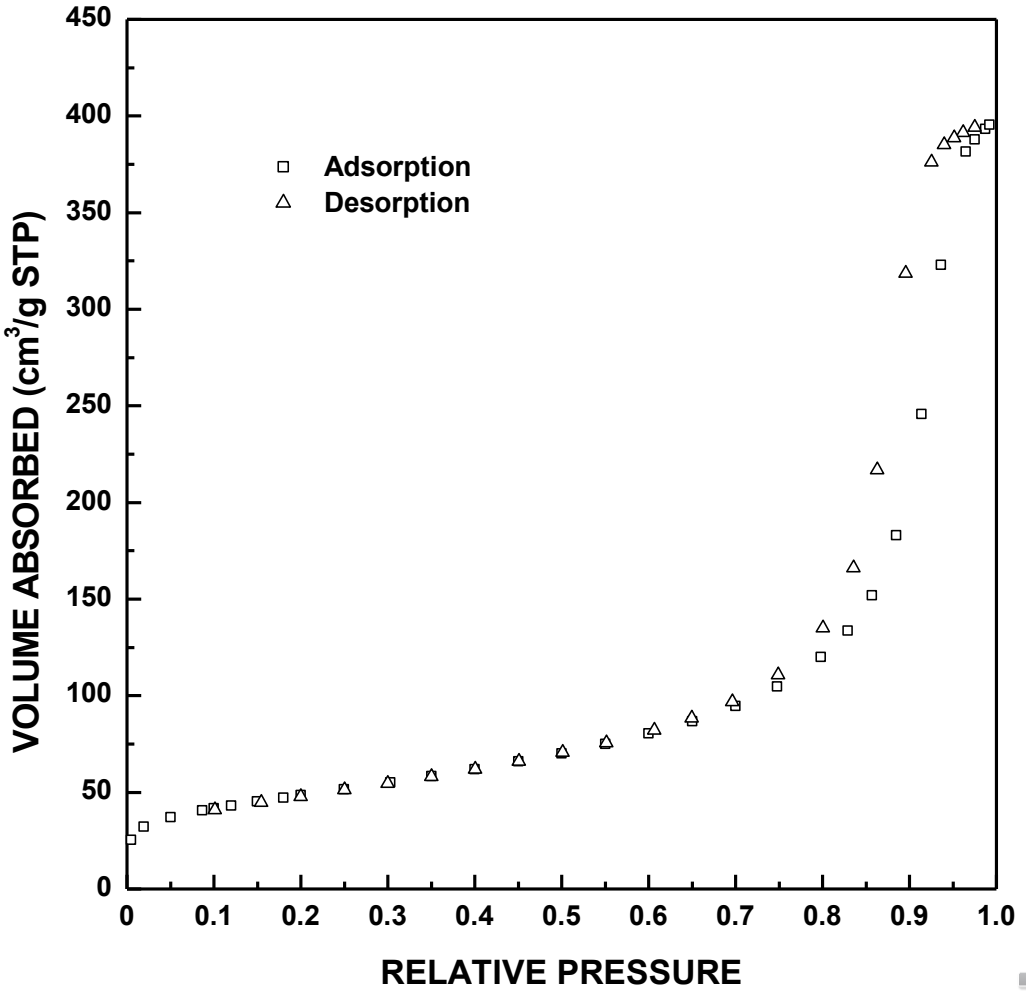
http://www.micromeritics.com/product-showcase/ASAP-2020-Physisorption.aspx

Example for Adsorption Isotherm

- Measured N_2 adsorption/desorption isotherm for nanocrystalline β-SiC with mesopores

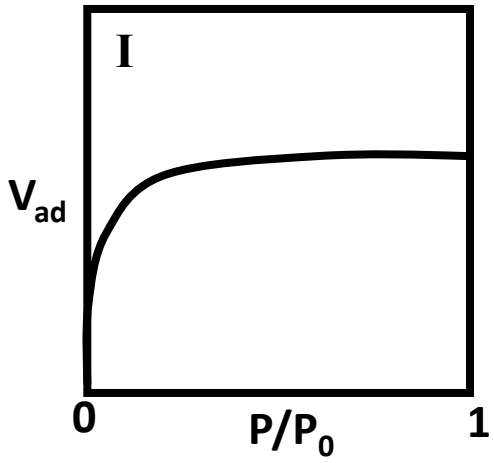


Zhe Cheng MS thesis, 2004

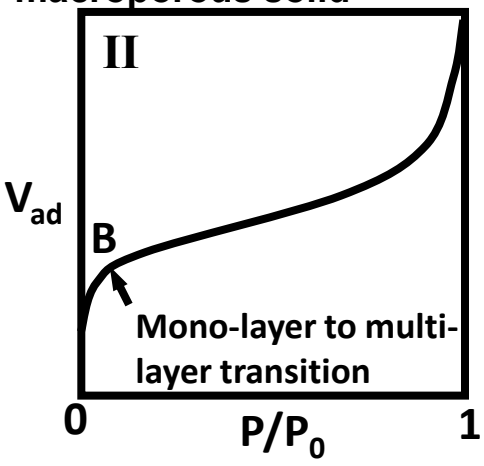


Common Adsorption Isotherms

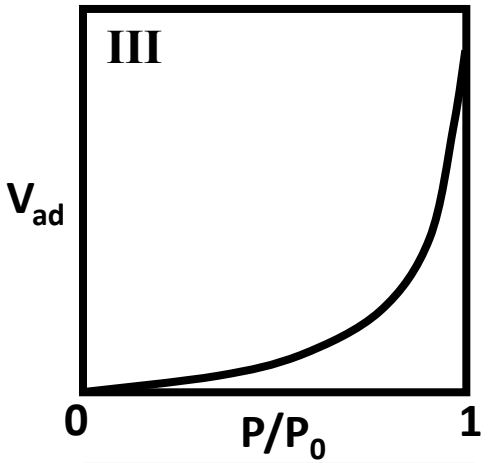
Microporous solid w/ small external surface

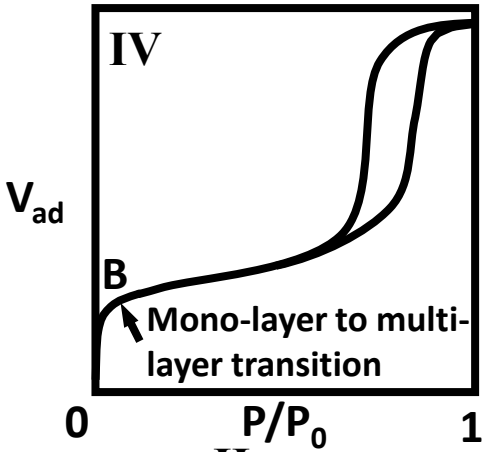


Unrestricted monolayer-multilayer adsorption on a non-porous or macroporous solid

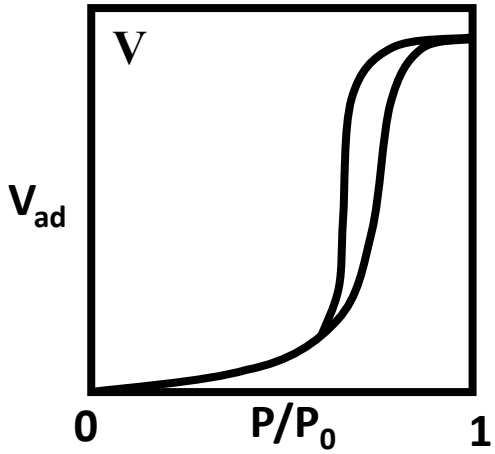


Weak adsorbate-adsorbent interaction

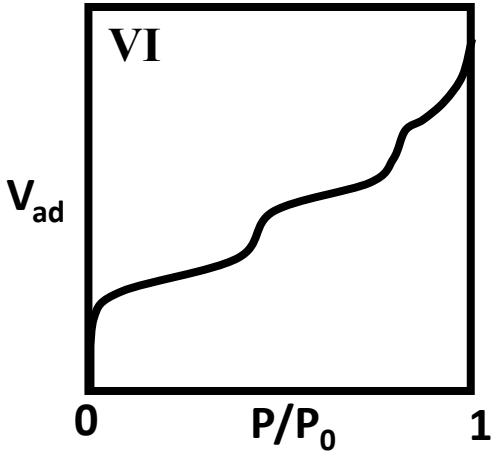




Similar to II w/ capillary condensation in mesopores & saturation



Weak adsorbate-adsorbent interaction w capillary condensation & saturation



Rare – non-polar gas adsorption on homogeneous surface

Langmuir Adsorption Isotherm (1)

❑Langmuir (monolayer) adsorption isotherm

Assumptions:

- Adsorption reaction: $A_g + S = A_{ad}$
- Only unoccupied surface sites are possible adsorption sites
- Under equilibrium, the rate of adsorption on unblocked sites is same as rate of desorption from occupied site

Define:

p_A Partial pressure of adsorbate gas

k_{ad} Adsorption rate constant

k_{de} Desorption rate constant

$[S]$ Available surface site (for adsorption) concentration

$[A_{ad}]$ Adsorbed (occupied) surface site concentration

Adsorption rate $r_{ad} = k_{ad} p_A [S]$ Desorption rate $r_{de} = k_{de} [A_{ad}]$

At equilibrium: $r_{ad} = r_{de}$ ➡ $k_{ad} p_A [S] = k_{de} [A_{ad}]$

https://en.wikipedia.org/wiki/Langmuir_adsorption_model#Background_and_experiments

Langmuir Adsorption Isotherm (2)

❑ **Continue from before**

https://en.wikipedia.org/wiki/Langmuir_adsorption_model#Background_and_experiments

$$k_{ad} p_A [S] = k_{de} [A_{ad}]$$

Therefore, $$\frac{k_{ad}}{k_{de}} = K_{eq} = \frac{[A_{ad}]}{p_A [S]}$$

Total surface site concentration [S_0] satisfy: $$[S_0] = [A_{ad}] + [S]$$

Therefore, $$[A_{ad}] + \frac{[A_{ad}]}{p_A K_{eq}} = [S_0] \quad \Rightarrow \quad \frac{1 + p_A K_{eq}}{p_A K_{eq}} \cdot [A_{ad}] = [S_0]$$

Define adsorbate surface coverage ratio

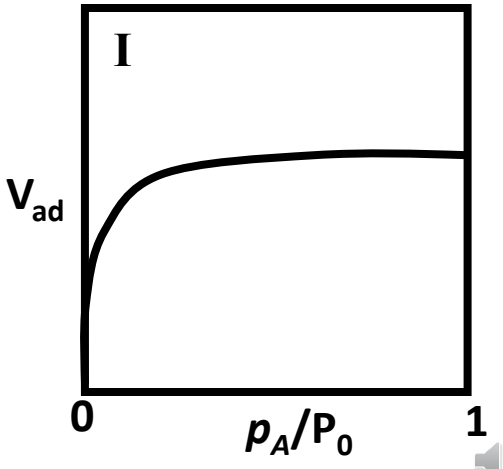
$$\theta_{ad} = \frac{[A_{ad}]}{[S_0]} = \frac{V_{ad}}{V_m}$$

V_{ad} ← **Equilibrium gas volume per unit mas of solid**

V_m ← **Gas volume per unit mass of solid to reach monolayer coverage**

Therefore,

$$\theta_{ad} = \frac{[A_{ad}]}{[S_0]} = \frac{K_{eq} p_A}{1 + K_{eq} p_A} \quad \& \quad V_{ad} = \frac{K_{eq} p_A}{1 + K_{eq} p_A} V_m$$



Specific Surface Area from Langmuir Adsorption Isotherm

❑Assuming monolayer surface coverage upon adsorption saturation

Define:

S_w Total sample specific surface area, in unit of m^2/g

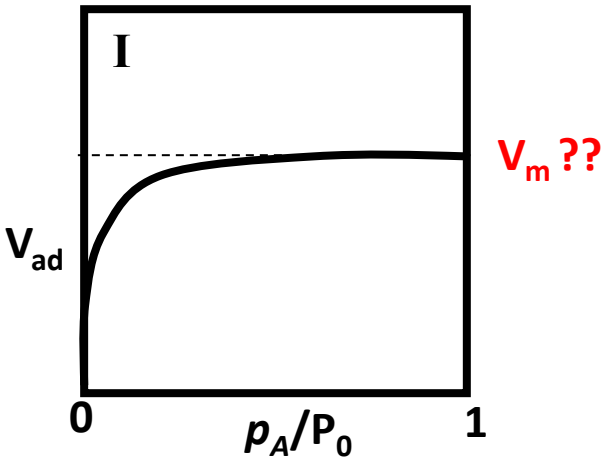
V_m Saturation adsorption gas volume under STP, in unit of cm^3/g STP

σ Adsorbate gas molecule area, in unit of m^2

N_A Avergadro's number $N_A = 6.02 \times 10^{23}$

Then

$$S_w = \frac{V_m}{22414 cm^3} \cdot N_A \sigma$$



Note for N_2 gas molecule, $\sigma = 16.2 \times 10^{-20}\ m^2$, $S_w = 4.35 V_m$ in unit of m^2/g

From measured Langmuir adsorption isotherm curve, to obtain V_m more precisely

$$V_{ad} = \frac{K_{eq} p_A}{1 + K_{eq} p_A} V_m \Rightarrow \frac{1}{V_{ad}} = \frac{1}{V_m} + \frac{1}{K_{eq} p_A} \cdot \frac{1}{V_m} \Rightarrow \frac{p_A / P_0}{V_{ad}} = \frac{p_A / P_0}{V_m} + \frac{1}{K_{eq} P_0} \cdot \frac{1}{V_m}$$

Therefore, plotting $\frac{p_A / P_0}{V_{ad}}$ versus p_A / P_0 , the slope will be $\frac{1}{V_m}$

BET Adsorption Isotherm

❑BET theory for monolayer-multilayer adsorption

Stephen Brunauer, Paul Hugh Emmett, and Edward Teller (1938)

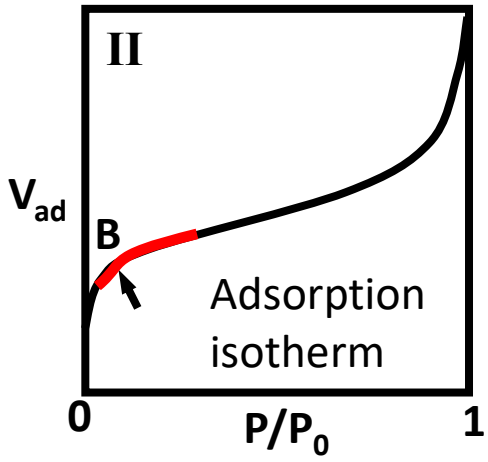
Assumptions (https://en.wikipedia.org/wiki/BET_theory):

- "gas molecules physically adsorb on a solid in layers infinitely"
- "no interaction between each adsorption layer"
- "the Langmuir theory can be applied to each layer"
- Additional assumptions
  - Only molecule interaction is that one adsorbed molecule can act as adsorption site for a molecule of the upper layer
  - Upper most molecule is in equilibrium with gas phase
  - Kinetic limited process with constant adsorption energy E_1 for the 1st layer and constant adsorption energy that equals to heat of liquidation E_L for all upper layers
  - At saturation, the sample is immersed in liquid phase of adsorbates

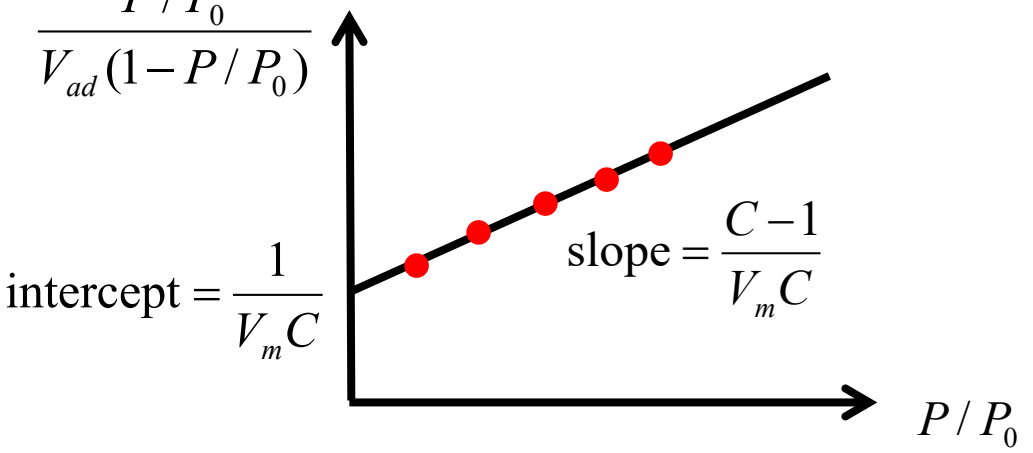
BET adsorption isotherm expression:

$$\frac{P/P_0}{V_{ad}(1-P/P_0)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\cdot\frac{P}{P_0}$$

Specific Surface Area from BET Adsorption Isotherm



Plotting $\frac{P/P_0}{V_{ad}(1-P/P_0)}$ versus P/P_0



$$\frac{P/P_0}{V_{ad}(1-P/P_0)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\cdot\frac{P}{P_0}$$

Specific surface area $S_w = \frac{V_m}{22414 cm^3}\cdot N_A \sigma$ in unit of m^2/g for V_m in STP cm^3/g

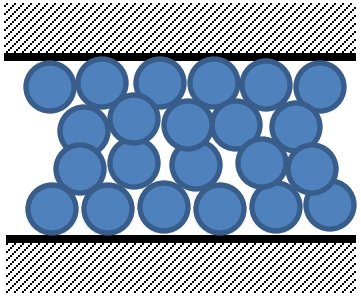
For N_2 gas molecule, σ = 1.62x10^{-19} m^2 , $S_w = 4.35 V_m$ in unit of m^2/g

- Five (or more) data points in the range of P/P_0 ~ 0.05 - 0.30 used
- C value roughly on the order of ~100 for reliable BET surface area
- N_2 (T_{bp} = -196 °C) and Ar (T_{bp} = -186 °C, σ = 16.6x10^{-20} m^2) used as adsorbates
- Kr (T_{bp} = -153 °C, σ = 19.5x10^{-20} m^2) used for very low SSA such as <1 m^2/g

Pore Analysis via Gas Adsorption (1)

❑Capillary condensation inside pores

When multilayer adsorption happens inside pores at **below boiling point** of the absorbate, actual state of multilayer adsorbate resemble liquid.



For cylindrical pore (capillaries) with radius r, if

P Actual gas pressure

P_0 Saturation gas pressure over a planar vapor/liquid interface

γ_{LV} Surface tension of the liquid-vapor interface (for the adsorbate)

V_L Molar volume of the (condensed) liquid

θ Contact angle between liquid and pore wall

r Capillary radius

Relative gas pressure in the capillaries when condensation occurs is governed by Kevin equation

$$\ln\frac{P}{P_0} = -\frac{2\gamma_{LV}V_L Cos\theta}{RTr}$$

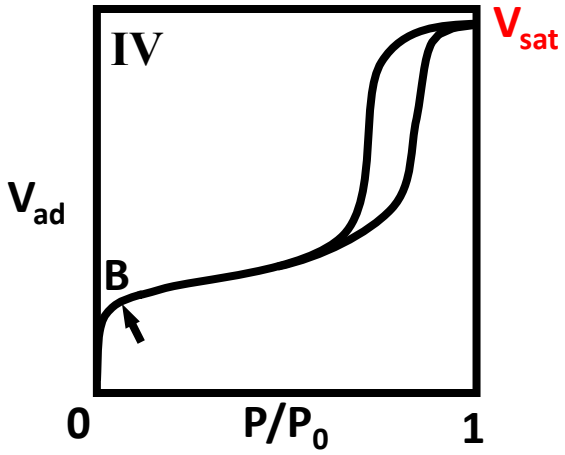
At pressure P ($< P_0$) and temperature T, capillary condensation would occur in pores with radius r determined by Kelvin equation

Pore Analysis via Gas Adsorption (2)

❑Continue from previous page

Pressure for capillary condensation & pore size satisfy

$$\ln\frac{P}{P_0} = -\frac{2\gamma_{LV}V_L Cos\theta}{RTr}$$



As relative pressure P/P_0 increases, larger pores get filled up with condensed adsorbate liquid.

Define:

V_{ad} - Adsorbate gas volume under **STP** needed to adsorb and fill up the pore at relative pressure P/P_0, in unit of cm^3/g

Total volume for pores with size smaller than r as determined by P/P_0 is

$$V_c(P/P_0) = \frac{V_{ad}M}{22414cm^3 \cdot \rho_L}$$

For N_2 as the adsorbate, M = 28 g/mol; Density of liquid N_2 at 77 K ρ_L = 0.808 g/cm^3

Therefore, for LN2, $V_c(P/P_0) = 1.547\times10^{-3}V_{ad}$ in unit of cm^3/g

V_c is also called cumulative (specific) pore volume

From Adsorption/Desorption Isotherm to Pore Size Distribution

❑ Cumulative pore volume & equivalent pore diameter

Kevin Equation $\ln\frac{P}{P_0} = -\frac{2\gamma_{LV}V_L Cos\theta}{RTr}$ ➡ $r = -\frac{2\gamma_{LV}V_L Cos\theta}{RT(\ln P - \ln P_0)}$

For liquid N_2, θ = 0; surface tension γ_{LV} = 8.72 x10^{-3} N/m; liquid molar volume V_L = 34.68x10^{-6} m^3/mol, T = 77K

$$r = -\frac{0.944}{\ln(P/P_0)}nm = -\frac{0.410}{\lg(P/P_0)}nm$$

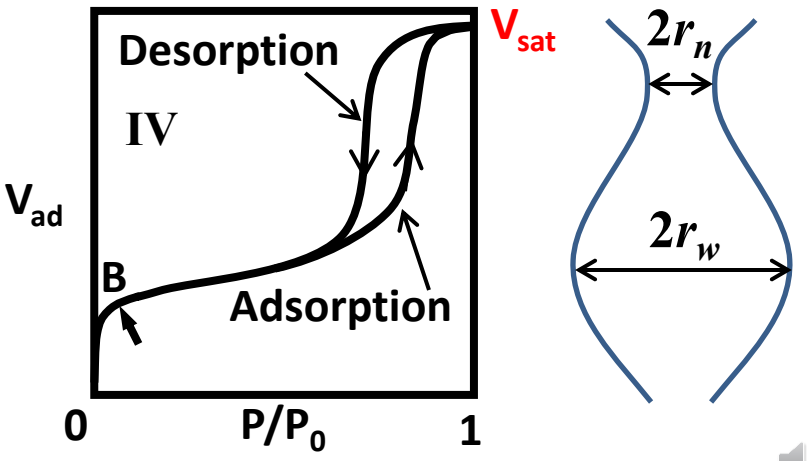
For any relative pressure of P_i/P_0, V_{ci} give the cumulative pore volume up to size r_i

Plotting a sets of V_{ci} vs. r_i data give the **cumulative pore volume plot** $V_c(r)$ vs. r

Differentiating the cumulative pore volume plot gives the pore size distribution $v(r)$

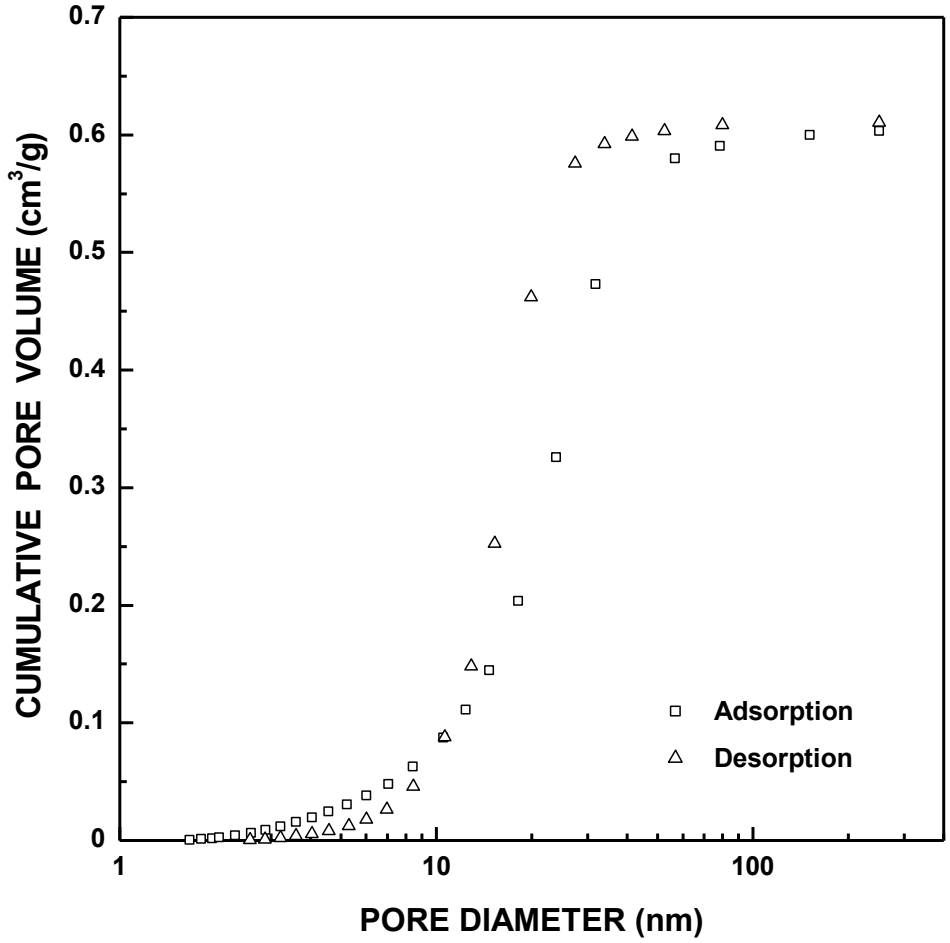
$$v(r) = \frac{dV_c}{dr}$$

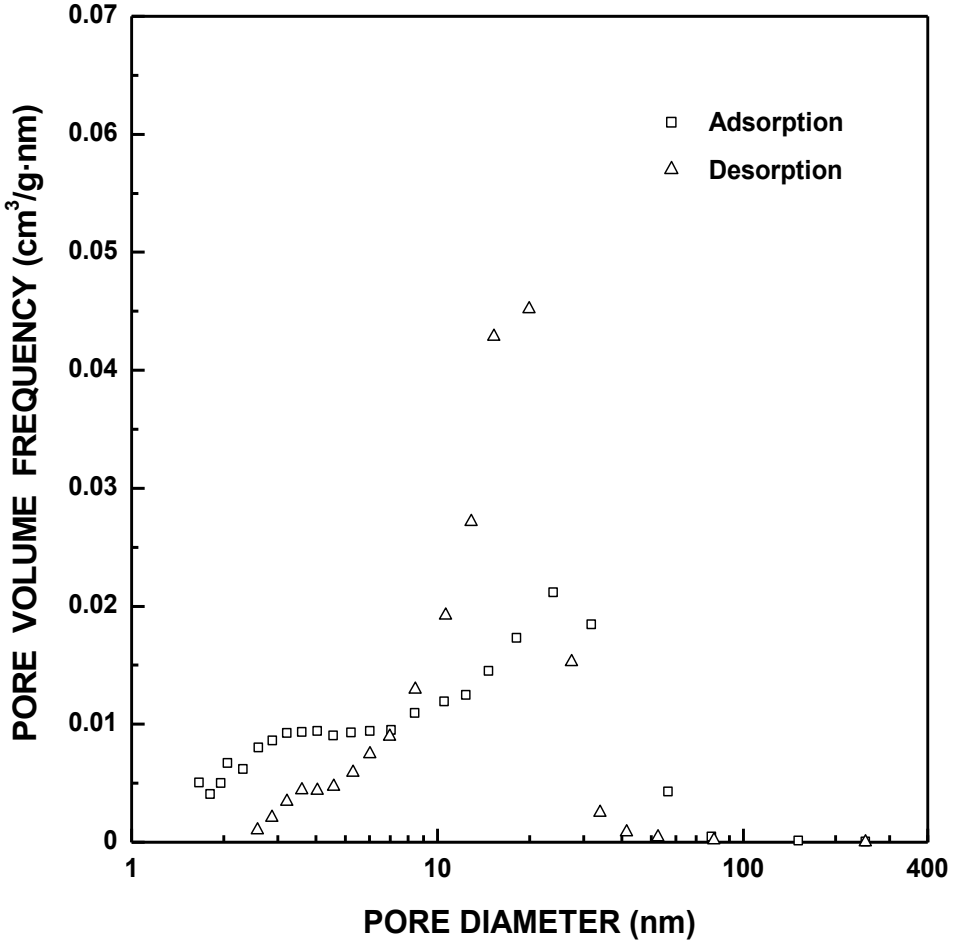
Hysteresis in adsorption/desorption isotherm



Examples of Pore Size Distribution

- Cumulative pore volume and derived pore size distribution plots for nanocrystalline β-SiC powder with mesopores





Zhe Cheng MS thesis, 2004

Specific Pore Volume & Relative (Open) Porosity via Gas Adsorption

❑Specific Pore Volume

When P approaches P_0, $r \to \infty$, all micropores and mesoporous pores get filled with condensed liquid, the volume of gas adsorbed (in unit of cm^3/g under STP) reaches saturation V_{sat}

Total specific pore volume V_w , in unit of cm^3/g is $V_w(P \to P_0) = \dfrac{V_{sat} M}{22414 cm^3 \cdot \rho_L}$

For N_2 as the adsorbate $V_w = 1.547 \times 10^{-3} V_{sat}$ in unit of cm^3/g

For actual measurement, V_{ad} value for P / P_0 = 0.995 is often used for V_w

❑Relative Open Porosity

Knowing total specific pore volume V_w, in unit of cm^3/g, and if the theoretical density of the fully dense solid powder is ρ_S in unit of g/cm^3

Relative **open** porosity ϕ_o will be

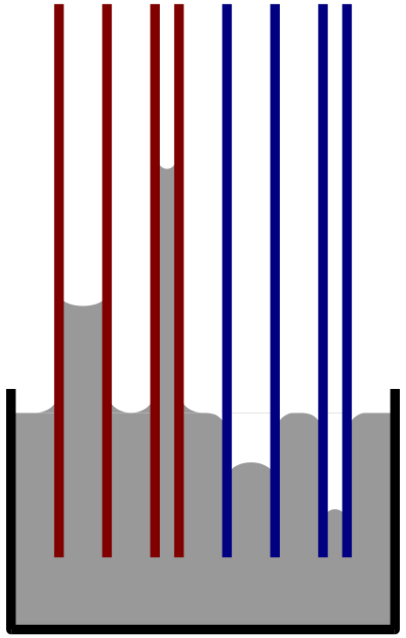
$$\phi_0 = \frac{V_w}{V_w + V_S} = \frac{V_w}{V_w + \dfrac{1}{\rho_S}}$$

Porosity/Pore Size Distribution via Mercury (Intrusion) Porosimetry (1)

❑Principle of measurement

For cylindrical capillary with radius r , the (effective) pressure difference ΔP between that inside the capillary above the curved liquid surface and that over planar surface outside capillary is given by Young & Laplace equation

$$\Delta P = -\frac{2\gamma_{LV} Cos\,\theta}{r}$$



https://en.wikipedia.org/wiki/Young%E2%80%93Laplace_equation#/media/File:CapillaryAction.svg

- When liquid wets the capillary wall, as in water on glass, $Cos\ \theta > 0, \Delta P < 0$, suggesting the liquid would rise up inside the capillary
- When using **Hg**, due to non-wetting, $\theta > 90^o$

  $Cos\ \theta < 0, \Delta P > 0$, Hg column inside capillary is depressed

In a closed system, by applying pressure, mercury could be forced into the capillaries in porous materials, and at different added pressure, capillaries with different radius got filled up by mercury.

Porosity/Pore Size Distribution via Mercury (Intrusion) Porosimetry (2)

❑Continue from previous page

$$\Delta P = -\frac{2\gamma_{LV} Cos\theta}{r}$$

$$r = -\frac{2\gamma_{LV} Cos\theta}{\Delta P} = \frac{0.735m}{\Delta P}$$

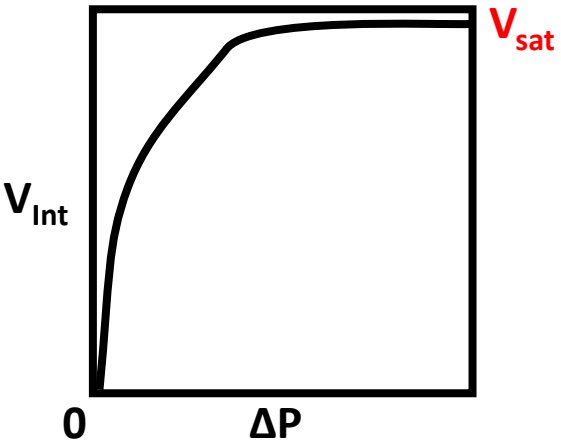
- For most solids, factors are constant for Hg:

γ_{LV} = 0.480 N/m and θ = 140°, $Cos\ \theta$ = -0.766

- The amount of Hg intruded into the powder sample gives the cumulative (specific) pore volume V_{int} for pores with size (i.e., radius) **greater than** r, as determined from applied pressure ΔP.

❑Features

- As applied pressure is increased, larger pores fill in first while smaller pores fill in later – opposite to gas adsorption
- Applicable for pore size ~5 nm-200 μm, but typically for **0.1-200 μm**
- More applicable to solids contain **macropores** for which gas adsorption cannot accurately measure
- Not very applicable for small mesopores due to inaccuracy at too high pressure

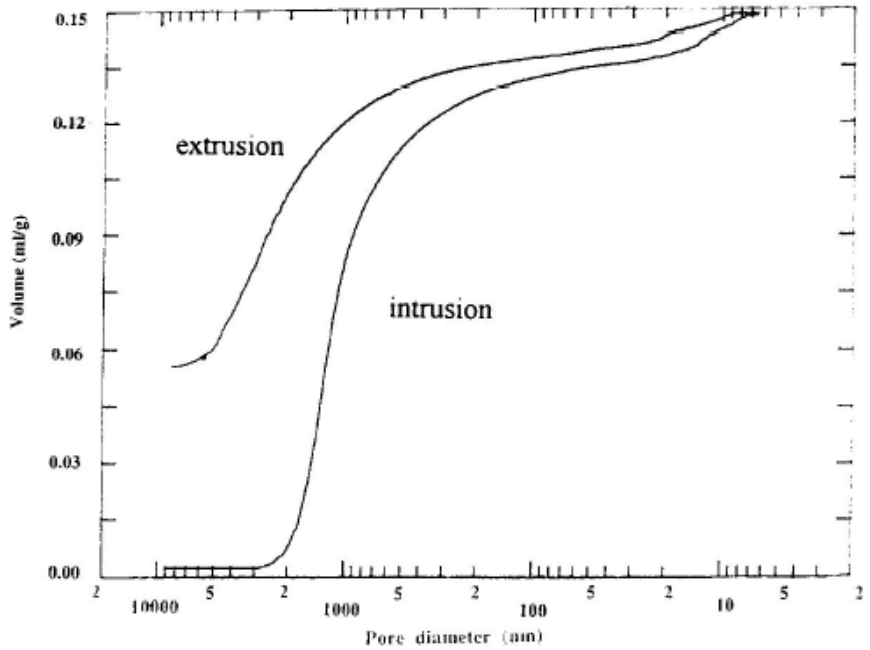


Porosity/Pore Size Distribution via Mercury (Intrusion) Porosimetry (3)

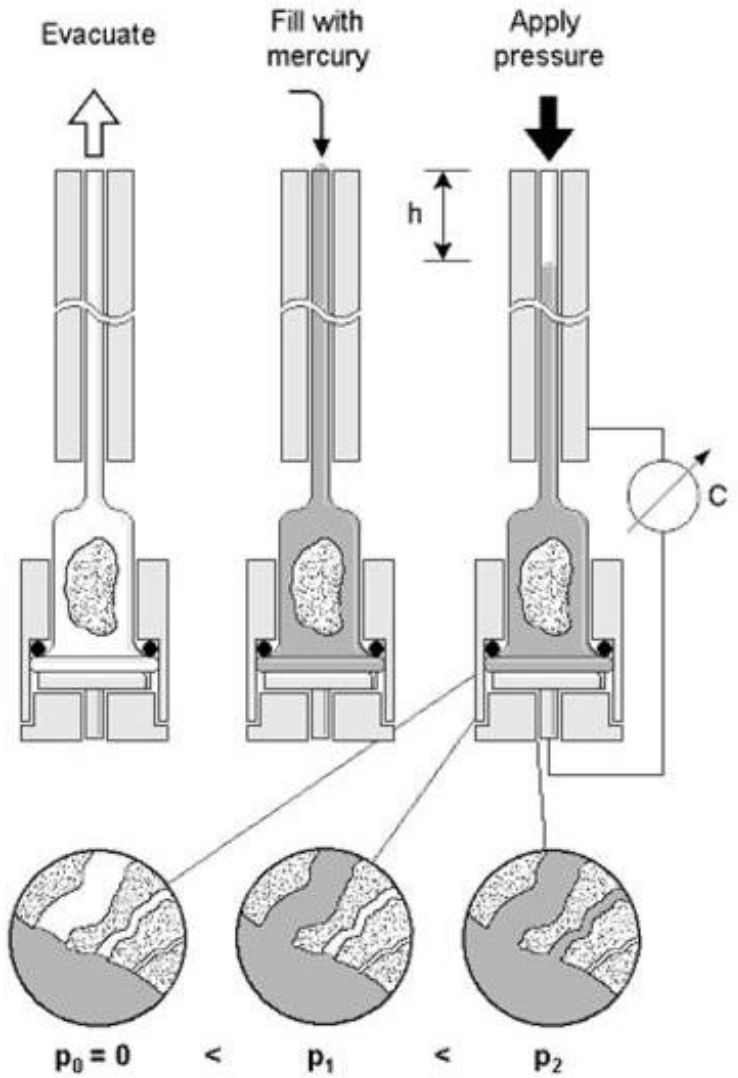
❑Typical steps

- Evacuate
- Back fill with Hg and gradually increase and then decrease pressure
- http://www.micromeritics.com/Repository/Files/Mercury_Porosemitry_Theory_poster_.pdf

❑Sample data



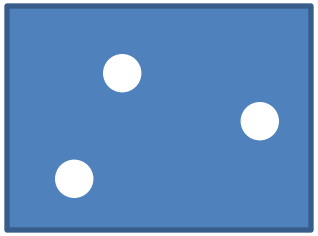
http://ethesis.helsinki.fi/julkaisut/mat/farma/vk/westermarck/ch2.html



http://particle.dk/methods-analytical-laboratory/mercury-porosimetry-pore-size/

Density/Closed Porosity Analysis via Pycnometry

❑ **For samples with closed pores**



M Mass of solid

V_S Actual volume occupied by solid

V_{ip} Volume of isolated (or closed) pores

Pycnometry, using liquid or gas (typically helium) measures total sample volume $V_S + V_{ip}$

Apparent density is $$\rho_a = \frac{M}{V_S + V_{ip}}$$

If solid theoretical density (i.e., fully dense) is ρ_S (from literature or others)

Relative **closed** porosity ϕ_c will be:

$$\phi_c = \frac{V_{ip}}{V_{ip} + V_S} = \frac{(V_{ip} + V_S) - V_S}{V_{ip} + V_S} = \frac{\frac{1}{\rho_a} - \frac{1}{\rho_S}}{\frac{1}{\rho_a}} = 1 - \frac{\rho_a}{\rho_S}$$

Relative density will be $$\rho_r = \frac{\rho_a}{\rho_S} = 1 - \phi_c$$

Homework

- Textbook Rahaman (2003) 3.2, 3.6