

Applying Quantum Mechanics to Physical Adsorption

It's simpler than you think

or Polanyi and DeBoer/Zwicker were right, but didn't know why.

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Presentation to the Columbian Catalysis Society

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Introduction - some preliminaries

To just talk about Physical Adsorption of Physisorption we need to have a common understanding of terminology, purpose and methods. The needs are:

1. A common set of definitions and symbols. A good starting point is the latest IUPAC (SIO) conventions - provided it doesn't restrict ones ability to communicate concepts or pursue other avenues of inquire.
2. A common understanding of experimental conditions and what can go wrong.
3. An understanding as to why there needs to be some changes in the thinking among researchers.

If you want to skip the preliminaries and go straight to the derivation, go to slide 10 - Part 1.

1st Topic - Physical Adsorption terminology and quantities

First we need to check on adsorption vocabulary:

1. Adsorptive - The gas phase in contact with solid phase.
2. Adsorbate - The phase that forms on the solid, originating from the adsorptive.
3. Adsorbent - The solid phase
4. Relative pressure - (symbol: P/P_{vap}) -The pressure of the adsorptive divided by the vapor pressure of the liquid phase of the adsorptive at the temperature of the adsorbent. (The symbol X in some papers.)
5. moles adsorbed - (symbol: n_{ads}) amount of adsorbate.
6. Monolayer equivalence* - (symbol: n_m) The moles of adsorbate that if confined to all being in contact with the adsorbent surface would constitute the amount reference classically as a monolayer.
7. Areal density* - (symbol θ) the number of molecules per unit surface area compared to n_m : $\theta = n_{\text{ads}}/n_m$ This could be total or per “layer”

* Not IUPAC in meaning. θ might be particularly problematic since it's used for “coverage.”

1st Topic - Physical Adsorption terminology and quantities

Secondly the experimental conditions need specified:

1. The Relative pressure (P/P_{vap}) is measured. Pressure above P_{vap} is not valid
2. The temperature is restricted to be somewhat below the adsorptive critical point and above the freezing point. (This can sometimes be extended some below the freezing point but there is no guarantee.)
3. Measurements of n_{ads} can vary, usually gravimetric or volumetric.
4. Measurements are normally isothermal.
5. Common experimental errors can make a very large difference
 - a. Temperature control - absence of thermal baffles. This is a common error. It makes interpretation of the high pressure portion at least difficult.
 - b. Absence of low pressure measurements. A ubiquitous error - The interpretation of the isotherm requires at least high vacuum technology or better yet, ultrahigh vacuum.
 - c. Insufficient outgassing procedure. Dead-space or buoyancy gasses tend to “stick” longer than one would expect* (more about this latter.)

*See this very important publication:

Silvestre-Albero J., Silvestre-Albero A. M., Llewellyn P. L., Rodrigues-Reinoso F. (2013) *J. Phys. Chem.*, **117** 16885-16889.

2nd Topic - What's wrong with classical theories?

Question: why would one want to do this? Everything is solved, for example BET and QSDFT.

Let's examine this question about BET* first. Until the 1980s, BET was the only theoretical treatment that yielded the surface area, A , as an output parameter.

However there are multiple problems:

1. BET is considered not mathematically compatible outside the relative pressure range, P/P_{vap} , or 0.05 to 0.35.
2. BET yields the surface area within a factor of ± 3 . At $P < .01P_{\text{vap}}$ it's too low, at $P > .05P_{\text{vap}}$ too high.
3. BET applies only to IUPAC Type II and Type IV (maybe.)
4. BET range 0.05 to 0.35 P/P_{vap} may need adjusting depending upon the C value.
5. BET has some anomaly problems. It is not valid for heterogeneous surfaces.
6. BET always predicts the wrong heats of adsorption - and other problems**

* Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., **60**, (1938) 309

** The list is quite long. See: "Surface Area and porosity measurements, 2d edition" Elsevier publishing, Amsterdam, (2020) pages 28-32 ISBN 978-0-12-818785-2

2nd Topic - ... and what about DFT, NLDFE and QSDFT?

DFT (Density Functional Theory) and its latest version QSDFT (Quenched Solid) are classical mechanical theories.

1. They have been tested against another classical mechanical treatment - the Monte Carlo method (by using the same assumptions one should get the same results.)
2. The method is best applied to porosity, but does not seem to be an improvement over the standard curve method.
3. For each adsorbent-adsorbate combination a standard curve is required. This is a problem because:
 - a. There is no assurance that the surface of the porous sample is the same as the non-porous standard. For example, even with different non-porous silica samples the energy of adsorption varies.
 - b. The energy of adsorption inside pores may be different from the outer surface and might even have a different composition
 - c. For an unknown adsorbent-adsorbate combination the calculation is not possible without extensive experimental calibrations.
4. The calculations are difficult and a computer is required or one needs a (large) catalogue of kernels, but the calculation is a digital integration. The practical possibility of covering everything is beyond present day capability.

3rd Topic - How is Quantum Mechanics an improvement?

What's the practical advantage of the Quantum Mechanical approach?

1. It is self-consistent. No standards are needed.
2. For flat homogeneous surfaces, it is stable and yields the correct value*
3. Calculations are relatively simple:
 - a. for homogeneous, flat surfaces there is one simple transformation and can be done without a calculator.
 - b. for heterogeneous, flat surfaces graphical representation is a good aid with some distribution to match.
 - c. for porosity, a simple least squares routine is needed, especially if the adsorbent is is also heterogeneous.
4. The graphical representation is the amount adsorbed versus average monolayer equivalents.
5. It does not introduce anything that has not been used before, such as an external potential that miraculously decays exponentially and does not need a variety of input energies of uncertain validity.

*most likely. It seems unlikely that QM would yield the wrong answer.

3rd Topic - Why use Quantum Mechanics?

What are the disadvantages? There are needs:

1. Excellent experimental data is needed
 - a. From ultrahigh (or at least high) vacuum ($<10^{-8}P_{\text{vap}}$) to nearly P_{vap}^*
 - b. Sample temperature is critical and temperature baffles are highly recommended.
 - c. Care must be taken that dead volume or buoyancy probe gases be thoroughly outgassed.*
 - d. Repeation is golden.
2. For analysis, especially for porosity, a computer is best to do a minimization least squares routine.
3. Initially the QM model and concepts are not intuitive.
4. There are a lot of details to be worked out.

One would think that the first need would be required for all the analyzes methods, but there is a lot of data in the literature that does not fit these requirements.

*Again, see this very important publication: J. Silvestre-Albero, A.M. Silvestre-Albero, P. L. Llewellyn and F. Rodriques-Reinoso, J. Phys. Chem. C, 117 (2013) 16885-16889. They point out that for the log-law plot there could be a irreproducible characteristic feature at the beginning of the isotherm that indicates this outgassing problem.

3rd Topic - Why to use Quantum Mechanics?

What are arguments against the QM calculation?

I believe that rejections have been more political than scientific. Dr. E. Loren Fuller was able to publish many papers without mentioning the theoretical aspects. He did analyze using the results of the QM calculation, but presented the results of the analysis without explanation.

I never received from reviewers the reasons for my publications being rejected other than “everyone knows” comments, outright mis-quotes or poor math on the reviewer’s part*.

If there are some scientific reason for rejection, I would like to hear about it.

One possibility could be the argument that quantum mechanics does not apply to objects as large as molecules. However, double slit experiments on the noble gases and C_{60} [‡] has demonstrated the quantum nature for these larger particles.

*A good example of poor math is the approximation given in equation (11). The reviewer said that as A gets large that a/A goes to 0 and the expression becomes 1. I objected to the editor of Langmuir that every beginning calculus student should know the definition of e , but the editor said the reviewer was right and I was wrong. It was the sole criticism of the paper. Can you figure out who was right and why?

[‡]See for example:

Carnal, O. and Mlynek, J. “Young’s Double-Slit Experiment with Atoms: a Simple Atom Interferometer” *Physical Review Letters*, **66** (1991) 2689-2692.

Nairz, O., Arndt, M. and Zeilinger, A., “Quantum Interference Experiment with Large Molecules” [C_{60}], *Am. J. Phys.* **71(4)**, (2003) 319-324.

Romero-Isart, O., Juan, M. L., Romain, Q. and Cirac, J. I., “Toward Quantum Superposition of Living Organisms” *New J. Phys.* , **12** (2010) 022015 (16pp)

Part I -Theoretical Development

The derivation consists of three parts

Topic 1: The energy of adsorption is derived from Quantum Mechanics Perturbation theory. A first order perturbation is justified by the “big box” assumption, that is, the adsorbing surface is much, much larger than the adsorbate molecule. This is also a very simplified derivation assuming a classically shaped well and a rectangular perturbation. This makes very little difference and calculations of error has been demonstrated elsewhere.

Topic 2: Insertion of this energy derivation into the Grand Canonical Partition function.

Topic 3: An additional implication of how the areal density “layers.” A useful concept for fitting to the isotherm.

1st Topic - The Perturbation Model

Assumptions used in the model

The following assumptions are made for the quantum mechanical model:

1. The wave function may be separated in two parts:
 - a. a two dimensional wave function in the plane of the surface
 - b. a one dimensional wave function normal to the surface.*
2. The adsorbate molecule is much smaller than any particular aliquot of the adsorbent (the “big box” assumption.)
3. The adsorbate molecule is totally mobile in the 2D direction with very little effect of the adsorbent particular atomic “muffin tin” potentials. Only an average potential of the adsorbent surface is needed. If this were otherwise, the case would be chemisorption.

*The normal direction,if needed, is handled with Leonard-Jones potentials and is very simple. It yields the density in the normal direction. This approach is used in some classical approaches and does not really add anything of interest at the moment. One problem for the normal calculation: What are the L-J parameters for the adsorbate molecule in direct contact with the adsorbent?

For more detail see: “Surface Area and porosity measurements, 2d edition” Elsevier publishing, Amsterdam, (2020) pages 147 - 160, ISBN 978- 0-12-818785-2. Sorry, details are in this book copyrighted by Elsevier, so get this book from the library or on interlibrary loan.

1st Topic - The Perturbation Model

Below is a diagram of the model proposed

The diagram below illustrates the perturbation model used. (Simplified 2D model)

The 1st adsorptive molecule, whose origin is the liquid, evaporates with the energy ϵ and enters the potential well.

For the 2nd molecule, it enters the potential well with a perturbation present of a length (simulating width) of l and height from the top of the well of ϵ .

The original wave equation is:

$$\hat{H}^0 \psi_n^0 = W^0 \psi_n^0 \quad (1)$$

where the wave functions are:

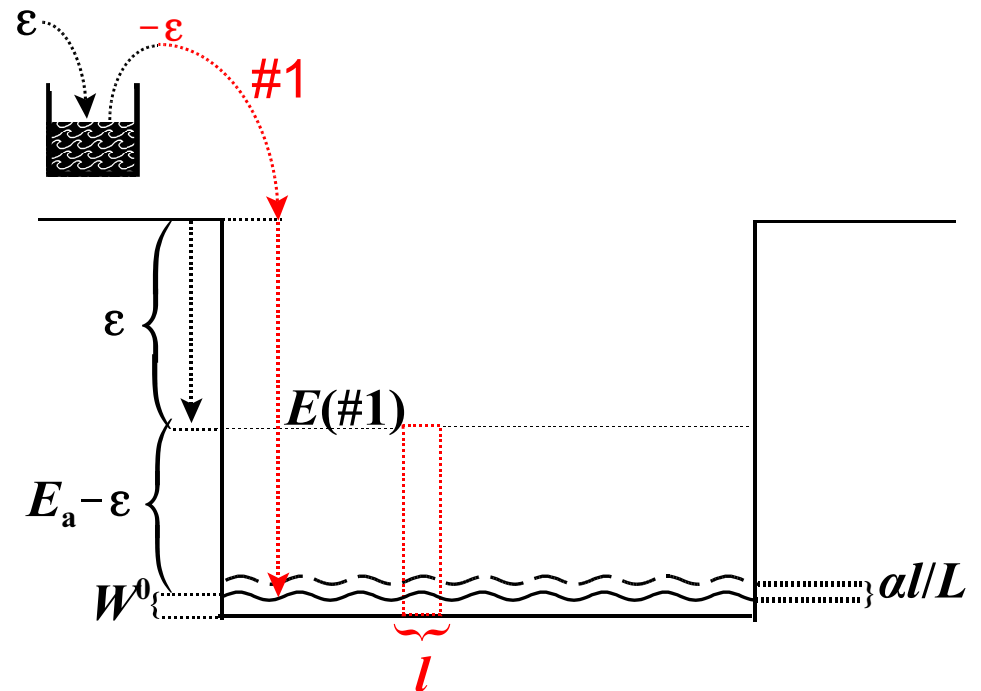
$$\psi_n^0 = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (2)$$

and the perturbation equation is:

$$(\hat{H}^0 + \hat{H}') \psi_n^0 = (W^0 + W'_n) \psi_n^0 \quad (3)$$

where by the diagram:

$$\hat{H}' = \alpha l$$



1st Topic - The Perturbation Model

First order approximation is simple

One uses the set of orthogonal equations, ψ_n^0 , given in equation 2 to give what needs to be added to the original ψ_n^0 s. Using the orthogonality the correction is:

$$\frac{2}{L} \int_{x-\frac{1}{2}l}^{x+\frac{1}{2}l} \sin^2\left(\frac{n\pi\tau}{L}\right) d\tau = \frac{1}{L} \left(\tau - \frac{L}{n\pi} \sin\left(\frac{n\pi\tau}{L}\right) \cos\left(\frac{n\pi\tau}{L}\right) \right)_{\tau=x-\frac{1}{2}l}^{\tau=x+\frac{1}{2}l} \quad (4)$$

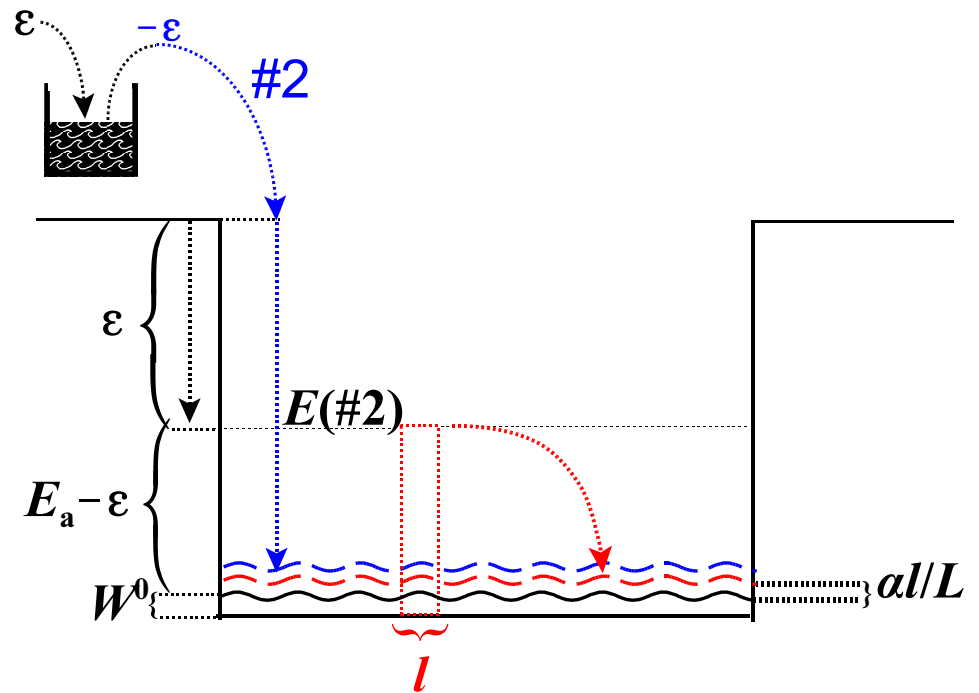
The new W ($W^{\#1}$) becomes:

$$W^{\#1} = \alpha \left(1 + \frac{1}{L} \left(\tau - \frac{L}{n\pi} \sin\left(\frac{n\pi\tau}{L}\right) \cos\left(\frac{n\pi\tau}{L}\right) \right)_{\tau=x-\frac{1}{2}l}^{\tau=x+\frac{1}{2}l} \right) \quad (5)$$

Evaluating, using the limits and the minimum and maximum values:

$$W^{\#1} = \alpha + \frac{\alpha l}{L} \left(1 \pm \frac{1}{n\pi} \right) \quad (6)$$

For $N_2(l)$, $n \approx 6 - 30$ which makes $1/n\pi < 1$, so the largest error ignoring that third term in (6) is 1% to 5%. But this varies with position so it should average out to be negligible.



1st Topic - The Perturbation Model

Some assumptions made

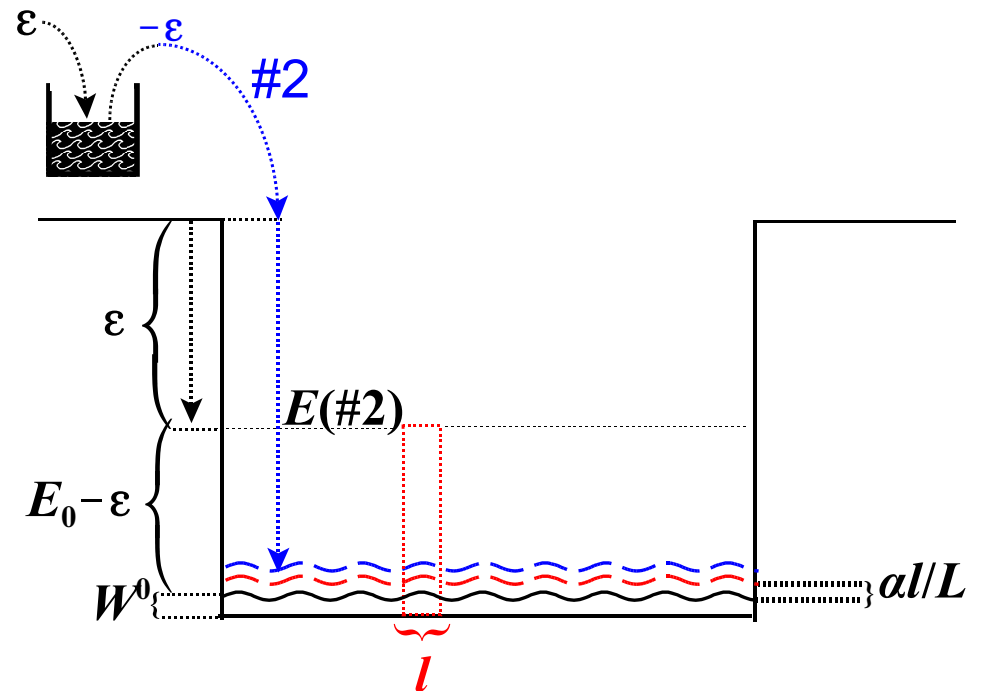
Equation (6) can be simplified with little loss in accuracy, that is simply:

$$W^{\#1} = \alpha + \frac{\alpha l}{L} \quad (6')$$

The 3rd assumption was made for the potential well, that is, the nanoscale variation in potential has little effect. This has to be the case, otherwise physical adsorption would be epitaxial, in other words, a solid phase would form. We know that this does not happen.

Likewise, the presence of adsorbate molecules, except for intermolecule attractions, also does not have a nanoscale effect upon the potential well model.

Furthermore, as illustrated by the red and blue wavy lines, these molecules are acting as spread-out waves. Only the energy·length product matters.



1st Topic - The Perturbation Model

Let's add more adsorbate molecules

Continuing the assumption of no nanoscale potential problem, for the third molecule:

$$W^{#2} = W^{#1} + W^{#1}l/L$$

$$W^{#2} = \alpha(1 + l/L) + \alpha(1 + l/L)l/L$$

$$W^{#2} = \alpha(1 + l/L)(1 + l/L) \quad (7)$$

$$W^{#2} = \alpha(1 + l/L)^2$$

This progression continues so that:

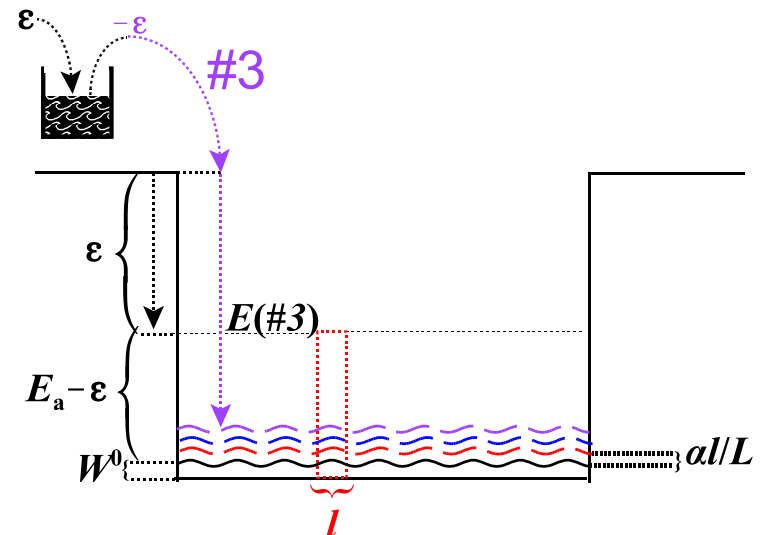
$$W^{#n} = \alpha(1 + l/L)^{#n} \quad (8)$$

This has been a 2D derivation but 3D is similar:

$$W^{#n} = \alpha(1 + a/A)^{#n} \quad (9)$$

Notice that this energy is from the energy W^0 up. Counting it from the top of the well down, this becomes:

$$E(\#n) = (1 - a/A)^{#n} \quad (10)$$



2nd Topic - The Grand Canonical Partition (GCP) Function

Entering into the GCP function with two terms left off.

In this version of the GCP function the translational losses, internal losses and rotational losses are ignored. For most simple adsorption they are negligible.

First notice that the “big box” assumption implies:

$$\mathbf{E}(N) = \alpha \left(1 - \frac{a}{A}\right)^N \quad \theta = \frac{Na}{A} \Rightarrow \mathbf{E}(\theta) = \alpha \left(1 - \frac{a}{A}\right)^{\frac{\theta A}{a}} \approx (E_a - \varepsilon) \mathbf{e}^{-\theta} \quad (11)$$

This last approximation* is due to $a \ll A$. Constructing the GCP with this:

$$\Xi = \ln(\lambda Z)^N \exp \left(\frac{\left\{ -\int_0^N (E_0 - \varepsilon) \mathbf{e}^{-\theta} - N\varepsilon \right\}}{kT} \right) \quad (12)$$

where the lateral interactions are added**. So in the usual fashion:

$$0 = \frac{\partial \ln(\Xi_{\max})}{\partial N} = \ln(\tilde{p}) + \frac{\left\{ -(E_0 - \varepsilon) \mathbf{e}^{-\theta} - \varepsilon \right\}}{kT} \quad (13)$$

...or:

$$-\ln(\tilde{p}) = \frac{\left\{ -(E_0 - \varepsilon) \mathbf{e}^{-\theta} - \varepsilon \right\}}{kT} \quad (14)$$

* The answer to the question, “Who was correct?” in slide 9. Substitute $-n$ for A/a and take $\lim(n) \rightarrow \infty$.

**This assumption is off by the loss proposed by Loren Fuller of $0.5RT$ for the first “layer” or $0.5RT(1 - \exp(-\Delta\chi))$. This will be clear later after the “layering” is explained. It might be important for calorimetry as demonstrated by the data by Dr. Berg.

2nd Topic - The Grand Canonical Partition Function

Almost to something simple - enters the threshold pressure

Simplify setting $E_a = (E_0 - \epsilon)$ and converting to moles and pressure:

$$-\ln(P) = \frac{\{-\bar{E}_a e^{-\theta} - \bar{\epsilon}\}}{RT} \quad (15)^*$$

First notice there are no entropy terms. This is the Dubinin “thermodynamic criterion,” $\Delta S_{la} = 0$. (l = liquid, a = adsorbate) Thus $\bar{\epsilon}/RT = \ln(P_{\text{vap}})$ and replacing the fugacity with pressure:

$$-RT \ln\left(\frac{P}{P_{\text{vap}}}\right) = -\bar{E}_a e^{-\theta} \quad (16)$$

Now for something contraversial: Notice as $\theta \rightarrow 0$, the pressure has a finite pressure. This pressure has been called the threshold pressure** and it signals the start of a new phase, specifically the liquid phase. This is according to Gibbs’ phase rule which all the “Henry’s Law” isotherms, which includes the BET, violate. Thus:

$$RT \ln\left(\frac{P_c}{P_{\text{vap}}}\right) = \bar{E}_a \quad (17)$$

* The overbar is a standard IUPAC symbol meaning “per mole,” used to keep subscript “m” to use for “monolayer.”

** Thus “c” will be used for threshold quantities.

2nd Topic - The Grand Canonical Partition Function

Almost done with “Almost to something simple”

Another way of expressing equation (17)*

$$-\ln\left(\frac{P}{P_{\text{vap}}}\right) = -\frac{\bar{E}_a}{RT} e^{-\theta} \quad (17')$$

Is to take the **ln** of both sides

$$\theta = -\ln\left(-\ln\left(\frac{P}{P_{\text{vap}}}\right)\right) + \ln\left(\frac{-\bar{E}_a}{RT}\right) \quad (18)$$

The two terms on the left have been given a special letter, χ :

$$\chi := -\ln\left(-\ln\left(\frac{P}{P_{\text{vap}}}\right)\right), \quad \chi_c := -\ln\left(\frac{-\bar{E}_a}{RT}\right) \quad (19)$$

Defining $\Delta\chi = \chi - \chi_c$ yield the χ equation for physisorption for non-porous adsorbent:

$$\frac{n_{\text{ads}}}{n_m} := \theta = \Delta\chi \mathbf{U}(\Delta\chi) \quad (20)$$

A plot of n_{ads} versus $\Delta\chi$ yields a plot of **amount** versus **monolayer equivalents!**

* E_a is exothermic

3rd Topic - Continuing to some other implications

Backing up, one can derive another set of equations

In the derivation, one sees that the quantity $\exp(-\Delta\chi)$ is the amount of that is not covered by “layers” of adsorbate, either in contact with the surface or with underlying “layers.” Thus the θ_1 , the molecule in direct contact with the surface is given by:

$$\theta_1 = 1 - \exp(-\Delta\chi) \quad (21)$$

Returning to the **ln** form, after some rearrangements, one ends up with:

$$\theta_1 = 1 + \frac{RT}{E_a} \ln \left(\frac{P}{P_{\text{vap}}} \right) \quad \text{note that:} \left(\theta_1 = \frac{n_1}{n_m} \right) \quad (22)$$

This is the log-law that is often observe for microporosity. Notice the following about this equation. As $P \rightarrow P_{\text{vap}}$, $\theta_1 \rightarrow 1$ and $n_{\text{ads},1} \rightarrow n_m$. As $n_{\text{ads}} \rightarrow 0$ and $\theta \rightarrow \theta_1 \rightarrow 0$ then $P \rightarrow P_c$. One may assume for the second “layer” that the potential provided by the first “layer” is insignificant localizing effect. If this is the case then for the second “layer” the equation is:

$$\theta_2 = 1 - e^{-\Delta\chi + \theta_1} \quad (23)$$

and for subsequent layers:

$$\theta_n = 1 - \exp \left(-\Delta\chi + \sum_{m=1}^{n-1} \theta_m \right) \quad (24)$$

Implications and Examples

Review of “layering” and interpretation

The letter θ is normally interpreted to be the “surface coverage” in classical adsorption theory. However, the quantum mechanics changes the meaning slightly. It should be interpreted as the relative areal density instead.

This holds true also for θ_1, θ_2 , etc.

This is important when considering microporous adsorbents. For each “layer” > 1 , adsorbate amount per surface area in the pores for these adsorbents is less than for an identical flat surface due to being physically barred from adsorption.

However, the areal density is the same provided the physical situation allows such a corresponding “layer” to form either in full or in part.

Furthermore, for the flat surface, one can demonstrate that:

$$\theta = \sum_{m=1}^{\infty} \theta_m \quad (25)$$

or:

$$\theta = \sum_{m=1}^{\infty} \left[1 - \exp \left(-\Delta\chi + \sum_{k=0}^m \theta_k \right) \right] \quad (26)$$

Continuing to some other implications

The individual layers may be handy for analysis using the log-law

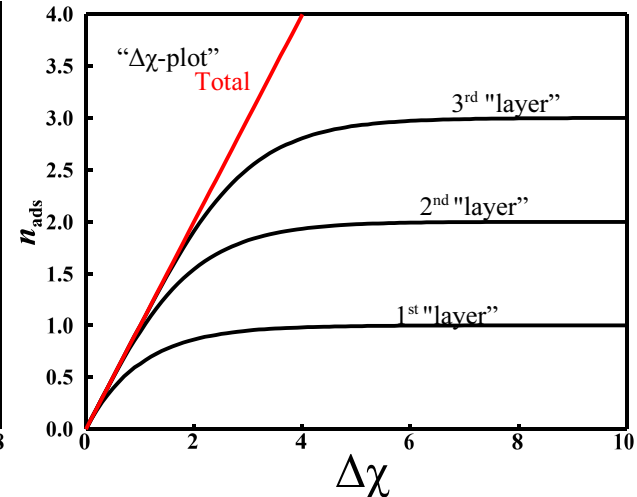
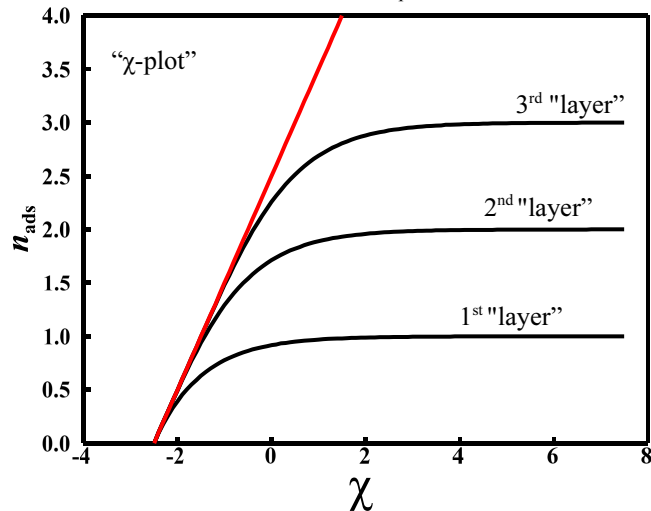
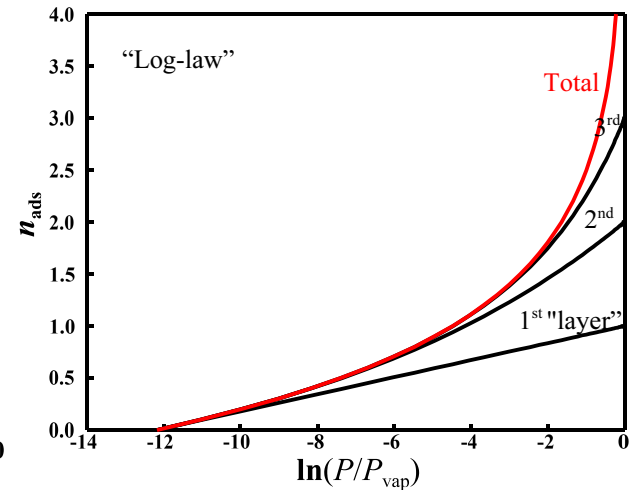
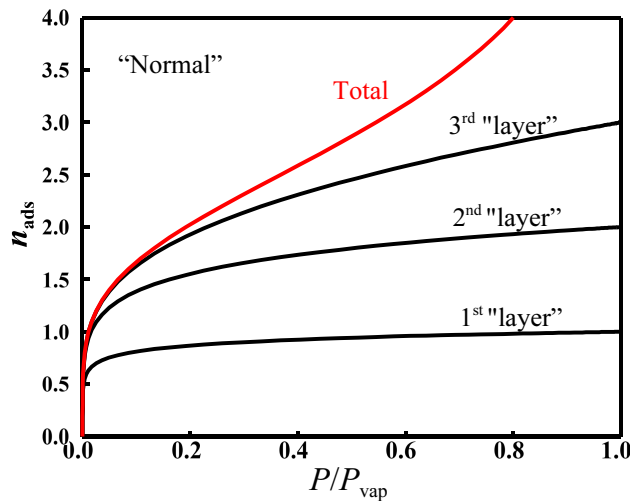
Below is are graphs of what layers look like in the various isotherm forms.

These are for the homogeneous nonporous adsorbents.

These “layer” lines do not show up in experiments, that is, one cannot restrict the “layer” filling arbitrarily.

Notice in the log-law plot the 1st “layer” is always present and is a straight line from the threshold pressure to the value of n_m .

Other layers can increase and decrease, but the higher the “layer” number the lower the areal density.



Part II Examples

χ -plots - 2, 3, 5, 6, etc. parameter models

The more complex the adsorbent-adsorbate pair, the more parameters are needed to describe the isotherm. This is only natural, and all the parameters have some physical meaning. Many isotherms fit into four categories, here listed first:

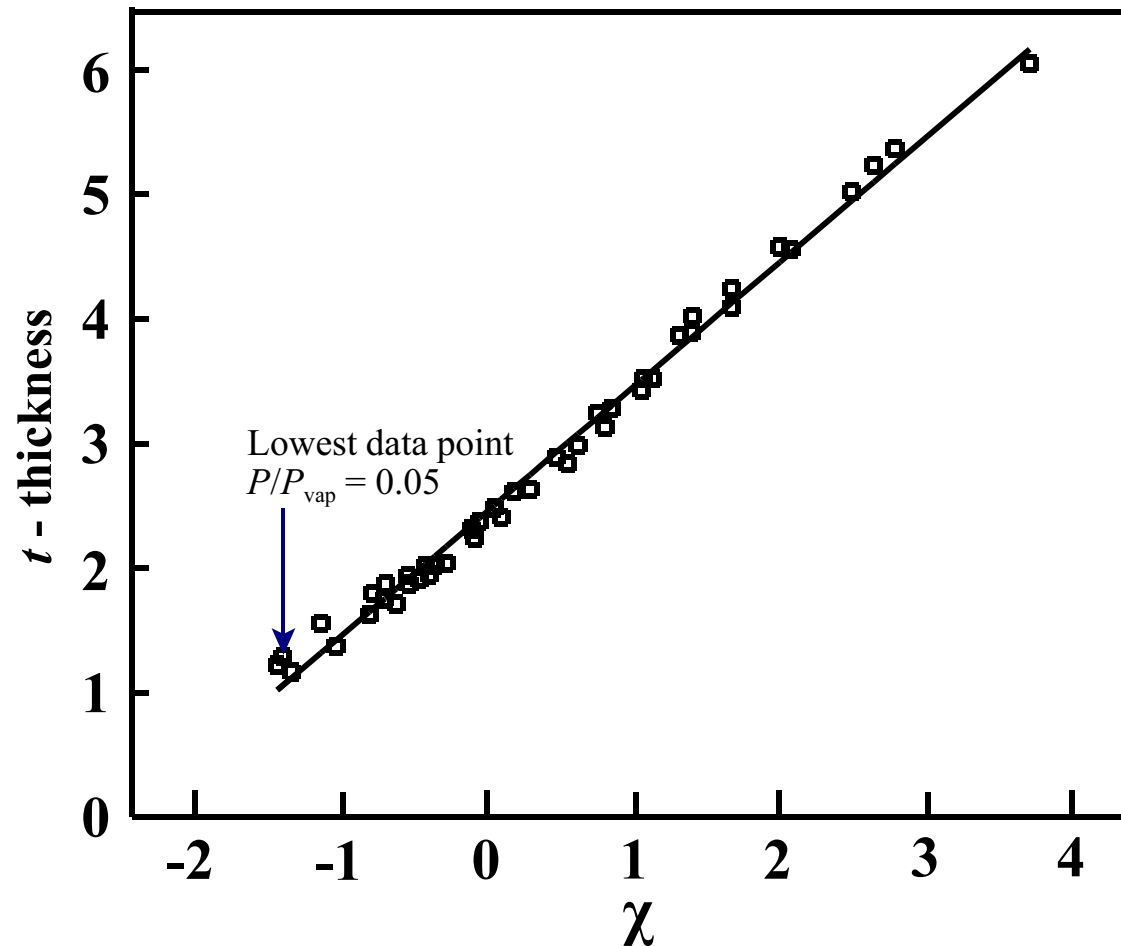
Parameters	Associated phenomenon(a)	χ -plot property(ies)
2	homogeneous nonporous	straight line (baseline)
3	heterogeneous nonporous	begins with positive curvature
5	homogeneous and single pore size	negative curvature* $\Delta\chi > \sim 1$
6	heterogeneous and single pore size	beginning positive curvature and a negative curvature* $\Delta\chi > \sim 1$
8	homogeneous and 2 pore sizes	2 negative curvatures* $\Delta\chi > \sim 1$
9	heterogeneous and 2 pore sizes	beginning positive curvature and 2 negative curvatures* $\Delta\chi > \sim 1$

* For mesoporosity there will be a preceding positive curvature before the negative.

2 parameters - Example 1

χ -plots - Homogeneous non-porous - Cranston and Inkley

The following is the data for Cranston and Inkley* t-curves and the χ -plot fit.



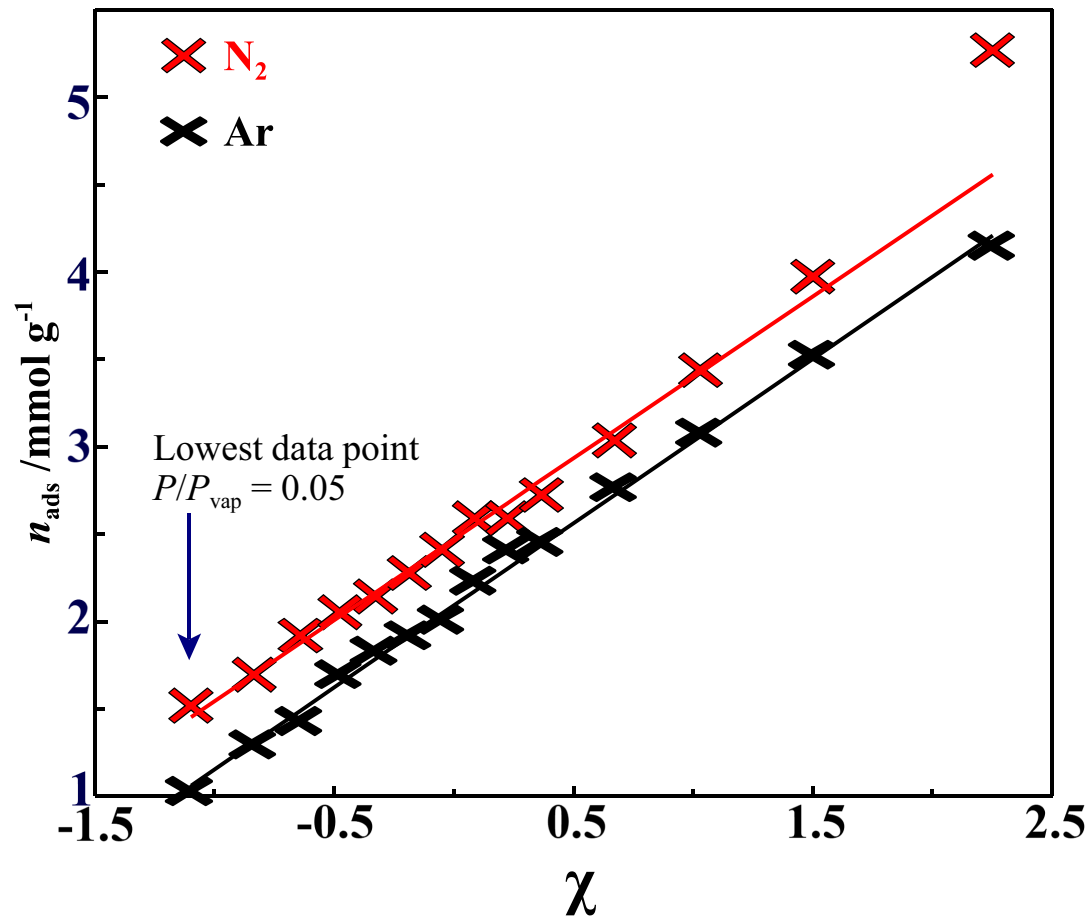
Due to uncertainty in conversions used, the original reported units are given here.

*Cranston R. W., Inkley F.A. (1957) *Adv. Catal.* **9** 143.

2 parameters - Example 2

χ -plots - Homogeneous non-porous - Sing's α -s

The following is the data for Sing's α -s curves of N₂ and Ar on SiO₂ ^{*‡}



*Sing K. S. W., in Everett D. H. and Ottewill R. H. (Eds.), (1970) *Surface Area Determination*, London: Butterworths 25.

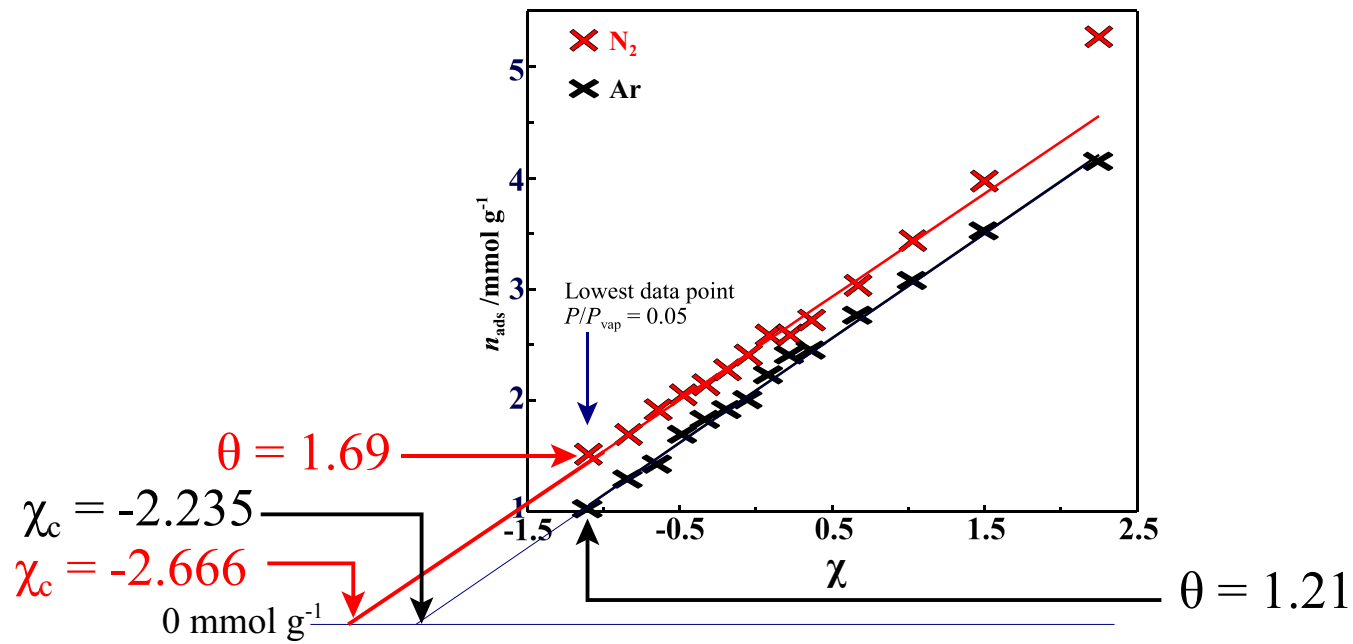
‡Bhanbhani M. R., Cutting R. A., Sing K. S. W., Turk D. H. (1981) *J. Colloid Interface Sci.* **82** 534.

2 parameters - Example 2

χ -plots - Homogeneous non-porous - an observation

It should be noticed that in this standard curve the data starts above one monolayer. This is normal for older standard curves.

The χ_c for the N_2 plot is -2.666 and the first data point has the monolayer equivalence of 1.57 mole g^{-1} . For the Ar plot the χ_c is -2.235 and the first point is 1.14 mole g^{-1} .^{*‡} You will see that this makes pore analysis difficult.

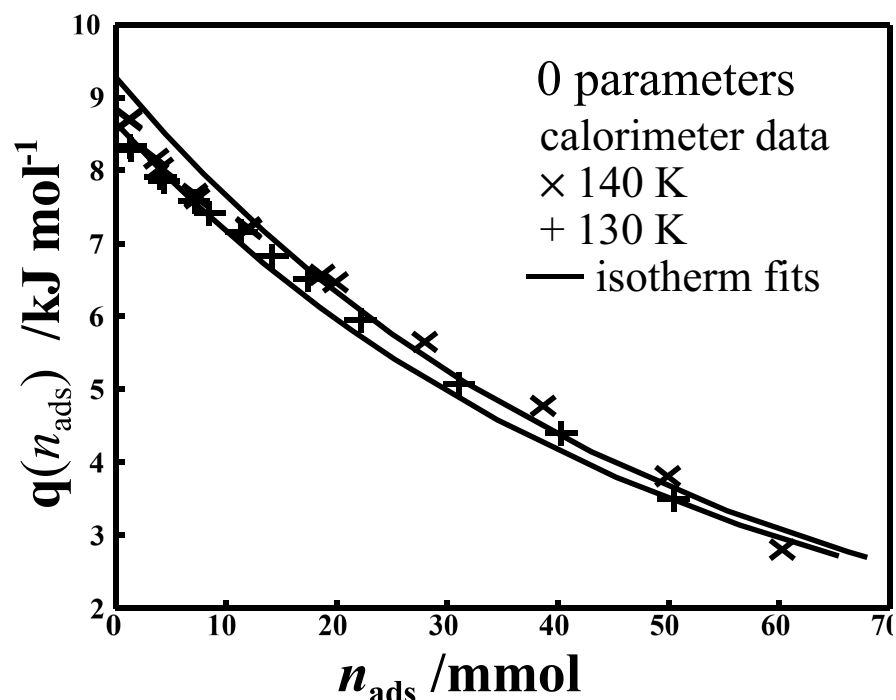
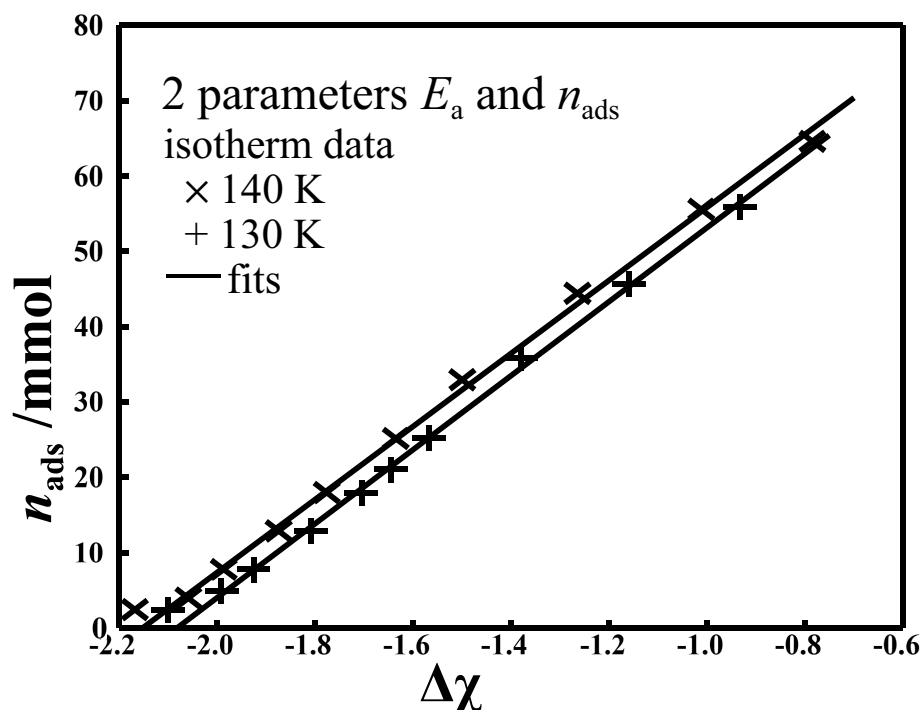


What you can't see won't both you, so don't look.

2 parameters - Example 3

$\Delta\chi$ representation and the heat of adsorption

There is not much information comparing the isotherm with calorimetric data in the literature. The best example I found is work by Berg, not accepted for publication, but is available from Case Western Reserve Library*. Below are graphs of the isotherm of Kr on Anatase. The isotherm fit was then used to calculate the differential heat. The sample size is **approximately** 50 g but not recorded. (This is not a problem for the point being made here.)



*Berg W. T., *Heat capacities from 15-140 K and entropies of krypton adsorbed on anatase* PhD thesis, Western Reserve University (now Case Western Reserve University) Cleveland, OH, USA, 1955. (Don't be fooled by the title.) I have posted his relevant data on the internet under fair use on Researchgate.com. It is also given here in slides 50-52.

3rd Topic - Modification for Heterogenous Surfaces

First consider an adsorbent with two E_a s

Assume an adsorbent is a mix of two independent powder samples. Assume they each have $n_m = 1$.

$$n_{\text{ads},a} = n_{m,a} (\Delta\chi_a \mathbf{U} \Delta\chi_a) \quad (27)$$

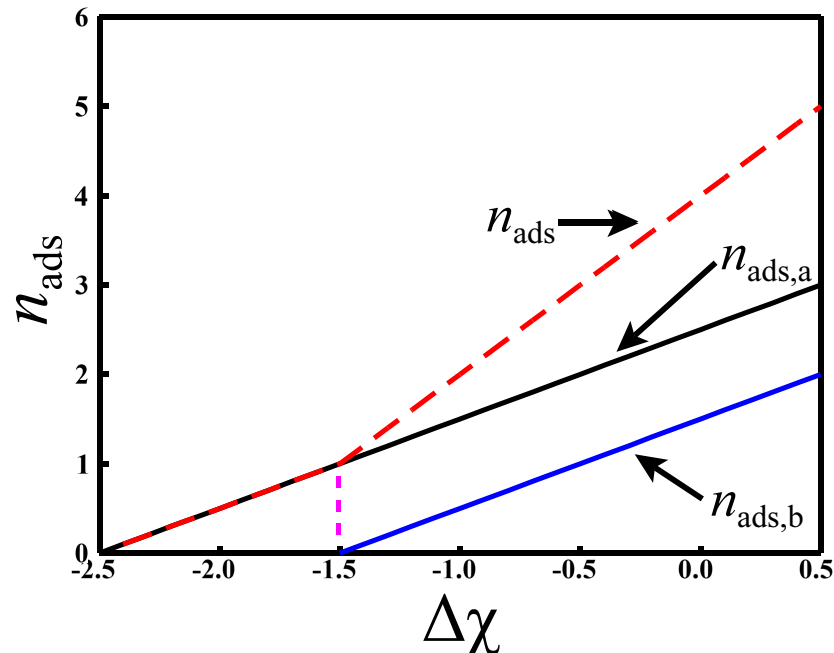
The first sample has an energy that has a $\chi_c = -2.500$. Using subscript “a”, then:

$$n_{\text{ads},b} = n_{m,b} (\Delta\chi_b \mathbf{U} \Delta\chi_b) \quad (28)$$

The second sample has an energy of $\chi_c = -1.500$. Using subscript “b:”

These may add as illustrated below:

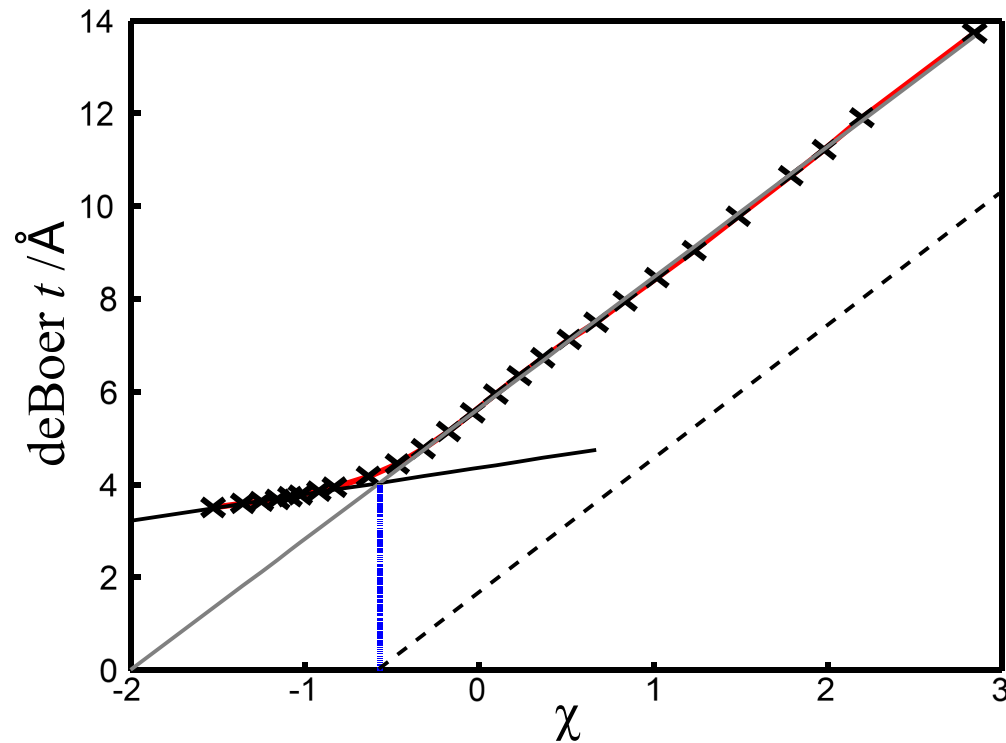
$$n_{\text{ads}} = n_{\text{ads},a} + n_{\text{ads},b} = n_{m,a} (\Delta\chi_a \mathbf{U} \Delta\chi_a) + n_{m,b} (\Delta\chi_b \mathbf{U} \Delta\chi_b) \quad (29)$$



3rd Topic - Modification for Heterogenous Surfaces

An example of an adsorbent with two E_a s

An example of adsorption on a material with two E_a s is the adsorption of N_2 on thoria high fire at 1000°C by Gammage, Fuller, and Holmes.*

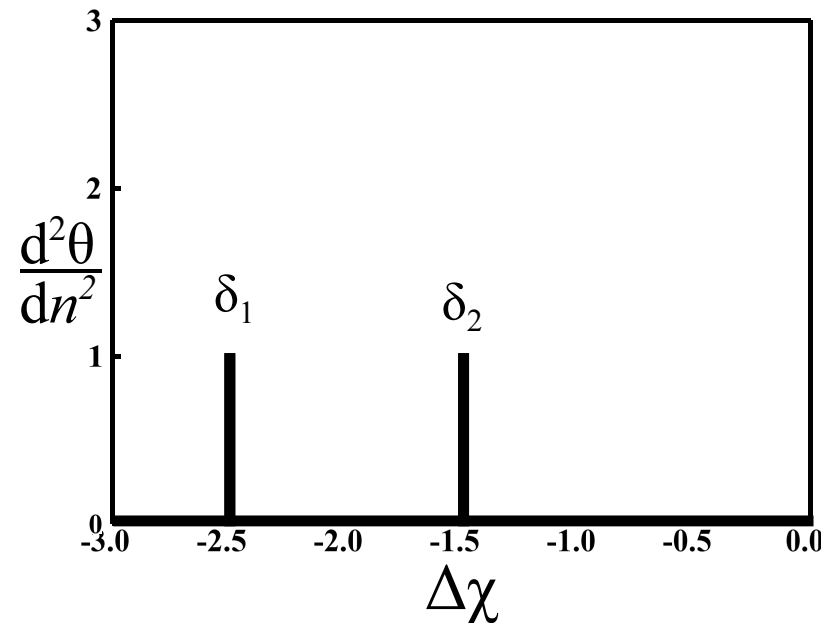
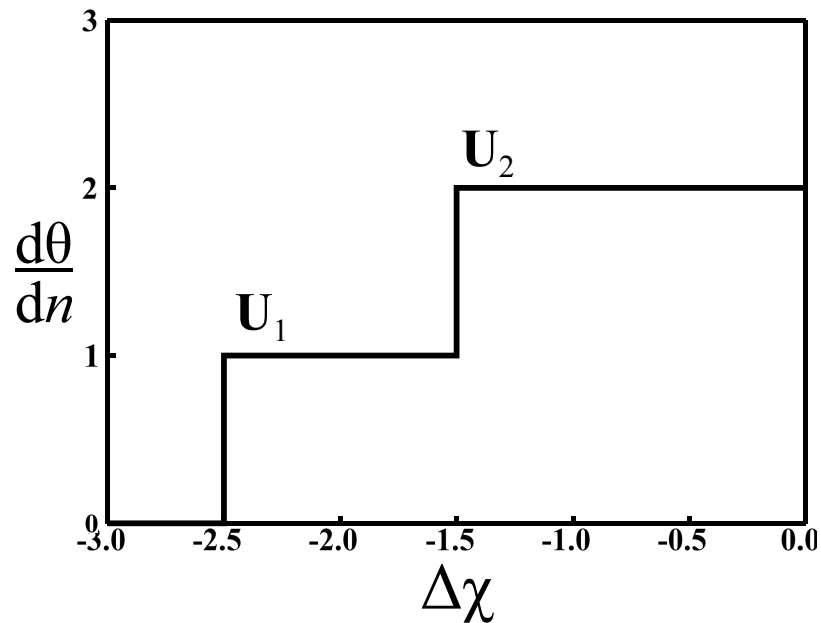


*Gammage R. B., Fuller E. L., Holmes H. F., (1970) *J. Colloid Interface Sci.* **34** 428.

3rd Topic - Modification for Heterogenous Surfaces

The use of a distribution

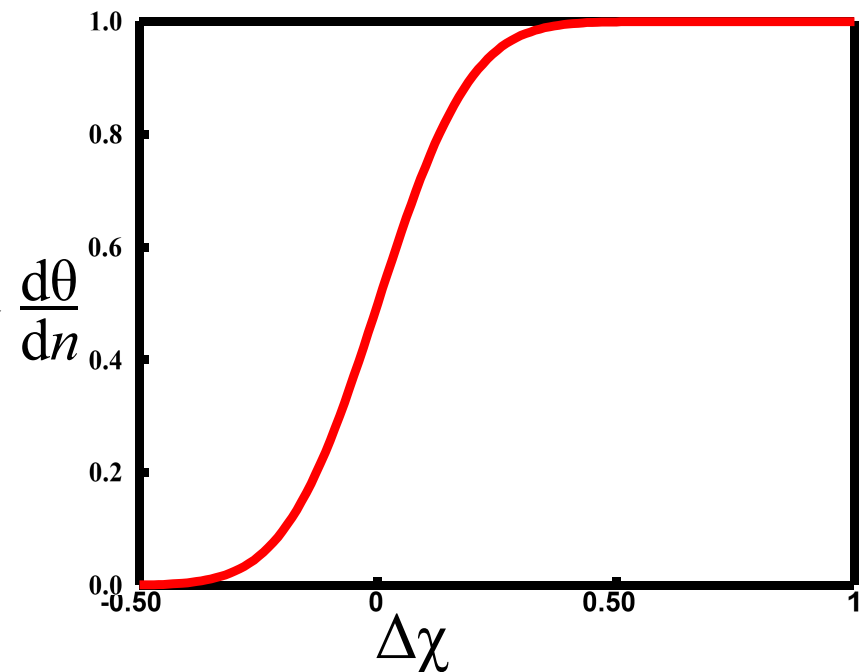
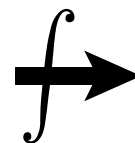
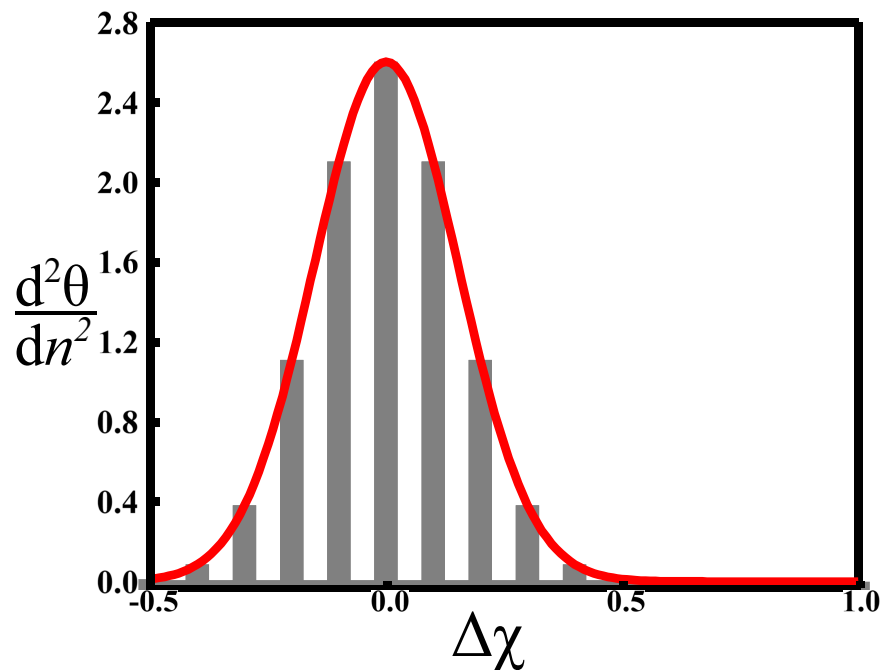
Differentiation of the added isotherms yields two step functions. Differentiation again yields two (δ) spikes corresponding to the χ s of the two energies.



3rd Topic - Modification for Heterogenous Surfaces

Intergrate the energies twice to yield the isotherm.

This process can be reversed by double integration if one knows the energy distribution. This could be arbitrary depending upon sample preparation, but for illustration the normal distribution, with respect to χ , is used. Another logical one would be the normal distribution with respect to E_a .



This is the normal distribution given the symbol $\mathbf{N}(\chi, \langle \Delta\chi_c \rangle, \mu, \sigma)$

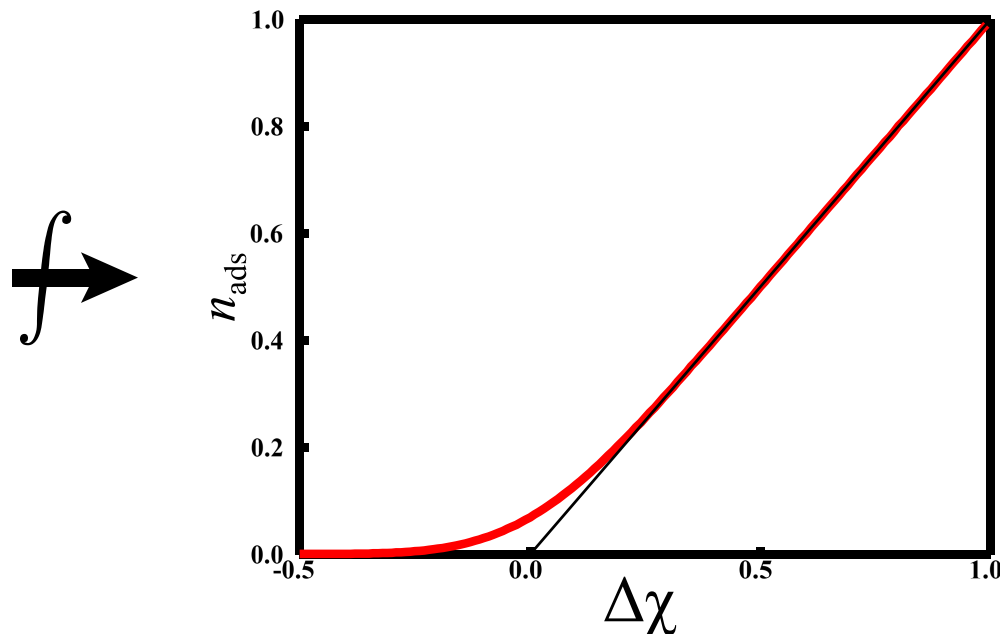
This is the cumulative normal distribution: $\mathbf{D}(\chi, \langle \Delta\chi_c \rangle, \mu, \sigma)$

3rd Topic - Modification for Heterogenous Surfaces

The second integration yields the probability “area function.”

The second integration yields the probability area function Z . This is given by the formula:

$$Z(\chi, \langle \chi_c \rangle, \sigma) = (\chi - \langle \chi_c \rangle) \mathbf{D}(\chi, \langle \chi_c \rangle, \sigma) + \frac{2\sigma^2}{\sqrt{\pi}} \mathbf{N}(\chi, \langle \chi_c \rangle, \sigma) \quad \text{and} \quad \therefore n_{\text{ads}} = n_m Z(\chi, \langle \chi_c \rangle, \sigma) \quad (30)$$



The asymptote line of this distribution ($\lim \rightarrow \infty$) passes through $\langle \chi_c \rangle$. This adds one more parameter to the fitting routine. Total parameters = **3**: χ_c (or E_a), n_m and σ

3rd Topic - Modification for Heterogenous Surfaces

It's highly unlikely one will find an example of a 3 parameter modeled isotherm in the literature.

Why is that? Until recently the low pressure region, where the effect shows up has rarely been investigated.

The reason is obvious. The BET does not apply to such a low range so why take the effort or have the equipment to make the measurement?

This may be changing as the high resolution adsorption experiments become used more widely.

The E_a distribution, however, is commonly observed with microporosity.

3rd Topic - Reminder of the “layer” representation

More modern standard curves - $\Delta\chi$ representation for microporosity

The individual “layers” are defined as follows:

1st “layer” : This consists of molecules in direct contact with the surface. The symbol for its areal density is θ_1 ($:= n_{\text{ads}}/n_{\text{m}}$.) Full density has the value of 1. Pores that are penetrable will have θ_1 when the pressure is equal to the vapor pressure of the liquid adsorbate (at T of the sample.)

The equation for θ_1 is: $\theta_1 = 1 - \exp(-\Delta\chi)$ (21')

or (the log law): $\frac{n_1}{n_m} = 1 + \frac{RT}{E_a} \ln\left(\frac{P}{P_{\text{vap}}}\right)$ (31)

Thus if only one monolayer can adsorb, then this log-law is followed.

The second “layer” is defined as the areal density that is separated by and in contact with the molecules of the first “layer.” The equation for θ_2 is:

$$\theta_2 = 1 - e^{-\Delta\chi + \theta_1} \quad (23')$$

The third “layer” is likewise defined as are subsequent “layers.” Beyond “layer” 3 there seems to be the possibility of mesoporosity.

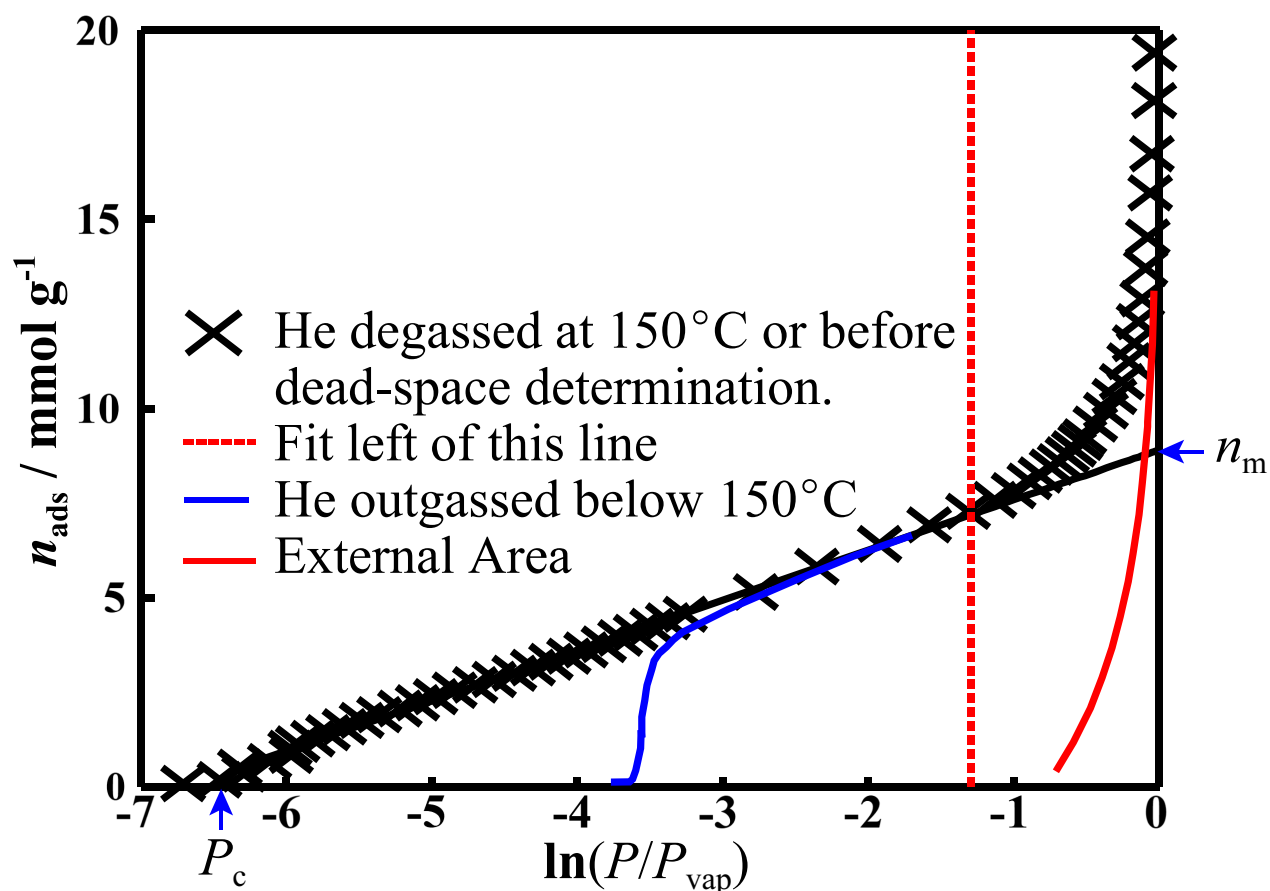
3rdTopic - “layer” representation and microporosity

The log-law is a plot of moles adsorbate versus P/P_{vap}

The data by Silvestre-Albero, Silvestre-Albero, Llewellyn and Rodrigues-Reinoso* illustrates the log-law and threshold pressure. This figure also illustrates the need for He dead-space gas removal properly at 150°C

Important points:

1. Dead-space He gas used interferes! Outgas at 150°C or above.
2. The log-law indicates only one “layer.”
3. UHV system is needed for the threshold pressure measurement.
4. There is considerable external area.



*Silvestre-Albero J., Silvestre-Albero A. M., Llewellyn P. L., Rodrigues-Reinoso F. (2013) *J. Phys. Chem.*, **117** 16885-16889.

More complex system require more parameters - pores

This new feature requires a distribution, perhaps 4 or 5 parameters.

\bar{E}_a (i.e. χ_c) may have a spread in values, as indicated in previous slides. The distribution form is arbitrary, but a normal distribution is a logical choice. The distribution would have an average $\langle \chi_c \rangle (= \mu)$ and n_m it has a spread, σ_c . In this case it is a 5 parameter fit. Without a distribution in \bar{E}_a it is a 4 parameter fit.

If the log-law is close to a straight line, the layer approach might work well. The 2nd “layer”, θ_2 , might have a cut-off. This cut-off distribution should be the antifection of the χ function*:

$$\sigma_{\text{pore}} = \theta_2^* \left\{ 1 - \exp \left[- \exp \left(\frac{x - \mu}{s} \right) \right] \right\} \quad (32)$$

where θ_2^* is the ideal θ_2 given by equation (23):

$$\theta_2 = 1 - e^{-\Delta\chi + \theta_1} \quad (23')$$

The next slide shows an example of a 4 parameter fit with a single \bar{E}_a .

The slide after that shows the physical quantity interpretation of the parameters.

* This is the consequence of the boundary not being sharply developed but is spaced out in the normal direction. If there is a significant distribution in E_a then σ observed for the pore is given by the sum: $\sigma_{\text{obs}}^2 = \sigma_c^2 + \sigma_{\text{pore}}^2$

Experimental Results

Below is an example of a 4 parameter fit as the χ -plot and the log-law plot

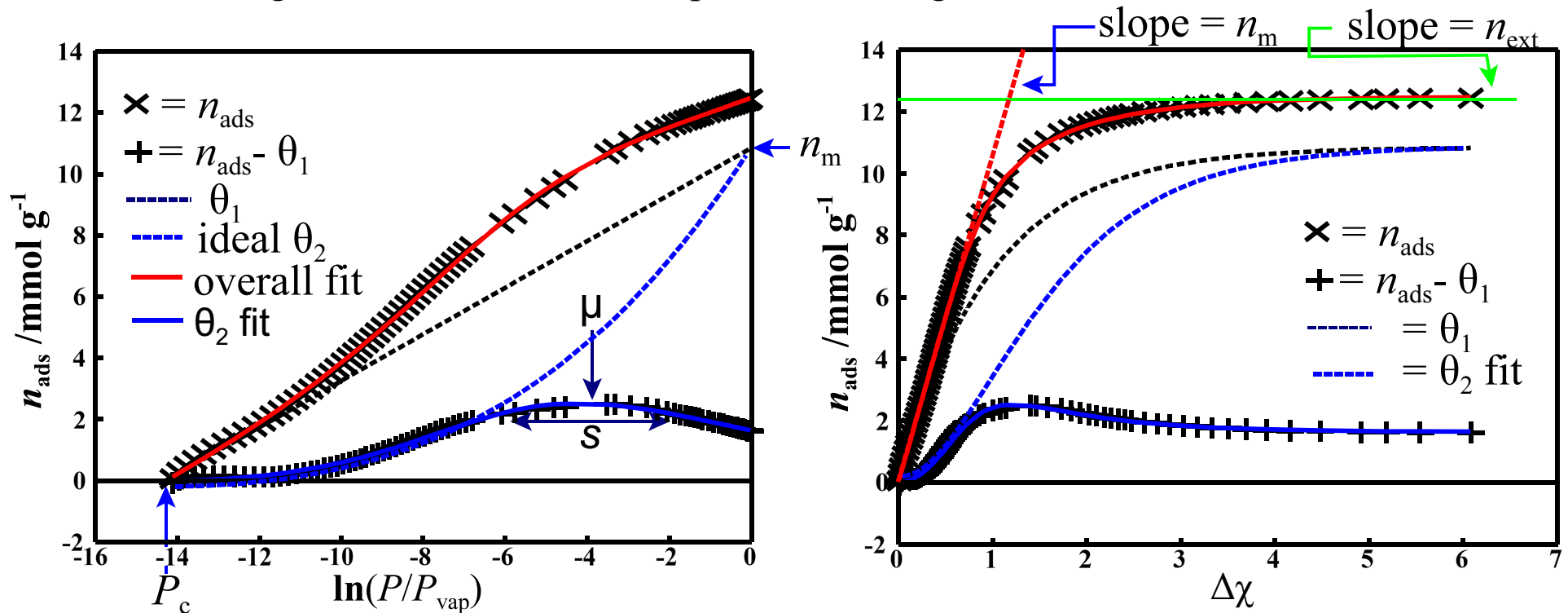
This is Ar on activated carbon samples*

The microporosity has a distribution due to the χ -distribution between “layers”

log-law parameters: $s = 2.541$, $\mu = -4.596$, $\ln P_c = -14.282$, $n_m = 10.8414$, $n_{ext} \approx 0.24$

χ values: $s = 1.245$, $\mu = 1.201$, $\chi_c = -2.659$, $n_m = 10.8414$, $n_{ext} \approx 0.24$

statistics for goodness of fit: $\sigma = 0.059$, percent full range = 0.47%



*From original data by: S. H. Madani, P. Kwong, F. Rodríguez-Reinoso M. J. Biggs, P. Pendleton, Microporous and Mesoporous Materials 264 (2018) 76–83 - kindly provided by Professors Madani and Pendleton.

Experimental Results

From the 4 parameter fit the following physical properties may be derived

quantities values

$$n_{\text{ext,f}} + n_{\text{pore}} = 12.48 \text{ mmol g}^{-1}$$

$$n_{\text{ext,f}} = 0.24 \text{ mmol g}^{-1}$$

$$n_{\text{pore}} = 12.24 \text{ mmol g}^{-1}$$

$$n_{\text{ext}} = 0.032 \text{ mmol g}^{-1}$$

$$V_{\text{ext,f}} + V_{\text{pore}} = 0.357 \text{ mL g}^{-1}$$

$$V_{\text{ext,f}} < 0.007 \text{ mL g}^{-1}$$

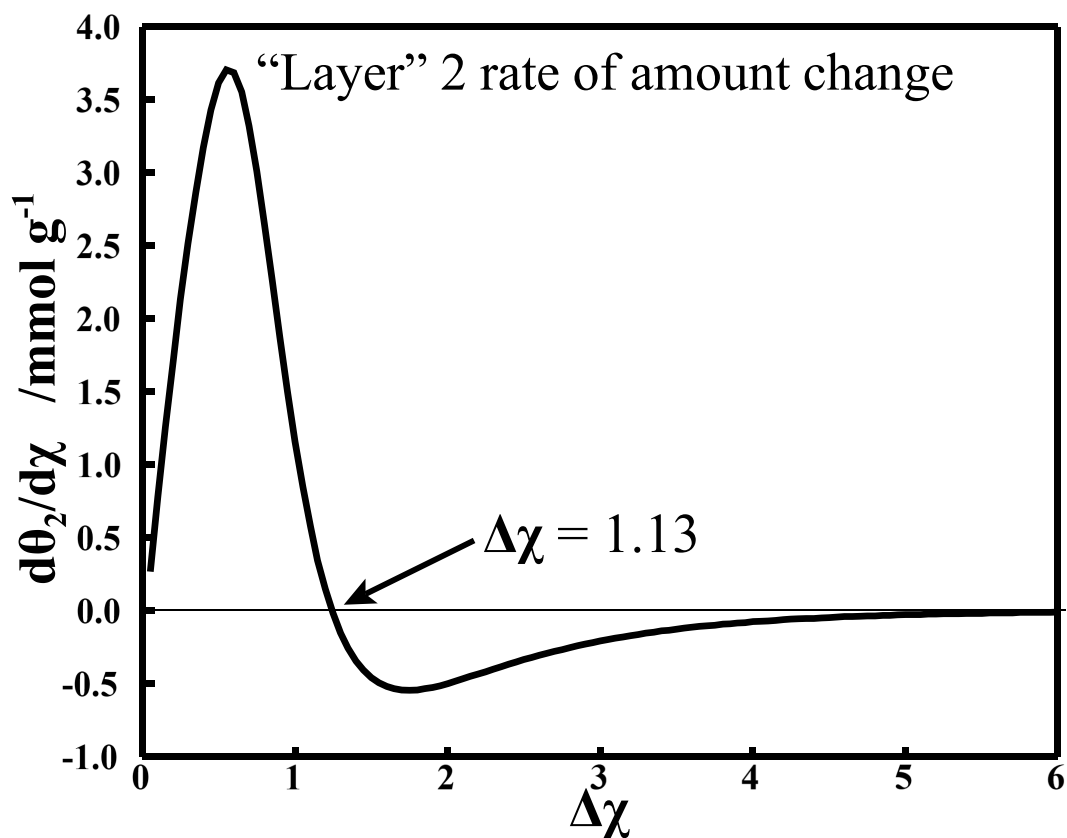
$$V_{\text{pore}} = 0.351 \text{ mL g}^{-1}$$

$$A_{\text{total}} = 932.3 \text{ m}^2 \text{ g}^{-1}$$

$$A_{\text{ext}} = 2.8 \text{ m}^2 \text{ g}^{-1}$$

$$A_{\text{pore}} = 929.5 \text{ m}^2 \text{ g}^{-1}$$

$$E_a = 10.37 \text{ kJ mol}^{-1},$$



Equation 26 (slide 21) indicates that there is an areal density for all “layers”, but here the pore walls restrict the layer amounts. This distribution does not indicate the pore distribution, but rather the amount of “layer” 2 that is added as $\Delta\chi$ increases.

Experimental Results

From the 4 parameter fit the following physical properties may be derived

It is easy to differentiate the fitted equation, specifically the 2nd layer part since one has an analytical function for it. The value or $\Delta\chi$ for the peak of the 2nd layer is easily read from the $d\theta/d\chi = 0$.

This indicate the point at which the pore begins to restrict the adsorption in the 2nd layer and thus the maximum areal density of this layer.

*From the experimental Results:

The t_{\max} value can be calculated from V_{pore} ($= 0.351 \text{ mL g}^{-1}$) and

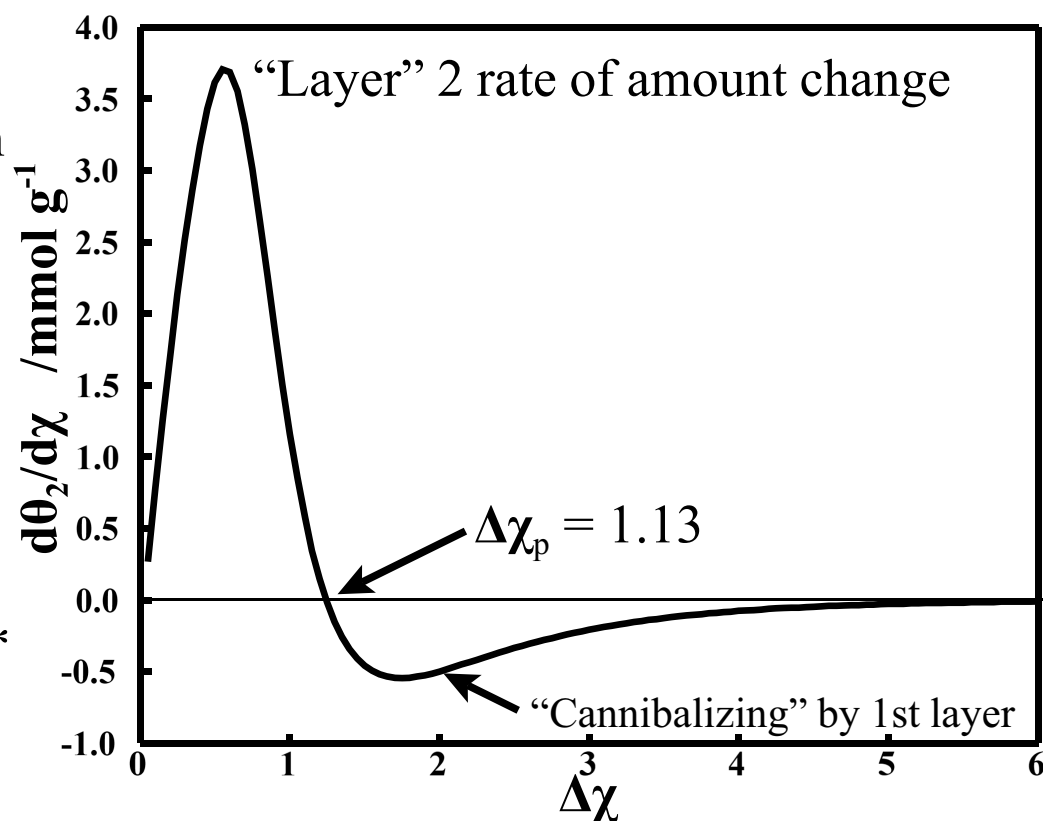
A_{pore} ($= 911.9 \text{ m}^2 \text{ g}^{-1}$) to yield:

from $V_{\text{pore}}/A_{\text{pore}}$, $r = 0.377 \text{ nm}$

and using $\Delta\chi_p$:

$$t_p = r = 0.333 \text{ nm} \times 1.13 = 0.376 \text{ nm}^*$$

*0.333 nm calculated from V_m and A_m .



The End of the Normal Presentation

The Following slides include additional Information

Error analysis for Ar and SF₆ on carbon isotherms - a four parameter fit

A short mesopore explanation and examples

The Data from Dr. W. Thomas Berg's Thesis

Binary adsorption - an easy and efficient estimate

More Lunar Soil - standard curves

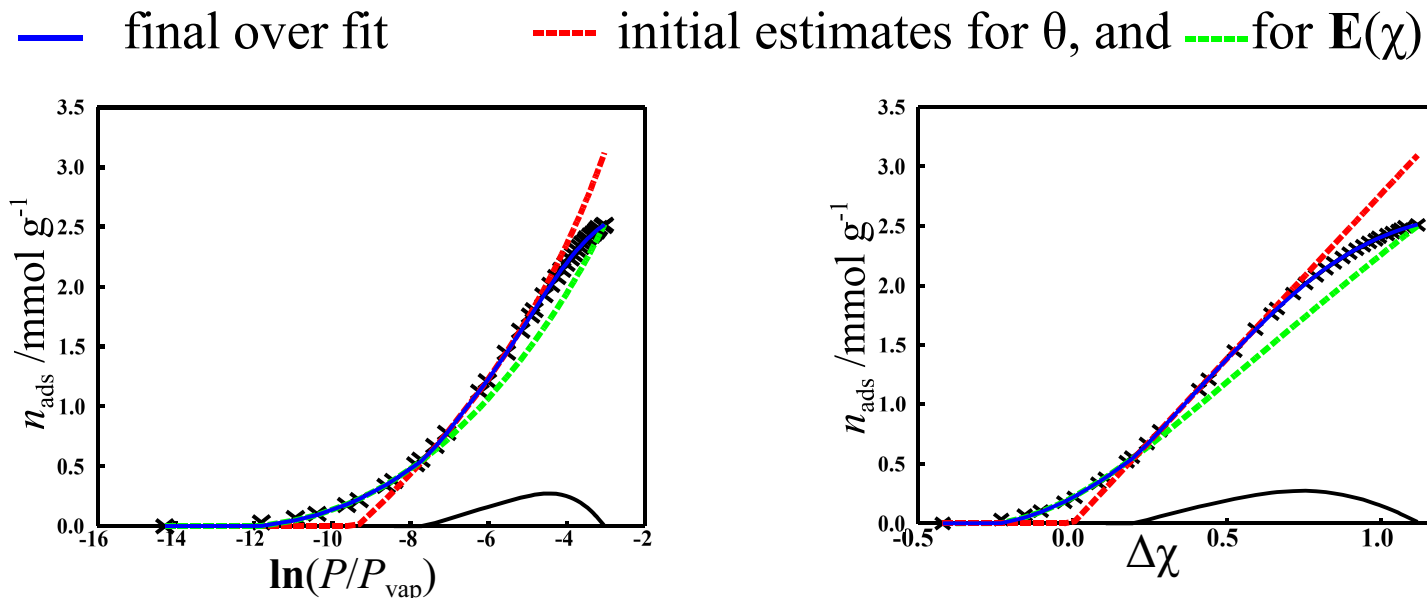
This slideshow is available at <http://www.genchem.net/ColumbianPresentation.pdf>

Also available as an HTML at <http://www.genchem.net/ColumbianPresentation/>

Error analysis for Ar and SF₆ on carbon

The following are the comparisons of fit deviation with 2σ for data points
The fit for Ar is in slide 37. Below is the fit for SF₆ on the same carbon.

Because of the overlapping distributions of the $\mathbf{E}(\chi)$ and the microporosity it may not be possible to separate everything cleanly. (This is least for the moment, but maybe some brilliant grad student will figure it out.) Below is analysis of SF₆ adsorbed on carbon. In this case, the analysis is NOT layer-by-layer but uses full isotherm approximation. The initial estimates were used in the 6 parameter fit.

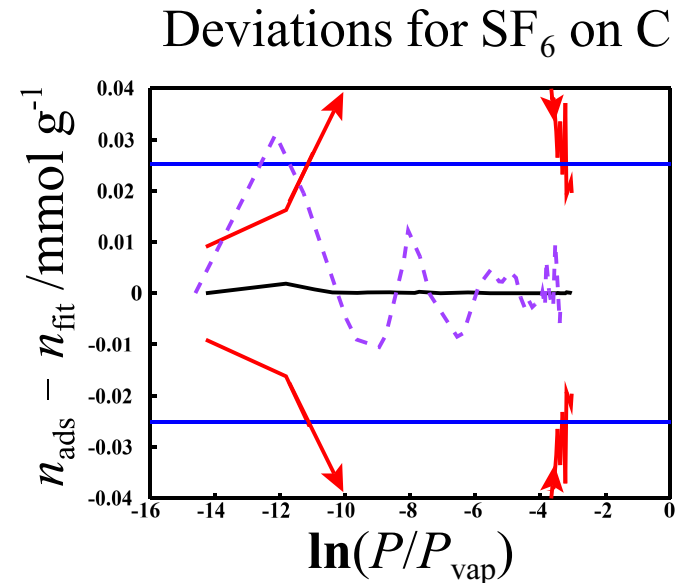
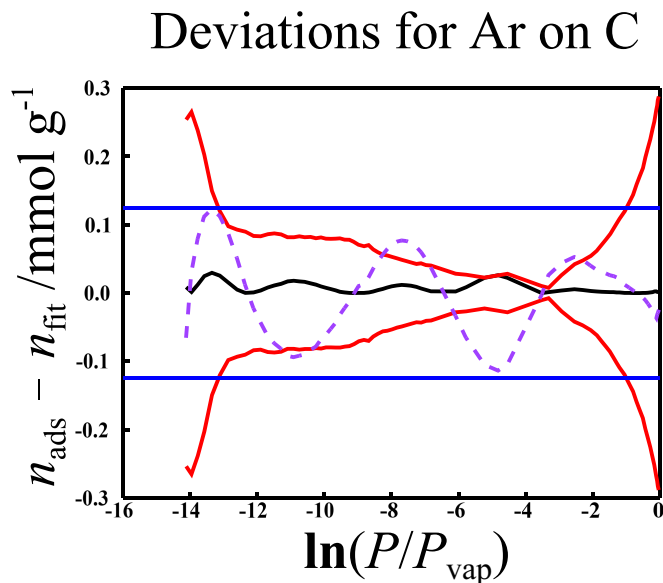


*From original data by: S. H. Madani, P. Kwong, F. Rodríguez-Reinoso M. J. Biggs, P. Pendleton, Microporous and Mesoporous Materials 264 (2018) 76–83 - kindly provided by Professors Madani and Pendleton.

Error analysis for Ar and SF₆ on carbon

Below are the deviations, 2σ , of the data points and of the model fit.

The data point 2σ values are in **red**, the deviations (2σ) from the fit are in **black**. The **blue** lines are the 1% full range value. The **Violet dashed** lines are the differences between the fit and the data points.



Additional Topic: Applying the QM to Mesoporosity

The combined micropore-mesopore equation for fitting θ is usually has been used successfully. The layered formulation is optional but provides some insight.

This micropore-mesopore equation for fitting θ equation is:

$$n_{\text{ads}} = n_m \mathbf{Z}(\chi, \chi_c, s_c) - (n_m - n_{\text{ext}}) \mathbf{Z}(\chi, \Delta\chi_p, s_2) + n_p \mathbf{D}(\chi, \Delta\chi_p, s_2) \quad (34)$$

$$\mathbf{Z}(x, \mu, \sigma) := (x - \mu) \mathbf{D}(x, \mu, \sigma) + \frac{2\sigma^2}{\sqrt{\pi}} \mathbf{N}(x, \mu, \sigma) \quad (35)$$

$$\mathbf{D} := \int_{-\infty}^{\chi} \mathbf{N}(x, \mu, \sigma) dx \quad (36)$$

$$\mathbf{N}(x, \mu, \sigma) := \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(x - \mu)^2}{2\sigma^2}\right) \quad (37)$$

$$s_2^2 = s_c^2 + s_p^2 \quad \text{if } s_c \text{ and } s_p \text{ are independent.} \quad (38)$$

Z is referred to as the statistical area function

D is the (normal) cumulative distribution function (CDF)

N is the normal probability distribution function (PDF)

(the Gausen distribution is a little different.)

Most spreadsheets contain the functions **N** and **D**.

You will probably need to construct **Z**.

This equation is for case of an energy distribution and one pore distribution

Applying the QM physisorption to mesoporosity

QM mesoporosity calculations are much easier to apply than micropore calculations. The reasons for this are:

1. The distributions for E_a and the pores are separated enough that a good measurement of n_m can be made
 - a. The underlying calculation of the surface area of the pores that needs to be subtracted before the mesopore filling is fitted. They should both have the same χ_p and σ as the micropores. No additional parameters are needed.
 - b. Thus the parameters χ_p and σ for the **Z** distribution for mesopores and **D** distribution for micropores are the same
2. The value for n_{ext} can be subtracted before the mesopore **Z** determination, provided there are enough higher pressure data*. Normally, however, $n_{\text{ext}} \approx 0$ relative to the total amount adsorbed.
3. If there is a sharp distribution for E_a and for s_p the determination is almost trivial.

Applying the QM physisorption to mesoporosity

An Example of a simple fit

Below is an example of a mesopore fit that was homogeneous and had apparently one pore size. This data is by R. Guillet-Nicolas, M. Wainer, L. Marcoux, M. Thommes and F. Kleitz,*(GWMTK.) This is KIT-6 that was calcined at 100°C for 48 hrs. The adsorptive is N₂ at 78 K.

physical properties:

$$\chi_c = -2.6513 \text{ mmol g}^{-1}$$

$$\Rightarrow E_a = 9.19 \text{ kJ mol}^{-1}$$

$$n_m = 5.719 \text{ mmol g}^{-1}$$

$$n_{\text{ext}} = 0.538 \text{ mmol g}^{-1}$$

$$\Delta n = 5.181 \text{ mmol g}^{-1}$$

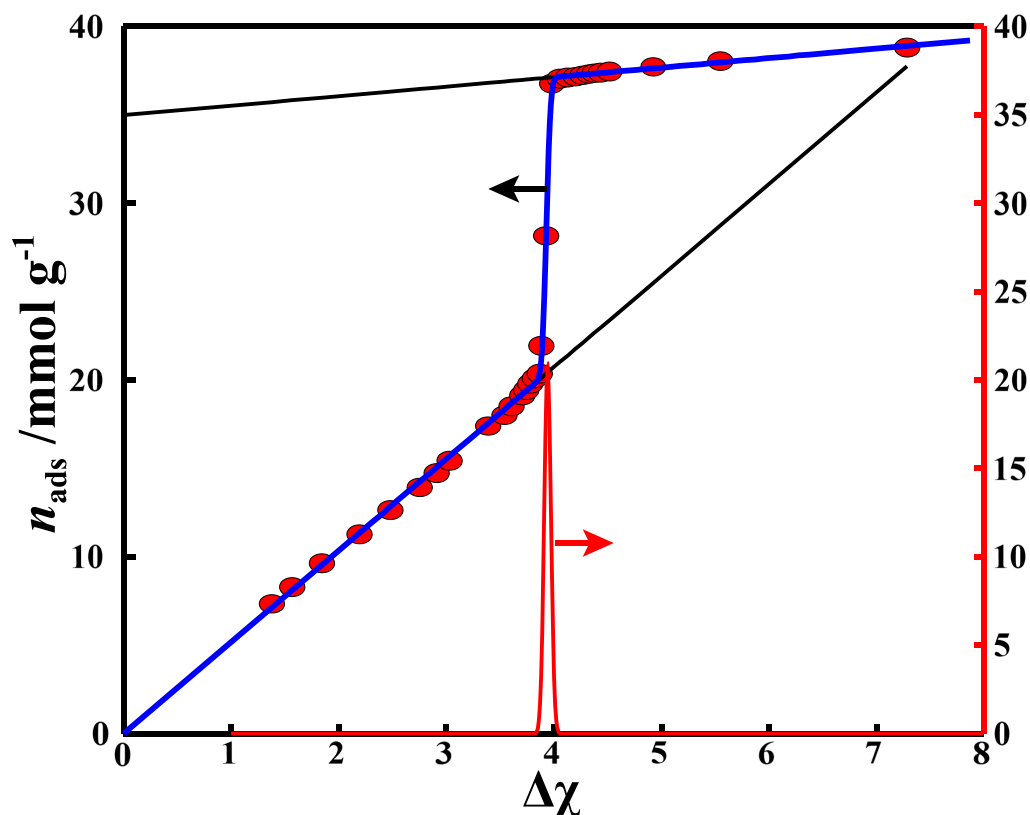
$$A_p = 453 \text{ m}^2 \text{ g}^{-1}$$

$$A_{\text{ext}} = 53 \text{ m}^2 \text{ g}^{-1}$$

$$n_p = 34.99 \text{ mmol g}^{-1}$$

$$V_p = 1211 \text{ mL g}^{-1}$$

$$V_p/A_p = 2.67$$

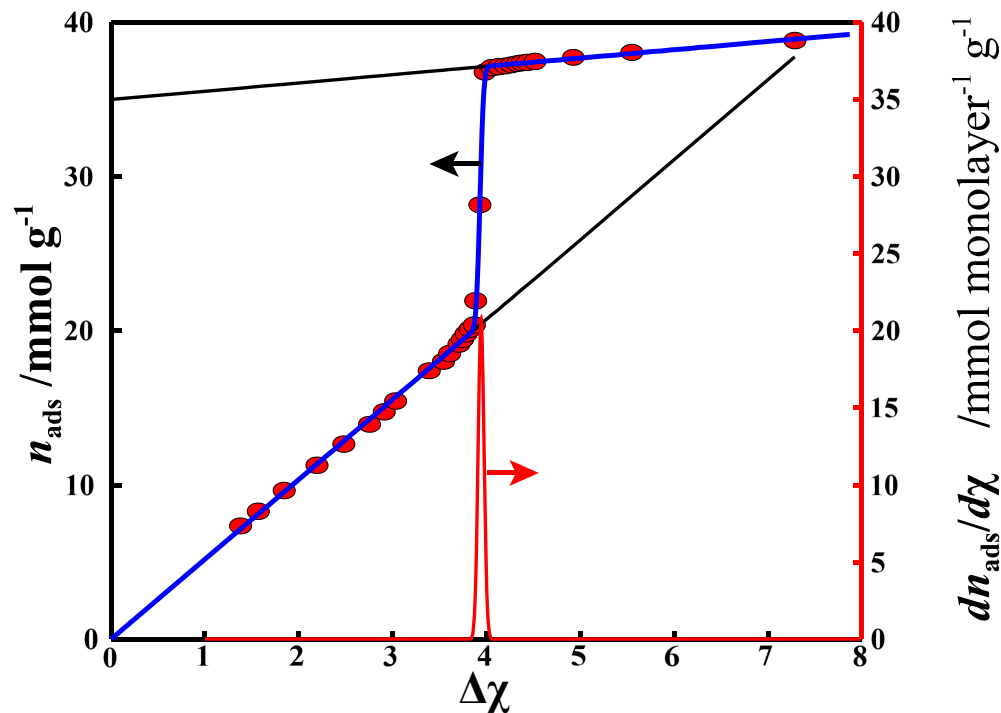


*Rémy Guillet-Nicolas, Magali Wainer, Louis Marcoux, Matthias Thommes, Freddy Kleitz, “Exploring the confinement of polymer nanolayers into ordered mesoporous silica using advanced gas physisorption,” J. Colloid and Interface Science, **579** (2020) 489–507

Applying the QM physisorption to mesoporosity

Comments about the data by R. Guillet-Nicolas, M. Wainer, L. Marcoux, M. Thommes and F. Kleitz (GWMTK)

Since σ_2 (observed σ) is very sharp. This means that both σ_p and σ_s must also be very sharp. Thus, the sample must be very homogeneous and very nearly one pore size. This makes finding the parameters very easy. The initial slope yields n_{ads} and the final slope yields n_{ext} . The peak, $\Delta\chi_p$ can be easily approximate by sight. Only a little adjusting of $\Delta\chi_p$ and σ_2 is needed to get the error below 1% of range.



Applying the QM physisorption to mesoporosity

Expanding the data out to see the details of the distribution:

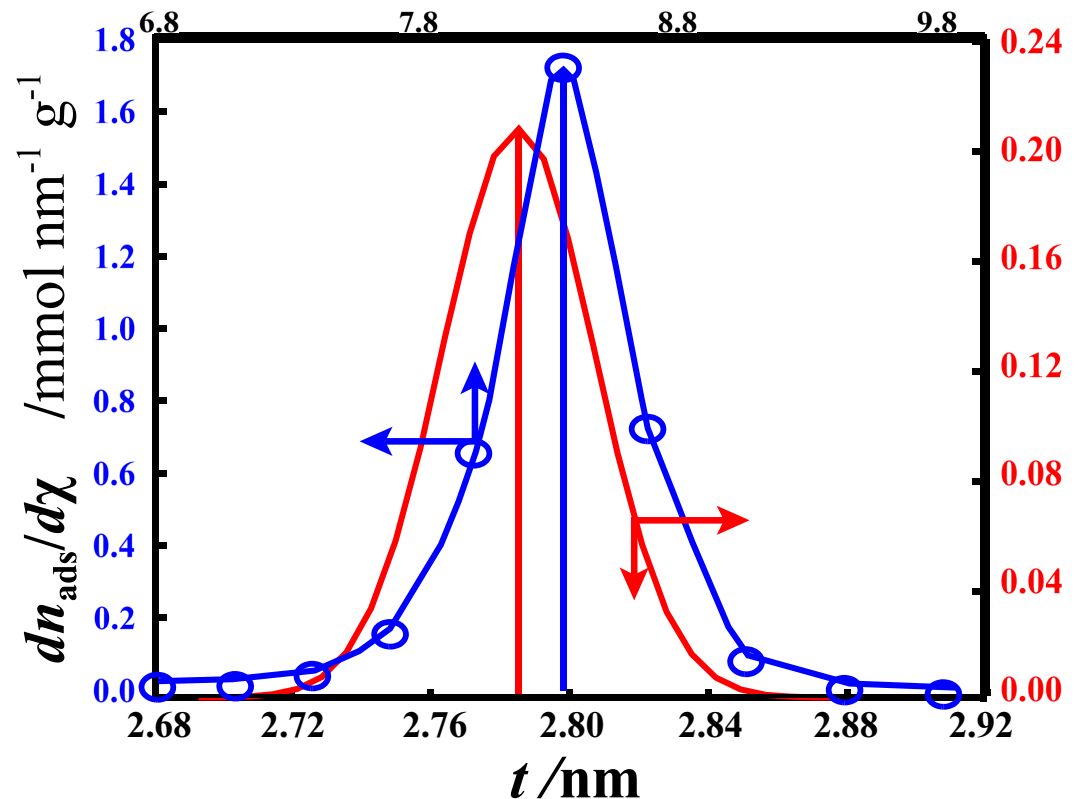
The σ_2 for the present calculation **in red** is especially sharp. The values for this are: $\mu (= \Delta\chi_p) = 2.78$ nm, $\sigma_2 = 0.022$ ($\sigma_c \leq 0.007$) nm.

For the GWMTK NLDFT, **in blue**, is $\mu \approx 8.4$ nm and $\sigma \approx 0.87$ nm

The present calculation is by definition normal and the NLDFT appears almost normal. However, notice the abscissa axes. There is a difference about a factor of 3* in $\Delta\chi$ centers and a factor of about 40 in width.

χ values are converted to nm for direct comparison. Conversion factor used was 0.709 nm for the thickness (d) of one "layer." (Literature VdW $r = 332$ pm.)

* This is the error expected for the BET over the 0.05-0.35 range. This error gets increased with the pore measurement.



Applying the QM physisorption to mesoporosity

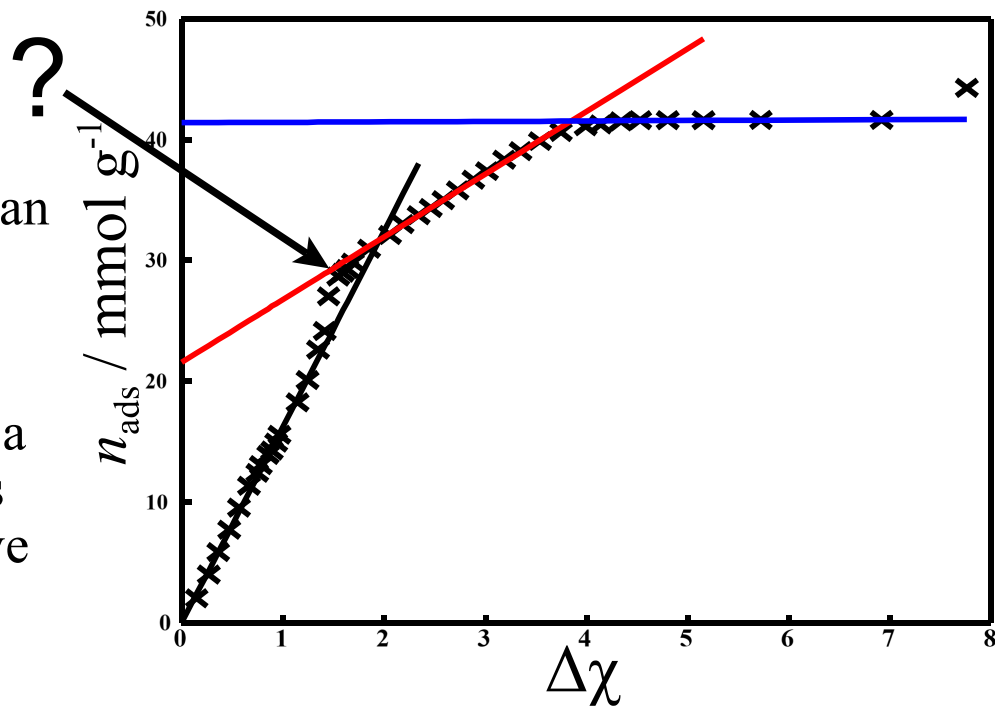
Now for a challenge, thanks to the Columbian group.

Here is some data from C. Ardila-Suárez, J. Rodríguez-Pereira, Víctor G. Baldovino-Medrano, and G.E. Ramírez-Caballero*. An adsorption curve.

One might be tempted to say, “Oh, that’s simple, it’s just two micropore fits. The problems with this assumption is:

1) For the first break, it is in the right range for microporosity, but something else is happening with an upward curvature before the intersecting lines.

What is it? It seems to be too low a $\Delta\chi$ ($\theta \approx 1.5$) to be mesopores. It’s not a fluk, the other isotherms have the same feature, even more extreme.



“An analysis of the Effect of the Zirconium Precursor of MOF-808 on its Thermal, Structural, and Surface Properties”
by C. Ardila-Suárez, J. Rodríguez-Pereira, Víctor G. Baldovino-Medrano, and G.E. Ramírez-Caballero

Applying the QM physisorption to mesoporosity

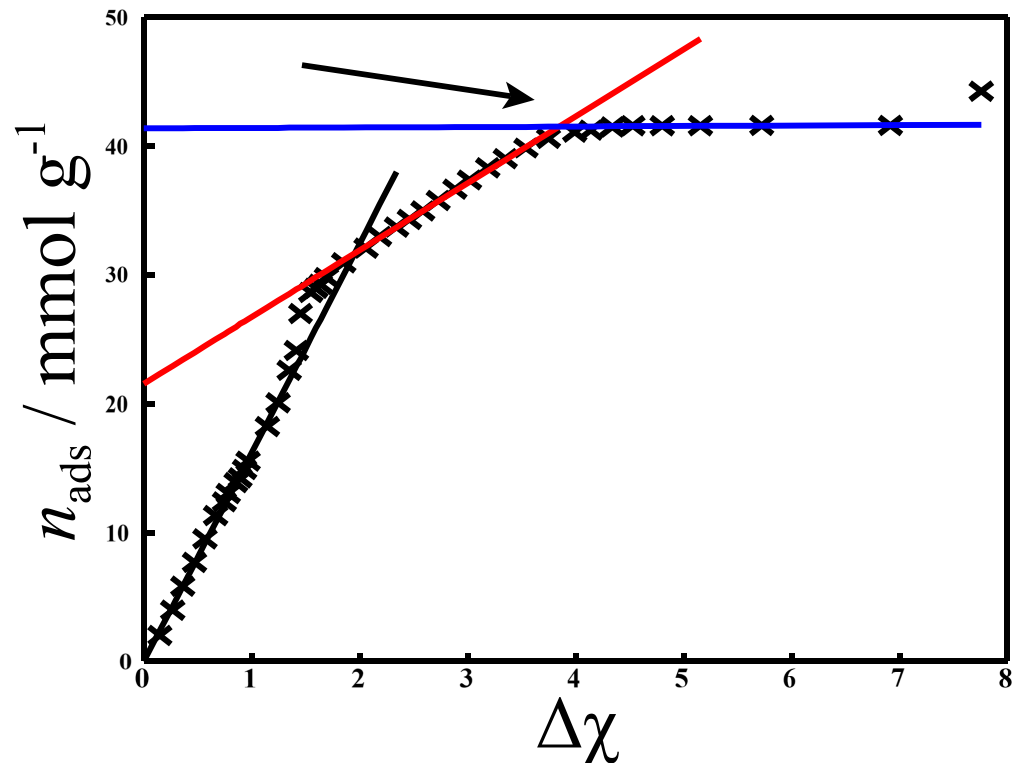
Now for a challenge, thanks to the Columbian group.

Here is some data from C. Ardila-Suárez, J. Rodríguez-Pereira, Víctor G. Baldovino-Medrano, and G.E. Ramírez-Caballero*. An adsorption curve.

2) For the second break, it is well out of the range for microporosity and, besides, there is a hysteresis loop evident on the desorption. This has to be mesoporosity. The hysteresis is there, but where is the pore filling up-curve? Is the volume too small?

So you ask, “OK, that might be fine, but what about the first break.” - My answer, “I haven’t a clue, and it’s in all the other isotherms. I see you’ve check the experiment with several more data points, so I don’t believe it’s experimental.”

Look’s like we need someone smarter than me to figure this one out.



Dr. W. Thomas Berg's data

The following is the “isosteric” heat data from Dr. Berg's thesis*

Isotherm data

130 K			140 K		
P /torr	n_{ads} /moles	P/P_{vap}	P /torr	n_{ads} /moles	P/P_{vap}
0.26	0.002386	0.000162	0.83	0.002382	0.000284
0.64	0.003926	0.000399	1.94	0.004913	0.000663
1.10	0.007756	0.000685	3.09	0.00774	0.001056
2.38	0.01287	0.001483	6.57	0.01282	0.002246
4.39	0.01796	0.002735	11.94	0.01788	0.004081
9.49	0.02514	0.005913	16.42	0.02103	0.005613
18.21	0.03290	0.011347	24.3	0.02518	0.008306
46.63	0.04441	0.029055	55.42	0.03577	0.018943
102.70	0.05558	0.063993	120.93	0.04563	0.041335
179.08	0.06460	0.111586	230.15	0.0558	0.078668

This information is available from the Archivist (Helen Conger) at:

Kelvin Smith Library
Case Western University Library
10900 Euclid Avenue
Cleveland, Ohio 44106-7151
email: library.case.edu/ksl

Title: “Thermodynamic of Krypton Adsorbed on Anatase,” by William Thomas Berg (June 1955)

It comes digitized in attached to an email: 66 pages @ \$0.25/page for total \$16.50

The red 0.03577 is a correction to the value 0.03977 (typo) in communication with Dr. Berg.

Dr. W. Thomas Berg's data

The following is the integral heat data from Dr. Berg's thesis*

Isosteric heat:					
130 K			140K		
n /mol	q / cal.	q^* / kJ	n /mol	q / cal.	q^* / kJ
0.001249	4240	8.708	0.001369	4170	8.332
0.001262	4235	8.687	0.001457	4160	8.290
0.003695	4110	8.163	0.004086	4070	7.913
0.004095	4080	8.038	0.004420	4055	7.850
0.007194	3995	7.682	0.007163	3990	7.578
0.007400	3980	7.619	0.008530	3950	7.410
0.011990	3885	7.221	0.011410	3890	7.159
0.012080	3880	7.200	0.014200	3810	6.824
0.018690	3730	6.572	0.017450	3735	6.510
0.019920	3705	6.468	0.022190	3600	5.945
0.027970	3510	5.651	0.031030	3390	5.066
0.038680	3300	4.772	0.040300	3230	4.396
0.049930	3070	3.809	0.050480	3015	3.496
0.060260	2830	2.804			

$$\varepsilon = \begin{array}{l} \mathbf{9.044} \text{ at 140 K} \\ \mathbf{9.1274} \text{ at 130 K} \end{array}$$

$$.5RT = \begin{array}{l} \mathbf{0.54041} \text{ at 140 K} \\ \mathbf{0.58198} \text{ at 130 K} \end{array}$$

*The following modification are needed. 1) ε is subtracted from q for the 3rd column, 2) $0.5RT \times \theta_1$ is subtracted from the calculation from the isotherm. (These heats are better described as differential heat.)

Dr. W. Thomas Berg's data

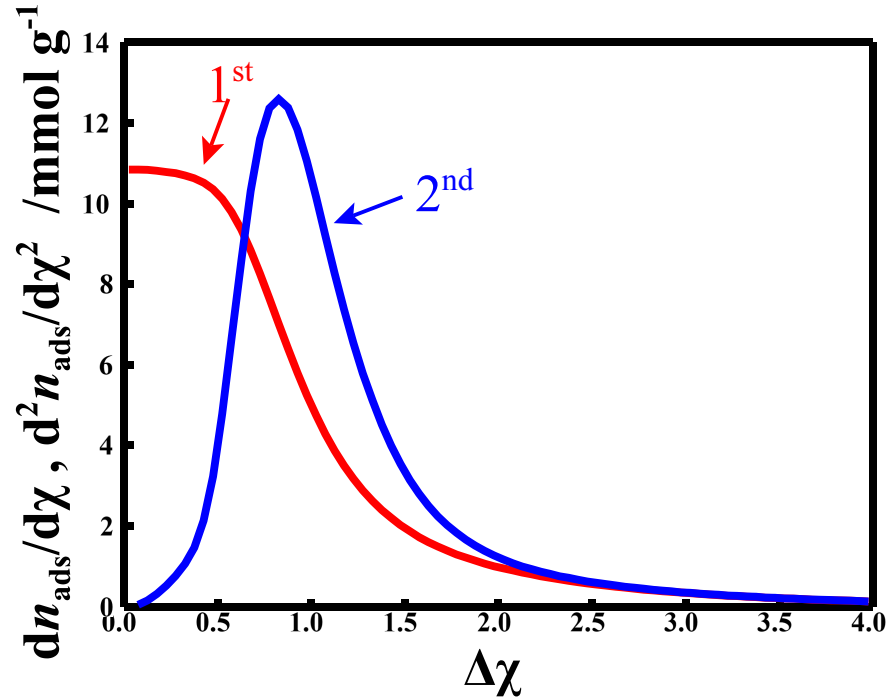
From the 8 parameter fit the following physical properties may be derived

integral heat					
	130 K			140 K	
n / mol	Q' / cal.	Q^* / kJ	n / mol	Q' / cal.	Q^* / kJ
0.002497	4240	8.708	0.002738	4170	8.332
0.002524	4235	8.687	0.002915	4160	8.290
0.004894	4175	8.435	0.005433	4115	8.101
0.005867	4150	8.331	0.005926	4105	8.059
0.009133	4085	8.059	0.008892	4085	7.976
0.009494	4090	8.080	0.01114	4035	7.766
0.01429	4020	7.787	0.01391	4000	7.620
0.01502	4005	7.724	0.01726	3955	7.431
0.02306	3910	7.326	0.02099	3910	7.243
0.02481	3885	7.221	0.02719	3825	6.887
0.03288	3790	6.824	0.03485	3730	6.489
0.04443	3685	6.384	0.04557	3610	5.987
0.0554	3545	5.798	0.05549	3450	5.317
0.06475	3445	5.379			

Converting this to differential heats is difficult. See Dr. Berg's thesis for details

1st and 2nd derivatives for slide 37

With the statistical functions used, it is easy to get precise derivatives:



It is possible that the statistical function used is characteristic only of slit pores. More research is needed to determine this and whether one can distinguish between slit pores and cylindrical pores.

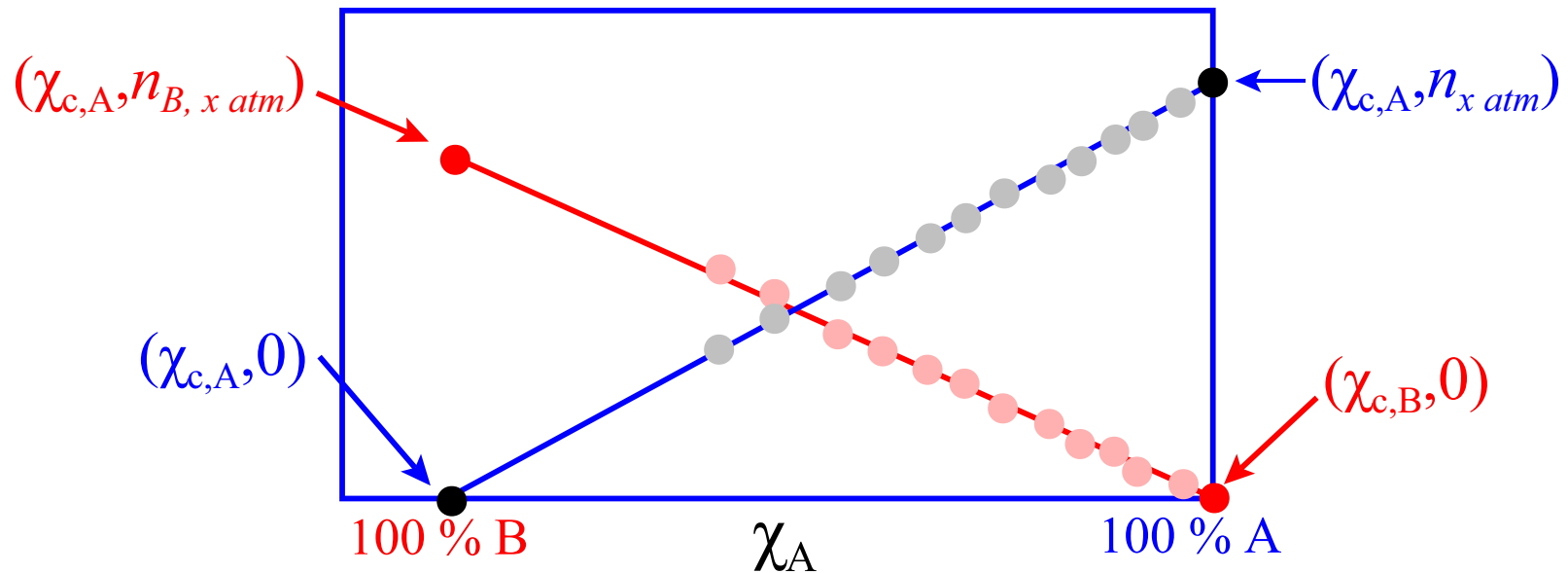
Binary Adsorption - strategy

It appears that calculations from the pure adsorbate to mixed adsorbate is simple

1. The adsorbate (label #1) with the highest $|E_a|$ will adsorb before the adsorbate with the lower (#2) $|E_a|$
 - a. since the pressure of adsorbative #2 is below its P_c .
 - b. However, #2 can adsorb in “layer” 2 by some binary liquid law, eg. Regular solution.
 2. After the pressure of #2 passes the P_c then the adsorbate-adsorbent attraction becomes possible.
 3. However, it may be that the “layer” 1 may be nearly completely covered by #1 on adsorbent surface and #2 cannot compete.
 4. The greater the difference between χ_c s of the adsorbate, the stronger will be the dominance of #1*
 5. If the χ_c of the two adsorbate are nearly identical, then they may adsorb together.†
 6. †However, the partial pressures must be used in this calculation.
- * This is the basis of the so-called Henry’s law dominance for the carrier gas method.

Binary Adsorption - strategy

The diagram below illustrates the method



In the single adsorbate isotherms, component A has the lowest χ_c (largest exothermic adsorption energy) so the abscissa is specified by it.

The four points needed are (χ_B, n_{ads}) are shown in the diagram above.

The data points are matched pairs in the binary experiment. The abscissa could be either values of χ , but only, in this case, A (the high energy species) is plotted. The low energy species, B, does not yield a straight line. (This is referred to as the “strong Henry’s law species.” But the BET theory does not support this assumption.)

Binary Adsorption - strategy

This seems complicated so here are step-by-step instructions:

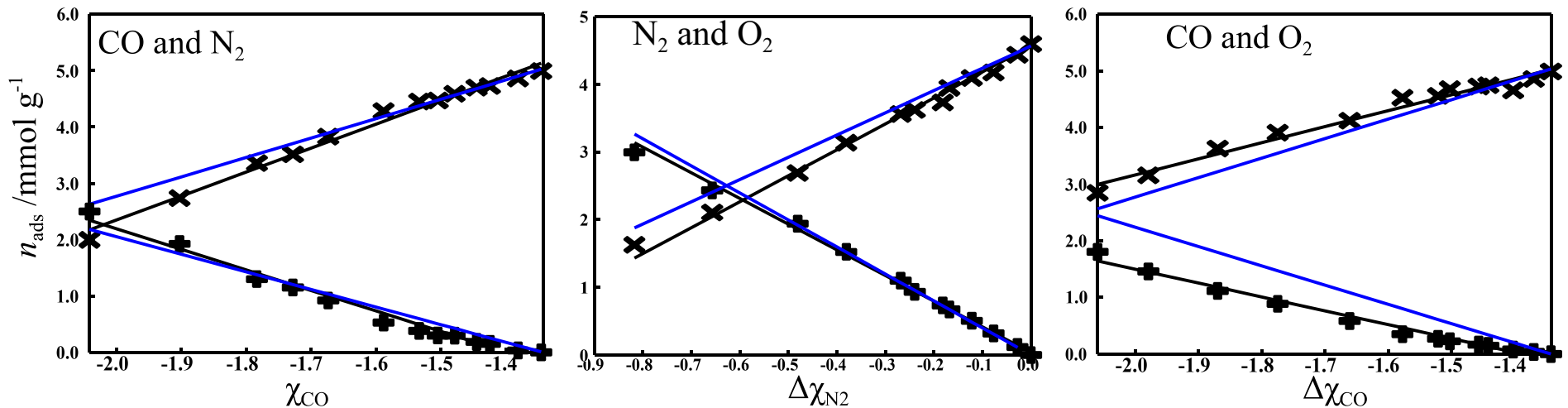
1. Do the χ -plot for both adsorbates
2. Determine what total pressure you wish to have the phase diagram for. (Let's call this p' .)
3. From the χ -plots, determine which adsorbate has the lowest value for χ_c . It may be difficult to do this, so try determining the value of χ_c from the log-law plot. (Let's specify this adsorbate "A")
4. Determine the value of n_{ads} from both isotherms of the adsorbates. (Let's call these n_A and n_B .)
5. If you have the data for the phase diagram, plot the data using as the abscissa the χ values of A over the range from χ_c to the value of χ at p' .
6. Draw straight lines from for
 - a. A: $\chi = \chi_c(A)$ and $n_{\text{ads}} = 0$ to $\chi = \chi(p'(A))$ and $n_{\text{ads}} = n_{\text{ads}}(p'(A))$
 - b. B: $\chi = \chi_c(A!)$ and $n_{\text{ads}} = n_{\text{ads}}(p'(B))$ to $\chi = \chi(p'(A!))$ and $n_{\text{ads}} = 0$

The "!" is placed here to emphasize that one uses only the χ values for A.

Binary Adsorption - Example results

Some examples will illustrate the principles - in the following plots the abscissa are the χ that has the lowest χ_c

The following are binary χ -plots of gas mixes on 5A zeolite by Danner and Wenzl*
The black lines are fits to the data. The blue lines are calculated from the pure χ -plot



The Xs and +s are the data, black lines are least squares fit and the blue lines are the χ -plot modeling.

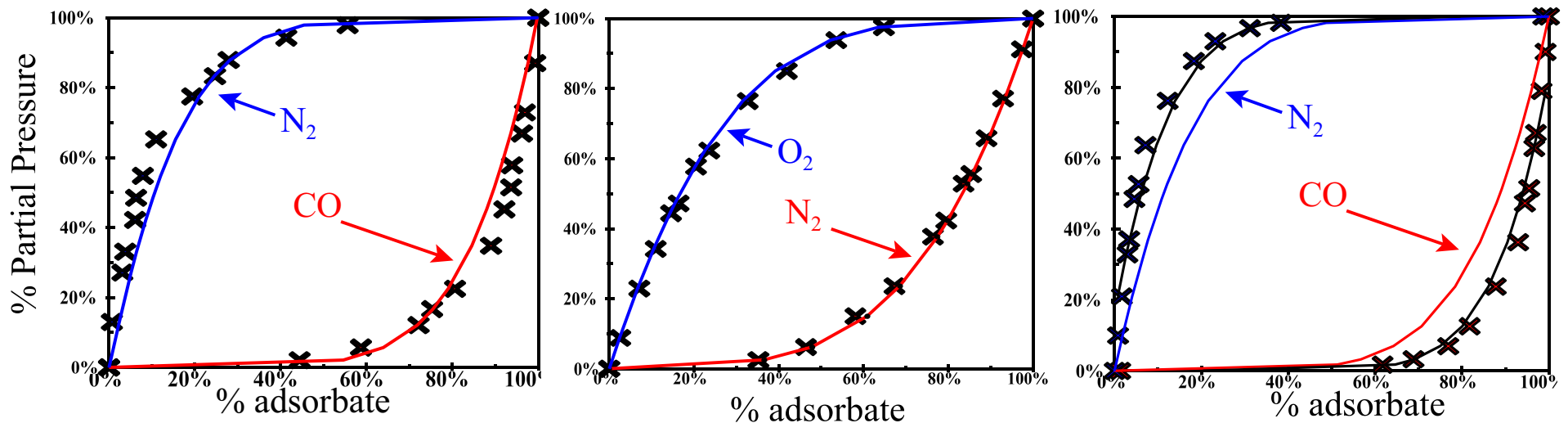
These data points and the theoretical calculations are shown in the binary phase diagrams on the next slide.

* Data by R. P. Danner and L. A. Wenzl, AIChE Journal, **15(4)** (1969) 515- 520

Binary Adsorption - Example results

Some examples will illustrate the principles.
In the following plots the abscissa are the χ that has the lowest χ_c .

The following are binary χ -plots of gas mixes on 5A zeolite by Danner and Wenzl*



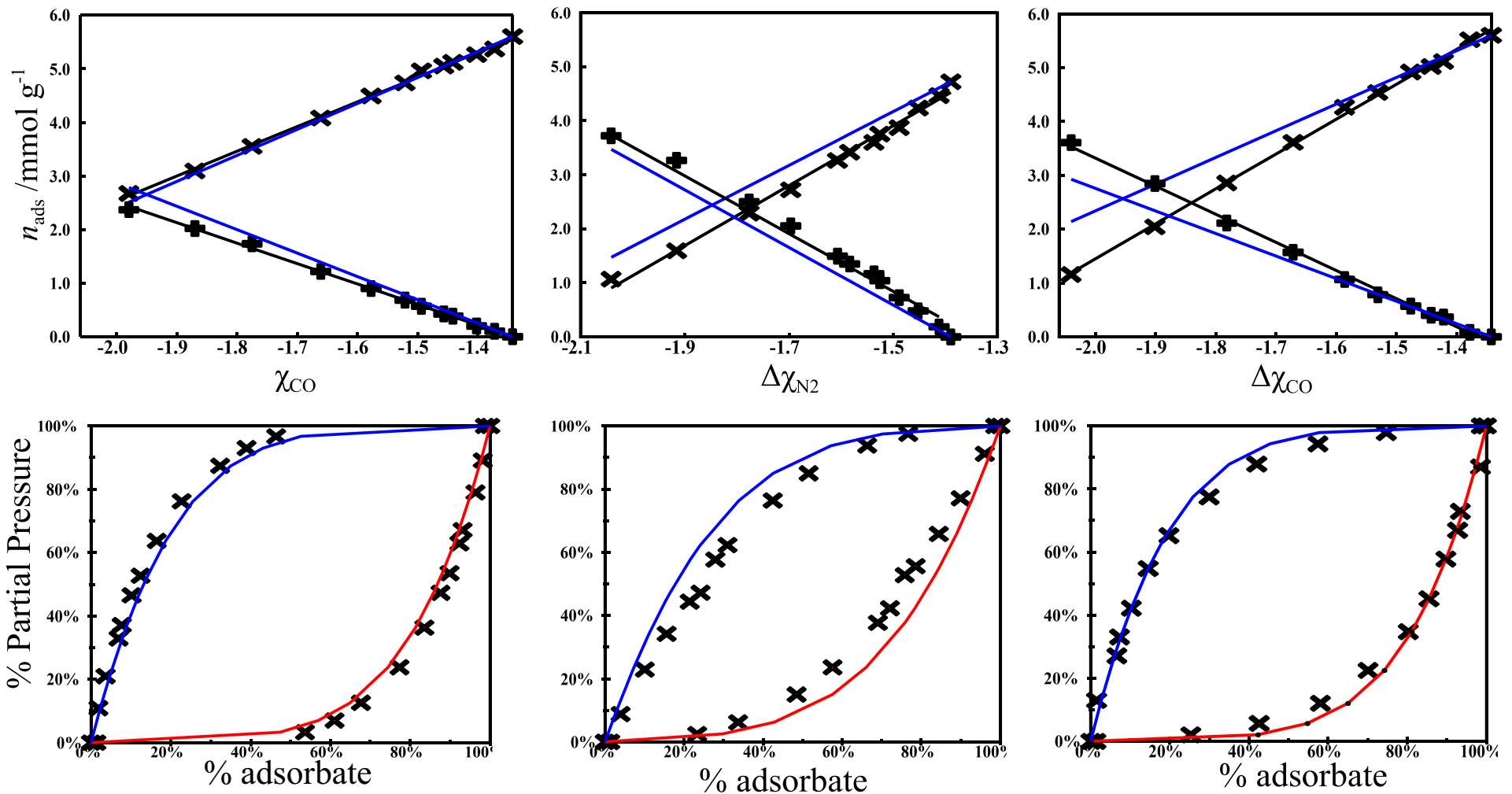
The biggest problem was the low pressure data needed for calculating χ_c s are not available. The log-law and linearly fit was used but there is still high uncertainty.

The red and blue lines are calculated from the individual isotherms. The black line for CO-O₂ is from the least squares fit. The experimental data was probably $\pm 5\%$. However, for χ_c it is $\sim \pm 12\%$. However, notice that the CO-N₂ diagram is fairly good; whereas, the CO-O₂ diagram is problematic.

Binary Adsorption - Example results

Some examples will illustrate the principles - in the following plots the abscissa are the χ that has the lowest χ_c

A similar results was obtained for the gas mixes on 10A zeolite by Danner and Wenzl*



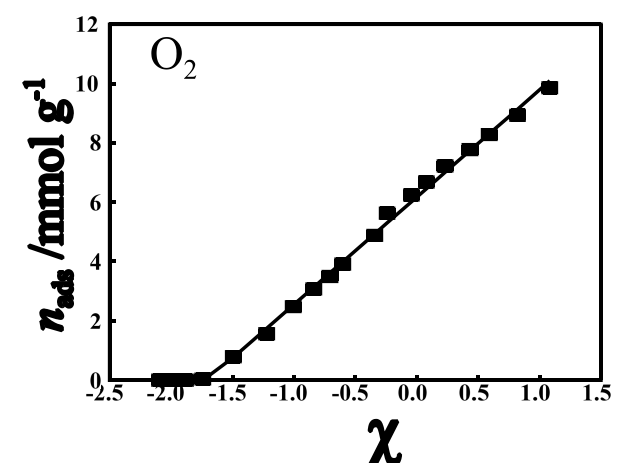
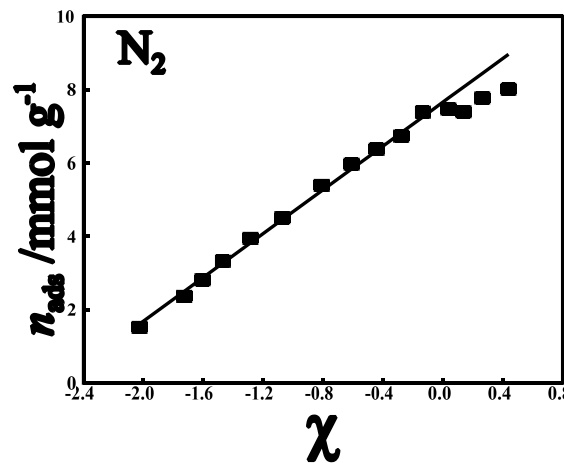
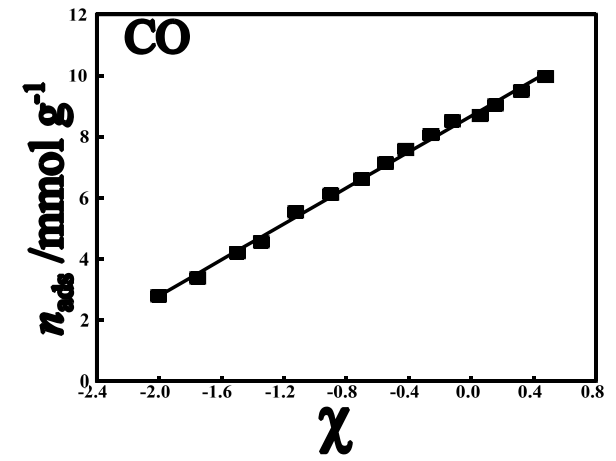
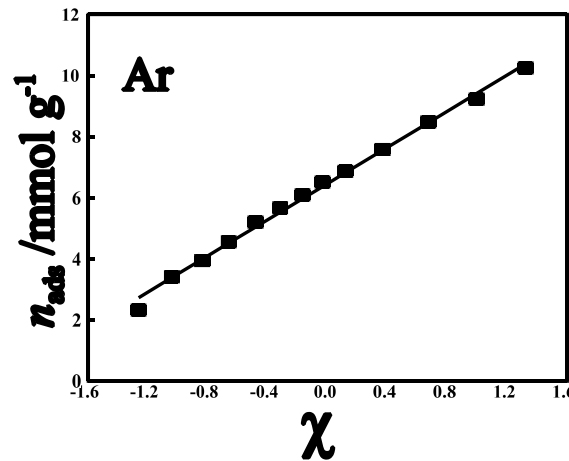
NASA Standard Lunar Soil Isotherms

Lunar soil has been outgassed very well and extremely clean. It illustrates the possibility of the χ -plot as being a good standard plot*

Generally the lunar soil shows linear χ -plot behavior.

Notice the threshold pressure for O_2 is quite obvious.

The loss in weight for the N_2 was probably loss in material or perhaps an earthquake shifting the balance. Oak Ridge has many active earthquake faults which often ruin runs



*Data by R. B. Gammage, H. F. Holmes, E. L. Fuller, Jr., D. R. Glasson, J. Colloid Interface Sci, **47** (1974) 350. and E. L. Fuller, Jr. P. A. Agron, "The reactions of Atmospheric Vapors with Lunar Soil. U." US Government Report ORNL-5129 (UC-34b), 1976

That's it for now

You may have figured it out that there are a lot of questions to be answered regarding this method.

It has not been critically tested by many researchers. Frankly, I would not be surprised if it were to be disproved. This would leave us in a peculiar situation similar to the pre-1930s, where there is no reliable way to measure surface area.

To test if it yields an approximation of the surface area, tests should be repeated on smooth surfaces. (Some were made early but disagreed with BET, so they were ignored.) These should be performed avoiding pit-falls. Needs are: 1) high and low pressure (UHV) measurements 2) better sample- T with baffles, etc. 3) more precision and accuracy 4) rigorously removing dead-space and/or buoyancy gasses.

More advanced theoretical work is need to understand binary adsorbent systems and better experiments to test the proposals. More work is needed to coordinate calorimetry and isotherm data with the same samples. More work is needed to obtain an automatic way to do the analysis -and there is much more. So if you want to help - you'll be busy.

You can send comments and suggestions to: condonjb@genchem.net Thank you.
This slideshow is at - <http://www.genchem.net/ColumbianPresentation.pdf>
or HTML at - <http://www.genchem.net/ColumbianPresentation/>