

**JoVE: Science Education**  
**Porosimetry of a Commercial Adsorbent or Catalyst**  
--Manuscript Draft--

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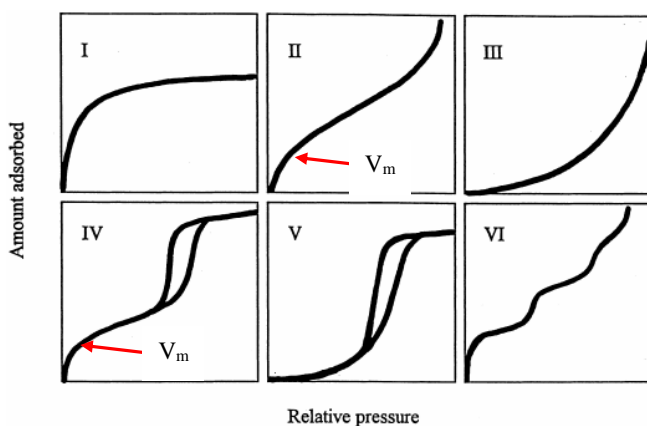
## Science Education Title: Porosimetry of a Commercial Adsorbent or Catalyst<sup>1</sup>

### Overview

Surface area and pore size distribution are porous solid attributes used by adsorbent and catalyst manufacturers and users to ensure quality control, and to determine when products are at the end of their useful lives. The surface area of a porous solid is directly related to adsorption capacity or catalytic activity. The pore size distribution of an adsorbent or catalyst is controlled such that pores are large enough to easily admit molecules of interest, but small enough to provide a high surface area per mass. Surface area and pore size distribution can be measured by the technique of isothermal nitrogen adsorption/desorption. Commercial devices (**porosimeters**) to do so are highly automated.

Surface areas of micro- (<2 nm pores) and mesoporous (2-50 nm pores) solids can be as large as several hundred m<sup>2</sup>/g. Accurate measurement requires an equation relating surface area to volume adsorbed ( $V_{ads}$ ) and pressure at constant temperature (the **isotherm**). One then regresses the isotherm equation to determine the fit parameters. The normal method of reporting the surface area is to divide the sample area in m<sup>2</sup> by the solid mass in grams to yield what is often called the **specific surface area, A**.

All adsorption isotherms can be divided into five classes (**Figure 1**).<sup>1-2</sup> But for physical adsorption, only types II or IV are relevant; the rest describe bonding isotherms (“chemical adsorption”). Points  $V_{ads} = V_m$  in types II and IV represent (approximately) the location of an adsorbed **monolayer**. The remainder of the curve represents multilayer adsorption and then capillary condensation.



**Commented [ASW1]:** What is this? Is it different than “regular” surface area?

**Commented [K2R1]:** That’s what many call it. Some just say “surface area”.

**Figure 1. Brunauer's classification of adsorption isotherms.** Type I is Langmuir. Types III and V are “swelling” isotherms often found with polymeric adsorbents.  $V_{\text{ads}}$  = amount adsorbed.

The three isotherm equations most frequently used are those due to Langmuir; Freundlich; and Brunauer, Emmett, and Teller (**BET**). Only the BET equation can relate  $V_m$  and the adsorption energy parameters of a **vapor** to **A**.

## Principles

An **adsorbate** is a compound in a gas or liquid phase that attaches to the surface of the solid adsorbent being investigated. **Physical adsorption** depends upon weak intermolecular forces only. The  $\Delta H$  of such adsorption is <3 times the heat of vaporization. It is only important at low temperatures near and below the adsorbate's saturation temperature. The  $N_2$  adsorption/desorption used here takes place at the normal boiling point of liquid  $N_2$  (77 K). The process is rapid and reversible. A **monolayer** is a single layer of molecules completely covering the pore surfaces of a porous material.

The BET isotherm assumes:

- Each molecule in the first adsorbed layer (the monolayer) provides only one site for the second and subsequent (multi-)layers. Adsorption initially takes place layer by layer.
- A heat of adsorption  $\Delta H_1$  applies to the first monolayer while the heat of liquefaction  $\Delta H_L$  of the vapor applies to adsorption in layers 2, 3 etc.

Brunauer *et al.* simplified the estimation of  $V_m$  and the energy parameters to the following isotherm equation:<sup>3</sup>

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c} \frac{P}{P_0} \quad (1)$$

$$c = \exp \left[ \frac{(\Delta H_L - \Delta H_1)}{RT} \right] \quad (2)$$

$P_0$  is the saturation pressure at a given temperature,  $T$ . This expression represents a type II or IV isotherm in the range  $0.05 < P/P_0 < 0.35$ .

There is a progression from multilayer adsorption ( $P/P_0$  to ~0.3-0.35) to capillary condensation (higher  $P/P_0$ ) in which the smaller pores become completely filled. This occurs because the fugacity (vapor pressure) in a small pore is reduced, in accordance with the Kelvin equation (**Equation 3**), by the surface tension ( $\sigma$ ).<sup>1</sup>

$$P_v/P_0 = \exp[-4 \sigma \rho_M \cos\theta / (D R T)] \quad (3)$$

**Commented [ASW3]:** Should this be 3 or 2?

**Commented [K4R3]:** What I said is correct.

**Commented [ASW5]:** You state in the Overview that these values are important to QC and product lifetime, but take it to its conclusion here. How do you use these values to determine QC and lifetime?

**Commented [K6R5]:** Answered in the “Applications”.

**Commented [ASW7]:**  $P/P_0$  is talked about a lot in the manuscript, but it's not really explained anywhere. What is its significance?

**Commented [K8R7]:**  $P_0$  is the saturation  $P$ , so it's the  $P$  at which bulk condensation occurs. They should know that from 1<sup>st</sup> Thermo.

The left hand side gives the  $P/P_0$  at which capillary condensation takes place in a **cylindrical** pore with adsorbate contact angle  $\theta$  and pore diameter  $D$ . The capillary effect is significant only in pores  $< \sim 200$  nm in diameter; but pores larger than this are uncommon in most commercial porous adsorbents and catalysts.

## Procedure

The interior of a porosimeter is just two chambers with one sensitive pressure transducer, a flow controller to chamber 1, and a vacuum pump. Chamber 1 contains the transducer and is held at room temperature. Chamber 2 contains the sample and sits in a liquid  $N_2$  bath. The control program proceeds as follows.

- (1) Evacuate both chambers, then close the valve connecting them.
- (2) Admit a small amount of gas into chamber 1 (step 2). The amount of gas admitted ( $\Delta N_1$ ) can be calculated from  $V_1$ , the pressure transducer, and the ideal gas law.

$\Delta N_1 = \Delta P V_1 / (R T_1)$ , where  $\Delta P_1$  is the increase in pressure read by the transducer.

- (3) Open the valve between the two chambers. Some time (typically  $\sim 5$  min) elapses for adsorption to occur in chamber 2; the system eventually comes to equilibrium. The adsorption onto the surface removes  $N_2$  from the gas phase, lowering the pressure read by the transducer. The amount adsorbed during this step is:

$$\Delta N_2 = \Delta N_1 - P [V_1/(R T_1) + V_2/(R T_2)].$$

- (4) Then steps (2-3) are repeated until a pressure near the saturation  $P_0$  is reached. This procedure constitutes the “adsorption branch” of the cycle. For desorption, the process is reversed.

As you might guess there is a lot more complex detail than presented here (*e.g.*, the sample volume must also be accounted for, the temperature of the liquid  $N_2$  bath must be known precisely, and a non-ideality correction is usually applied). For each cycle of steps (2-3) we collect one datum of amount adsorbed (usually expressed as gas volume  $V_{ads}$ , again using the ideal gas law) vs. pressure (expressed as  $P/P_0$ ). The full collection of data at a fixed temperature is called an **adsorption isotherm** (when we are raising  $P_2$  successively) or a **desorption isotherm** (when we are lowering it).

The sample setup procedure is:

1. Weigh the plastic tube holder, sample tube, glass insert, and plastic valve that screws into the top of the tube. Then load the sample and weigh again.
2. The goal is to get at least  $20 \text{ m}^2$  of total surface area in the tube. You can look up a typical surface area range for the type of solid you are using. In other words, if you think you have an  $\sim 200 \text{ m}^2/\text{g}$  solid, you only need 100 mg. However, never use less than 50 mg no matter how high you think the surface area is.

**Commented [ASW9]:** 1) This is too much like a lab write-up. Use more general wording. 2) Write steps 1-3 (in the opening paragraphs) in our numbered list format. 3) The software steps seem specific to your system. Write them more generally.

**Commented [K10R9]:** I put them in a numbered list, but this software is NOT specific to our system. I've owned 3 of these porosimeters over the years from 3 different companies (3 out of the only 4 that make them worldwide, and all 3 follow basically the same procedures.

3. Click → File → New Sample. Then select a Method (Instructor will supply the Method).
4. Enter both weights (apparatus and apparatus + sample) into the program. Rename the sample. Load sample and O-ring into the degas port.
5. Click → Degas Conditions to adjust the degas (drying) procedure. Normally the sample is heated and evacuated to 12  $\mu\text{m}$  of Hg at a low temperature (*e.g.*, 90 °C, this is the “Evacuation Phase”). Then it is ramped to the desired final temperature (usually 300 °C for inorganic materials and carbons) and held for the desired time (the “Heating Phase”). The Instructor will show you how to modify the Degas Method parameters, if necessary.
6. Load the sample tube and O-ring into the sample port. You must push up on the tube slightly before turning the nut, so that the pin that opens the plastic valve can engage. **DON'T WIGGLE THE TUBE. HOLD IT VERTICAL. USE 2 HANDS.**
7. Use a lab jack to support the heating mantle. Put the mantle on first, then raise the jack slowly until it supports the mantles. Again, don't wiggle the bulb – hold the mantle firmly.
8. Show the degas schematic by clicking under “Degas” → “Show degas schematic”
9. Click → Unit 1 → Start Degas. Click → Browse to select your sample file(s), then Start.
10. The Degas phase is absolutely necessary in order to remove all traces of water and CO<sub>2</sub> from the sample before the adsorption experiment. N<sub>2</sub> cannot displace water and CO<sub>2</sub>! However, you can “skip” through any degas step to the next step once the desired pressure and temperature have been reached.
11. When the Degas phase reaches the “cooldown” step you should lower the heating mantle, let the sample tube cool to near room temperature (use a finger to tell), and then skip to the next step. The backfill step (fills with helium) is last and it **MUST** be completed. If it is not getting to 800 mm Hg this means the sample tube has popped down from the fitting. **You can hold it in place yourself if necessary.**
12. Wait for Degassing to complete. Weigh the sample and apparatus. Open the sample file again and edit the mass.
13. Fill a Dewar flask until near top with liquid N<sub>2</sub>.
14. Place the sample tube in the port above the Dewar flask. Remember O-ring. Put the plastic tube jacket on first, as far down as it will go. Also use the plastic insulating cover on the Dewar – put it near the sample port.
15. Click → Unit1 → Sample Analysis
16. Browse for the degassed sample file.
17. Click → Start.

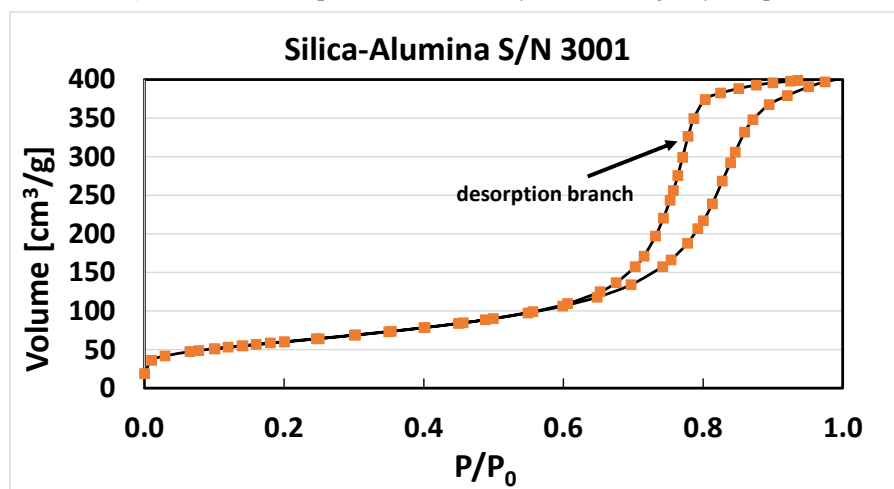
**Commented [ASW11]:** Is this best practices?

**Commented [K12R11]:** Yes, this step only takes a minute at most.

18. You only need be present for the first step – the initial evacuation. If that fails, try re-setting the tube in the port (check O-ring, re-tighten the nut). When this step completes, the rest of the experiment is totally automated but takes several hours. Results can be downloaded into an Excel spreadsheet at any later time.

## Representative Results

In the capillary condensation region the isotherm generally shows hysteresis so that the apparent equilibrium pressures observed in adsorption and desorption experiments are different (**Figure 2**). The desorption branch is always at lower fugacity and pressure.



**Figure 2.** Volume adsorbed (gas phase basis) vs. relative pressure (the **isotherm**) for N<sub>2</sub> adsorption on silica-alumina S/N 3001. The hysteresis begins at  $P/P_0 \approx 0.6$ , where capillary condensation begins to dominate the adsorption process, although the pore size distribution algorithm uses the entire isotherm. The calculated total pore volume, using the ideal gas law and the molar volume of liquid N<sub>2</sub>, is 0.63 cm<sup>3</sup>/g.

Two explanations for this effect have been proposed.<sup>1</sup> (1) During adsorption, multilayers build up on pore walls, but a complete meniscus is not formed until saturation is reached. Therefore the surface area for adsorption (the wall surfaces) exceeds that of desorption (meniscus only) in the capillary condensation region. The adsorption branch of the isotherm is therefore governed by a multilayer isotherm analogous to the BET equation, but desorption in the capillary condensation region is governed by the Kelvin equation (**Equation 3**). (2) The differences in the branches arise from a difference in the shape of the meniscus. During adsorption the pore fills radially and a cylindrical meniscus is formed. During desorption the meniscus is hemispherical and the Kelvin equation applies. By either argument, only the desorption isotherm should be used to calculate the pore size distribution in the hysteresis region, although neither argument is entirely correct. Disagreements from theory arise from deviations in the shape of the pores from simple cylindrical geometry (can look like snakes, can vary in D, or be more slit-like),

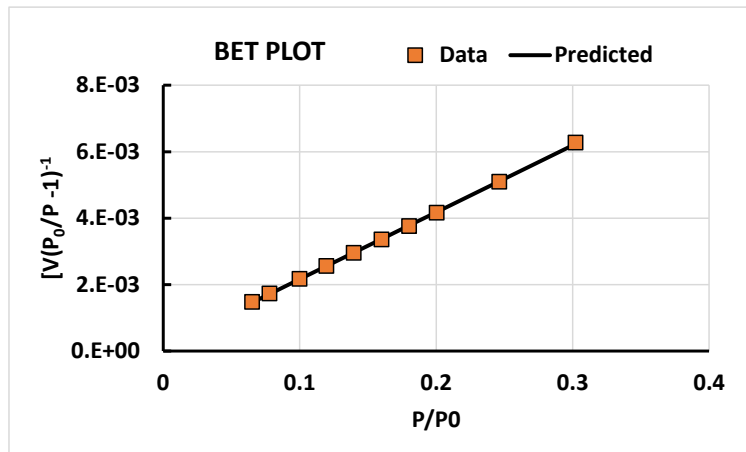
and from the fact that transmission electron microscopy and other techniques suggest that BOTH explanations are partly correct. In particular, the physics of adsorption dictates that there must be some adsorbed material in the pores, clinging to the walls even below the Kelvin  $P_v/P_0 = P/P_0$ . The space occupied by this multilayer adsorbed material must be corrected for in the Kelvin pore size calculation – this is called a “t-plot correction” in the literature. Various theoretical equations can be used to calculate this adsorbed layer thickness (=  $t$ ), as a function of  $P/P_0$ . For our system, the Halsey-Faas correction to obtain  $t$  is used automatically in the machine software, and the pore size distribution for both branches computed automatically.

The BET equation yields a straight line if plotted linearly (see **Equation 1**), to give  $V_m$  and  $c$  from the slope and intercept. The specific surface area  $A$  is found assuming the average area occupied by one molecule of adsorbate ( $a_m$ ) is known (for  $N_2$ ,  $0.1620 \text{ nm}^2$ ):<sup>4</sup>

$$A = (V_m/22,414) a_m L \cdot 10^{-18} \quad (4)$$

where  $V_m$  [=]  $\text{cm}^3/\text{g}$ ,  $A$  [=]  $\text{m}^2/\text{g}$ , and  $L$  = Avogadro’s number.

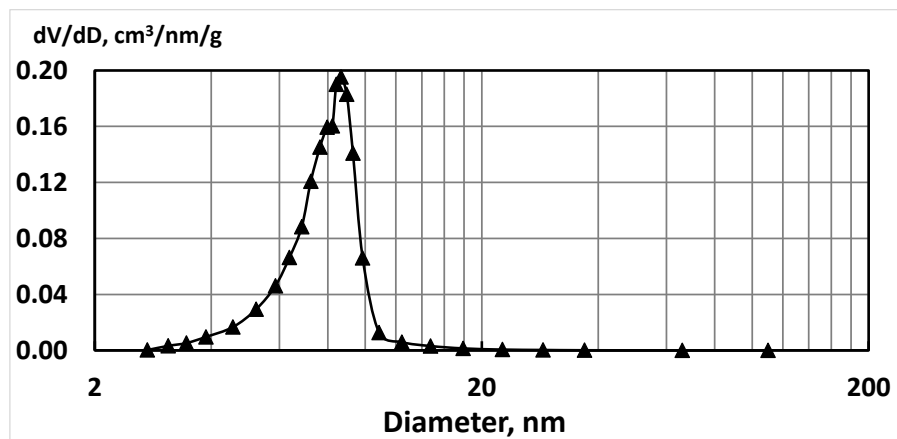
A typical BET plot (**Figure 3**) showing data and regression fit is shown below. The value of  $R^2$  (correlation coefficient) and the average relative deviation of the fit are reported. The confidence limits on the slope and intercept from the linear regression can be used to estimate the confidence limit on  $A$ , from propagation of error theory.



**Figure 3.** BET plot for sample silica-alumina S/N 3001. The regressed (predicted) values are:  $c = 139$ ,  $V_m = 49.3 \text{ cm}^3/\text{g STP}$ ,  $A = 214 \text{ m}^2/\text{g}$ ,  $R^2 = 0.9998$ ,  $ARD = 0.59\%$ .

As explained above, the exact calculation of the pore size distribution  $dV/dD$  is complex, so let the software generate it. A typical distribution for the same sample is shown in **Figure 4**. Use both the adsorption and desorption  $dV/dD$ 's to determine average pore diameter using the properties of a probability distribution. Note  $(dV/dD) \times (dD)$  is the

probability of adsorbed volume, expressed as a gas phase volume, at  $D$ . The desorption average  $D$  is always smaller than the adsorption one, as predicted by **Equation 3**, because as shown in **Figure 2** its fugacities ( $P_v$ 's,  $P_v = P$ ) at a given  $V_{ads}$  are smaller.



**Figure 4.** Calculated pore-size distribution of the data in Figure 2, desorption branch. For this sample, the average pore  $D$  from the distribution was calculated as 8.6 nm, while the cylindrical pore estimate ( $4 PV/A$ ) was 8.0 nm ( $PV$  is pore volume/mass). This is fairly good agreement, suggesting that these pores are roughly cylindrical.

## Summary

The method of measurement and calculation presented here has almost no rival. The mercury porosimetry technique is still an alternative, but its high pressures and possibility of exposure to mercury has caused its eclipse. Better pressure transducers, vacuum pumps, and software have greatly extended the utility of  $N_2$  porosimetry, and the method gives all 3 key adsorbent or catalyst morphological measurements ( $A$ , pore volume, pore size distribution) in one experiment. It can even be used to provide information on *pore shape*, as discussed below.

## Applications

(1) Quality control and lifetime determinations. Commercial catalysts and adsorbents are often manufactured to tight pore size specifications. The fastest way to determine if the correct morphology is present is to measure the pore size distribution. For example, uneven temperature control in the calcining (heat treatment) step during manufacture can greatly alter the distribution. For many catalysts, lifetimes are greatly shortened if larger pores are not present, even if the surface area is still high, because these large pores often serve as gateways for the removal of oligomeric carbon residues (“coke”) that otherwise would poison many active sites.



(2) Determination of pore shape – an example. For cylindrical pores the average pore diameter,  $D$ , should also equal  $4 \cdot PV/A$  ( $PV$  is pore volume/mass). The software reports the cylindrical estimates for both adsorption and desorption branches, and the magnitude of their differences from the average diameters calculated from the distributions themselves gives an idea of the porous material's deviation from perfectly cylindrical pores. Some solids have pores that are slit-like, with a critical short dimension ( $h$ ) analogous to the diameter of  $2 \cdot PV/A$  for very long and wide slit pores, and then determine if the porous solid is more slit-like, comparing the different branch estimates to more exact values generated from the probability distributions. If both cylindrical and slit estimates are significantly in error, what could this mean? Similar calculations could be done to test for other pore shapes.

(3) Application to materials other than typical catalysts and adsorbents. The same instrument used here is easily adapted to measure surface areas as low as  $0.01 \text{ m}^2/\text{g}$  (*e.g.*, in concretes, although  $\text{Kr}$  or  $\text{Xe}$  are used instead of  $\text{N}_2$ ) and pore sizes below  $1 \text{ nm}$  (*e.g.*, in zeolites, although  $\text{Ar}$  is used and special procedures necessary).<sup>6</sup> While it is true that zeolites are important catalysts and commercial adsorbents, their primary use is in detergents, where they can bind almost all the grime removed from laundry.

(4) Pharmaceutical applications. The morphological properties of tableting materials such as excipients (lubricants) and binders are extremely important in controlling the pill tableting process and controlling the dissolution and degradation of the outer shell to ensure controlled release of the active pharma ingredient *in vivo*.<sup>7</sup>

## Legend

**Figure 1. Brunauer's classification of adsorption isotherms.** Type I is Langmuir. Types III and V are "swelling" isotherms often found with polymeric adsorbents.

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Commented [K14R13]: It is correct.

**Figure 2. Volume adsorbed (gas phase basis) vs. relative pressure (the isotherm) for  $\text{N}_2$  adsorption on silica-alumina S/N 3001.** The hysteresis begins at  $P/P_0 = \sim 0.6$ , where capillary condensation begins to dominate the adsorption process, although the pore size distribution algorithm uses the entire isotherm. The calculated total pore volume, using the ideal gas law and the molar volume of liquid  $\text{N}_2$ , is  $0.63 \text{ cm}^3/\text{g}$ .

**Figure 3. BET plot for sample silica-alumina S/N 3001.** The regressed (predicted) values are:  $c = 139$ ,  $V_m = 49.3 \text{ cm}^3/\text{g STP}$ ,  $A = 214 \text{ m}^2/\text{g}$ ,  $R^2 = 0.9998$ ,  $\text{ARD} = 0.59\%$ .

**Figure 4. Calculated pore-size distribution of the data in Figure 2, desorption branch.** For this sample, the average pore  $D$  from the distribution was calculated as  $8.6 \text{ nm}$ , while the cylindrical pore estimate ( $4 PV/A$ ) was  $8.0 \text{ nm}$  ( $PV$  is pore volume/mass). This is fairly good agreement, suggesting that these pores are roughly cylindrical.

## References

<sup>1</sup>For almost everything on this subject, the best references are: S.J. Gregg and K.S.W. Sing, *Adsorption, Surface Area, & Porosity*, 2nd Ed., Academic, 1982, and D. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.

<sup>2</sup><http://www.nottingham.ac.uk/~eczehl/catalysis/isotherms.htm>

<sup>3</sup>The original reference is: S. Brunauer, P.H. Emmett, and E. Teller. *J. Amer. Chem. Soc.*, 60, 309-319 (1938). A good summary of the technique can be found at: <http://particle.dk/methods-analytical-laboratory/surface-area-bet-2/>. The derivation can also be found in Gregg and Sing.

<sup>4</sup>The value of  $a_m$  for an adsorbate other than  $N_2$  can be estimated assuming close packing of spherical molecules at the van der Waals diameter. The  $a_m$  is close to  $(\rho_M L)^{-2/3}$  for nonpolar adsorbates, where  $\rho_M$  is the molar density. There is a good discussion of this in ref. 1. To use the estimating equation there is a correction factor, which also corrects the units to per molecule in the denominator. For  $N_2$  the correction factor is  $\sim 1.09/\text{molecule}^{1/3}$ .

<sup>5</sup>A good discussion of the concept of propagation of errors in experimental work is by V. Lindberg: <http://www.rit.edu/~w-uphysi/uncertainties/Uncertaintiespart2.html>, or at <http://www.itl.nist.gov/div898/handbook/mpc/section5/mpc55.htm>, both accessed 9/23/16.

<sup>6</sup>[http://www.micromeritics.com/Repository/Files/ap139\\_0.pdf](http://www.micromeritics.com/Repository/Files/ap139_0.pdf)

<sup>7</sup><http://www.micromeritics.com/Repository/Files/ap87.pdf> and [http://www.micromeritics.com/Repository/Files/Application\\_Note\\_153.pdf](http://www.micromeritics.com/Repository/Files/Application_Note_153.pdf)

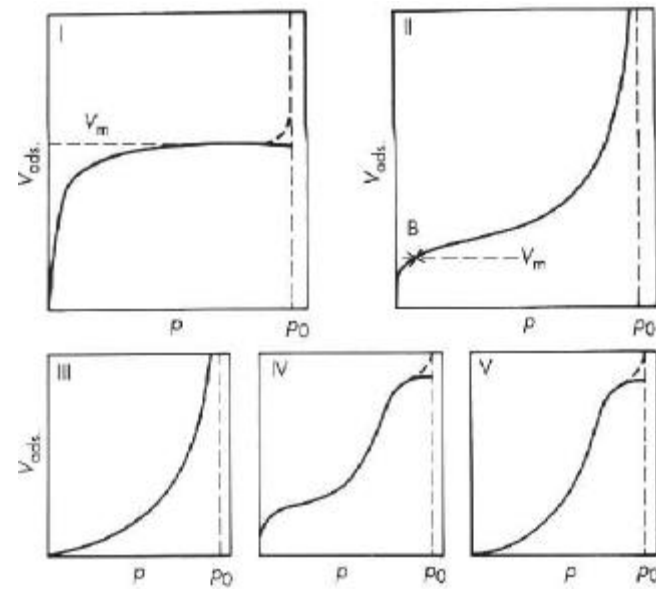


Figure 1

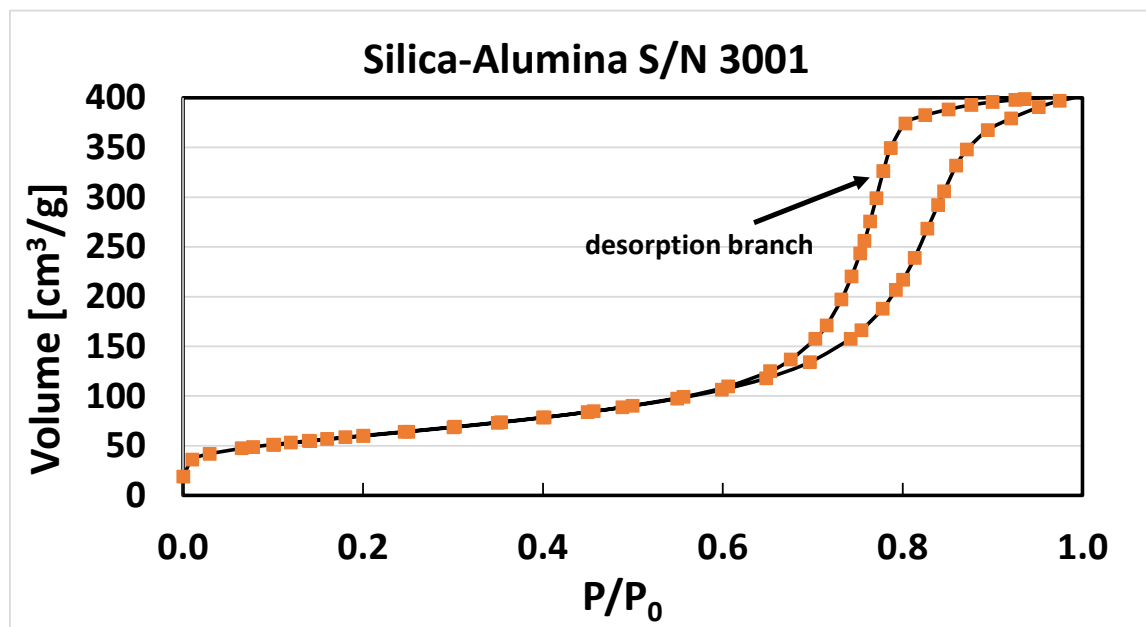


Figure 2

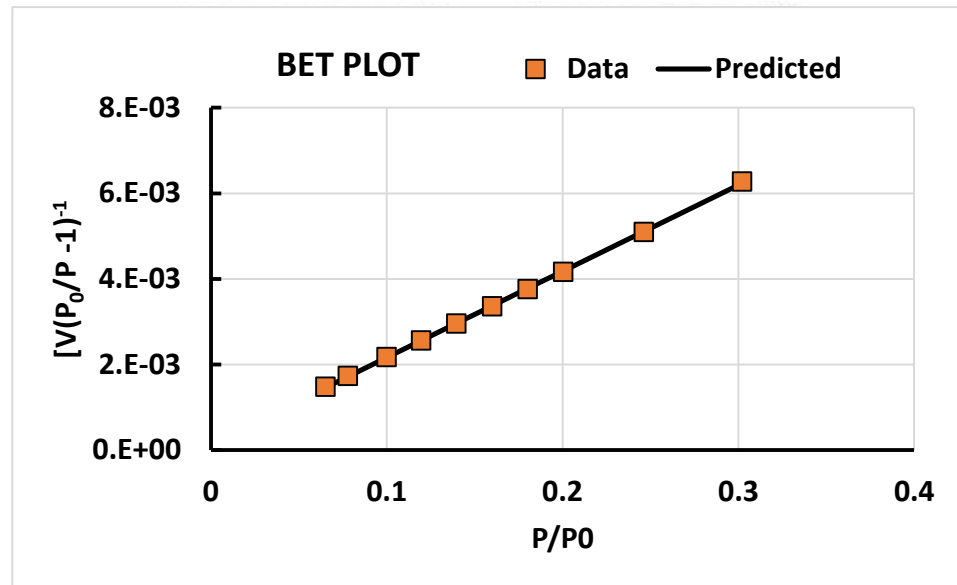


Figure 3

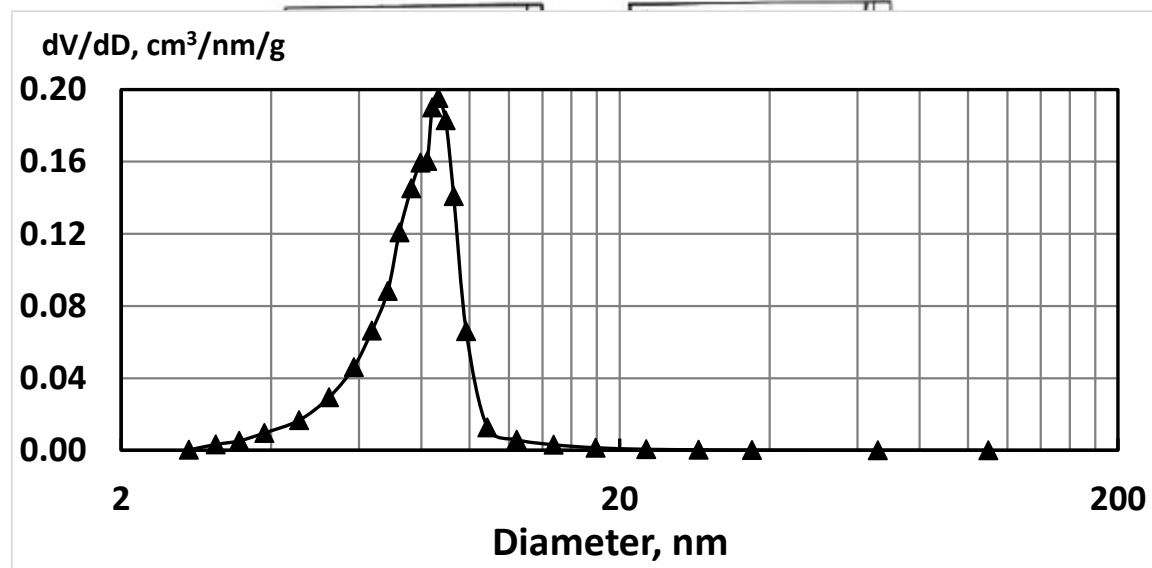


Figure 4