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Particle Characterization

Introduction to Gas Adsorption

Or everything you ever wanted to know about physisorption but were afraid to ask!

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What is gas adsorption

- **Adsorption** – the accumulation of a substance at a surface of a material

- **Gas adsorption** – the build up of gas molecules on the surface of a solid, which is reversable

- Not to be confused with **aBsorption** – the accumulation and distribution of a substance throughout a material

- Physical adsorption (**physisorption**) another name for gas adsorption which is reversable

- Chemical adsorption (**chemisorption**) higher energy, non-reversable adsorption (bonding) on selected sites of a material primarily used for characterizing catalysts

Why is it important

- Adsorption occurs in nature

- Materials which separate gases (gas purification, gas separation, poison gas protection – gas masks)

- The surface of pharmaceutical APIs and excipients affects performance

- Activated carbons adsorb impurities from water for purification

- Paints, pigments and coatings all require certain surface characteristics to perform optimally

- Oil refining by catalysts require specific surface design to be effective

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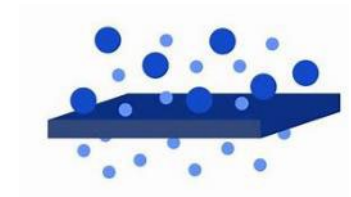
What causes a gas to adsorb

- **Van der Waals forces** – weak intermolecular forces which increase as molecules become closer together
- Within a material, Van der Waals forces are satisfied by the neighboring molecules of the substance
- However, at the edge of a solid or the interface with surrounding gas or liquid, those Van der Waals forces have nothing to satisfy them. No neighboring molecules

Some definitions

- **Adsorptive** – gas available to be adsorbed

- **Adsorbate** – gas which has been adsorbed

- **Adsorbent** – the material adsorbing the gas

Adsorptive

Adsorbate

Adsorbent
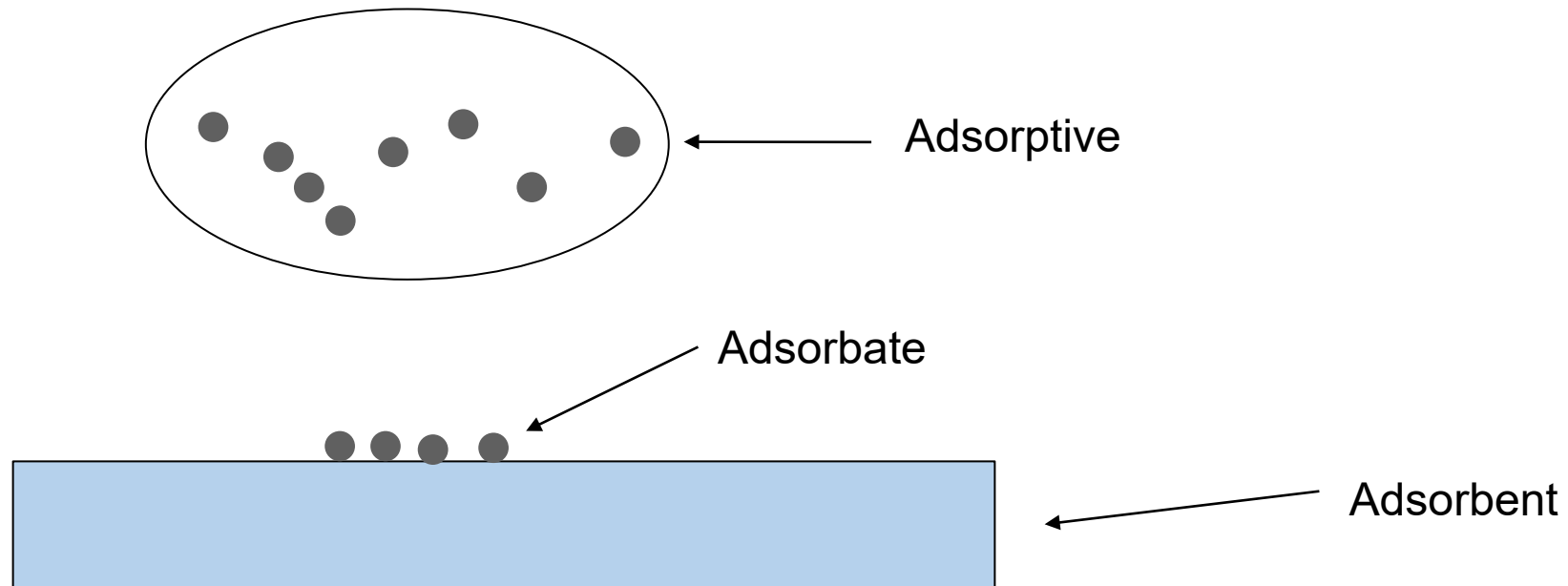
What causes a gas to adsorb continued

- In nature, at this interface or edge of a solid, the Van der Waals forces attract water molecules or other vapors from the surrounding atmosphere.
- This satisfies the unmet potential energy
- Flat surfaces are lowest in adsorption energy
- Adsorption energy increases as pores become smaller

Increasing adsorption energy
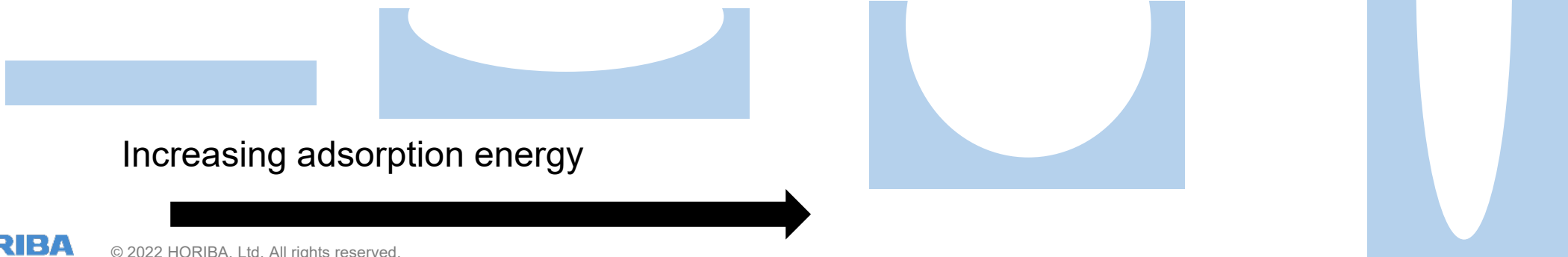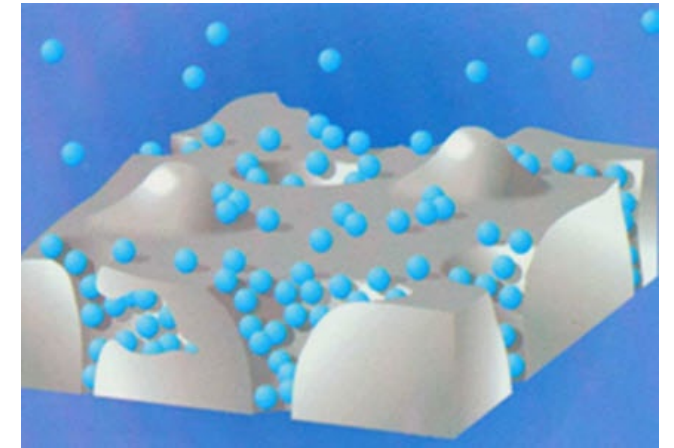
Classification of pores

- **Macropores** – > 50 nm diameter

- **Mesopores** – 2 to 50 nm diameter

- **Micropores** – < 2 nm diameter

- Generally, materials with larger pore sizes tend to have lower total surface area.

- Materials with smaller pore sizes, alternatively, tend to have higher surface areas.

- And of course, non-porous materials are lowest in surface area.

What else causes adsorption to occur

- In a gas adsorption experiment, the sample, which has been placed in a sample holder and appropriately prepared (we'll get to that), is immersed in a cryogen (typically LN_2) which cools the surface of the sample – in the case of LN_2, to approximately 77.3K.

- Gas which is admitted to the sample holder loses thermal energy and again, as a result of the surface energy of the material, gas molecules adsorb.

The Adsorption Process

At low pressure, isolated sites on the sample surface begin to adsorb gas molecules
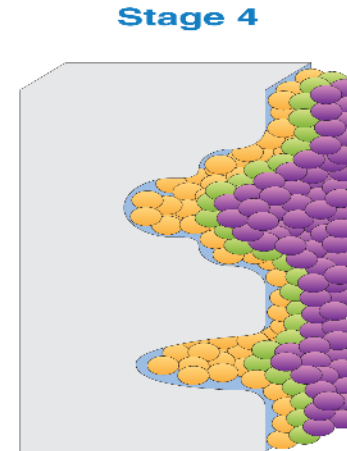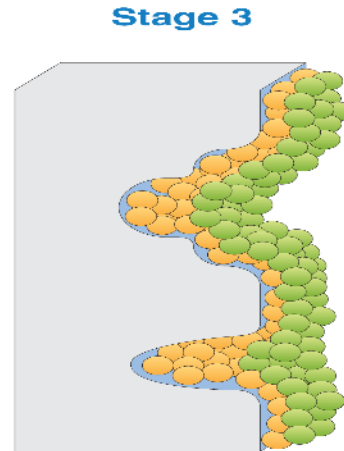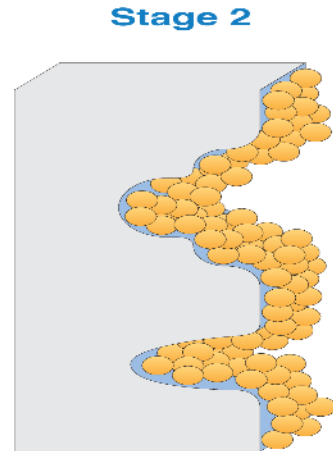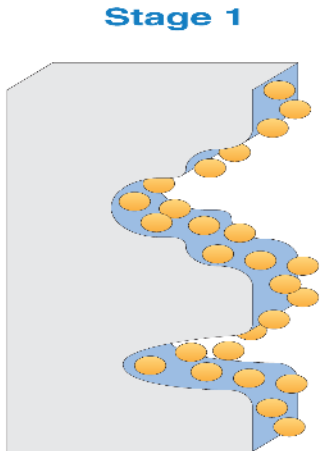
Increasing gas pressure causes the beginning of multi-layer coverage. Smaller pores in the sample will fill first. The BET equation is used to calculate the surface area.

Stage 1 **Stage 2** **Stage 3** **Stage 4**

As gas pressure increases, adsorbed molecules increase to form a monolayer one molecule thick.

Further increase in gas pressure will cause complete coverage of the sample and fill all the pores.

What effect does particle size have on surface area?
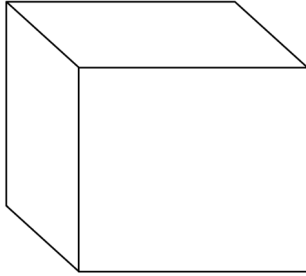
A 1 cm^3 cube would measure 6 cm^2 in area
1 x 1 x 6 faces
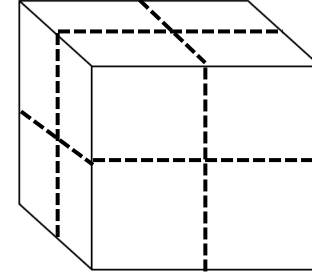
Trisecting the same cube into 8, ½ x ½ cm cubes creates 12 cm^2 of area
½ x ½ x 6 faces = 1.5 cm^2
1.5 x 8 = 12 cm^2

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A few additional terms

- **Isotherm** – the raw data from a test at constant temperature (typically 77.3K) plotted as volume of gas adsorbed (y axis) vs pressure (x).

- **Saturation pressure** – the pressure of a gas which is in equilibrium with its liquid – expressed as P_o

- **Relative pressure** – a means to "normalize" data from different labs which may be at differing atmospheric pressures where the absolute pressure is divided by the saturation pressure of the test gas, frequently written P/P_o. Typically expressed as 0.05, 0.1, 0.2, etc.

- **Desorption** – removal of adsorbed gas from the surface of a substance.

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Types of Isotherms as defined by IUPAC

Microporous solids with limited external surfaces e.g., activated carbon, zeolites, porous oxides.

Nonporous or macroporous solids. Point B if sharp corresponds to completion of monolayer coverage.

Mesoporous solids – adsorption and desorption follow different paths due to pore shapes (hysteresis).

Also rarely seen. Here, interaction between adsorbent and adsorbate is very weak but as pressure increases some pore filling occurs.
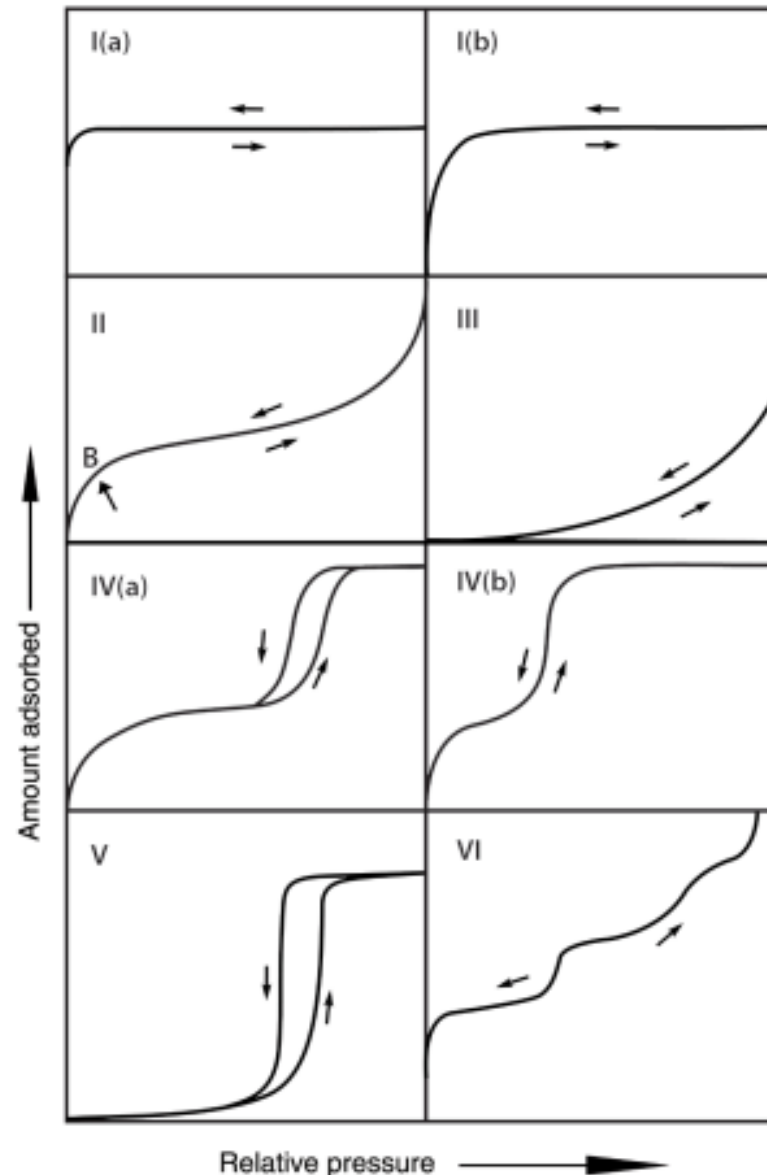
Microporous solids having pores over a wider range – possibly as large as 2.5 nm.

Rarely seen. Here, interaction between adsorbent and adsorbate is very weak. Examples are Bromine on silica gel or Iodine on silica gel.

Mesoporous solids – adsorption and desorption follow same path due to smaller mesopores or cylindrical closed end pores

Layer by layer adsorption on a uniform non-porous surface – again, rarely seen.

What data can I obtain?

- The Isotherm is the raw data – again, volume of gas adsorbed (y) vs pressure (normally expressed as relative pressure – P/P_o) (x)
- Using different ranges of the pressure axis, different characteristics of a material may be calculated.
- Surface area – Langmuir, BET (multi-point and single point)
- Micropore volume and area (t-plot, MP method)
- Micropore size distribution (Horvath-Kawazoe, Dubinin, others)
- Meso and macropore size, area and volume distributions (BJH)
- Density Functional Theory for area and pore volume distribution
- Total pore volume

Isotherms – most common types

Filling of macropores

Micropore filling at low pressures

Build up of gas on surface / higher energy sites (filling of the monolayer)

Development of multi-layer adsorption

Filling of mesopores (adsorption) and emptying (desorption) may demonstrate hysteresis – indicating differences between pore cavities and openings
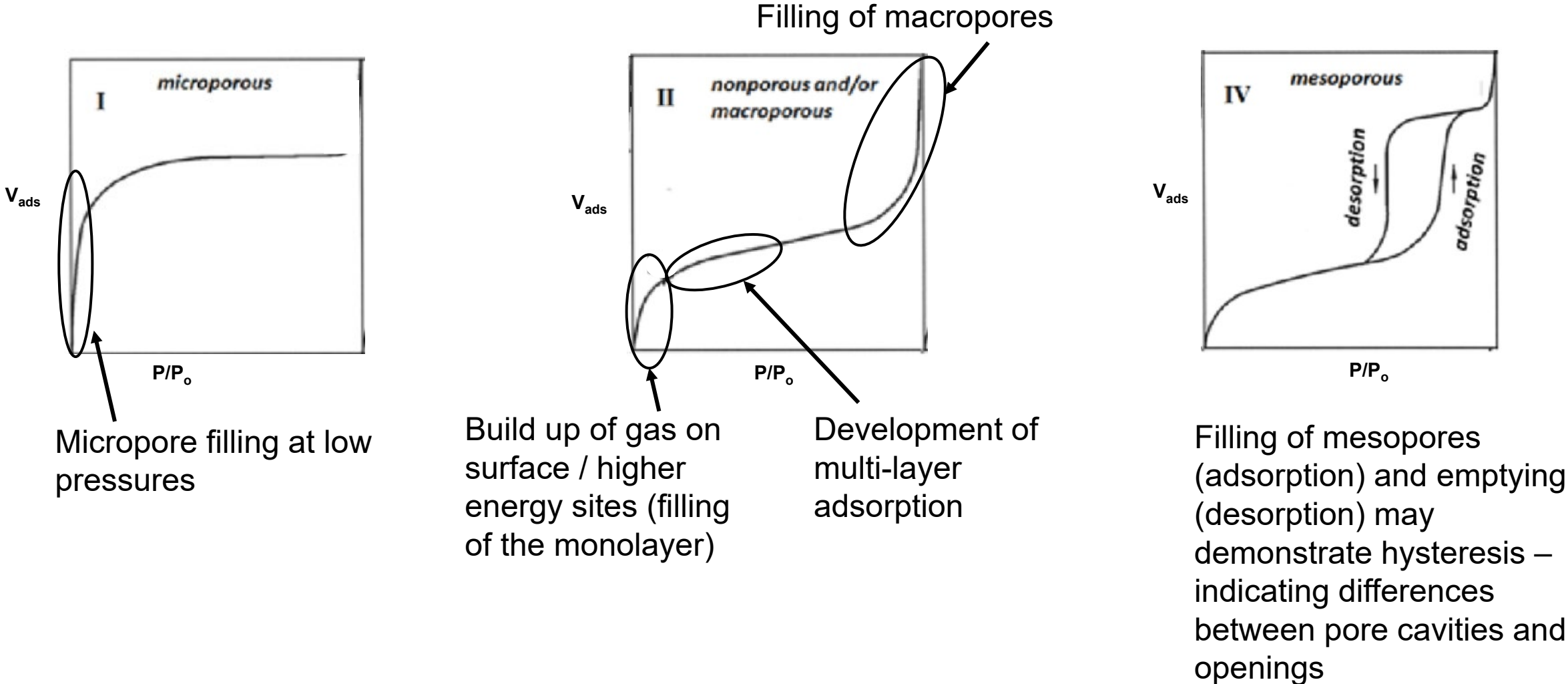
Data collection

- In this presentation we will focus upon surface area calculations
  - Early work by Langmuir (1919) on charcoal indicated that gas molecules adsorb in only a single layer after which negligible adsorption occurred
  - Brauneur, Emmitt and Teller (BET) in 1938 theorized that multi-layer adsorption was more the norm and developed a formula to explain this phenomena
  - Data is taken from the isotherm in the linear region where multi-layer adsorption takes place – most typically between 0.05 – 0.3 P/Po
  - Brauneur also first assigned designations to type I through V isotherms
  - Commercial laboratory instrumentation began to be developed in the late 1950's

Adsorption layers

Ideal

Actual

i^{th} layer

3rd layer

2nd layer

1st layer
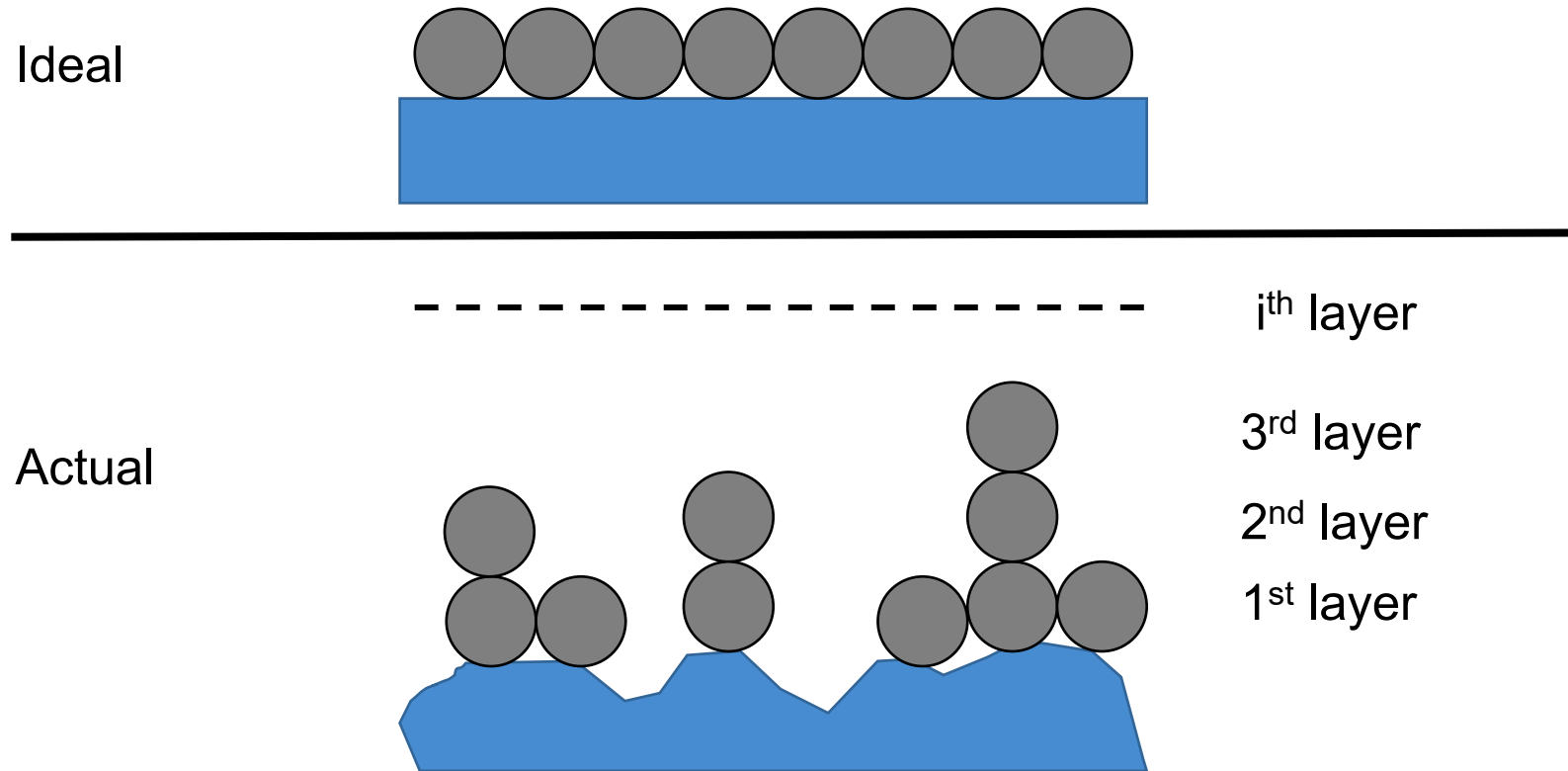
The BET equation (in linear form)

$$\frac{P}{V_a(P_o - P)} = \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right) + \frac{1}{V_m C}$$

$$\text{y} \quad = \quad \text{m(x)} \quad + \quad \text{b}$$

Where: V_a = Volume of adsorbed gas

P = Absolute pressure

P_o = Saturation pressure

V_m = Mono-layer gas volume – what we're seeking!

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

The BET equation (linear) for multi-point analysis

$$\frac{P}{V_a(P_o-P)} = \frac{C-1}{V_mC}\left(\frac{P}{P_o}\right) + \frac{1}{V_mC}$$

$$\text{y} \quad = \quad \text{m} \;(\text{x}) + \text{b}$$
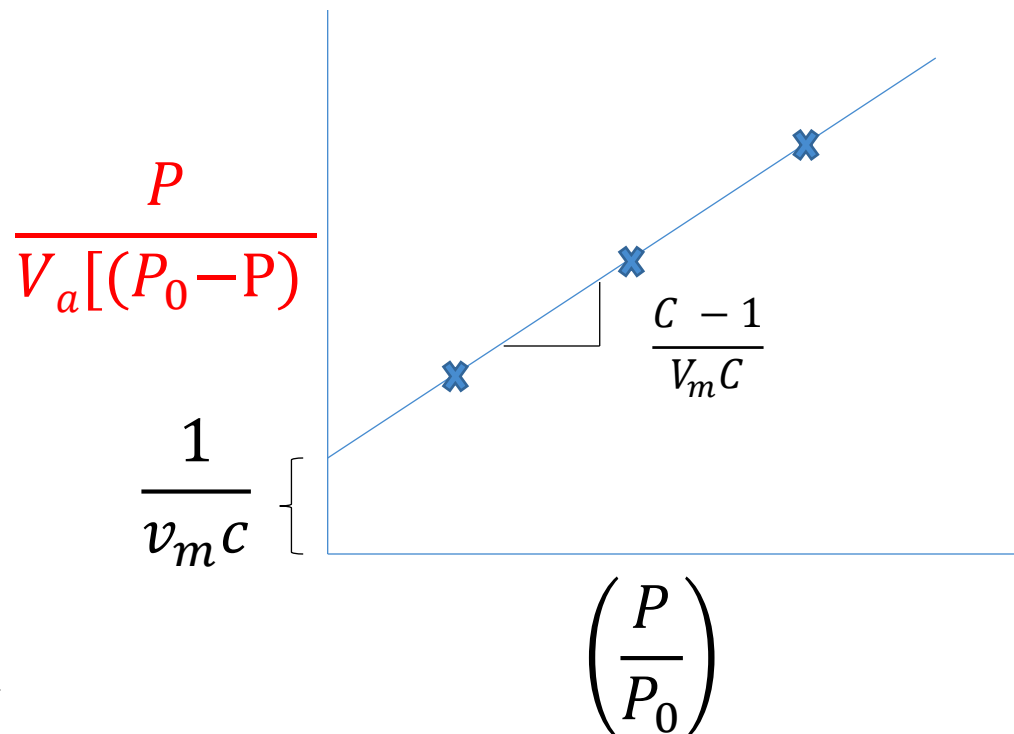
And from this linear regression

$$\text{slope} = \frac{C - 1}{V_m C}$$

$$\text{intercept} = \frac{1}{V_m C}$$

$$V_m = \frac{1}{\text{slope} + \text{intercept}}$$

$$C = 1 + \frac{\text{slope}}{\text{intercept}}$$

Calculating surface area from V_m

$$S_{BET} = \frac{V_m * L * \alpha_m}{M}$$

Where:

S_{BET} – Total surface area under test

V_m – Monolayer volume

L – Avagadro's number - 6.02×10^{23} molecules/mol

α_m – Cross sectional area of gas molecule - 0.162 nm^2 for N_2

M – molar volume – 22414 L / mol

Dividing S_{BET} by sample mass gives specific surface area (m^2/g)

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Single point calculation from the BET equation

- When C is very large – $1/V_mC$ approaches 0

- Meaning y-intercept is very close to 0

- Regression can be forced through the origin without substantial error (change to slope)

- Likewise, C-1≈ C. Thus, C-1$/V_mC$ becomes $1/V_m$, simplifying our equation to:

$$\frac{P}{V_a(P_o - P)} = \left(\frac{1}{V_m}\right)\left(\frac{P}{P_o}\right)$$

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So how do we use all of this?

- We take advantage of these Van der Waals forces
- We prepare a sample by removing these adsorbed molecules thus "reenergizing" the surface of the material we wish to measure.
- Next, we perform a controlled adsorption of gas on the surface to measure it

Horiba SA-9603MP

Preparation options

- Preparation of a sample requires
  - Time
  - Elevated temperature *
  - Clean environment (in a sample tube)

Note: Rule of thumb – apply temperature which will not change the structure of the material but will drive off adsorbed water / vapor.
Note 2: If prep temp is unknown, a general rule of thumb is to determine melting point of material and never apply more than 50% of that temperature.
Note 3: Many pharmaceutical APIs or excipients cannot be degassed at temperatures above ambient.

How does preparation work? AKA Degassing

- Typically, a sample is placed in a clean sample tube.

- The sample tube is connected to an instrument and a source of heat

- Heat is then applied, and while being heated….

- A source of dry gas flows through the sample tube
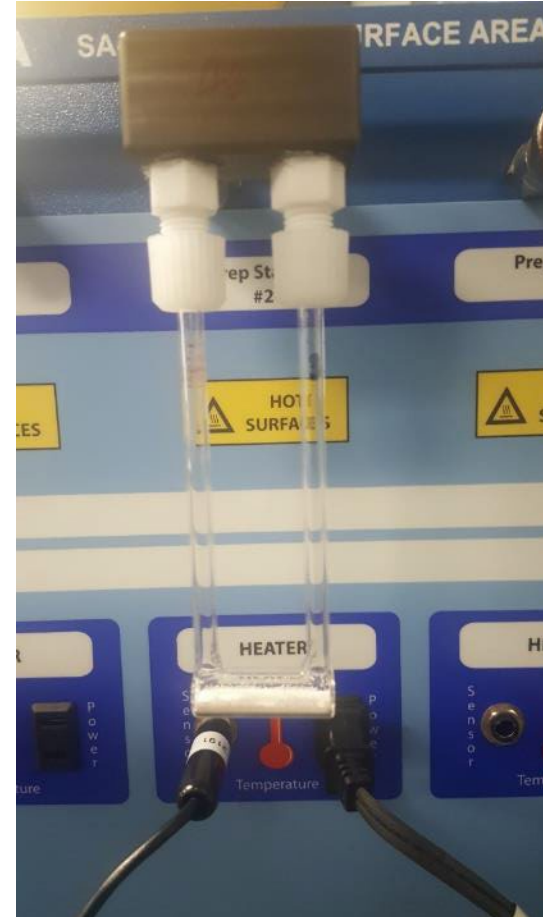
Sample tube with sample installed on degas port

Sample with degas heating mantle in place

That's interesting but what really happens?

- As the temperature rises, the molecules adsorbed on the surface are heated
- They begin to move more rapidly and overcome the weak Van der Waals forces
- Then as they break free from the surface of the sample material, they are swept away by the flowing gas
- That leaves the Van der Waals energy again unsatisfied. Sometimes this is referred to as being "activated."
- It is important that the sample remain unexposed to atmosphere as much as possible after this preparation.

Types of gas adsorption instruments

- Volumetric – manifold of known volume, volume of sample tube known, PV=nRT Gas dosed according to pre-defined table of pressures or volumes

- Dynamic – flowing gas, TCD on gas inlet and on gas outlet. Conductivity difference of gas on inlet vs outlet measured as adsorption or desorption

- Gravimetric – sample is placed in a sensitive microbalance and mass of adsorbed gas is measured

Comparison of gas adsorption instruments

Volumetric

- Requires volume calibration data
- Typically, slow, step wise data collection
- Must dose multiple times per data point
- Research applications
- Can collect many data points
- Can be configured to measure extremely low-pressure data. (micropores)
- Complex designs (cost to purchase and cost to maintain)

Dynamic

- Typically, very fast (for single point SA)
- Good tool for in process control of product
- Excellent for rapid material screening in research applications
- Inexpensive to purchase and maintain
- Very reliable and robust
- Use of quick connect fittings avoids exposure of sample atmosphere
- Very small footprint

Gravimetric

- Uses a microbalance in a "chamber"
- Very small amount of sample used
- Balance is tared at the start of analysis
- As gas flows into chamber and sample adsorbs, mass increases and is measured by balance.
- Typically these are more expensive research grade instruments
- Popular application for water / vapor adsorption

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Why does Horiba promote flowing gas / dynamic?

- Dynamic instruments are of straightforward design

- Lower cost to purchase

- Very robust and reliable

- Very low maintenance costs

- Extremely fast data collection

- Excellent choice for production environments

- Self sealing bulkhead fittings avoid contamination

- Simple to operate

Now to the measurement

We must know the precise mass of the sample we are testing – but it must be the mass after preparation!

- This requires a tare weight of the empty sample cell
- A known mass of sample is added (Many times people record this mass.)
- Preparation (degassing) of the sample takes place
- After the analysis is complete, we will weigh the sample tube to determine the sample mass. (post analysis sample + tube weight - sample tube tare weight = degassed sample weight)

The Horiba approach – Dynamic gas alternative

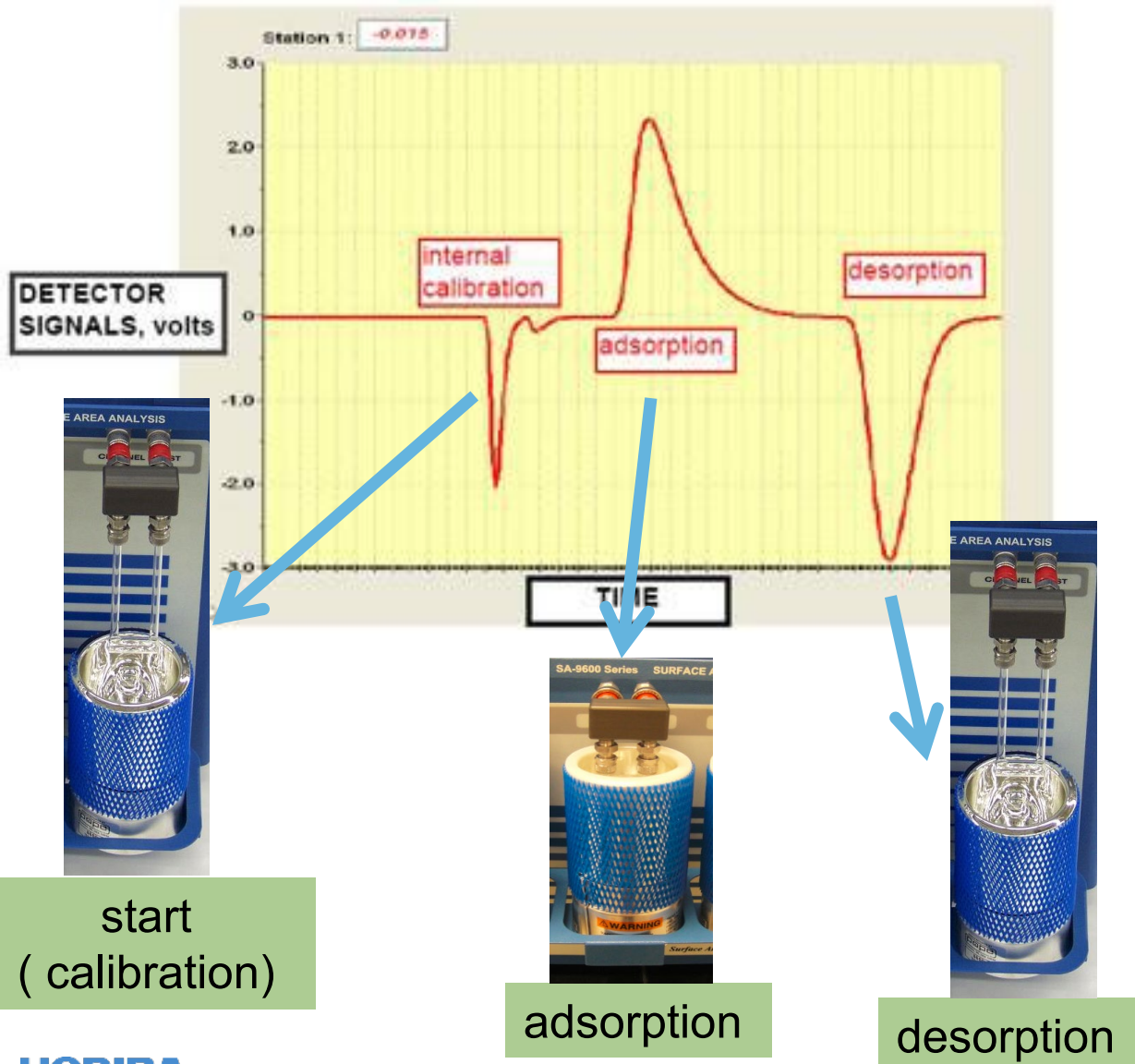## The SA-9600 Series of Surface Area Instruments

Degas stations

Analysis stations

9601 Single Point
9601 Multi Point

9603 Single Point
9603 Multi Point

Automatic dynamic sorption process

DETECTOR SIGNALS, volts

internal calibration

adsorption

desorption

TIME

start (calibration)

adsorption

desorption

- Analysis initiated from PC software or integrated computer
- Gas flows across sample
- $1cm^3$ N_2 is injected for calibration
- Dewar is raised / sample cools
- Gas begins adsorbing
- When adsorption ends, Dewar is lowered
- Gas desorbs rapidly providing integratable peak for V_a
- Complete if single point, repeated 2-5 times if multi-point
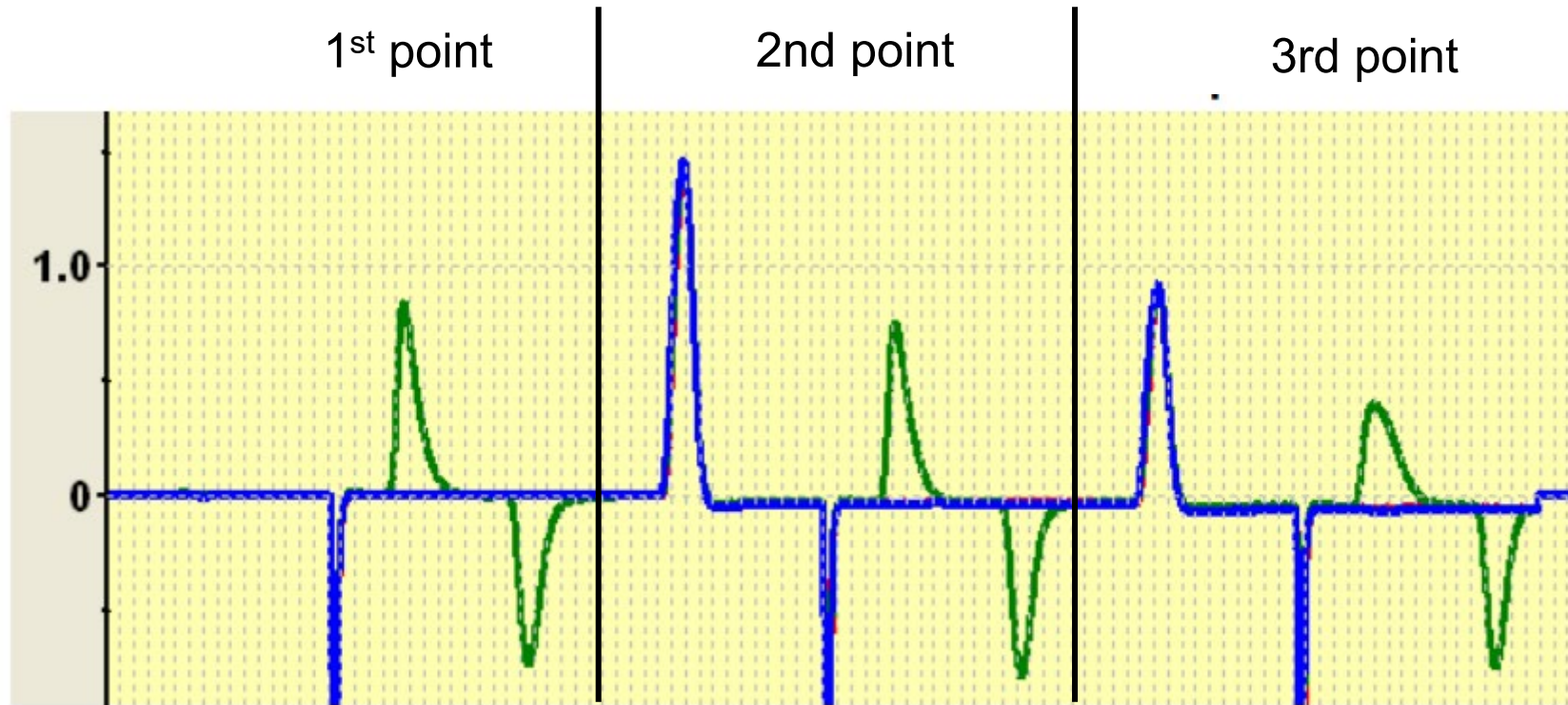
Small total surface area vs large
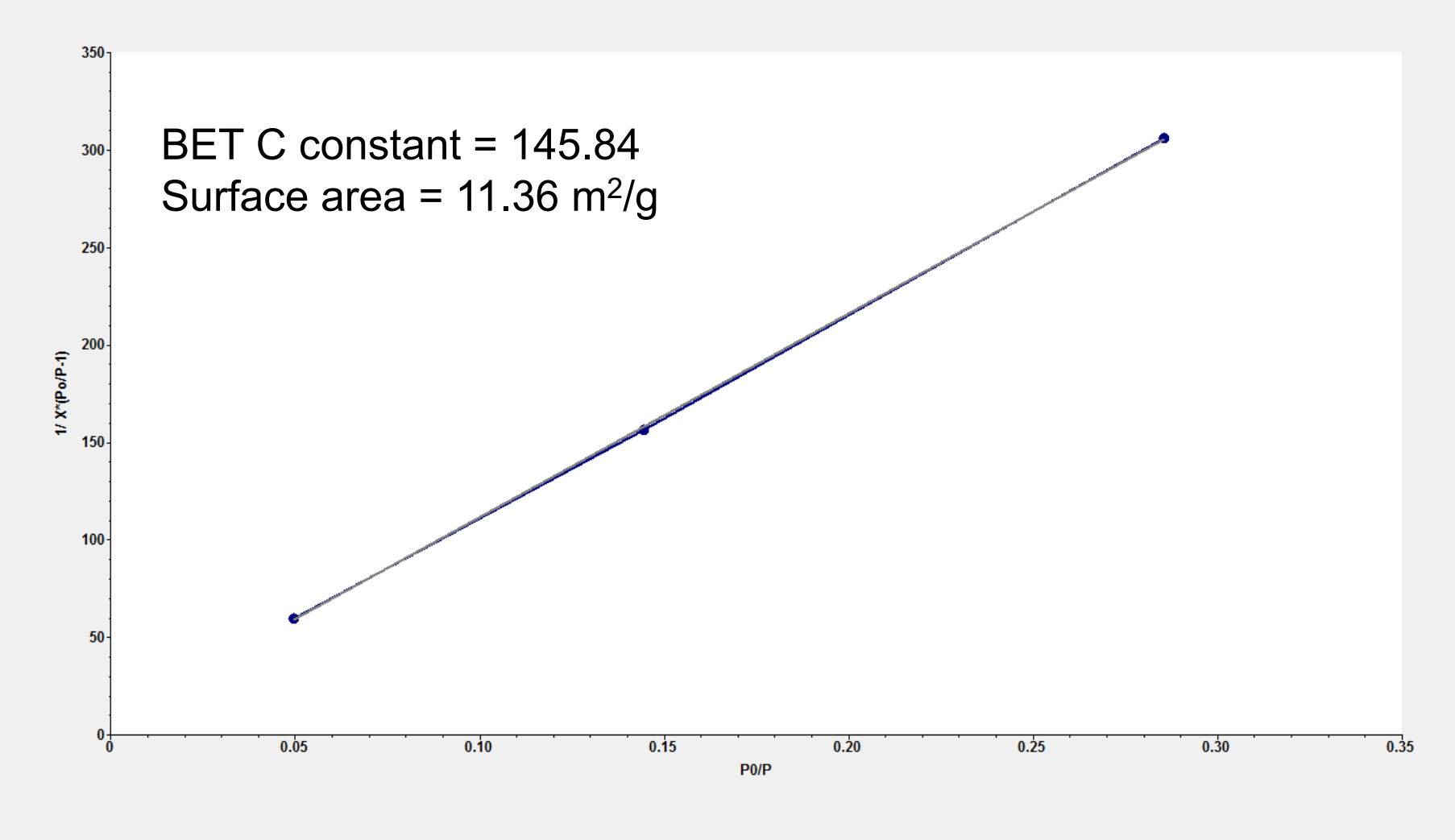
Small Surface Area
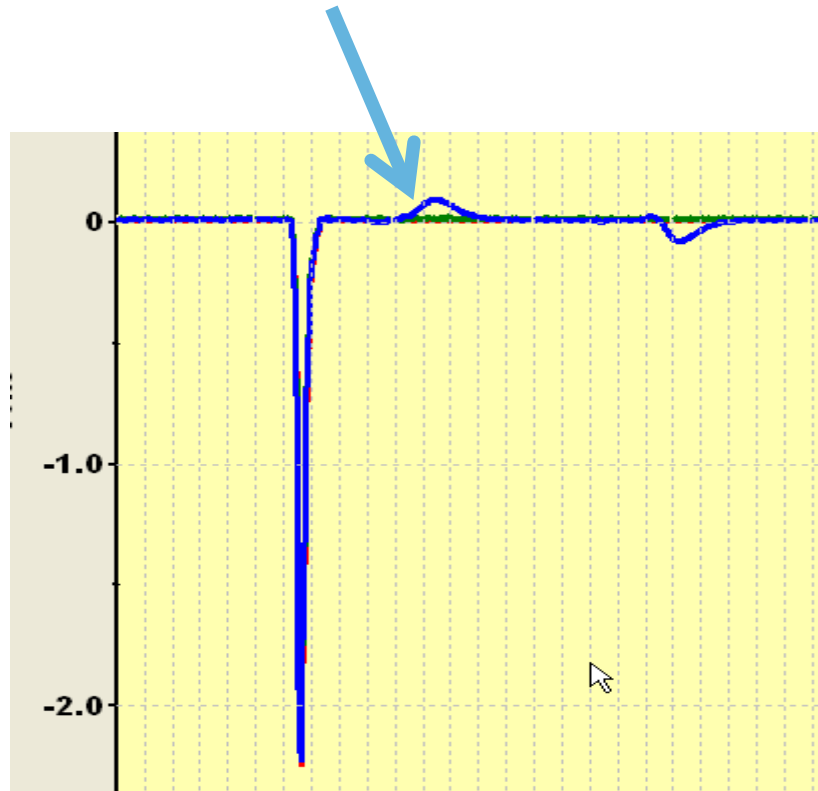
Large Surface Area
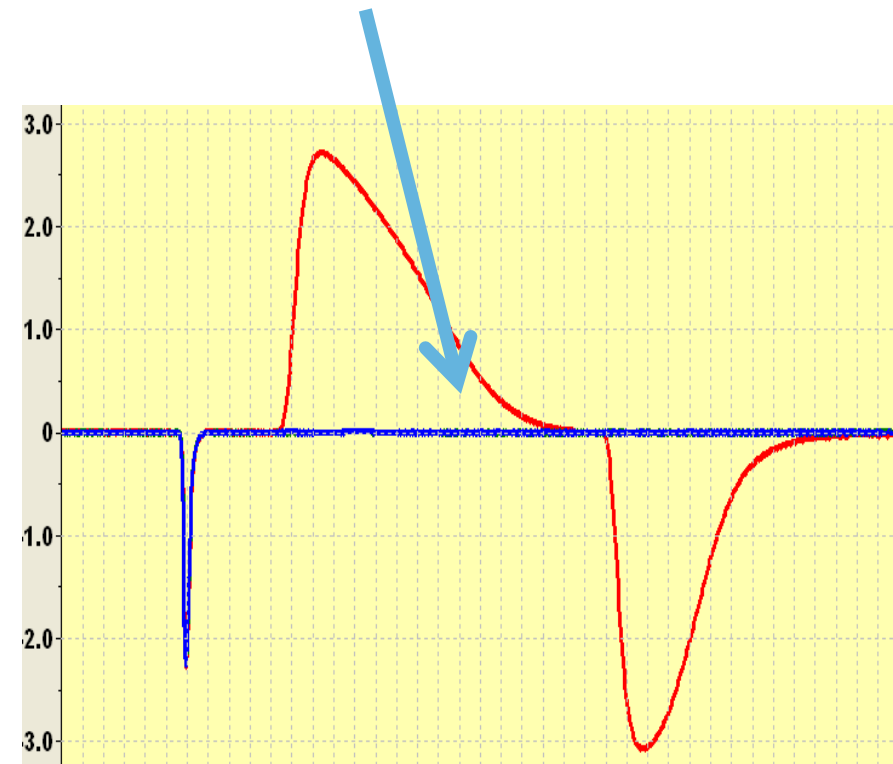
BET Multi-point example

Plot at least 3 points to obtain multi-point plot

BET C constant = 145.84
Surface area = 11.36 m²/g

Example data – Calcium Carbonate

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	2.28	2.47	2.13	
Test 2	2.31	2.36	2.2	
Test 3	2.21	2.3	2.12	
Average	2.27	2.38	2.15	2.26
STDEV	0.05	0.09	0.04	0.11
COV	2.26%	3.63%	2.03%	4.96%

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	2.32	2.4	2.26	
Test 2	2.32	2.4	2.26	
Test 3	2.27	2.28	2.25	
Average	2.30	2.36	2.26	2.31
STDEV	0.03	0.07	0.01	0.06
COV	1.25%	2.94%	0.26%	2.54%

Single point analysis

Multi-point analysis

Example data - Kaolin

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	21.29	21.89	21.72	
Test 2	21.27	21.83	21.66	
Test 3	20.95	21.55	21.4	
Average	21.17	21.76	21.59	21.51
STDEV	0.19	0.18	0.17	0.31
COV	0.90%	0.83%	0.79%	1.42%

Single point analysis

Column1	Sample 1	Sample 2	Sample 3	Grand Totals
Test 1	21.47	21.11	21.8	
Test 2	21.26	21.77	21.48	
Test 3	20.66	21.37	21.06	
Average	21.13	21.75	21.45	21.44
STDEV	0.42	0.37	0.37	0.43
COV	1.99%	1.70%	1.73%	2.01%

Multi-point analysis

Other materials

Material	Single point	Multi-point
Alumina	173.74	177.76
Bentonite	12.31	12.29
Calcium Hydroxide	13	13.35
Graphite	5.75	5.97
Hydroxyapatite	56.28	56.88
Kaolinite	7.9	8.1