Evaluation of Surface Area and Porosity Utilizing Physisorption Isotherms: Nonporous Materials.

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Physical sorption can be presented as a function of: 1. Relative pressure (isotherms); 2. Logarithm of relative pressure (Characteristic curve); or 3. AutoShielding Potential (ASP ---- Logarithm of Polanyi sorption potential). For nonporous materials the general shape of these curves are sigmoidal, exponential and linear, respectively, with an enhanced sorption component for interparticulate condensation (IPC) in the pressure region where capillary condensation occurs.

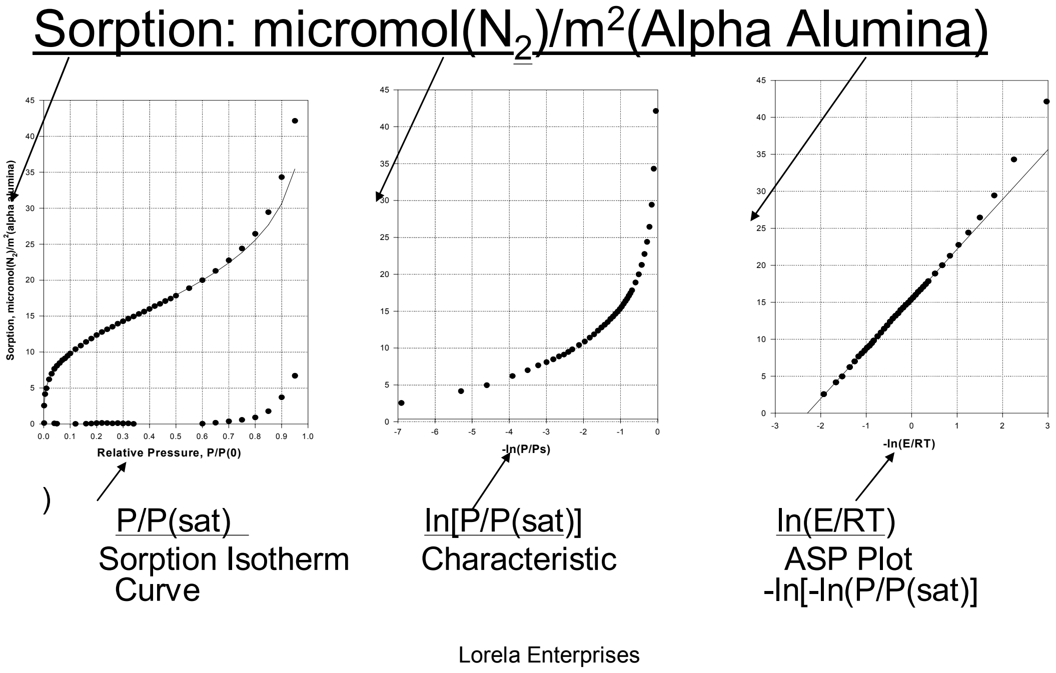

Figure 1. Alternative presentations of sorption isotherm data for nitrogen sorption on alpha alumina standard at 77 K.. Left: adsorption isotherm with relative pressure ordinate, lower curve defines the capillary condensation. Center: Same data with natural logarithm ordinate. Right: Same data with natural logarithm of Polanyi Potential as ordinate.

Graphical presentations show the merits of the alternate methods of analyses for *Nitrogen sorption on alpha alumina at 77K: Phys. Chem. Chem. Phys.* <u>*3*</u> *5078(2001)* ASP plots for physisorption on known homogenous nonporous materials indeed are rectilinear for multilayer coverage. The ASP assumes that there is a finite sorption potential for the first sorption increment followed by the decrease exponential decrease to zero at saturation pressure. Intermolecular condensation becomes more prominent for greater specific surface areas (smaller particle size, more interparticulate voids). The ASP plot slope = monolayer capacity (6.734 μmol/m^2, based on BET) and Intercept = threshold sorption potential (1501 cal/mol, or P= 5.14e^{-5} P(0)) fitted to the data with a correlation coefficient of 0.9997. The lower isotherm curve is the excess ICP, over and above the extrapolation prediction based on ASP. These ASP parameters would serve well as a method of calculating a reference (t. n, α_s. etc) isotherm, although it is more informative to plot the sorption in the ASP format directly and attribute additional effects to micropores, mesopores, chemisorption, morphology, surface chemistry, etc. One is hard put to assure that the reference isotherm has the same surface chemistry and structure.

By comparison, the BET methodology is considerably less definitive since, although it is referred to as a multilayer theory, it:

- is only applicable in a restricted range (0.05-0.35P(0)), ca 0.8 to 1.2 monolayers
- does not quantitatively delineate the amount and mechanism of the inevitable IPC
- does not give an estimate of the threshold sorption energy (pressure),

Introduction

Classically, sigmoidal shaped physisorption isotherms depict the amount of sorbate associated with the surface of a solid sorbent. If indeed the sorbent is nonporous, the monolayer is formed at low pressure and is normally assumed to be completed near 0.1 saturation pressure, P(sat). The physisorption curves have a smaller slope to ca. 0.04 P(sat) inflection which is followed by an exponential rise to 1.0 P(sat) as shown in Figure 1 (left). The mathematical analyses for this type of behaviour is extensive and is varied. A comprehensive review is available in reference 2. At present, the BET "Multilayer" equation is used most often to obtain numerical values for monolayer capacities even though it is only applicable in the "BET region"[3] of 0.5 to .35 P(sat) --- 0.8 to 1.2 monolayers, θ. This is questionable methodology for quantitative definition of multilayer phenomena at higher pressures where capillary condensation of liquid sorbate is an important contribution in addition to multilayer formation. .

An alternative paradigm is available based on thermodynamics of the sorption processes. "A still different approach to multilayer adsorption considers that there is a potential field at the surface of a solid into which adsorbate molcules 'fall".[4] This potential field is equal to the reversible work required to change the system pressure from that of the saturated sorbate liquid, P(sat), to that of the equilibrated system, P:

$$E = -RT\ln\left[\frac{P}{P(sat)}\right] \qquad \textbf{Equation 1}$$

The initial sorption potential has a finite magnitude, E(0) =(-RTln {P(0)/P(sat)} and is shielded by the presence of preadsorbed species:[5]

$$E = E(0)\exp\frac{-\Gamma}{\Gamma(m)} = E(0)\exp(-\theta) \qquad \textbf{Equation 2}$$

Data analyses utilize the natural logarithmic form

$$\Gamma = \Gamma(m)\,\{\ln[E(0)/RT] - \ln[E/RT]\} \qquad \textbf{Equation 3}$$

Such a plot is noted in Figure 1, right and the two relavent parameters are for nitrogen sorption on the standard alpha alumina

$$\text{Slope} = \Gamma(m) \qquad \textbf{Equation 4}$$

And

$$\text{Intercept} = \ln[E(0)/RT) \qquad \textbf{Equation 5}$$

These graphical define the multilayer formation and note capillary condensation as pressures approach that of the liquid bulk phase at this temperature. Young and Laplace analyses have shown that the principle radii of clurvature are well defined and applications have been made to interparticulate condensation in beds of particles in the higher pressure, 0.5 to 1.0 P(sat), realm. [6] In general the effective radius of curvature is related to the sorption potential: [7]

$$r(eff) = k/\ln[P/P(sat)] = k\,(E/RT)^{-1} \qquad \textbf{Equation 6}$$

with k depending on the geometry of the interparticulate void. There is a fractal dimension relationship between the amount (volume) adsorbed and the effective radius as measured by equation 6;

$$\text{Pore Volume}\ \alpha\ \Gamma(cond)\ \alpha\ r(eff)^{D} \qquad \textbf{Equation 7}$$

This fractal dimension, D, should be near unity, if indeed all of the mesopores exist as voids emanating from point contacts. If a plot of Γ(cond) versus $(E/RT)^{-1}$ is linear, one can be reasonably assured that there is minimal convolution of the surfaces. [6]

Results

In the sequence of Figure 1, the extensive abcissa is expressed in pressure, logarithm of pressure, and logarithm of the sorption potential. These plots show more linearity and define the intercept associated with E(0), As instrumentation and techniques have improved, more investigators have begun to study the low pressure region which is emphasised in the "Characteristic Curves" [6] (logarithmic plots akin to Figure 1). These curved plots become quite rectilinear when presented in the ASP format. With excessive interparticulate pore condensation occurring exponetially as the system pressure approaches the liquidus where (P/P(sat) =1, -ln(P/P(sat) = zero, and –ln(E/RT) = infinity. Note that the ordinate is linear and unchanged in the computational sequence presented here.

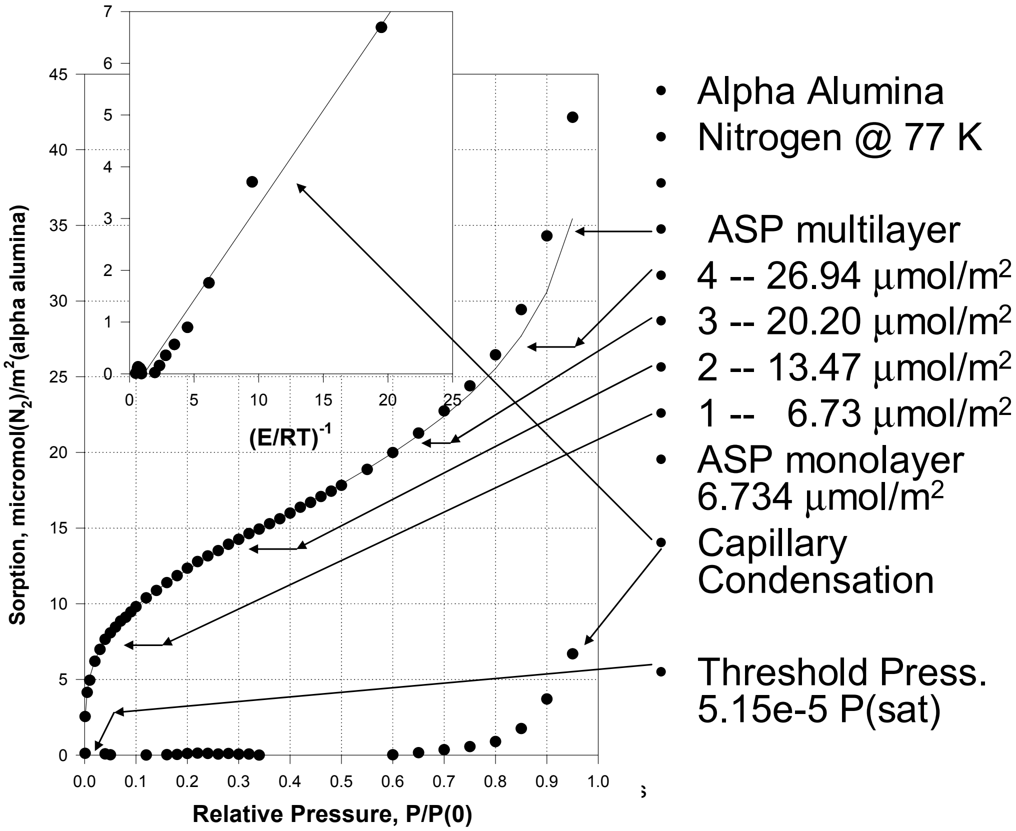

Figure 2. Nitrogen Sorption Isotherm for Alpha Alumina Standard Material.

At this writing it is informative to show the details of the analyes to evaluate sorption on this nonporous material. Figure 2 shows the details of the isotherm plot, where the monolayer capacity and energy (pressure) threshold were evaluated from the ASP plot (Figure 3) where the linearity is noted in the presentation. The line of Figure 2 is based on the slope and intercept parameters of the ASP plot (Figure 3). The excess sorption, over and above that of the extrapolated ASP calculation, is attributed to IPC and is shown in the inserted graph with respect to the effective radius expressed in free energy terms. The linearity is evident and the intercept corresponds well to the statistical limiting size where the thermodynamic treatment is not valid.

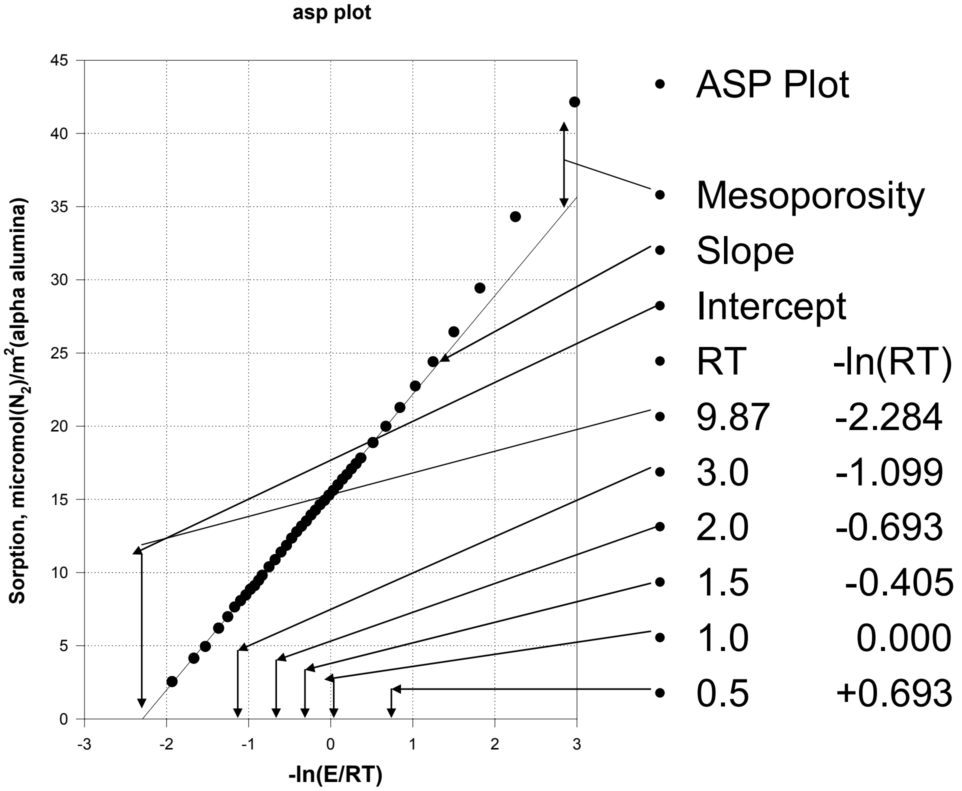

Figure 3. Nitrogen ASP Plot for Alpha Alumina Reference Material

The ASP plot Figure 3 shows a small linear extrapolation to the intercept, followed by the linear multilayer range

$$9.87\ RT < E < 0.5\ RT \qquad \text{Equation 8}$$

Which is indeed in the domain of physical adsorption involving only the weak dispersion forces. [3,4] The low coverage extrapolation may be tentative because it covers the realm where micropore filling, chemisorption, surface defect, etc. can occur. Most sorption systems do not achieve the base vacuum required to obtain data at this low coverage. The slope (6.734 µmol(N2)/g(alpha alumina)) was calculated by a linear least squares analyses of the ASP data with correlation $r^2 = 0.9997$. The adherence to the ASP paradigm is noted in the calculated curve of Figure 2 that defines the sorption isotherm very well for the first three monolayers:

$$5.15 \times 10^{-5}\ P(sat) > P/P(sat) > 0.6065\ P(sat) \qquad \text{Equation 9}$$

Note that the excess sorption, over and above that calculated by the linear extrapolation, occurs at very low energy (<< 0.5 RT), verifyng that both the multilayer and IPC sorbate are virtually structurally identical to the liquid nitrogen at this temperature. This condensation is linearly related to the effective radius, in terms of sorption potential, as shown in the insert of Figure 1. The linearity of this plot is a result of the low degree of convolution of these packing voids emanating from point contacts[6] between the particles in the sample holder. Compaction of the sample would lead to closed pores and limited sorption at the very high pressures, P(sat).
The transition region is obvious in Figure 2 and lends credence to the choice of 0.4 P(sat) or 1.0 monolayers for normalization factors for the α_s and θ (n) plots

Comparative Plots?

Many investigators have used comparative plots (n, θ, t, α_s, etc.) to compare sorption on an experimental sample to that of a nonporous material of similar or identical surface chemical composition. [2] Ostensibly any differences would be attributable to porosity and/or chemisorption. The transition region is obvious in Figure 2 and lends credence to the choice of 0.4 P(sat) or 1.0 monolayers for normalization factors for the α_s plots. In view of the ASP analyses for this and other nonporous materials, the intermediate step to comparison plots seem somewhat of a waste of time and resources. Indeed, a direct ASP plot of sorption data for porous materials is just as informative, as will be shown in Part 2 that will be offered as a poster presentation today, E. Loren Fuller Jr. *Evaluation of Surface Area and Porosity Utilizing Physisorption Isotherms: Porous Materials* ,

Engineering Aspects

Energy and mass balance calculations are more easily evaluated by the conventional presentation such as that shown in Figure 4. This is naught but a reversal of coordinates of Figure 3 and shows the high energy of adsorption at very low coverage varying exponentially with coverage to the lesser energy in the region of IPC.

References

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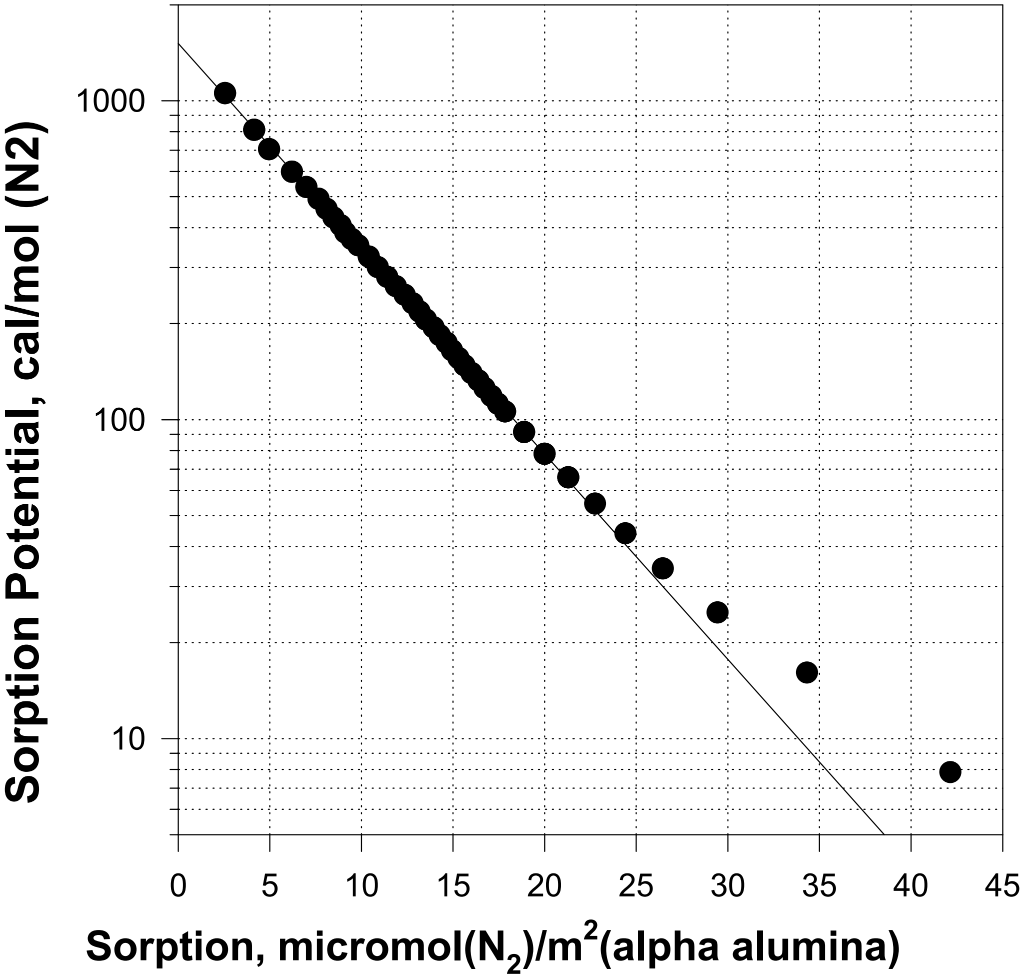

Figure 4 Nitrogen Sorption Potential for Nitrogen on Nonporous Alpha Alumina.

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