QM-Based Calculations of Porosity

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Abstract:

Calculation of surface areas and pore sizes have been successfully performed using the quantum mechanical formulation referred to as chi theory. The modification which allows the accurate calculation of the surface area is the introduction of the van der Waal excluded area into the calculation as opposed to the simple molecular radius and the introduction of the QM symmetry rules into the probability in the grand canonical partition function. A small correction from the hard sphere approximation using a Lennard-Jones 6-12 potential is also introduced. The results of the calculation are very accurate for the pore data available (from d = 2 to 4 nm).

This, along with previous successes of the theory, is very strong evidence for the accuracy of chi theory. It is a generalized theory for any adsorbate and adsorbent and completely characterizes the surface of fine powders with respect to the surface area, pore size, pore size distribution, surface energy, energy distribution, and covers the entire isotherm. Atomic details and parameters, such as those required for DFT, are not needed. The only input parameters are sample temperature and boiling point and liquid density of the adsorbate.

1. Introduction:

The chi theory of physical adsorption has had several successes as recorded in the literature. Included in these successes are:

- The analytical expression which fits within experimental error most of the known standard curves, especially for adsorbents which are of a simple nature such as silica, alumina, thoria[1 ,2], Polytetrafluoroethylene[3], etc.
- The derivation of the Dubinin types of isotherms and the Tóth isotherms.[4, 5]
- Confirmed calculations of the isosteric or heats of adsorption from the isotherm over the entire range of the isotherm.[6]
- Isotherm fits for the entire range of the isotherm without parameters.[1]
- Calculations of microporosity.[7]
- Prediction[8] and discovery[9] of the threshold phenomenon.

The questions remaining are whether the calculation can accurately measure the surface area and if the porosity calculation in the mesopore range is also accurate. Confirming both of these is difficult because one needs independent measurement of these physical quantities in order to make a confirmation. Measurements on non-porous and macroporous surfaces seemed to yield the right answer, but there has always been the uncertainty about the surface roughness. For mesoporous samples, independent measurements of the pore sizes are difficult to find. However, with such measurements of pore sizes, one can confirm both the surface area question and the porosity question as well. This is the goal of this presentation and the future challenge is to find more data against which to test the theory.

2. Background - Chi Theory:

Conceptually, chi theory is very simple. It assumes that the surface acts as a potential well for the adsorbate molecules. The first adsorbate on the surface is like a single "particle-in-the-box". The second particle acts similarly but sometimes "sees" the other particle as a "tooth" of lower potential. For the second particle, this will happen half the time it encounters the first particle, but the same scenario holds for the first particle. The third adsorbate is a particle that now could "see" two "teeth", one "tooth", or none to yield the permutations. Continuing this process, it is easy to show that these permutations lead to the expression:

$$C = \frac{\sum_{M=2}^{N} M \frac{N!}{M!(N-M)!}}{\sum_{M=2}^{N} \frac{N!}{M!(N-M)!}} \approx \frac{N}{2} \qquad \textbf{(1)}$$

where N is the number of adsorbate molecules. The area of each "tooth" is approximately the van der Waal excluded area (modified by the considerations below) which is 4 times the molecular area in the liquid phase. It is easy to show that if the thermal wave length is considerably less than the size of a perturbation, such as the "tooth" being referred to here, and if one holds the wave number constant, the energy becomes a area weighted average of the potentials of the perturbed and unperturbed portions. This leads to the following grand canonical ensemble for a surface with only one surface energy:

$$\Xi = \sum_{N} (\lambda z)^{N} e^{-\frac{\sum_{M=0}^{N} E_a e^{-\frac{M a_{ex}}{2 A_s}} + \varepsilon N + NkT + \frac{1}{2} NkT \left(1 - e^{-\frac{N a_{ex}}{2 A_s}}\right) + N f(T)}{kT}} \qquad \textbf{(2)}$$

Where A_s is the surface area and E_a the energy between an adsorbate molecule and the adsorbent surface.

The following operations are performed to yield the simple chi equation:

- the inner sum is replaced by an integral,
- the most likely Ξ is found by setting ∂(max term ln Ξ)/∂N to zero,
- the small exponential term outside the inner sum is combined with the term containing E_a,
- **f**(T), which is due to differences in heat capacity from the bulk liquid to the adsorbed phase, is recognized as very small and that $\partial\mathbf{f}/\partial N$ is even smaller and both are therefore ignored,
- it is recognized that negative Ns are not allowed, and
- the limit as P approaches P_s, the saturated vapor pressure, yields the bulk liquid.

After these operations one obtains:

$$\frac{Na_{ex}}{2A_s} = \Delta\chi\,\mathrm{U}(\Delta\chi) \tag{3}$$

Where **U** is the unit step (Heaviside) function and:

$$\Delta\chi = \chi - \chi_c \tag{4}$$

where:

$$\chi = -\ln\left[-\ln\left(P/P_s\right)\right] \quad \text{and} \quad \chi_c = -\ln\left(E_a/kT\right) \tag{5}$$

The question then becomes, "what is a_{ex}?" That is, what is the area of the surface that each molecule excludes from other molecules, provided the other molecular wave function is above the molecule in question? This area would be the van der Waal area if the molecules behaved as hard spheres. In terms of the liquid molar volume, V_m, this hard sphere area, a_{hs}, would be:

$$a_{hs} = 4\,(V_m)^{2/3}\,(N_A)^{-2/3} \tag{6}$$

(from the liquid the molar area, A_m, which is:

$$A_m = (V_m)^{2/3}\,(N_A)^{1/3} \qquad) \tag{7}$$

However, this assumes that the potential is suddenly discontinuous as a test molecule travels from the bare surface over the adsorbed molecule. This may be modified by the following treatment.

A Lennard-Jones 6-12 potential is assumed for both the adsorbate and the surface atoms. Since the adsorbate molecules are free to travel over the surface, the 6-12 potential is considered a uniform average in the parallel plane of the surface. By referring to Fig. 1 the following geometrical arguments may be made.

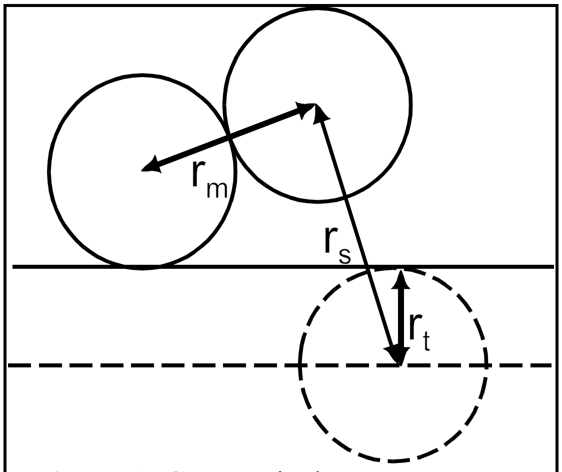

Figure 1 Geometrical arrangement to calculate the potential seen by a adsorbate molecule passing over another adsorbate molecule.

The L-J potential has a distance, r_o, designated in the 6-12 equation by:

$$E = 4\varepsilon\left[\left(\frac{r_o}{\mathbf{r}}\right)^{12} - \left(\frac{r_o}{\mathbf{r}}\right)^{6}\right] \tag{8}$$

and is related to the other r values by:

$$r_0 = 2^{-1/6}\left(r_m + 2r_t\right) \tag{9}$$

where r_m is the center-to-center distance between adsorbate molecules and r_t is the radius of the immobile surface atom or ion, that is, center-to-edge.

By simple geometry from Fig. 1 the distance between the average surface molecule or ion and the molecule that is rolling over is:

$$r_s = \frac{r_m\left(\sqrt{r_m^2 - r^2} + \tfrac{1}{2}r_m + r_t\right)}{r} \tag{10}$$

Where *r* is the distance between centers in the plane of the surface. Using this, the effective fraction of the excluded area compared to the hard sphere ratio, *s*, may be calculated from the expression:

$$s = \frac{\int_0^{r_m} 4\varepsilon\left[\left(\frac{r_o}{r_s}\right)^{12} - \left(\frac{r_o}{r_s}\right)^{6}\right](2\pi r)\,dr}{\int_0^{r_m} E(2\pi r)\,dr} \tag{11}$$

Making the appropriate substitution for r_s and evaluating numerically *s* is given as:

$$s = -0.0967\frac{r_t}{r_m} + 0.9653 \tag{12}$$

Defining a factor $f = 2s$ it follows that since $a_{ex} = sa_{hs}$ Eq. **(2)** becomes:

$$\frac{nfA_m}{A_s} = \Delta\chi\,\mathrm{U}(\Delta\chi) \tag{13}$$

The ratio of r_t to r_m is always greater than 0 and is unlikely to be greater that 0.5. Therefore the reasonable range for *f* is from 1.83 to 1.93. This value is independent of the value for E_a or the adsorbate intermolecular force. It depends upon the ratio of radii but not upon the absolute values of the individual radii.

3. Capillary Filling and the Kelvin Equation.

The capillary filling equation theory, that is the Kelvin equation as modified by Cohen[10], can be expressed for cylindrical pores as:

$$-\ln\left(\frac{P}{P_s}\right)=\frac{2\gamma}{RTr_c} \qquad \textbf{(14)}$$

with γ = the surface tension of the liquid adsorptive, r_c = the core radius, which is the pore radius, r_p, minus the "thickness" of the adsorbed layer, t. In light of chi theory this is modified to:

$$\mathrm{e}^{-\chi_p}=\frac{2\gamma V_m}{RT(r_p-t)} \qquad \textbf{(15)}$$

Here the χ_p is the value of χ at which the capillary filling takes place. (In the case of a distribution of pores it will be the mean value.) The value of t is obtainable by using the difference between χ_p and χ_c, or $\Delta\chi_p = \chi_p - \chi_c$, since this would be related to the overall thickness by:

$$t=\frac{\Delta\chi_p V_m}{fA_m} \qquad \textbf{(16)}$$

Thus, for r_p:

$$r_p=\frac{2\gamma V_m}{RT\,\mathrm{e}^{-\chi_p}}+\frac{\Delta\chi_p V_m}{fA_m} \qquad \textbf{(17)}$$

For d then, $d = 2r_p$.

4. Method of analysis

Fig. 2 (data by Krug and Jaroniec[11]) illustrates the parameters to extract from the χ plot (a plot of n adsorbed versus χ value). The analysis using the chi theory is similar to that used for standard curves such as the α-s[12, 13] except a standard from a similar non-porous material is not necessary. The following symbols apply to this analysis:

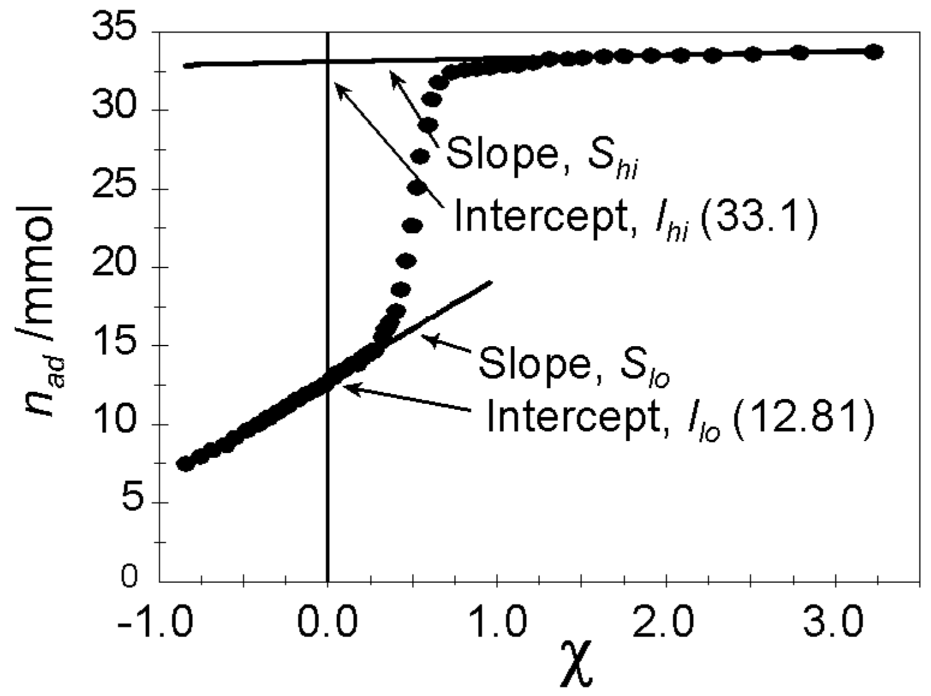

Figure 2 Preliminary parameters obtained from the isotherm to analyze surface area and porosity. Data by Krug and Jaroniec[10]

A_p = surface area inside pores
A_w = surface area of outside walls
A_o = area of pores openings
V_p = total pore volume

Then:

$$S_{lo} = \frac{\left(A_p + A_w\right)}{fA_m} \tag{18}$$

and:

$$S_{hi} = \frac{A_{ex}}{fA_m} = \frac{\left(A_o + A_w\right)}{fA_m} \tag{19}$$

The value of χ_c is required to make the subsequent calculations, this is given by:

$$\chi_c = -\frac{I_{lo}}{S_{lo}} \tag{20}$$

The pore volume is then:

$$V_p = V_m \left(S_{hi}\chi_c + I_{hi} \right) \tag{21}$$

If $A_w << A_p$ then A_p can be obtained from Eq. **(18)** directly otherwise it is true that:

$$A_p \leq f A_m S_{lo} \tag{22}$$

These consideration may be used to make one of the estimates of the pore pore diameter, *d*. From the determined values:

$$d \geq \frac{2V_m \left(S_{hi} + I_{hi} \right)}{f A_m S_{lo}} \tag{23}$$

This is one estimate of the average pore diameter. The other estimate, the modified Kelvin equation, yields the diameter along with the pore size distribution. For the data analyzed here this distribution is assumed to be a normal distribution in χ. A more detailed analysis does not seem justified by the number of data points in the transition zone.

5. Modified Kelvin Equation Analysis

Eq. **(14)** along with the chi equations leads to a pore radius as given in Eq. **(17)**. This equation is specifically dependent upon χ and therefore any positive deviation from the straight projected line in the chi plot can be interpreted as capillary filling. Initially, a probability normal mass function (PMF) in χ is assumed. To go beyond this assumption is in principle not difficult but for the data presented here does not seem justified. The PMF, **P**, is:

$$\mathbf{P}(\chi) = \frac{\mathbf{e}^{-\left(\chi-\chi_p\right)^2 / 2\sigma^2}}{\sqrt{2\pi\sigma^2}} \tag{24}$$

Where σ is the standard deviation in the pore size distribution. A method of successive approximations is used to obtain χ_p and σ. Using an initial estimate for χ_p and setting σ to a very low value, a probe value for the fit to the isotherm data, η_j, is created from the equation:

$$\eta_j = \mathbf{P}\left(\chi_j - \chi_p\right) + \sum_{i=2}^{j}\left[\left(\chi_i - \chi_{i-1}\right)\left(S_{lo} - S_{hi}\right)\left(1 - \mathbf{P}\left(\chi_i - \chi_p\right)\right)\right] \tag{25}$$

A new value of χ_p is calculated from a weighted average of χ using the square of the difference as the weighting factor. That is:

$$\chi_p = \frac{\sum_{i=k}^{l} \chi_i \left(n_{ad,i} - \eta_i\right)^2}{\sum_{i=k}^{l} \left(n_{ad,i} - \eta_i\right)^2} \tag{26}$$

Using this new χ_p, new estimates are made for η. This is repeated until convergence is satisfactory. If the fit at both sides of the transition had similar data scatter, the above method would work very well. However, there are different numbers of data points on two sides of the transition which weigh into the summations. To avoid this problem, it is best to select data points that are judged to be in the transition zone, along with roughly a few additional data points on either side of the transition.

The value of σ is obtained by a similar successive approximations method.

$$\sigma_{new} = \sigma_{previous} + \nu \sum_{i=k}^{l} \operatorname{sign}\left(\chi_i - \chi_p\right)\left(n_{ad,i} - \eta_i\right) \tag{27}$$

Where ν is a factor set for the sensitivity of the convergent. It should be set small enough to avoid oscillations between approximations. (In place of the function behind the "Σ" one could use other functions to provide convergence such as "$(n_{ad,i} - \eta_i)^3$". However, this latter function seems to be considerably less stable.)

6. Surface Area and Pore Analysis Results:

In order to test the methodology of this treatment original data is required. Dr. S. Z. Qiao*[14] kindly supplied data from nitrogen adsorption experiments to be used for testing this method. The data, obtained on MCM-41 type zeolites, had the advantage that X-ray data was available

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Table 1 - Analysis of MCM-41 zeolites by the chi theory method.

Sample designator	X-ray d_{100} /nm	d_{max} from A_s and V_p /nm	d by pore filling /nm	σ of the pore size /nm
C-10 adsorb	2.866	2.00	1.95	0.36
C-12 adsorb	3.246	2.84	2.61	0.19
C-14 adsorb	3.560	3.21	2.76	0.21
C-16 adsorb	3.872	3.15	2.89	0.23
C-18 adsorb	4.244	3.80	3.25	0.22
C-22 adsorb	4.877	3.83	4.13	0.18
C-10 desorb	2.866	2.00	1.92	0.42
C-12 desorb	3.246	2.79	2.52	0.23
C-14 desorb	3.560	3.17	2.79	0.16
C-16 desorb	3.872	3.32	3.02	0.12
C-18 desorb	4.244	3.77	3.27	0.26
C-22 desorb	4.877	3.61	3.92	0.18

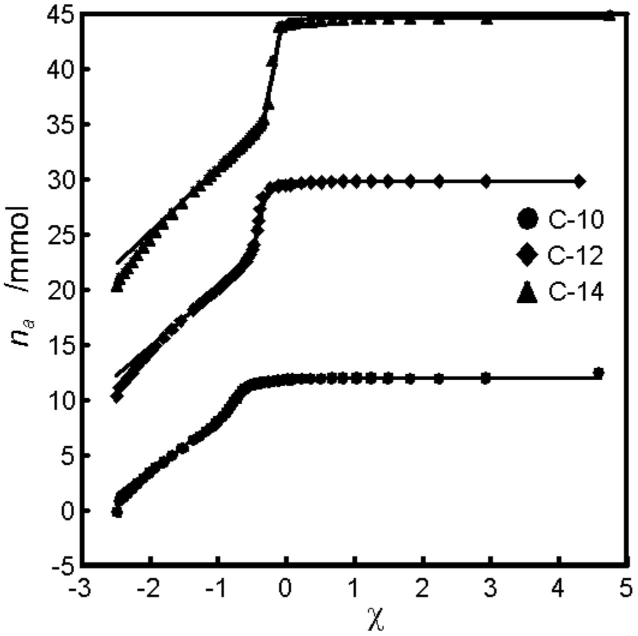

Figure 3 Chi theory fit for the adsorption of N_2 on MCM-41 zeolites. See Table 1 for sizes of samples C-10, C-12 and C-14.

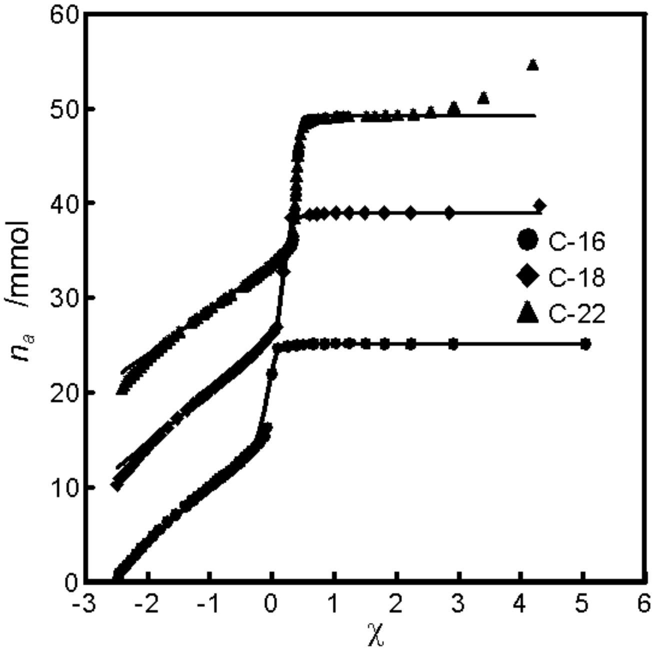

Figure 4 Chi theory fit for the adsorption of N_2 on MCM-41 zeolites. See Table 1 for sizes of samples C-16, C-18 and C-22.

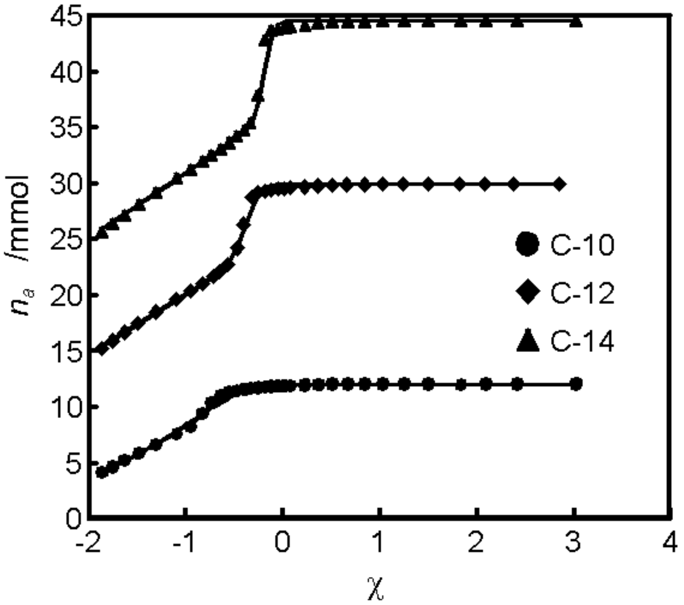

Figure 5 Chi theory fit for the desorption of N_2 on MCM-41 zeolites. See Table 1 for sizes of samples C-10, C-12 and C-14.

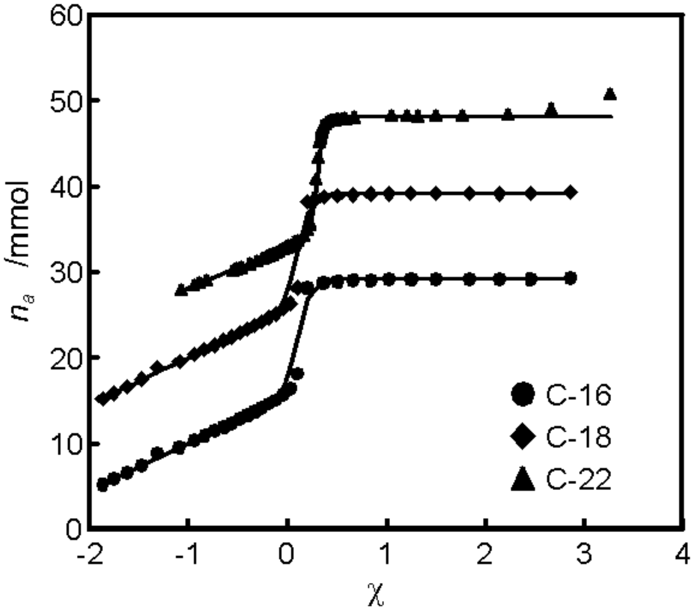

Figure 6 Chi theory fit for the desorption of N_2 on MCM-41 zeolites. See Table 1 for sizes of samples C-16, C-18 and C-22.

for determination of the pore diameters. In Figs. 3 through 6 are the fits determined for the isotherms. A summary of the results of the calculation is given in Table 1.

The data are consistent with the normally accepted wall thickness of 0.80 nm for these materials. For all the samples except the C-22 samples the *d* calculated from Eq. **(22)** are greater than the *d* calculated from Eq. **(17)** as expected. The pore size distribution is given as a normal distribution in χ, however for the values of χ_p observed this is very nearly a normal distribution in pore size as well. Therefore, the σ shown in table 1 is in terms of pore diameter with dimensions of nanometers.

7. Discussion

This investigation along with the previous successes are strong evidence that the chi theory is correct. As listed in the introduction, these include fits to the entire isotherm, especially standard isotherms, parameter-free calculations of the heats of adsorption, demonstration of the identity to the Dubinin class of equations and Tóth isotherm and fits for microporosity. (There is some question as to whether the microporosity calculations are correct and probably they need to be corrected with the factor *f* as well.) The prediction of the threshold phenomenon[7] and its confirmation with lunar soils[8] and Polytetrafluoroethylene[3] is further evidence. This latter phenomenon is predicted <u>not</u> to be present by all other theories of adsorption. The present work adds to this list the possibility that it does indeed yield an accurate measure of surface area and mesoporosity.

Even at this stage of development one must conclude that it is certainly superior to any method based upon the BET[15,16] formulation. The final formulation of the BET method uses only a portion of the isotherm and the trials to correlate the BET surface area with known samples have failed[17].

One aspect that is missing is a calculation of the depth profile of the adsorbate. Indeed, chi theory does not depend upon the depth profile and by itself would not yield the depth profile. Furthermore, it seems to indicate that such a calculation would depend upon the specific geometry under consideration, since the amount adsorbed on a flat surface versus a curved surface (assuming everything else identical) is the same if the capillary filling is not involved. This aspect implies that a geometrical argument of adsorption as utilized by Barrett, Joyner and Halenda[18] does not work. This may cause considerable philosophical problems for some but is consistent with the quantum mechanical nature of the formulation. A successful calculation normal to the surface probably involves multiple calculations of QM harmonic oscillators. Such calculations have been made by this author and look promising, however, comparison to experimental data (not other calculations) at this time would seem to not be possible.

It is, however, too early to attach a high confidence in the surface area measurement. After all, one set of data is not enough to indicate that. This does indicate that more research should be done on a variety of adsorbates and adsorbents and investigators should remain open to the possibility that the chi theory might work.

8. Conclusions:

In addition to the former successes of the chi theory as listed in the introduction, the calculations made here are strong indication that the theory can be used to accurately measure the surface areas of fine powders and pore sizes of zeolites. To obtain this success, the various combinations of adsorbate molecules “rolling under” and “rolling over” other adsorbate molecules in contact with the surface needs to be accounted for. Such considerations modify the energy calculation and the effective amount of excluded area each adsorbate molecule requires. Calculations of pore radii from the surface area and pore volume yields a maximum answer due to the uncertainty in the wall surface area. On the other hand, the Kelvin-Cohen equation appears to be very accurate with the details of adsorbate “thickness” supplied by chi theory.

The method is very easy and straight-forward, especially compared to theories such as density functional theory, and can be done with a simple spread sheet calculation.

9. References:

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