

**Lessons in Chi hypothesis - Application of Quantum Mechanics to Physical Adsorption - and its connection to the Thermodynamic ESW, Excess Surface Work**  
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([https://www.genchem.net/Lessons\\_in\\_Chi\\_hypothesis.pdf](https://www.genchem.net/Lessons_in_Chi_hypothesis.pdf))

**Notice:**

**This is a preliminary and partial draft of “Lessons in Chi hypothesis - Application of Quantum Mechanics to Physical Adsorption”** It basically covers the QM material and the implications described in the 2<sup>nd</sup> edition of the book “Surface Area and Porosity Determination by Physisorption - Measurement, Classical Theories and Quantum Theory” plus some additional important information.

About **Columbian presentation**: There have been some important new information since the June 2021 presentation. If you were there, you might want to look at these lessons. Some modifications also were made to: <http://www.genchem.net/ColumbianPresentation.pdf>

**Incomplete**: As time goes on, I will complete and update the information.

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**Being modified:**

- 1) partial completion of the section **Lesson XII - What Happens when  $|\epsilon| > |E_a^0|$ ?**
- 2) Calculation of the mesoporosity onset using competing energies.

**What's New?**

There is more evidence that the trade-off between the QM energy calculation and the Kelvin-Freundlich gas liquid interface formation is correct. The problem is that the value of  $\chi_c$  can shift from adsorption to desorption, perhaps due to residual gas in the pores at the beginning of the experiment (unknown.) This shifts the desorption even further. However, it appears that the change from  $m = 1$  to  $m = 2$  is the main driver of this effect. The change in energy is only about 10-20 J mol<sup>-1</sup> (not kJ!) and compared to typical  $E_a$ s of 5-20 kJ mol<sup>-1</sup> it is trivial, less than 1 ppt. Thus, it is not normally visible beyond the  $m$  factor correction in the  $\Delta\chi$ -plot.

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## Forward

The modern day analysis of the physical adsorption should be based, not just upon thermodynamics but also upon quantum mechanics. The modern thermodynamic theory, referred to here as the **Excess Surface Work**, or ESW, was developed at about the same time as the quantum mechanical derivation, referred to as  $\chi$ , hypothesis. The ESW is based upon classical thermodynamic, classical ideal gas law and a modern theory of film dynamics, referred to as disjoining theory. This latter theory includes and accounting for the 2 dimensional surface tension of the two sides of a film along with the a tensor that expresses the stresses and strains between and on the two sides. This sounds complicated, but for the physical adsorption on a flat surface, is not as complicated as it first seems. The form of the final derivation leaves nothing to adjust, however to obtain an answer for the number of molecules in a monolayer a decay constant is reasonably assumed to be exactly 1. If combined with  $\chi$ , however, this assumption is proven to be correct. For a more comprehensive derivation of the ESW see the articles by Jürgen Adolphs, et al., given in references [1], [2], [3] and [4].

In these lessons, except for the derivation of  $\chi$ , everything that applies to  $\chi$ , also applies to ESW. Since I was trained by nature in the  $\chi$ -hypothesis, I will teach these lessons from that point of view. Furthermore, it is a much easier concept when expanding the analysis to other questions, such a what is here called “layering” and layer density or even areal density. Knowing the “unusual” properties of quantum mechanics help with advanced concepts.

Quantum mechanics is the most powerful calculation technique that is used in chemistry. One can easily get away using classical chemistry, such as equilibria and solution theories such as regular solutions; however, these are only macroscopic approximations to describe submicroscopic processes. The mathematical connection between microscopic processes to the macroscopic observations is statistical thermodynamics. If the submicroscopic mechanics is not correct, it is not possible to formulate the correct macroscopic mathematics needed to compare with the macroscopic observations. (This has indeed been tried by many investigators with little generalized success.)

In the distant past, there were attempts to use thermodynamics to explain almost all of the macroscopic observations. Some believed that the four laws of thermodynamics derived all the macroscopic properties and cite the multiplicities of predictions. However, one can not get very far without assumed macroscopic models of materials’ behavior. A simple and vital example is the perfect gas law. It’s debatable that thermodynamics could have progressed very far without it. It is also dependent upon classical mechanics, although people don’t even notice when they have strayed out of the realm of the 4 laws. Thus, a mechanical model is needed for thermodynamic to do it’s magic. You will see this in the thermodynamic section on ESW.

Quantum mechanics is, unfortunately, not the forte of most chemist who not do it as part of their field. Indeed, many quantum mechanical calculations are performed today with canned programs, whose users have only a cursory knowledge of how they work. When it comes to practical chemical calculations, the overwhelming use of classical techniques are preferred. For many types of calculations the classical approach has been supported by an extensive literature of support and testing. Unfortunately, in some fields the classical approach is sadly lacking.

The question then is, why is the classical approach always considered first and the quantum modeling comes latter or not at all? I believe the following are the reasons.

- 1) The most important reason is that classical calculations are more intuitive. Classical mechanics seem to most as natural, we believe that we observed these classical mechanics daily. This is a bit deceptive. A good example of this deception is to look at old paintings of battles. Cannon projectiles that are aimed high are shown rising up and then suddenly falling out of the sky. It was widely believe that the object would continue upward until the ran out of ability to fly and suddenly drop. Even to very good observers, they get the flight path incorrect because of their point of view is at the point of launch, so when they draw the path from the side, it is distorted in the direction of the sudden drop belief.
- 2) Most investigators are not really familiar with quantum mechanics. They do not run into it in their field. Most general chemistry teacher shy away from quantum mechanics with the excuse that it does not apply, except for the results of other peoples calculation, to the subject they are teaching. I believe in truth, they do not understand quantum mechanics. For example, they might teach about quantum numbers, give the rules and how they apply to the periodic chart, but do not give an explanation in terms of how these are calculated. (I can hear the howls of objections now, but this is my observation. There are ways of explaining quantum mechanics without calculus. However, if one is teaching second year chemistry students, they should have had calculus.)
- 3) They are stuck in a “tradition.” This tradition in physical adsorption is the BET theory<sup>2</sup>. It is even designated the “gold standard” by IUPAC - an unjustified mistake.

Thus, the classical theories of classical mechanics has dominated the field of physical adsorption. Firstly, with the BET equation - the overwhelming favorite, and today, in response to frustration, methods such as the “Monty Carlo” technique and the various iterations of classical mechanical density functional theory (DFT, QSDFT, etc.) which requires tables of integration kernels, what I would call “look up tables.” This latter technique is basically a complicated way of making standard curves. Originally, it was based upon the assumptions that BET used and later assumed an assumption that is used in the quantum mechanical, that is delocalization in NLDFT and QSDFT.

The argument that many make is that their particular method, including those mentioned above, is that the theories correctly predict the pore volume. I call this argument a “no-brainer.” If the amount of material adsorbed on the outside surface of the porous sample is insignificant, then the eponymous Gurvitsch rule, stated more that 100 years ago works well. (If the outer surface is significant then one can reliably obtain the pore volume only with the quantum mechanical method. More about this either in my book or read on.) In the rule, the pores become filled as one approaches the vapor pressure of the gas being adsorbed. There are various ways of extrapolating to this pressure, since obviously the sample will be dripping when that pressure

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<sup>2</sup> Others classical based theories are also sometimes used, maybe out of frustration. (I was certainly frustrated with the BET when I first start making physical adsorption calculations. But, then, a very good mathematician pointed out the anomaly in the BET I was working against.)

reached. That is why I call the claim a “no-brainer” since all theories, and even no theory, can do a decent job of measuring this.

The quantum mechanical calculation of surface area and porosity has been proven to be very successful, as you will see in the following lessons. Obviously not all potential cases of adsorption have been analyzed nor even the majority. This is because there have been only two people consistently working on this problem, myself and the late Dr. E. Loren Fuller. A few others have contributed. One of special note is Dr. Jürgen Adolphs whose work on the Excess Surface Work (ESW) and disjoining pressure had contributed to the thermodynamics.

I hope you read this forward, but if you didn't at least take to heart this piece of advise:

**All theoretical development are considered tentative, even what is being presented herein. If you want you work to survive through time, it is OK to present some theory, but record and present the data you have in an untransformed condition. It may be in digital (preferred) form or in sharp, uncluttered graphic form. Otherwise, your work might be lost forever!**

I have run into many publications where the BET results are listed or some other theory listed, but no or poorly readable data. For these cases, the data has become useless. Other problems are the data has been transformed in another unretrievable fashion or the data is present in graphs which are very hard to read the data, for example, with several data sets in one graph. In these cases, I choose not the believe or use the information presented and so should others.

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## Lesson I - Introduction

### Sub-Lesson #1: Definitions and Symbols

Some of the vocabulary is familiar but has a slightly different meaning when working with the quantum mechanical (QM) derivation. Here are some familiar ones:

- 1) adsorbent: The solid material upon which the gas molecules will adsorb
- 2) adsorbate: The molecules originating in the gas phase that adsorb on the adsorbent.
- 3) adsorptive: The gas phase from which the adsorbate is sourced.

Here are some modified terms to either be consistent with modern IUPAC or with the QM.

- 4)  $P_{\text{vap}}$  the vapor pressure of the adsorptive at the temperature of the adsorbent. (IUPAC)
- 5)  $n_{\text{ads}}$  the number of moles of adsorbate on the adsorbent surface. (IUPAC)
- 6) “touching” atoms or molecules in close enough to be in a pseudo-harmonic oscillation (QM)
- 7)  $n_{\text{m}}$  the number of moles of adsorbate that would be required to completely cover the adsorbent surface IF they were all touching the surface (and thus each other.)
- 8)  $\theta$  is the normalized areal density of the adsorbate molecules. For a flat surface  $\theta = n_{\text{ads}}/n_{\text{m}}$  (QM.) In classical mechanics, this called the “surface coverage,” which is a little misleading in the QM picture.
- 9)  $n_1$  is the number of adsorbate moles whose molecules are touching the adsorbent surface. (QM)
- 10)  $\theta_1$  the areal density of the molecules touching the adsorbent surface,  $\theta_1 = n_1/n_{\text{m}}$  on a rigid adsorbent always. (QM see Lemma #1) These molecules are referred to being in layer 1.
- 11)  $n_2, n_3, \dots, n_n$ , are the number of adsorbate molecules touching molecules that are in the class  $n_1, n_2, \dots, n_{n-1}$ , but not lower (higher is possible and probable.) These are referred as being in the 2<sup>nd</sup>, 3<sup>rd</sup>, ... n<sup>th</sup> layer.
- 12)  $\theta_2, \theta_3, \dots, \theta_n$  are the areal densities of the 2<sup>nd</sup>, 3<sup>rd</sup>, ... n<sup>th</sup> layer.  $\theta_x < n_x/n_{\text{m}}$  for concave surfaces,  $\theta_x = n_x/n_{\text{m}}$  for flat surfaces and  $\theta_x > n_x/n_{\text{m}}$  for convex surfaces. (QM)
- 13)  $P/P_{\text{vap}}$  is the “relative” pressure sometimes given the letter “X.” (IUPAC and traditional)

These concepts may be a little confusing or puzzling, but there is a need to break away from classical thinking to appreciate the power of the QM derivation.

The symbol list is given in **Table 1** on page 9. Most symbols are latest IUPAC symbol and others are unique to the  $\chi$ -hypothesis. Some symbols used are combinations involving the main symbol and a subscript modifier, so be sure to look at both.

**Table 1** Symbol list - “X” and “y” are used as the descriptors.

Symbol	Description	units	*see notes
$\Delta\bar{S}(y)$	The entropy function as a function of $y$	$\text{kJ mol}^{-1} \text{K}^{-1}$	(1), (2), (5)
$\Delta_1^a \bar{S}(y)$	entropy change from liquid to the adsorbed state <sup>†</sup>	$\text{kJ mol}^{-1} \text{K}^{-1}$	(1), (2), (5)
$\Delta_1^a \bar{E}(y)$	energy change from liquid to the adsorbed state <sup>†</sup>	$\text{kJ mol}^{-1}$	(1), (2), (5)
$\Delta Q$	Steps in the integral heat for experiments	$\text{kJ mol}^{-1}$	(5), (8)
$\varepsilon$	$\varepsilon = \Delta_1^a \bar{E}(y)$		(3)
$\bar{\varepsilon}$	$\bar{\varepsilon} = \Delta_1^a \bar{E}(y)$	$\text{kJ mol}^{-1}$	(3)
$\theta,$	Relative adsorbate areal density, $\theta = n_{\text{ads}}/n_m$		(3)
$\theta_1$	Relative first “layer” areal density		(3)
$\theta_n$	Relative nth “layer” areal density		(3)
$\theta_{1,1}, \theta_{1,2}, \theta_{2,1}$	The relative density in the “first layer” of the: 1 <sup>st</sup> adsorbate, 2 <sup>nd</sup> adsorbate,... , 2 <sup>nd</sup> layer 1 <sup>st</sup> adsorbate,...		(3)
$A, A_a$	Surface Area	$\text{m}^2 \text{g}^{-1}$	(1)
$a$	molecular area	$\text{m}^2 \text{g}^{-1}$	(1)
$\bar{E}(y)$	Internal energy function dependent on $y$	$\text{kJ mol}^{-1}$	(1), (2), (5)
$\bar{E}_a$	molar “internal energy” first adsorbate molecule	$\text{kJ mol}^{-1}$	(2), (6)
$E_a$	Adsorption energy of the first adsorbed molecule		(6)
$N_A$	Avogadro’s number	$\text{mol}^{-1}$	(1)
$n_{\text{ads}}$	amount of adsorbate	$\text{mol g}^{-1}$	(1)
$n_{\text{ads},1}$	amount of adsorbate molecules in the first “layer”	$\text{mol g}^{-1}$	(3)
$n_{\text{ext}}$	monolayer equivalent on the non-pore “external” surface	$\text{mol g}^{-1}$	(3)
$n_{\text{pore}}$	on the non-pore “external” on the pore surfaces	$\text{mol g}^{-1}$	(3)
$n_{\text{pore},V}$	total amount in the pores (includes $n_{\text{pore}}$ )	$\text{mol g}^{-1}$	(3)
$n_m$	total monolayer equivalent moles	$\text{mol g}^{-1}$	(3)
$n_X$	moles of type “X”	$\text{mol g}^{-1}$	(1)
$n_1$	$n_1 := n_{\text{ads},1}$ (for convenience)	$\text{mol g}^{-1}$	(3)
$P$	Pressure of the adsorptive.	(7)	(1)

$P_{\text{vap}}$	adsorptive vapor pressure at adsorbent temperature	(7)	(1)
$P_{\zeta}$	pressure for adsorption	(7)	(6)
$\tilde{p}$	fugacity	1 bar	(1)
$q$	Differential heat of adsorption, $q = \bar{E}^{\ominus}(y)$	$\text{kJ mol}^{-1}$	(5), (8)
$Q$	Integral heat of adsorption	$\text{kJ mol}^{-1}$	(5), (8)
$R$	The gas constant, = $8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$		(1)
$\bar{X}$	Molar quantity of “X”	$\text{mol}^{-1}$	(1), (2)
$X(\text{a})$	adsorbed phase of “X”		(1)
$X(\text{g})$	gas phase of “X”		(1)
$X(\text{l})$	liquid phase of “X”		(1)
$\mathbf{X}(y)$	A function (bold type) of $y$		(4)
$X_{\text{g}}^{\text{ada}}$	“X” of gas to adsorbate (or $X_{\text{g}}^{\text{a}}$ )		(1)
$X_{\text{l}}^{\text{ads}}$	“X” of liquid to adsorbate		(1)
$X_{\text{l}}^{\text{g}}$	“X” of liquid to gas (or $X_{\text{l}}^{\text{a}}$ )		(1)
$X^{\ominus}$	“ $\ominus$ ” indicates the standard state is 1 bar for “X”		(1)
$X_{\zeta}$	“ $\zeta$ ” indicates threshold quantity for “X”		(6)
$X_{\text{ads}}$	“ $\text{ads}$ ” indicates “of adsorption” for “X”		(1)
$X_{\text{m}}$	“ $\text{m}$ ” indicates monolayer quantity for “X”		(1)
$X_{\text{vap}}$	“ $\text{vap}$ ” means vaporization of adsorptive		(1)
$X$	mole fraction		(1)
* The following numbered notes indicate what convention is used. Subscript convention is also followed for designations.			
(1) This is according to 2013 IUPAC “Green Book” [5] and normal standard state is 1 bar.			
(2) This uses the alternate designation from the 2013 “Green Book” so as to avoid conflict with the symbol for monolayer.			
(3) $\chi$ symbolism or definition. May have classical equivalent.			
(4) IUPAC does not distinguish between the differential and integral heat in the “Green book,” so this distinction, which is traditional in some quarters, used. Also $q \approx \Delta Q/\Delta n_{\text{ads}}$			
(5) traditional (IUPAC makes no distinction between a variable and a function.)			
(6) Unique to adsorption since it was unknown to IUPAC. Standard State is $\mathbf{P}_{\text{vao}}(T_{\text{adsorbent}})$			

(7) Pressure units depend upon data source. Often torr or atm. Normally pressure is held constant or as an independent variable, therefore its symbol is italic and not normally bold.

(8) Somewhat traditional with standard state of 1 bar

† Since the topic is adsorption, the  $i^a$  will often be left off if there is no ambiguity. Quantities in the Physisorption writing, specific quantities means compared to the adsorbent mass.

Symbols used for the quantum mechanical derivation are given at the beginning of that Lesson.

### Sub-Lesson #2: General analysis concepts:

In most analyses of physical adsorption there are plots that are made to express the adsorption in an alternate way other than the normal isotherm, which is  $n_{\text{ads}}$  on the ordinate and relative pressure,  $X$ , on the abscissa.

For example, the BET isotherm representation uses  $X$  on the abscissa, but uses  $X/[n_{\text{ads}}(1-X)]$  on the ordinate, Henry's law and Freundlich isotherm use  $\ln(X)$  on the abscissa and  $\ln(n_{\text{ads}})$  on the ordinate. There are many other laws which use different transformations. Two of these laws are used for the QM model. They have been used in the past, apparently to express the isotherm in a more linear and wider range, without proper recognition of why they worked.

What are laws?

In science laws are a way of grouping repeatable observations. They may or may not be based on any theoretical foundation. For example, Newton's laws had no solid theoretical bases for hundreds of years but they worked unflinchingly until recently. Laws can be situational, for example chemical kinetics have multiple possible laws, first order, second order, etc. but are very handy for predictive purposes once the law is figured out. Many of the laws for adsorption in the literature are extremely situational to the extent that predictions are very uncertain.

In these lessons, the primary laws are derived from QM but have been observed in the past. They will be referred to as the log-law and the  $\chi$ -hypothesis. These laws, however, were observed first and then puzzled over for about 50 years.

Why make these transformations? The simple answer is, physical scientists love to see straight lines, and supposedly when one uses a transformation that yields a straight line, it proves the theoretical development. This is sadly incorrect. Firstly, no theory can be proven, only disproven. One can only gain confidence in a potential theory or law by critically testing it enough times. (How long? They are still testing Einstein's General Theory of Relativity.) This is philosophically uncomfortable since humans abhor uncertainty, but it is good to keep in mind.

### Sub-Lesson #3: Why BET and why not BET?

I will only mention the BET here shortly since it is the prevailing hypothesis of the moment. Firstly, it is a lousy theory. It makes incorrect predictions, it is imprecise and inaccurate. I do not want to spend much efforts on this, but you can read about the problems in publications by Kenneth Sing or the section in the 2<sup>nd</sup> edition of my book. The question is, “If the BET is so bad, why has it predominated the field for over 80 years?” The answer is simple, it was the only hypothesis which yielded a number convincingly for the surface area of a powder. There was, however, no indication that this was actually true. Indeed, efforts to make such measurements were dismissed as being experimentally flawed instead of the BET being wrong.

I end this section with the following recent quote and observation:

“Science is designed to test the boundaries of our existing knowledge in these efforts to get closed to the truth. But in challenging hypotheses and gathering data, new studies will inevitably show that some previous results don’t hold up anymore, whether regarding novel diseases such as COVID-19 or many other areas of research. Insisting the citizens [this includes scientists] simply trust the science on any given study [or theory] is not only disingenuous, it is likely unethical. It also undermines science’s fundamental claim as society’s impartial arbiter of what we know and don’t know.”<sup>3</sup>[6]

Unfortunately, I have observed much unethical behavior among science authors in the literature and by reviewers especially with respect to the BET theory. Any theory or hypothesis should be subject to revision or even rejection when scientific based data indicate this is appropriate. This includes the hypothesis presented here, called the  $\chi$ -hypothesis.

#### **Sub-Lesion #4: What is physical adsorption or physisorption?**

Firstly, it is the tendency for gas molecules to bond, or perhaps a better word would be to stick, to the surface of a solid. The word bond seems to imply a chemical bond, that is a covalent bond or possibly an ionic bond. Such a bonding is referred to as chemisorption. Physisorption does not rely on chemical bonds but rather the usually weaker and more delocalized intermolecular attractions. These include:

- 1) dipole-dipole attractions
- 2) dipole-induced dipole attractions
- 3) in the case of conductive adsorbents dipole-reflective dipole attraction
- 4) “hydrogen bonding”
- 5) London forces, induced dipole-induced dipole

These forces are not confined to particular “sites” on the surface unless the temperature is below the freezing point of the adsorbate. Instead, unobserved (QM), the adsorbate “flows” over the adsorbent much as a liquid would do. No doubt, the surface consists of potential pockets like muffin tins, but the energy of translation for the adsorbate molecules is too great to be caught in

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<sup>3</sup> N. M. Keause, D. A. Scheufele, I. Freiling and D. Brossard, “The Trust Fallacy,” American Scientist, A Sigma Xi publication, **104 (4)** 2021, 230. I have added the words in [ ] to expand this insight.

one of these muffin tins. Thus, physisorption is referred to as a delocalized process rather than localize as is the case with chemisorption.

There will be some arbitrary limits in addition to the temperature being above the adsorbate freezing point. (Even this restriction may not be totally correct since there has been evidence of delocalization below the adsorbate freezing point in some cases, but to be safe, here the restriction is maintained.) The other arbitrary limit is that the temperature and pressure be below the critical point of the adsorbate. Physical adsorption does occur above the critical point, but at this time, working this out is not high priority. One problem is how to calculate the fugacity to use to take the place of  $P_{\text{vap}}$  and the ability to find the thermodynamic data to do this.

The delocalized forces are a basic assumption, and are even a part of the definition of physisorption. Thus:

**Definition: physisorption over the temperature range for which the adsorptive is a liquid is delocalized and therefore the details of the condition of the surface, other than the overall adsorption energy, are not relevant.**

**Sub-Lesion #5: The  $\chi$  function and the inverse  $\chi$  function.**

The  $\chi$  function is being introduced here to eliminate any mystery about it. The  $\chi$  function is simply:

$$\chi(x) = -\ln(-\ln(x)) \quad (1)$$

and the inverse  $\chi$  function is:

$$\chi^{-1}(x) = \exp(-\exp(f(x, \mu, \sigma))) \quad \text{where} \quad f(x, \mu, \sigma) := -\frac{x - \Delta\chi_y}{\sigma} \quad (2)$$

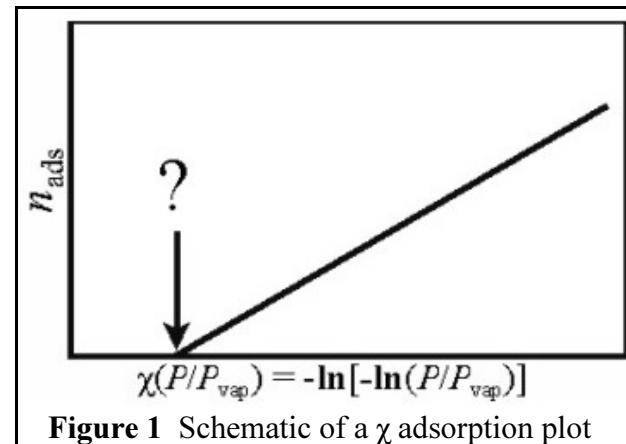
a delta  $\chi$  function is:

$$\Delta\chi(x, y) := \chi(x) - \chi(y) \equiv -\ln(-\ln(x)) + \ln(-\ln(y)) \quad (3)$$

Since the  $\chi$  function and  $\Delta\chi$  function will be used over and over, the arguments in the parenthesis will be usually be left off. The arguments remain fixed and will be specified by subscripts. The arguments for the inverse, however, need to be specified and vary according to circumstances.

The  $\chi$ -plot will be the plot consisting of the  $\chi$ -function of the relative pressure,  $\chi(P/P_{\text{vap}})$ , on the abscissa and  $n_{\text{ads}}$  as the ordinate. This plot, theoretically for a flat surface, looks like **Figure 1**.

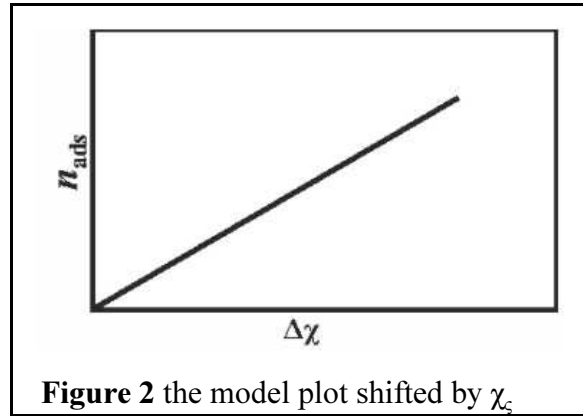
If this plot is linear for the adsorption (later on you will find out why and when it is) then the plot crosses the abscissa where the question mark is. This is impossible, since  $n_{\text{ads}}$  cannot be negative. This point is given the symbol  $\chi_c$  and the



**Figure 1** Schematic of a  $\chi$  adsorption plot

pressure at which this happens is been given the symbol<sup>4</sup>  $P_\zeta$ .

This has been referred to as the threshold pressure. The threshold pressure is impossible according to the BET and other “Henry’s law” isotherms and if were to be found would convincingly disprove them. This form can then be modified by subtracting the value of  $\chi_\zeta$  from  $\chi$  one obtains a plot of  $\Delta\chi$ :



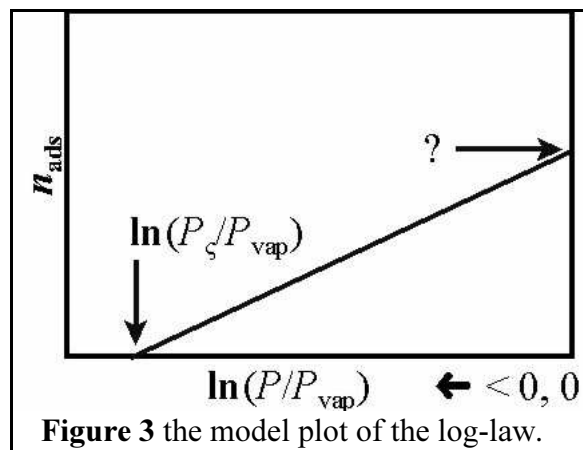
This  $\Delta\chi$ -plot is shown in **Figure 2** with the appropriate shift. You will discover the intuitive advantage of this plot later.

The other plot that is important is the log-law plot. For this plot the transform is simply the log of the relative pressure as the abscissa and the ordinate remains as the  $n_{\text{ads}}$ . This law serves a different purpose from the  $\chi$ -plot. This law is illustrated in **Figure 3**. This is the case for a linear plot. Notice now that there are two intercepts, one on the abscissa and one on the ordinate. The one on the abscissa is the same intercept as in the  $\chi$ -plot. The one on the ordinate (right side at  $\ln = 0$ ) is not available in the  $\chi$ -plot. (It turns out to be  $n_m$  but more about that later.)

These plots show up in the QM derivation, so they are very useful for extracting the output parameters that one needs to characterize the adsorbate-adsorbent pair.

Many samples can be analyzed simply with these graphs. Unfortunately, Mother Nature often does not supply simple answers and simple analysis needs to be expanded to include higher order fitting routines. But first, we need the QM description and then examine some simple isotherms. This will be started after a short section on the experimental pitfalls. These pitfalls, if not avoided, can make it impossible to provide an accurate answer about the nature of the adsorbent-adsorbate pair.

Be warned, read about the pitfalls! Your data might be useless otherwise.

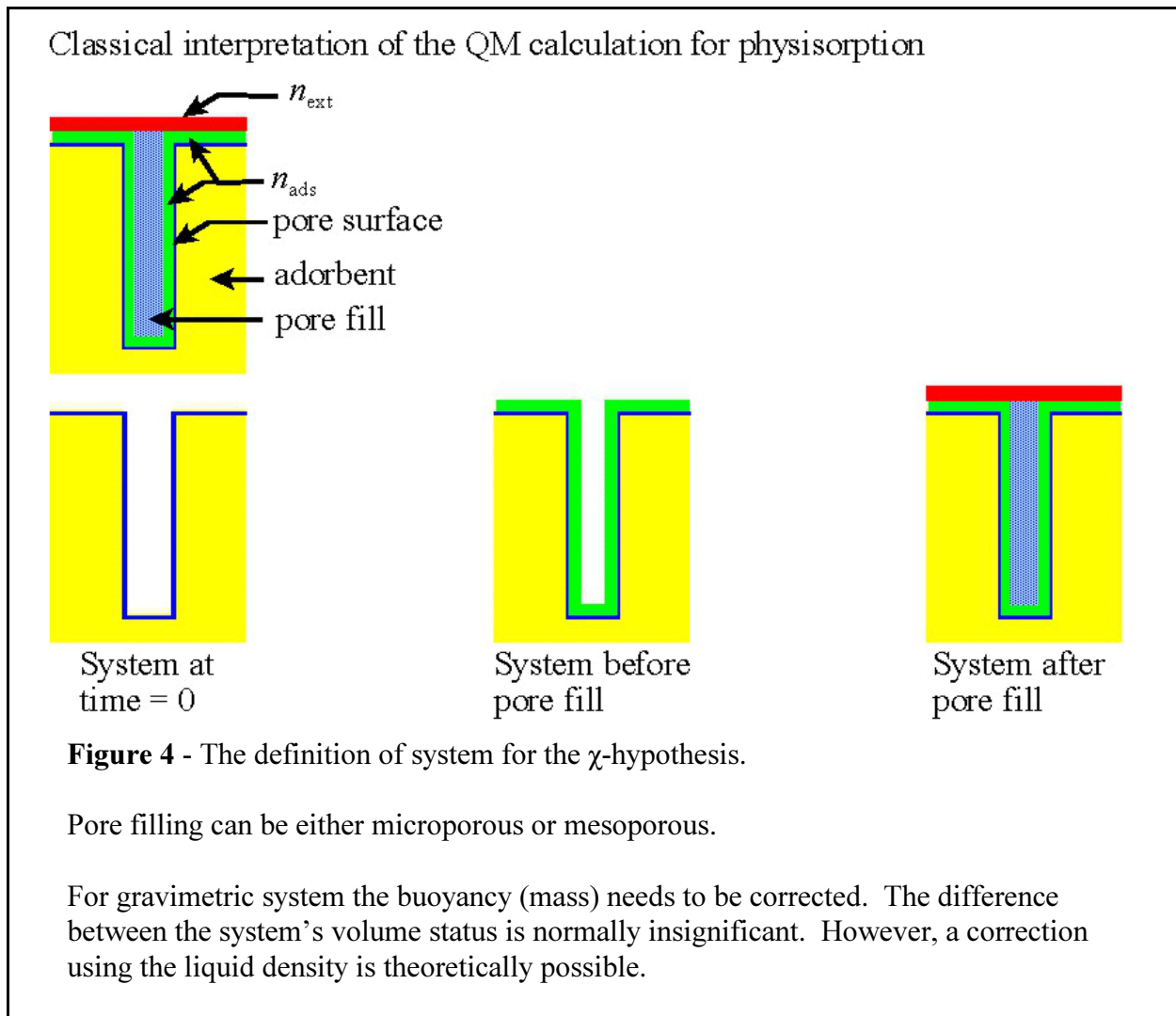


<sup>4</sup> The subscript is being modified from “c” and “p” to “ $\zeta$ ” for consistency and to distinguish the  $P_\zeta$  from the critical pressure of the adsorptive liquid/gas,  $P_c$  (NIST standard).

**Sub-Lesion #6: System Definition:**

I end this section with some comments about the thermodynamic concept of “system.” Thermodynamics is independent on the fine structure of matter<sup>5</sup>[7], and the concept of “system” is a macroscopic property. A system is usually defined as a physical space defined by specified (macroscopic) spatial boundaries. Properties of the system may change according to what passes through the boundaries or how the boundaries change in space. However, even though these boundaries might be conceptually considered “thin,” this is a difficult, and unnecessary, concept to apply. The concept of the thin boundary for a surface was a problem the Gibbs attempted to by-pass with the concept of surface excess.

This definition is inappropriate for physical adsorption, especially in the light of the Quantum mechanic and the  $\chi$ -hypothesis. For the gravimetric method, this means the adsorbate mass increase is the vital property for the system definition, since it is assumed that the adsorbent mass remains constant. Any spatial boundary changes do not affect this definition. This means that



<sup>5</sup> Wording from Denbigh expanded upon to be more relevant to physical adsorption.

a change in the buoyancy correction should be trivial even up to multiple monolayers. At any rate, this change is easily performed if there is some doubt.

An illustration of this concept is showing in **Figure 4**. A similar treatment may be used for the volumetric system. But in that case, there is a small adsorbent volume change for the “dead” space. Again, for low pressures, this correction due to increasing volume of the system may be insignificant, but more likely than in the gravimetric system. Therefore, one should remain cognizant of the possibility and make a few quick calculations.

The potentially small corrections for adsorption can be seen from **Figure 4**. This include changes in  $n_{\text{ads}}$ ,  $n_{\text{ext}}$ , and  $n_{\text{pore}}$ . The largest would probably be  $n_{\text{pore}}$ , especially for mesoporosity. For microporosity, that is restricted to only 1 to 2 monolayers, the correction should be insignificant.

What about high pressure, even approaching the critical point? Corrections for compressibility of the adsorbed state and the material in the pores might need have to be considered. If the adsorbent is compressible, this would be an additional complication. There is a difference in the volume needed to be used for the buoyancy calculation. The buoyant volume decreases with adsorption in the pores and increases slightly as adsorbate builds up on the external surface. This along with the densification of the adsorptive, also needed for the buoyancy calculation, are difficult problems to solve before the measurement. However, the definition of the system need not change. Again, at low pressures these complications are insignificant.

Here are some questions that might come up:

*What counts as adsorbate?*

This question is really answered by the definition of the system.

*What molecules qualify to be an adsorbate molecule?*

*Classical explanation:* Of course, the system is in equilibrium with the surrounding adsorptive. The classical explanation would state: Any particular molecule at a particular time may be an adsorbate molecule or an adsorptive molecule. It may be close enough to the surface to switch back and forth. When an adsorptive molecule releases energy due to the approach to the surface and remains, at least momentarily, without gaining energy to escape from the surface, it is an adsorbate molecule. If an adsorbive molecule is reflected from the surface with no energy change it is not counted as an adsorbate molecule. When an adsorbate molecule randomly obtains enough energy to break free from the near surface area, it becomes an adsorptive molecule. Equilibrium implies there is a balance between these two processes.

*Quantum mechanical explanation:* The quantum definition is in the mathematics of the derivation of the  $\chi$ -hypothesis given later.

*Why would a molecule “stick” to the surface?*

By “sticking” to the surface, Helmholtz energy is released with the molecule being held by intermolecular forces. This is an important point, and will be visited again in the section on

mesoporosity and the formation of a liquid-gas surface. This latter formation releases energy in competition with the adsorption energy function. Approach to the minimum in these forces is what releases the energy. To become “unstuck” the molecule needs to escape from these forces which requires energy. The thermodynamic equilibrium is maintained by a balance of these processes among many molecules averaging as no net gain or loss in overall energy.

This latter explanation hints at how mesoporosity can be predicted.

## Lesson II: - A short description of possible errors - the pitfalls.

In the text book, I devote an entire chapter to equipment and a considerable amount of space to errors. Many investigators buy their equipment, usually volumetric, ready-to-go. Not only that, but the equipment is automatic and even the analysis the data automatic with questionable algorithms. My experience with manufacturers is that they are very reluctant to change anything, either in the hardware or software to aid the user to obtain more reliable information.

### Big error #1 - pressure range:

Error: the equipment is not capable of measuring the full range of pressures. This includes at least down to  $10^{-6}$  of  $P_{\text{vap}}$ . This is usually the high vacuum range, but ultra-high vacuum might be needed. One doesn't necessarily know what range is required before starting an experiment, so this problem is tricky. The higher the vacuum, the more expensive the equipment is. See if you can find someone to do trial runs before you buy. You need to get down to the  $P_{\zeta}$  (see page 14) since it contains vital information. Reaching down to the  $P_{\zeta}$  pressure is important to determine the energy function,  $\mathbf{E}(\chi) = E_a \exp(\chi)$ , for which the constant  $E_a$  needs measuring and  $E_a$  is available at the appearance of  $P_{\zeta}$ .

### Big error #2 - sample radiative heating and other temperature problems:

If the temperature range is below of above room temperature, one needs to worry about radiative heating. For cryogenic temperatures, this is critical. A  $1^{\circ}\text{C}$  radiative heating error of the adsorbent creates a big shift at higher pressures and distorts the isotherm. This is particularly a problem for the big tubing for a gravimetric system, and baffles in the cold zone are called for.

For the volumetric systems, if they have metal walls, the problem is much smaller, especially if there is a bend in the tubing to block direct line-of-sight to room temperature. However, most volumetric systems have glass hang-down tubes and the radiative heating from above is considerable.

Another problem for those who use liquid coolant is atmospheric pressure. This may sound like a ridiculous worry but the liquid coolant is only at the temperature of the coolant boiling point only if the atmospheric pressure is at 1 bar. A 0.10 K error in temperature is very significant at 77 K. (... and by the way, one can tell when a researcher is not paying attention to sample temperature if it is given only to the nearest 1 K as written here. The adsorbent temperature should be recorded to the nearest 0.01 K.

This seems to be a big shift in how one operates the system. The simplest method to measure the temperature is with a gas/liquid thermometer using the same gas/liquid as the adsorptive. This is a very old technique, which seems to have been abandoned. Make sure the bulb of the gas/liquid thermometer is physically close to the adsorbent and shielded by the same technique that is used for the adsorbent (preferably in the same shield.)

A gravimetric system, also needs a good measuring device, however the radiative heating is not as severe since the internal baffles keep the cold zone uniform (assuming one is using these baffles as recommended.)

This error has long been known, documented by deBoer and Zwiiker[8], and ignored by almost everyone since. (After all, why believe something in a discredited publication?)

### **Big error #3 - insufficient outgassing**

One must make sure that dead-space measuring gas, usually He, is sufficiently out-gassed. One way of eliminating this problem is to do the isotherm of interest first then do the dead-space measurement. Alternatively, do the isotherm several times, a good idea anyway, to see if you get reproducibility without intervening dead-space analysis, which is not necessary. (A second advantage of doing the isotherm three times is to get a measure of the data standard deviation without fitting a model to the data.) It may also be a good idea to characterize what temperature to out-gas is best for the adsorbent. 150°C has been recommended, but there is not enough information in the literature to cover a variety of adsorbents. For this a little trial and error is in order.

The gravimetric system has a similar problem, since one needs to measure the buoyancy correction.

### **Big error #4 - Insensitivity to the laminar flow-turbulent flow/molecular flow transition.**

The problem was first related by Langmuir<sup>6</sup>[9] and is described in detail by Ross[10]. There are ways to either avoid the problem or correct for the problem. Langmuir calibrated the individual hang-down tubes in his volumetric system. In the Oak Ridge gravimetric system, the hang-down tube had a large enough diameter and long enough transition zone to avoid the problem. This problem will yield the incorrect abscissa in the isotherm  $\chi$ -plot. This is a very very important quantity to be measured correctly, or one obtains nonsense. It should be avoided or corrected.

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<sup>6</sup> If you haven't read or tried to analyze Langmuir's data, I suggest that you do so. You will realize in attempts to fit the data, that the data is not worthy of modern acknowledgment. Of the many sets, only one could be interpreted as supportive. Remember, Langmuir did not get the Nobel Prize for the "Langmuir isotherm," but for his work on aqueous monolayer films.

**.Other techniques:**

The gravimetric and volumetric techniques are the two most widely used for investigating physical adsorption. Mostly through out this course, these are the techniques being addressed. The theoretical concepts, however, obviously apply. Some of the more widely used techniques to investigate physisorption are:

1), Calorimetry. This technique is conceptually easy but in practice very difficult and an improperly designed calorimeter is a disaster. If one were to use this technique, the measurement of the isotherm is also necessary for interpretation. It's important, however, for comparing the energies obtained by the isotherm measurement and calculated then from the  $\chi$ -hypothesis. Agreement is required on the same adsorbent sample.

2), Another technique is the flow system, similar to chromatography. This technique is used primarily for engineering problems, but unlikely to yield, at least at this point, the fundamental parameters for adsorption. The QM model for analysis has not yet been applied to this method. It may actually be easier than the conventional analysis, which uses either Henry's law or the Langmuir equation modified for multiple adsorbates. Both the Henry's law and the Langmuir equation are really inappropriate for this analysis. So, good luck.

### Lesson III: The QM perturbation model?:

The QM model for physisorption (physical adsorption) is a modified particle-in-the-box with a perturbation, or several, present. A modification is to make the standard state pressure at the end of the derivation be  $P_{\text{vap}}$ . Thus, the energies will be compared to  $P_{\text{vap}}$  and there are three possibilities. These possibilities compare the energy of adsorption of the first adsorbed molecule,  $E_a$ , to the energy require to vaporize the adsorptive from the liquid state,  $\epsilon$ .

#1  $\epsilon < E_a^\ominus$  most common case<sup>7</sup>

#2  $\epsilon \approx E_a^\ominus$  probably very rare indeed

#3  $\epsilon > E_a^\ominus$  rare but observed.

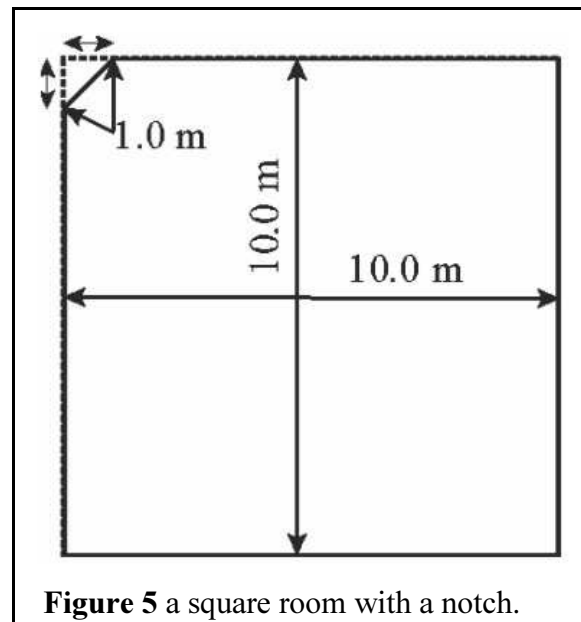
First some simple classical examples of the philosophy behind perturbation theory. After this, the QM derivation for the simplest case, that is homogeneous, flat (nonporous) adsorbate surface and uncomplicated, simple adsorptive molecule, for which internal modes of vibration and internal rotation can be ignored. The change in translational modes is also small but in some cases detectable, but this will also be ignored until the explanation of “layering” is presented<sup>8</sup>.

#### Sub-Lesion #1: QM perturbation theory

Perturbation theory is not a new concept. Indeed, the principles are used traditionally in classical mechanics before the advent of computers. The idea is to solve a problem similar to the real problem being addressed, but is easier to do. One then adds perturbations to simulate the real problem and modifies the first answer. Let's take a simple example:

Calculate the area of a square room that is 10.00 m  $\times$  10.00 m but has a triangular notch which measures out from a corner by 1.00 m in both directions. See diagram at the right.

Of course this is easy. Most students can do this just in their head. The important point is, “What are the specific steps?”



**Figure 5** a square room with a notch.

Firstly, attack the simple problem, the area of the square. This is:

<sup>7</sup> What's the connection to the standard state, “ $\ominus$ ”, of 1 bar? This is fixed by the reference to the liquid heat of adsorption, which in turn is referenced to the 1 bar standard state normally.

<sup>8</sup> The notations, in addition to IUPAC, will be similar to that for the classical adsorption theories, **however**, there are subtle differences in meaning. “Layer” is one of those to be defined later.

$$A(\text{square}) = l \times w$$

$$A(\text{square}) = 10.00 \text{ m} \times 10.00 \text{ m} \quad (4)$$

$$A(\text{square}) = 100.0 \text{ m}^2$$

Then one calculates the area of the triangle in the corner:

$$A(\text{triangle}) = \frac{1}{2} l^2$$

$$A(\text{triangle}) = \frac{1}{2} (1.0 \text{ m})^2 \quad (5)$$

$$A(\text{triangle}) = 0.50 \text{ m}^2$$

And now, we subtract the triangle area from the square area:

$$A(\text{odd shape}) = A(\text{square}) - A(\text{triangle})$$

$$A(\text{odd shape}) = 100.0 \text{ m}^2 - 0.50 \text{ m}^2 \quad (6)$$

$$A(\text{odd shape}) = 99.5 \text{ m}^2$$

This section may seem a bit too elementary, but it illustrates some important considerations when it comes to quantum mechanics and basically the concepts are easy to understand, although the math might be somewhat tangled getting there.

### **Sub-Lesion #2: The big box and homogeneity:**

The next question is, “Does it make any difference which corner has the notch as far as the final answer is concerned?” The answer is obviously not. How about if it is moved to the middle of the room, maybe inconvenient but the answer does not change. What if we break the triangle up in little pieces? Again, no change.

As long as the floor space is not something strange, like having different areas as a function of position (huh?), it makes no difference where the triangle is, the answer is the same.

This illustrates another concept in physical adsorption. If it does not matter where the position of the triangle is, the system is considered to be “homogeneous.” But what if near the walls the value of the square area changes (huh?) OK, another illustration would be helpful.

Say that this area is not a uniform room but rather a coal pile. The height of coal piles are not normally uniform, so if one were to take a core sample, that is a column of coal, out of the coal pile, the amount one obtains would depend upon location. Usually, the middle is higher than toward the edges, so one would get more core sample from the middle.

But now assume the coal pile is very large, say  $100 \text{ m} \times 100 \text{ m}$  and the manager of this pile is very fussy and always wants the bulldozer driver to level it off perfectly. Well, of course, this can be done in the middle of the pile, but becomes difficult toward the edges, unless there is a restraining wall. Thus, at the edges, the coal pile slopes at a  $42^\circ$  angle. If the slope extend only a few meters into the pile, however, it is most likely in taking random core samples, that one will obtain the same answers.

This latter example, is an analogy to what is being referred to here as the “big box” assumption. The surface of the (usually) powder adsorbents is broken up into many pieces, but even so, each piece of the surface, or surface aliquot, is very much larger than an individual adsorbate molecule. Molecules are on the scale of nanometers whereas the surface aliquots are on the scale of micrometers. Thus, the ratio of adsorbate molecule to surface aliquot is 1:10<sup>6</sup>, a big box indeed. This is the first assumption for the  $\chi$ -hypothesis.

**Assumption 1, the first order approximation: the “Big Box:”**

- 1A: An adsorbed molecule is a perturbation in the particle-in-the-box problem and it makes little difference where the perturbation resides on the adsorbent surface aliquot.**
- 1B: The area of this perturbation is extremely small compared to the surface aliquot it resides on.**
- 1C: The same is true of additional perturbations from other adsorbate molecules.**

The next assumption comes directly from QM and the particle in the box calculation. Many students are familiar with this and in General Chemistry courses I have taught this in preparation for atomic structure discussions. It may be that you are familiar with this and don't need this section.

**Sub-Lesion #3: Particle in the Box**

The following are symbols used in this section:

$\hbar$  : reduced Plank's constant

$m$  : particle mass

$V$  : potential energy

$\Psi(x,t)$  : time dependent particle wave

$\psi(x)$  : Steady state particle wave

$\phi(t)$  : Time portion of the particle wave

$W$  : Separation constant that translates to an energy

Quantum mechanics consists of 5 assumptions. These assumptions and the resulting wave equation are not presented here and assumed as settled as far as chemistry is concerned. The time dependent wave equation is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) = -\left(\frac{\hbar}{i}\right) \frac{\partial \Psi(x,t)}{\partial t} \quad (7)$$

The  $y$  and  $z$  dimension may be added in with term similar to the first term. In one dimension this equation is “separable” in time and space, by writing:

$$\Psi(x,t) = \psi(x)\phi(t) \quad (8)$$

Dividing both sides by  $\Psi$  and rearranging:

$$\frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) \right] = -\left(\frac{\hbar}{i\phi(t)}\right) \frac{d\phi(t)}{dt} \quad (9)$$

Since the separated equation retains its equality and is therefore an identity, both sides of this equation are equal to a simultaneous constant. This constant is usually given the letter  $W$ , but there can be several values for it, which will be distinguished by subscripts,  $W_1, W_2, W_3, \dots$

Setting both sides to  $W$  and rearranging into normal differential equations one obtains<sup>9</sup>:

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(W - V(x))\psi(x) = 0 \quad \text{and} \quad \frac{d\phi}{dt} = -\frac{iW}{\hbar} \quad (10)$$

The right equation is easily solved so long as  $W$  is a constant and the left equation determines the value(s) of  $W$ . The particle-in-the-box uses a constant  $V(x)$  and boundary conditions on  $x$  to solve the equation.

The particle-in-the-box is formed by setting  $V = 0$  and specifying  $\psi = 0$  at  $x = -L$  and  $+L$ :

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}W\psi(x) = 0 \quad \text{and} \quad \psi(0) = 0 = \psi(+L) \quad (11)$$

One can end up with several solutions with different particular values of  $W$ . The first solution is:

$$\psi_1 = A_1 \sin\left(\frac{\pi x}{L}\right) \quad \text{with} \quad W_1 = \frac{\pi^2 \hbar^2}{2mL^2} \quad (12)$$

According to the fourth assumption, the integral:

$$\int \psi^* \psi dx = 1 \quad (13)$$

and in order for this to be true then for  $A$ :

$$A = \sqrt{\frac{2}{L}} \quad (14)$$

This is not the only solution. Others solutions for this are<sup>10</sup>:

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{with} \quad W_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (15)$$

Another important property for these wave functions is orthogonality:

$$\int_{-\infty}^{\infty} \psi_m \psi_n dx = 0 \quad m \neq n \quad (16)$$

Also:

$$\int_{-\infty}^{\infty} \psi_m \psi_m dx = 1 \quad (17)$$

The question is, what is the probability of finding the particle if all of space from  $-\infty$  to  $+\infty$  is included. Obviously, the answer is 1. This is what has been assumed is the meaning of this last equation. Thus, what is inside the integral, must be the differential probability of finding that

<sup>9</sup> The “ $i$ ” creates complex numbers for the solution. If we were interested in the time dependance then the complex solutions would be needed. Here we will ignore the  $\Im$  portion of conjugates without any lose in rigor.

<sup>10</sup> For  $x$  and  $y$ , if separable, the  $W$ 's for  $x$  and  $y$  add for the total energy.

particle is at  $x$ :<sup>1</sup>

$$\mathbf{P}(x) = (\psi_m(x))^2 \quad (18)$$

Where  $\mathbf{P}(x)$  is the probability density. Thus for  $\psi$  from equation 15:

$$\mathbf{P}(x) = \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) \quad (19)$$

For the first molecule this describes the  $x$  “density distribution” of the molecule. Obviously it can be proven that in the potential box of dimension  $L$ :

$$\int_{-\frac{1}{2}L}^{+\frac{1}{2}L} \mathbf{P}(x) = 1 \quad (20)$$

The above equations used the hard-set boundary conditions to specify the boundaries of the potential box in which the particle is contained. Of course, Mother Nature is not that way. The potential “wells” can be escaped (at least on earth) with enough energy to get out of the well. So, how is this picture different.,,

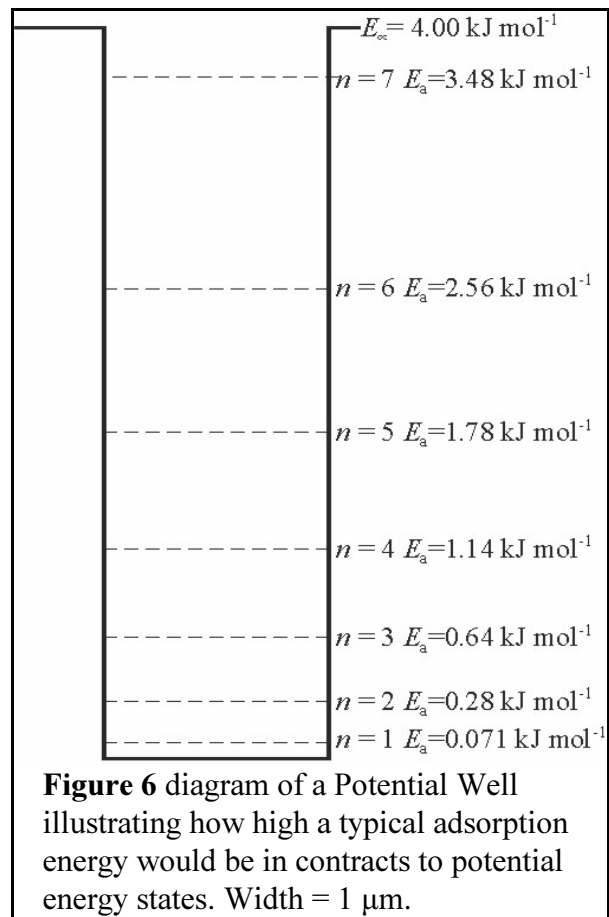
The first case, that is the potential box, is like a well with an infinitely high wall. The second case, more realistic, is a well with a finite energy wall. This finite case is illustrations in the figure 5. It is highly unlikely that an adsorbate particle would thermally jump to level 2, much less exit this well without a free energy drive. Normally,  $4.00 \text{ kJ mol}^{-1}$  is a low value for physisorption.

#### Sub-Lesion #4: Effect of changing to a finite box.

On a narrow box, it can make a difference whether the box has infinite walls or finite walls. However, for a “big box” it makes a trivial difference. The reason is that the translational motion is retained and may be approximated by the deBroglie wave function. The calculation of this wavelength is given by:

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} \quad (21)$$

where  $\Lambda$  is the wavelength,  $h$  is the (normal) Plank’s constant and  $k$  is the Boltzman’s constant. For example  $\text{N}_2$  at 78 K has a deBroglie wave length of  $3.7 \times 10^{-3} \text{ nm}$ . Thus, the tail-off of the thermal wave function is extremely small compare the the surface aliquot of about  $1 \mu\text{m}$  and the wave function is almost



<sup>1</sup> The Arial **P** will be used for probability to avoid confusion with pressure.

thermally identical to that in the infinite wall case.

Even without these considerations, the half-distance for the diagram in figure 5 for  $n = 1$  is calculated to be about  $x_{1/2} = 1 \times 10^{-20}$  m.

Thus, there is not much difference in the wave functions in a finite box with walls close to the energy of physical adsorption and the infinite wall case.

### Side bar #1

Some quick comments regarding some objections:

1) "The ground state and the energy in the well are not the same. Doesn't this distort the calculation?"

A quick calculation for some intuition is appropriate here. For for nitrogen and a surface aliquot of 1  $\mu\text{m}$  that is in the ground state,  $n = 1$ , yields a  $W_1 = 0.07 \text{ kJ mol}^{-1}$ . The initial energy of physical adsorption is normally in the range of 5 - 20  $\text{kJ mol}^{-1}$ . Thus, the difference between the energy at the bottom of the potential well and the ground state is almost insignificant.

2) "Don't you have to continue fill up the states in the well and after just a few molecules, the energy is greater than the well depth?"

Firstly, that applies to Fermions.

Secondly, For most physisorption measurements, the adsorbed molecules are overwhelmingly in the potential well ground state. How can this be since (if they are Fermions) they cannot be in the same quantum state. However, this ignores the translational modes of which there are many.

3) "Well what have you left off by ignoring  $\Im$  and using only  $\Re$ ?"

$\Im$  is the time dependence of the wave equation. For a stationary wave, the probability oscillates from positive to negative in  $\Re$ , thus passing through zero overall, and the  $\Im$  does the same out of sync. Thus, when one multiplies the  $\Im$  part with the  $\Re$  part, the product stays constant over time. (...and all is well with the universe.)

4) Oh, come on now. Molecules can be treated as classical particles. One need not worry about translation of molecules in the gas or liquid state, there are too big and heavy to need a quantum treatment. Haven't you heard of the correspondent principle?

This is essentially the argument made by most investigators in the field. I goes like this, except for bonding, viewed more or less like balls and sticks with electrons behaving as quantum waves, the molecules are believe to be classical particles with force field around them. This have been disproved in the literature by demonstrating that large particles, up to  $\text{C}_{60}$  bucky balls can be diffracted in double slit experiments. Some have suggested that even some viruses can also be diffracted.

**Sub-Lesion #5: A Particle in the Box with a Tooth:**

Up to this point, only one dimension,  $x$ , has been dealt with. There are obvious 3 dimensions, 2 in the plane of the surface and one normal to the surface. An assumption needs to be made about separability of the dimensions to continue.

**Assumption #2 - Separation of variables:**

**The adsorbate molecule wave function is separable into two parts:**

**#1; The two dimensions parallel to the adsorbent surface and**

**#2; The third dimension that is normal (perpendicular) to the plane of the adsorbent surface.**

The parallel 2D wave function portion will be affected by the perturbation and yields most of the properties of the  $\chi$ -hypothesis. The normal direction calculation is only needed if one wished to assign a thickness parameter to the results of the  $\chi$ -calculation. This assignment involves an assumption about what the “thickness” of a molecule. For this the IUPAC convention is as good as any other guess. Use of something like the Lennard-Jones potential and interlayer vibration yields an interesting picture, but doesn't seem to supply any useful information.

Again, we use the particle in a box description, using only one of the 2D dimensions. The first molecule adsorbed is the perturbation for the second molecule. The first molecule will be simulated by a rectangular perturbation. The energy of interaction between this perturbation is given by “ $\epsilon$ ” and the interaction distance is “ $l$ .” This is shown in **Figure 7** for Case °1 and Case °3.

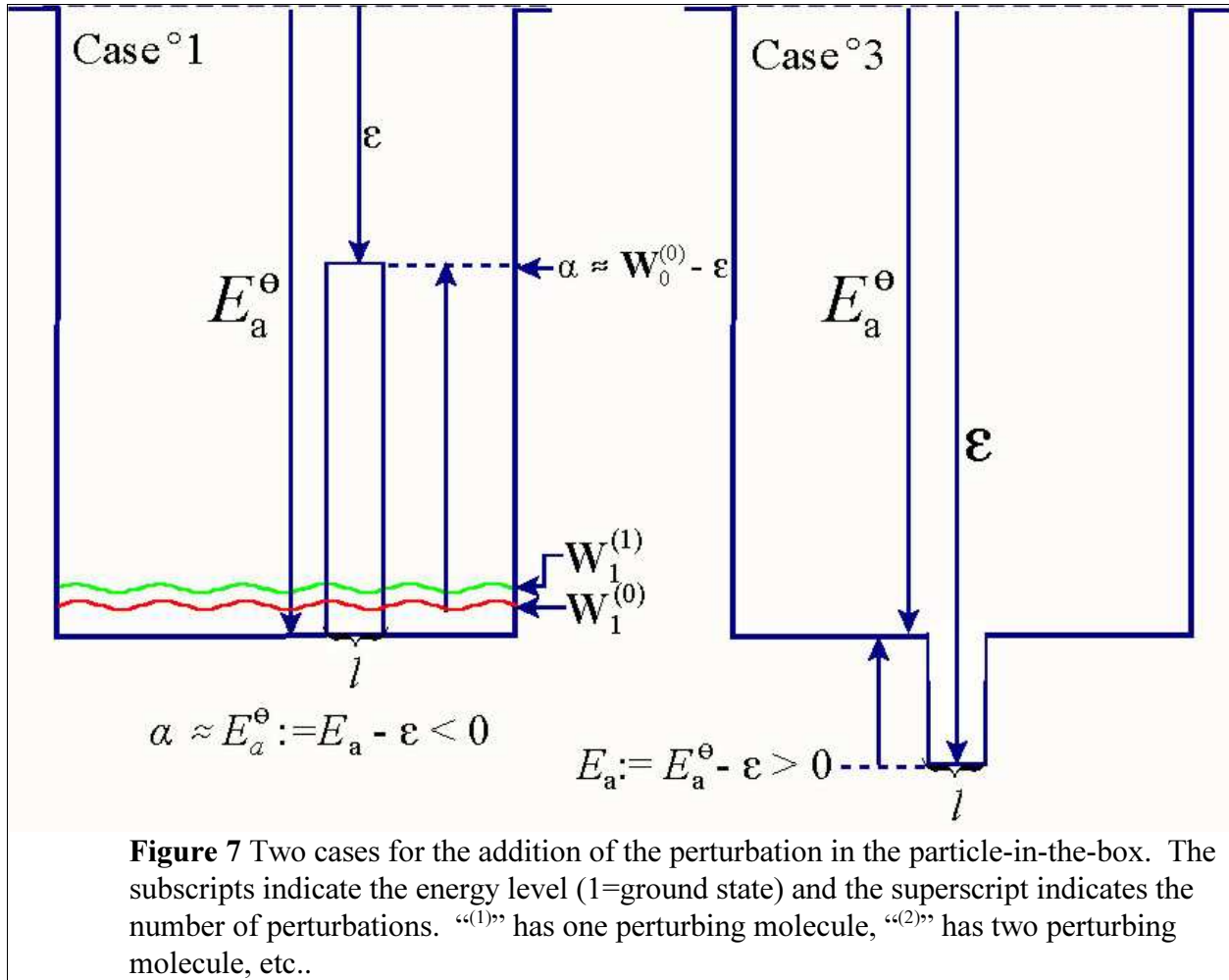
In these figures the energies are being counted from the top of the well. This is the normal thermodynamic convention, with the standard state being 1 bar of the adsorptive. A shift will be made to the normal reduced pressure by selecting  $P_{\text{vap}}$  as the comparison state but first the calculation for these diagrams.

Another normal convention is that  $E_a^\ominus$ , for example, is exothermic with respect to the adsorbent sample, and therefore negative<sup>1</sup>. For the quantum mechanical convention, the signs are turned around since the calculation is from the **bottom** of the empty well. So in Case °1 the perturbation is positive and in Case °3 it is negative.

The QM calculation will be for Case °1 which is the most common case, and then Case °3 will be discussed with the appropriate changes. The crudeness of the particle-in-the-box, and potential arguments about the classical representation will be addressed after the derivation.

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<sup>1</sup> The superscript  $\ominus$  indicates that the standard state referenced is 1 bar. This comes about because  $\epsilon$  is normally referenced against 1 bar.



The equations for the unperturbed well are given in equations (12) and (15). These will be referred to as the base functions. The first part of equation (10) can be rearranged and written as:

$$\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = W \psi(x) \quad (22)$$

or in general shorthand form:

$$\mathbf{H}^0 \psi_n^0 = \mathbf{W}_n^0 \psi_n^0 \quad (23)$$

Where only the original unperturbed waves, with superscript 0 are used. The subscripts  $n$  (an integer) indicates that there are several distinct solutions that are appropriate as mentioned above. For simplicity, only  $n = 1$  for  $\mathbf{H}$  and  $\mathbf{W}$  will be modified here<sup>1</sup>. To express the perturbation a  $\mathbf{H}'$  (like the triangle in the square room) is added to  $\mathbf{H}$  (like the whole room) to a certain extent,  $\lambda$  such that if  $\lambda = 0$  there is no perturbation and if  $\lambda = 1$ , the total perturbation is applied:

<sup>1</sup> Otherwise  $\mathbf{H}'$  becomes a matrix and things can get confusing. All states other than ground state are likewise modified.

$$\mathbf{H} = \mathbf{H}^0 + \lambda \mathbf{H}' \quad (24)$$

The perturbation, which in this case is an additional potential energy. Similarly  $\mathbf{W}$ s will respond with full perturbation at  $\lambda = 1$  and none at  $\lambda = 0$  but there is no guarantee of a linear relationship, so series are normally used. The convenient series to use would have the properties that they are not dependent upon each other mathematically, in other words, the waved functions are orthogonal, which is (equation (16).) A companion assumption is made for the  $\mathbf{W}$ s. So:

$$\begin{aligned} \mathbf{W}_n &= \mathbf{W}_n^0 + \lambda \mathbf{W}_n' + \lambda^2 \mathbf{W}_n'' + \dots \\ \psi_n &= \psi_n^0 + \lambda \psi_n' + \lambda^2 \psi_n'' + \dots \end{aligned} \quad (25)$$

Where the  $\mathbf{W}_n$  and  $\psi_n$  are the energy “eigenvalues” and the corresponding wave equations of the original equation. The orthogonality of the  $\psi_n$ s are useful later. The power of  $\lambda$  is what designates the order of the approximation. If only  $\lambda$  is used, the order is called first order. This is the first approximation to be made. If then one also goes back and uses  $\lambda^2$  is is call the second approximation, etc. The larger the approximation the higher the order that is needed. However, in the present case, the “big box” approximation<sup>1</sup>, only the first order is needed, since the initial approximation is only 1 part in  $\sim 10^6$  from the original. In other words, one adsorbed molecule, does not distort the potential well very much, but things will build up. Substituting into (23) into (22) without  $\lambda^2$  and greater powers:

$$(\mathbf{H}^0 + \lambda \mathbf{H}')(\psi_n^0 + \lambda \psi_n') = (\mathbf{W}_n^0 + \lambda \mathbf{W}_n')(\psi_n^0 + \lambda \psi_n') \quad (26)$$

Multiplying the right side out and, again, ignoring the  $\lambda^2$  terms:

$$\mathbf{H}^0 \psi_n^0 + \lambda \mathbf{H}^0 \psi_n' + \lambda \mathbf{H}' \psi_n^0 = \mathbf{W}_n^0 \psi_n^0 + \lambda \mathbf{W}_n' \psi_n^0 + \mathbf{W}_n^0 \lambda \psi_n' \quad (27)$$

Noticing that the first term of the left and right are the original equation and cancel leaving only the first order terms so the  $\lambda$ s cancel:

$$\mathbf{H}^0 \psi_n' + \mathbf{H}' \psi_n^0 = \mathbf{W}_n' \psi_n^0 + \mathbf{W}_n^0 \psi_n' \quad (28)$$

or rearranging:

$$(\mathbf{H}^0 - \mathbf{W}_n^0) \psi_n' = (\mathbf{W}_n' - \mathbf{H}') \psi_n^0 \quad (29)$$

one then has an equation that solves for the perturbation alone (to the first order) if one introduces the orthogonal of the of the series  $\psi_n^0$  to create a new set of functions that satisfy equation (27).

This can be done by using weighing constants on  $\psi_n^0$  of  $a_j$  to yield the complete set  $\psi_n'$  from the complete set of  $\psi_n^0$ :

$$\psi_n' = \sum_j a_j \psi_n^0 \quad (30)$$

This is merely a shift in the original basis set used in equation (23). The values of  $a_j$  for each value of  $n$  are to be determined, but the sum of  $a_j$  for each  $n$  adds up to 1. Substituting into

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<sup>1</sup> The “big box” approximation was used almost without comment in the first publication of the  $\chi$ -hypothesis in 1988. Even though the publication gave a classical analogy, the theoretical developments has always followed the QM route. (It was not possible in 1988 to publish it without a classical explanation. In my opinion, the reviewers and editors did not really understand QM.)

equation (27)

$$\left(\mathbf{H}^0 - \mathbf{W}_n^0\right) \sum_j a_j \psi_j^0 = \left(\mathbf{W}_n' - \mathbf{H}'\right) \psi_n^0 \quad (31)$$

Since  $\mathbf{H}\psi_j^0 = \mathbf{W}_j^0\psi_j^0$  then the constants  $\mathbf{W}$  can replace the Hamiltonian on the left side so:

$$\sum_j a_j \left(\mathbf{W}_j^0 - \mathbf{W}_n^0\right) \psi_j^0 = \left(\mathbf{W}_n' - \mathbf{H}'\right) \psi_n^0 \quad (32)$$

Now one uses the orthogonal properties or  $\psi^*\psi$  by multiplying every thing from the right by  $\psi_n^{0*}$ :

$$\sum_j a_j \left(\mathbf{W}_j^0 - \mathbf{W}_n^0\right) \psi_n^{0*} \psi_j^0 = \left(\mathbf{W}_n' - \mathbf{H}'\right) \psi_n^{0*} \psi_n^0 \quad (33)$$

Where the “\*” indicates the complex conjugate.<sup>1</sup> Taking advantage of the orthogonal properties:

$$\int_{-\infty}^{+\infty} \psi_i^* \psi_j dx = 1 \text{ if } i = j \quad \text{and} \quad \int_{-\infty}^{+\infty} \psi_i^* \psi_j dx = 0 \text{ if } i \neq j \quad (34)$$

integration over all space is perform on both sides: Since all  $\mathbf{W}$  s are constants, they may remain outside the integrals.

$$\sum_j a_j \left(\mathbf{W}_j^0 - \mathbf{W}_n^0\right) \int \psi_n^{0*} \psi_j^0 dx = \mathbf{W}_n' \int \psi_n^{0*} \psi_n^0 dx - \int \mathbf{H}' \psi_n^{0*} \psi_n^0 dx \quad (35)$$

Or since the left side is 0 and  $\mathbf{W}_n$ 's are being multiplied by 1:

$$\mathbf{W}_n' = \int \mathbf{H}' \psi_n^{0*} \psi_n^0 dx \quad (36)$$

For those familiar with Fourier transforms this might sound normal especially at this point. The solution then is the solution for an up and down unit step function.

It is assume in the following model that there are no degenerate states. Degenerate states are first unlikely in the many translational modes. Secondly, it obviously can be handled with little practical consequences in this case. Degeneracy is a very important topic in QM with far reaching consequences, but it seems to be a little more than what is needed here.

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<sup>1</sup> We can use sin functions all the way through this derivation, so the complex conjugate,  $\psi_n^{0*}$ , in this case is the same as  $\psi_n^0$ . We are in this case only interested in the time independent part. If one wants to see how fluctuations occur one would go back an include the  $\Im$  part. But at this point, I don't see any reason to do so but kinetics might prove otherwise.

## Lesson IV - Application of Perturbation to the Models:

### Sub-Lesson #1: Applying the Perturbation to Physical Adsorption:

In Lesson III and IV the quantum mechanics and perturbation theory were laid out. Many students are familiar with QM Perturbation Theory, so they have the option of simply scanning or skipping the previous section. (Now he tells me.) Also, it might be a good review for some or maybe a different approach than they have seen before, so all is not in vain.

The perturbation in Case <sup>o</sup>1 is the function:

$$E = E^\Theta \quad 0 < x < x_0 - \frac{1}{2}l \quad \text{and} \quad x_0 + \frac{1}{2}l < x < L \quad (37)$$

$$E = \alpha := \left( \mathbf{W}_0^0 - \varepsilon \right) \approx \left( E_a^\Theta - \varepsilon \right) \quad x_0 - \frac{1}{2}l < x < x_0 + \frac{1}{2}l \quad (38)$$

where  $x_0$  is the center point of the perturbation,  $l$  is the distance across the perturbation and  $L$  is the distance across the surface aliquot. The selection of coordinates are relative but here the standard state of 1 bar is appropriate with the superscript symbol  $\Theta$ . This is obviously a 1 dimensional (1D) solution, but the surface is 2D. However, the 2D perturbation is very similar to the 1D solution exception for the obvious addition of the sin functions in  $y$ .<sup>1</sup>

The wave equations for the well are given in equation (15) and the integration over all space is from just  $x_0 - \frac{1}{2}l$  to  $x_0 + \frac{1}{2}l$  since for the rest of space the value is 0.

$$\int \mathbf{H}' \psi_n^* \psi_n d\tau = \frac{2\alpha}{L} \int_{x_0 - \frac{1}{2}l}^{x_0 + \frac{1}{2}l} \mathbf{sin}^2 \left( \frac{n\pi\tau}{L} \right) d\tau = \mathbf{W}_n' \quad (39)$$

( $\tau$  is used for a dummy integration variable stand-in for  $x$ .) Integrating:

$$\mathbf{W}_n' = \frac{\alpha}{L} \left( \tau - \frac{L}{n\pi} \mathbf{sin} \left( \frac{n\pi\tau}{L} \right) \mathbf{cos} \left( \frac{n\pi\tau}{L} \right) \right) \Bigg|_{\tau=x_0 - \frac{1}{2}l}^{\tau=x_0 + \frac{1}{2}l} \quad (40)$$

or:

$$\mathbf{W}_n' = \frac{\alpha}{L} \left( \tau - \frac{L}{2n\pi} \mathbf{sin} \left( \frac{2n\pi\tau}{L} \right) \right) \Bigg|_{\tau=x_0 - \frac{1}{2}l}^{\tau=x_0 + \frac{1}{2}l} \quad (41)$$

Placing in the limits:

$$\mathbf{W}_n' = + \frac{\alpha l}{L} - \frac{\alpha}{2n\pi} \left( \mathbf{sin} \left( \frac{n\pi \left( x_0 + \frac{l}{2} \right)}{L} \right) - \mathbf{sin} \left( \frac{n\pi \left( x_0 - \frac{l}{2} \right)}{L} \right) \right) \quad (42)$$

The first term is the perturbation first order correction for  $\mathbf{W}_n$  and the second term expresses the fluctuation, or uncertainty with respect to position, of this correction. Since  $l \ll L$ , the two sine functions are extremely close to each other and almost cancel. For a typical example, if

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<sup>1</sup> It's not worth while doing that here, but one can readily see that the problem gets broken up into 6 pieces (4 solutions). Let some grad student do this for a thesis.

$l = 1 \times 10^{-3} L$  and  $n$  is in the ground state,  $n = 1$  then the difference is  $\pm 0.003$  or a deviation of 0.05 %. Thus, one can write simply:

$$\mathbf{W}_n^{(1)} = \mathbf{W}_n^{(0)} + \mathbf{W}_n' \cong \mathbf{W}_n^{(0)} + \frac{\alpha l}{L} \quad (43)$$

Here the (1) indicates that if there is 1 adsorbed molecule, then the energy of the next adsorbed molecule will be  $\mathbf{W}_n^{(1)}$ .

What does this mean for the finite well? The original distance from the top of the well to the first energy level for the first adsorbate molecule given as:

$$\mathbf{W}_n^{(1)} = \mathbf{W}_n^{(0)} - \frac{\alpha l}{L} \quad (44)$$

### Sub-Lesion #2: Beyond the first molecule:

The energy of adsorption for the first molecule is  $\mathbf{W}_n^{(0)}$  which is not much different from  $E_a^\ominus$  as is obvious from the discussion associated with **Figure 6**. The difference for a typical 1  $\mu\text{m}$  length was about 0.07  $\text{kJ mol}^{-1}$ , quite insignificant for most cases of physical adsorption. The following is a very good approximation to equation (41)

$$\mathbf{W}_n^{0(1)} = \alpha \left( 1 - \frac{l}{L} \right) \quad (45)$$

Proceeding to the second molecule, equation (43) becomes the new  $\mathbf{W}_n^0$ . This is the result of the original definition of physical adsorption, that is delocalized with no change in components versus chemisorption, which is localized with a change in the number of components.

Repeating the process using the symbolism  $\mathbf{W}_n^{0(1)}$  in place of  $\mathbf{W}_n^0$ , one obtains:

$$\mathbf{W}_n^{(2)} = \mathbf{W}_n^{(1)} + \mathbf{W}_n' \cong \mathbf{W}_n^{(1)} + \frac{\mathbf{W}_n^{(1)} l}{L} = \alpha \left( 1 - \frac{l}{L} \right)^2 \quad (46)$$

It can easily be shown by inductive proof that:

$$\mathbf{W}_n^{(N)} = \alpha \left( 1 - \frac{l}{L} \right)^N \quad (47)$$

where  $N$  is the  $N$ th molecule that has adsorb after the first.

### Sub-Lesion #3: Switching to adsorption notation, referencing $E_a^\ominus$ and $E_a$ :

Some modifications are needed for equation (45):

Equation (45) can now be written for the 2D (recall, the 3<sup>rd</sup> dimension has been separated) case by replacing  $l$  and  $L$  with  $a$  and  $A$  (recall, the 3<sup>rd</sup> dimension has been separated.). The derivation is the same except for separated  $x$  and  $y$ .

$$\mathbf{W}_n^{(N)} = \alpha \left( 1 - \frac{a}{A} \right)^N \quad (48)$$

In a previous section it was pointed out what the interpretation of  $\psi^2$  was. Here the letter  $\theta$  will

relate substitute for the previous  $\mathbf{P}$ :

$$\theta = \iint \mathbf{P}(x_1, y_1 \dots x_N, y_N) dx_1 dy_1 \dots dx_N dy_N = \iint (\psi(x_1, y_1 \dots x_N, y_N))_m^2 dx_1 dy_1 \dots dx_N dy_N \quad (49)$$

On a flat, nonporous surface this is classically given as the “coverage.” Defining the monolayer equivalence by the following:

$$n_m = A / aN_A \quad (50)$$

where dividing by Avogadro’s number,  $N_A$ , yields the number in terms of moles. Thus, on a flat, nonporous surface of a rigid adsorbent this classically gives the “coverage:”

$$\theta = n_{\text{ads}} / n_m \quad (51)$$

In the  $\chi$  formulation, however, this is in general the areal density of the molecules, in other words, the (algebraic) projection of all the adsorbate onto the surface. If for example there is 70% of the molecules touching the surface, 40% not touching the surface but touching the molecules that are touching the surface, called the first “layer” molecules, and 10% touching this 2<sup>nd</sup> “layer,” then  $\theta = 1.2$ .

Hopefully, these definitions are clear, since there is a difference between  $\theta$  and  $n_{\text{ads}}/n_m$  in other cases. In general for a rigid adsorbent

$$\theta \geq n_{\text{ads}} / n_m \quad (52)$$

Why this is referred to a an areal density and not an amount. You might have noticed in this discussion, that how to specify  $a$  is not mentioned. This could be a bit of a problem for those who insist upon the classical approach and dependent upon, say, the IUPAC convention. A more general definition is to specify  $n_m$  and not surface area. However if the latter is specified, the convention that is used should be listed so that information is not lost.

Continuing the derivation starting with equation (46) on page 32 and referencing **Figure 7** on page 28, the energy referenced from the top of the potential well is given by<sup>1</sup>:

$$\mathbf{E}(N) = + \left( E_a^\ominus - \varepsilon \right) \left( 1 - \frac{a}{A} \right)^{N-1} + N\varepsilon \quad (53)$$

The last term should be obvious. It is the interaction with all the other adsorbate molecules. Using the relationship and defining  $m \approx N - 1$ :

$$N = \frac{\theta A}{a} \quad m = -\frac{A}{a} \quad \therefore N = -\theta m \quad (54)$$

then, with  $E^\ominus - \varepsilon = E_a$ :

$$\mathbf{E}(N) = +E_a \left( 1 + \frac{1}{m} \right)^{-m\theta} + N\varepsilon \quad (55)$$

where, in addition, the reference state has been changed from 1 bar to the vapor pressure of the adsorptive at the sample temperature the integral is replaced with a continuous function. This is justified, since  $m$  is an extremely large number, one may make an approximation that  $m \rightarrow \infty$  and by

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<sup>1</sup> The extra  $\varepsilon$  accounts for the fact the first adsorbed molecule “sees” no adsorbate-adsorbate attractions nor masking of the adsorbent. This makes the  $E_a^\ominus$  the energy of the first adsorbed molecule. Because the quantities are very large, this 1 will be left off.

the definition of the function  $\mathbf{e}$ :

$$\mathbf{E}(N) = +E_a \mathbf{e}^{-\theta} + N\epsilon \quad (56)$$

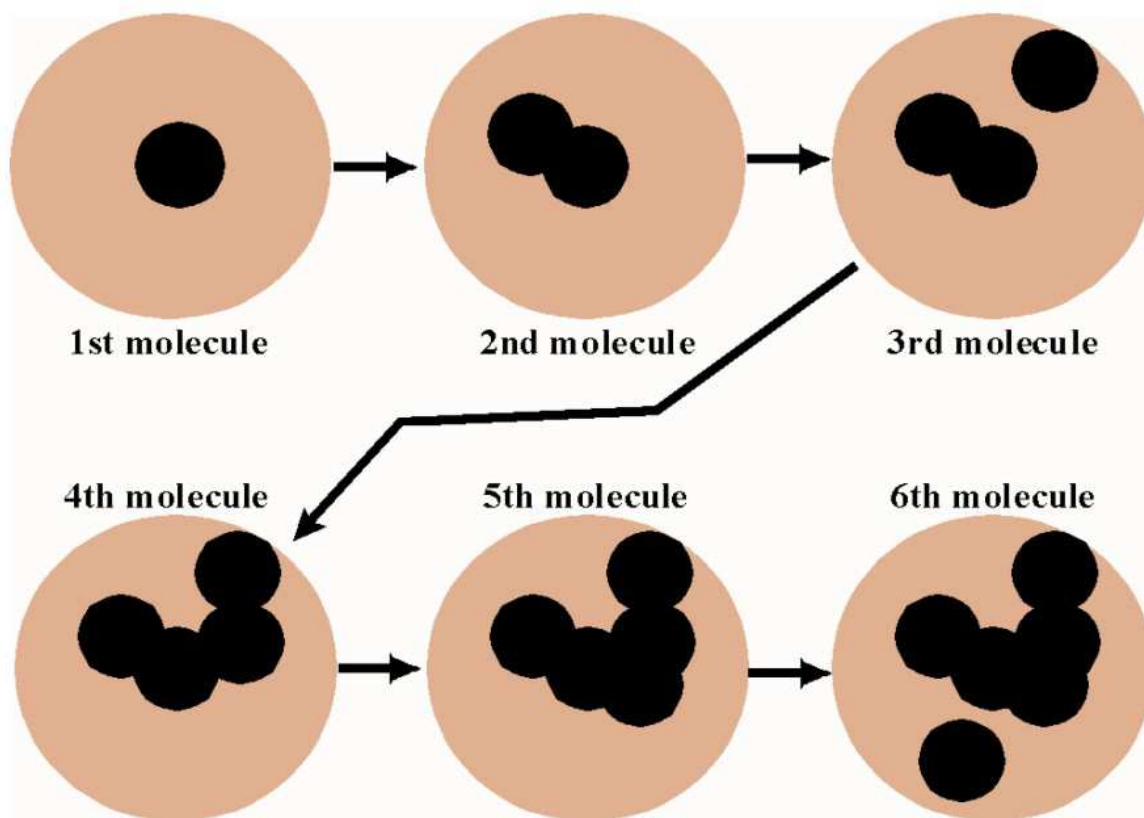
Notice that  $E_a^\circ - \epsilon \equiv E_a$  for Case  $^\circ 1$  is negative.

Now that the energy of the adsorption is figured out, one can plug this into the Grand Canonical Partition Function and obtain the Grand Potential and the thermodynamic properties of adsorption and the relationship between adsorptive pressure and adsorbate areal density. The areal density is something that thermodynamics alone cannot yield.<sup>1</sup>

#### Sub-Lesson #4: Fuller's Classical Explanation

“As you ramble on through life, brother,  
What ever be your goal,  
Keep your eye upon the doughnut,  
And not upon the hole. ”

- the advertizement for Mayflower Donuts, - author unknown.



**Figure 8** A classical explanation for the  $\chi$ -hypothesis. The donut disappears by random bites.

<sup>1</sup> The ESW, Excess Surface Work, theoretical development by Dr. Jürgen Adolph, et al., comes about as close to doing this as possible, but there is still an assumption, however reasonable, that needs to be made. See the text book for details and references

Many students and researchers are puzzled by the results of the QM treatment. It's not that they do not believe the results, it is just not intuitive. As the old advertizement for donuts stated, "Don't concentrate on the hole, but concentrate on the donut!" In this case the donut is the high energy of the adsorbent surface and the hole is the low energy of attraction to the adsorbate molecule. Let's say we can more easily eat around the donut hole illustrated in **Figure 8**.

If the process is random, sometimes the bites overlap, sometimes they are completely where another hole is and sometimes they are a clean bit. However, concentrating on the holes *is* confusing, but concentrating on the donut if the bites are random, then the donut disappears with an exponential decay. Since the brown area is the high energy area, and the black holes are the low energy areas, the decay starts at the energy of the high energy and decay asymptotically to the value of the "bites."

This looks very much like the BET assumption, but it is not. It is very different. One could say the each bit skim off a little of the surface of the donut, perhaps that would help since the concept of area density is involved. However, any classical interpretation falls short of the QM wave mechanics. Arguments need to be confined to the QM derivation. This illustration is only to take the mystery out of the QM derivation - concentrate on the donut.

This is a lot simpler, but quite limited in implications. Fuller knew this as well, but it was a much easier concept for most people to understand.

## Lesson V - The Grand Canonical Partition Function (GCPF):

### Sub-lesson #1 First some definitions:

There are several definitions for “heat” in the literature. For the case of physical adsorption theories, the experiments are performed in such a way that the energies of interest are the “Helmholtz’ Free Energy” and the “Internal Energy.” For the isotherms, the standard condition that one uses for comparison is the vapor pressure for the adsorbent at the temperature of the adsorbent. In contrast, the standard comparison condition for calorimetry is normally the thermodynamic standard state, which is 1 bar for the adsorptive. Thus, the calorimetric values include the latent heat of vaporization at the temperature of the adsorbent.

Another qualification is the definition of the “system” used in the description. The definition might be defined differently for low pressure versus high pressures. However, for most of the experiments have been performed at low pressures, so the system is defined as the adsorbent plus the adsorbate that is clearly different from the adsorptive. (At higher pressure approaching the critical point, this may have to be modified to avoid interpretive nonsense.)

For definitions of the various energy terms, Table is provided here.

symbol	meaning	comparison state
$\bar{E}_a$	The energy of adsorption of the first adsorbate molecule	liquid state
$\mathbf{E}(x)$	The differential heat of adsorption with respect to $x^*$	liquid state
$q$	The differential heat of adsorption with respect to $n_{\text{ads}}$	1 bar of adsorptive
$Q$	The integral heat of adsorption with respect to $n_{\text{ads}}$	1 bar of adsorptive
$q_{\text{st}}$	The isosteric heat of adsorption with respect to $n_{\text{ads}}$	liquid state
$\Delta H_1^{\text{ads}}$	The enthalpy of change from the liquid to the adsorbent	self compare
$\Delta S_1^{\text{ads}}$	The entropy of change from the liquid to the adsorbent	self compare
* $x = P/P_{\text{vap}}$ or $\chi$		

Before beginning, there is an important point to notice. The function  $\exp(-\theta)$  is the amount of the surface that has not coverage in the classical model. At  $\theta = 0$ , there is no adsorbate on the surface and  $\exp(-\theta) = 1$ , that is  $\theta_{\text{empty}} = 1$ . At  $\theta = 1$ , the  $\theta_{\text{empty}} = 0.36$  and at  $\theta = \infty$ ,  $\theta_{\text{empty}} \approx 0$ . Think of it as a Swiss bank account with a negative compound interest, with  $\theta_{\text{empty}}$  being what the bank gets.

### Sub-lesson #2 The Grand Canonical Partition Function (GCPF) and Grand Potential:

So, the following is the classical GCPF for this system. Perhaps there is some purpose to using the QM GCPF in some cases, for example, with mesoporosity. The GCPF uses the changes in energy of all components in the system. Since this is an open system these energies include the potential change for the adsorbate-adsorbent interactions including material changes and, thus, adsorptive change. Equation (54) the energy terms for the adsorbate-adsorbent interaction. The adsorptive canonical ensemble is appropriate, that is  $kT \ln(\tilde{p})$  where  $\tilde{p}$  is the gas fugacity that can be held constant by resupply from outside the system. The GCPF,  $\Xi$ , is then:

$$\Xi = \sum_N (\lambda Z)^N \mathbf{exp} \left( \frac{E_a}{kT} \sum_{n=0}^{n=N} \left[ \mathbf{exp}(-\theta) + \frac{N\varepsilon}{kT} \right] \right) \quad (57)$$

The second summation, since  $N$  is very large and the increments small, may be replaced by an integral from 0 and  $N$ .<sup>1</sup>

$$\Xi = \sum_N (\lambda Z)^N \mathbf{exp} \left( \frac{E_a}{kT} \int_{n=0}^{n=N} \left[ \mathbf{exp}(-\theta) + \frac{N\varepsilon}{kT} \right] \right) \quad (58)$$

The first summation is handled in a couple of ways. Here the simplest way is used, that is assume that the most probable configuration represents the thermodynamic properties. This is then the maximum term of  $\Xi$ :

$$0 = \frac{d(\text{max term } \ln(\Xi))}{dN} = \ln(\tilde{p}) + \frac{E_a}{kT} \mathbf{exp}(-\theta) + \frac{\varepsilon}{kT} \quad (59)$$

This is also the definition for the Grand Potential,  $\Phi$ :

$$0 = \Phi = \ln(\tilde{p}) + \frac{E_a}{kT} \mathbf{exp}(-\theta) + \frac{\varepsilon}{kT} \quad (60)$$

which is the Helmholtz Energy with the added proviso of an open system for one, or more components.

### Sub-lesson #3 For some equations that look like chemistry:

For chemist, rearrange and use molar quantities (with the alternate over-line IUPAC convention) and for low pressure substitute  $\tilde{p}$  with  $P$  (obvious inappropriate for very high pressures.)

$$-\ln(P) = \frac{\bar{E}_a}{RT} \mathbf{exp}(-\theta) + \frac{\bar{\varepsilon}}{RT} \quad (61)$$

Notice that as  $\theta \rightarrow 0$  then the energy is  $\bar{E}_a$  is the energy of adsorption of the first adsorbate molecule. The quantities are converted to molar quantities as well. (Reminder: by thermodynamic convention both  $\bar{E}_a$  and  $\bar{\varepsilon}$  are  $< 0$ .)

It is handy to use the  $\chi$  notation for the equation. First, notice that as  $\theta \rightarrow \infty$  that:

$$\theta \rightarrow \infty \Rightarrow P \rightarrow P_{\text{vap}}, \quad \ln(P_{\text{vap}}) = \frac{\bar{\varepsilon}}{RT} \quad (62)$$

Substituting the  $\ln(P_{\text{vap}})$  for the energy term yields:

$$-\ln\left(\frac{P}{P_{\text{vap}}}\right) = \frac{\bar{E}_a}{RT} \mathbf{exp}(-\theta) \quad (63)$$

and notice that as  $\theta \rightarrow 0$  something traditionally controversial pops up:

That is, pressure is finite, in opposition to the physisorption “Henry’s law.” This pressure has been named the “threshold pressure” and has been experimentally demonstrated multiple times by a variety of researcher. It should be now considered a reliable experimental observation and

---

<sup>1</sup> A picky point:  $N = 0$  stands for the first molecule adsorbed with  $\theta = 0$  and the value of  $E_a$  is its energy of adsorption.

“Henry’s law” for physical adsorption is strongly disproved. The symbol being given here for this pressure is  $P_\zeta$ . (It is good idea not to use the subscript “c” to avoid conflict with the critical point designation. How about subscript “ $\zeta$ ”? - OK I’ll use it from here out.) So:

$$-\ln\left(\frac{P_\zeta}{P_{\text{vap}}}\right) = \frac{\bar{E}_a}{RT} \quad (64)$$

Substituting this into equation (61) one obtains:

$$-\ln\left(\frac{P}{P_{\text{vap}}}\right) = -\ln\left(\frac{P_\zeta}{P_{\text{vap}}}\right) \exp(-\theta) \quad (65)$$

Taking the **ln** of both sides and rearranging:

$$\theta = -\ln\left(-\ln\left(\frac{P}{P_{\text{vap}}}\right)\right) + \ln\left(-\ln\left(\frac{P_\zeta}{P_{\text{vap}}}\right)\right) \quad (66)$$

Using definition of equation (1):

$$\theta = \chi\left(\frac{P}{P_{\text{vap}}}\right) - \chi\left(\frac{P_\zeta}{P_{\text{vap}}}\right) := \chi - \chi_\zeta \quad (67)$$

Here some short-hand is written for the normal isotherm adsorption. There is one qualification, that is that  $\theta$  cannot be negative and  $\chi > \chi_\zeta$  always. This can be written even more compactly with the indication of the non-negative  $\chi$  by:

$$\theta = \Delta\chi \mathbf{U} \Delta\chi \quad (68)$$

Where **U** is the unit step function<sup>1</sup> and  $\Delta\chi = \chi - \chi_\zeta$ .

For a rigid, homogeneous, non-porous surface:

$$\theta = \frac{n_{\text{ads}}}{n_{\text{m}}} \quad (69)$$

#### Sub-lesson #4: “Layers”

Inspecting equation (54) (page 34), the question is what is  $\exp(-\theta) = \exp(-\Delta\chi)$ ? If  $\Delta\chi = 0$  the function is 1, clearly not the  $\theta$ , but if  $\Delta\chi = \infty$  the function is 0. It can be demonstrated that the function is the adsorbent surface which empty of the material represented by  $\theta$ . (See the donut analogy for an intuitive understanding.) In other words, it is the free surface,  $\theta_{\text{free}}$ . If that is the case than the areal density of the first layer,  $\theta_1$  is given by implication:

$$\theta_{\text{free}} = \exp(-\Delta\chi) \Rightarrow \theta_1 = 1 - \exp(-\Delta\chi) \quad (70)$$

for  $\theta_2$ :

$$\theta_2 = 1 - \exp(-\Delta\chi + \theta_1) \quad (71)$$

etc.

---

<sup>1</sup> The unit step function is a handy way of approaching the heterogeneous energy distributions later on instead of using  $\Delta\chi \geq 0$ .

$$\theta_n = 1 - \exp\left(-\Delta\chi + \sum_{m=1}^{n-1} \theta_m\right) \quad (72)$$

These are called the “layering” equations. They indicate the areal density of each “layer set” as defined on page 8.

It is possible to show that:

$$\theta = \theta_1 + \theta_2 + \dots = \sum_{n=1}^{\infty} \left\{ 1 - \exp\left(-\Delta\chi + \sum_{m=1}^{n-1} \theta_m\right) \right\} \quad (73)$$

These equations are quite useful, especially for microporosity but also for determining  $E_a$  for some difficult cases.  $\theta_1$  equation is especially useful because it yields the quite common log-law.

$$\theta_1 = 1 + \frac{RT}{E_a} \ln\left(\frac{P}{P_{vap}}\right) \quad (74)$$

Form the observation that equations (68) must always be true provided the adsorbent is rigid, one derives a law dependent upon the validity of the  $\chi$ -hypothesis:

**Lemma #1: Areal density of the first “layer” - If the adsorbent does not change geometrically during adsorption, the areal density of adsorbate,  $\theta_1$ , in direct contact with the available surface will always be given by equation (68) and the moles of adsorbate in direct contact with the surface,  $n_{ads,1}$ , will always be given by:**

$$n_{ads,1} = \theta_1 n_m \quad (75)$$

**and thus:**

$$n_{ads,1} = n_m + \frac{n_m RT}{E_a} \ln\left(\frac{P}{P_{vap}}\right) \quad (76)$$

For simplicity the symbol  $n_1$  may be use in place of  $n_{ads,1}$ .

On a log plot of  $n_1$  ( $= y$ ) versus  $\ln(P/P_{vap})$  ( $= x$ ) the intercept on the abscissa (at  $n_1 = 0$ ) is  $(P_c/P_{vap})$  or  $\ln(-E_a/RT)$ . The very low pressure extrapolation to the ordinate yields the value of  $n_m$ . At any rate, the ordinate intercept is always greater than  $n_m$ , which can be also be determined from the initial slope of the  $\chi$ -plot.

## Lesson VI - Applications of $\chi$ -equations - supporting experiments: for Eqs. (66) and (72)

### Sub-Lesson #1: Examples of flat, homogeneous surfaces:

When looking at the literature for standard curves, one needs to keep in mind the **Big Errors**. Much of the older literature indicates a more or less cavalier attitude toward these problems. This is not to say that the investigators were negligent or careless, they were doing the best of practices of the day. The creation of standard curves has also been distorted by insistence that the BET be vindicated. Thus, check against the standard curve is useless. Luckily, in many cases the data is available as well as the assumed contiguous standard curves. Data after about 1970 is likely to be reliable, especially if the experimental details indicate cognition of the **Big Errors** and attempts to avoid them. It is, however, very common for the assumed temperature to be incorrect which distorts the entire isotherm, but especially as the pressure tends toward the high end.

According to QM, a standard curve should follow the  $\chi$ -equation. So a plot of  $n_{\text{ads}}$  versus  $\chi$  should be a straight line, whose slope is  $n_m$  and whose intercept to the abscissa is  $\ln(-E_d/RT)$ . If one subtracts the abscissa intercept,  $\chi_c$ , from  $\chi$  one obtains the  $\Delta\chi$  as the abscissa. This is referred to as the  $\Delta\chi$ -plot.

Recall, that the  $\chi$ -plot is a plot of  $\ln(-E/RT)$  and the  $\Delta\chi$ -plot is a plot of monolayer equivalents.

### Sub-Lesson #2: Modern “Standard Curves:”

One of the problems with “standard curves” is, in the past, there was too little attention to the assurance that the temperature of the adsorbent was correctly measured. Often, it was assumed that the temperature of the adsorbent, and also adsorbate, was the same as the cooling bath or that a liquid-gas thermometer buried below yielded the correct  $P_{\text{vap}}$ . Although the latter is a better method, neither one assures temperature control. Most egregious are some of the modern commercial instruments with sample holders made of glass or quartz with little regard for the **Big Error #2** - radiant heating.

Given this particular problem, the examples in which more confidence should be given, are those that specifically avoid the **Big Errors**. Here, these are given for the NASA lunar soil sample, the DOE thorium and beryllium samples. The traditional  $\alpha$ -s curves and some others but not for the  $t$ -curves since the value of  $P_{\text{vap}}$ , even in the straight isotherm representation, appears that the temperature is between 0.5 K and 1.0 K higher than recorded. Another problem is that the curves themselves may not be a good representation of the data. (This is before wide-spread use of computers to analyze data.) There appears to be a bias toward fitting the BET, which is not particularly surprising. Thus, the actual data, where available, is used in these analyses.

**Side bar #2**

What are standard curves and why do they exist?

If you have wondered this, good for you. First, why they exist. They are used to get around the weaknesses of the BET. The BET and its followup, the N-layer BET, were miserable failure for any isotherm other than Type II. (There are six to nine types with various modification for hysteresis.) Even for Type II isotherm it is restricted to relative pressure of 0.05 to 0.35. (Even this range is sometimes modified in order to avoid a BET “C” constant that is, impossibly, negative.) Beyond the Type II isotherms are very many isotherms of interest, including porous adsorbents and high or low energy surfaces. It was assumed that porosity modifies the isotherm in pressures only above 0.35 relative pressure and below 0.35 there was little effects from porosity, so the surface area could be measured by the BET. (Both assumption are, by the way, false.) Thus, the standard curves were created to account for porosity.

This is the method. One first obtains a nonporous sample and measure the BET surface area and create an isotherm that is the standard. This data is “smoothed,” at the time with a spline but later by polynomial fits, and data from the fit recorded at usually even increments of  $P/P_{\text{vap}}$  and scaled and published as a table. The scaling was often performed by dividing the fitted data by that of  $P/P_{\text{vap}} = 0.40$  and a proportionality constant if given to obtain the surface area of a sample. This becomes the standard.

For the investigator looking at a chemically similar porous sample the plot the data point obtained from the sample against the “standard curve.” For a nonporous sample, one obtains a straight line, the slope of which is proportional to the stated surface area of the standard. For a porous sample, the amount of material missing in the sample versus standard is due to the pore filling. The intercept to the ordinate is an indication of the pore volume according to Gurvitsch (Gurvich) rule.

Sounds good - so what are the problems?

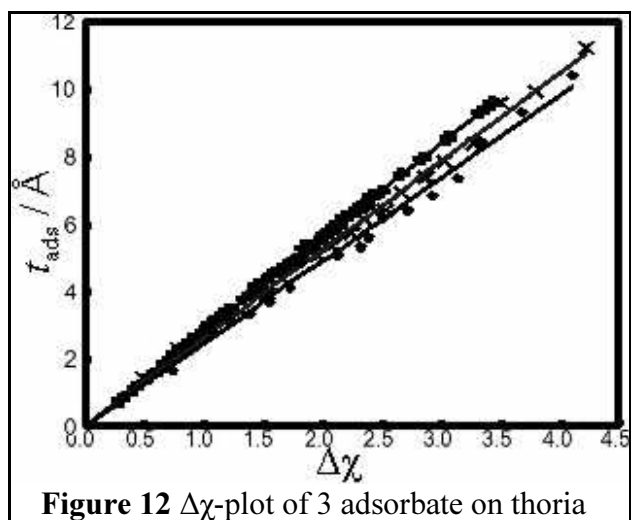
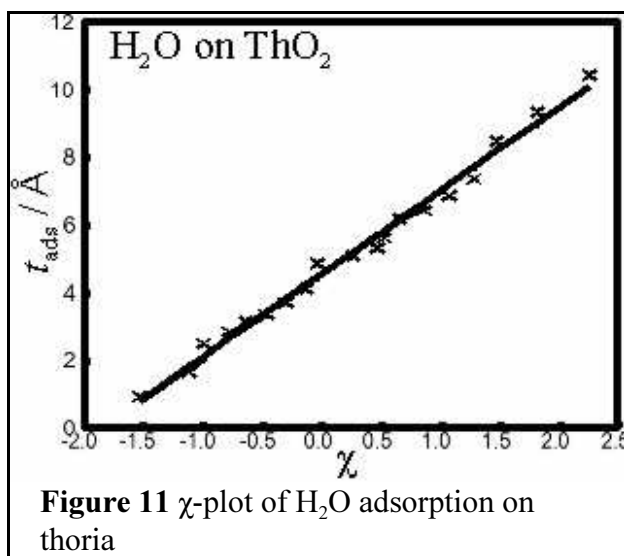
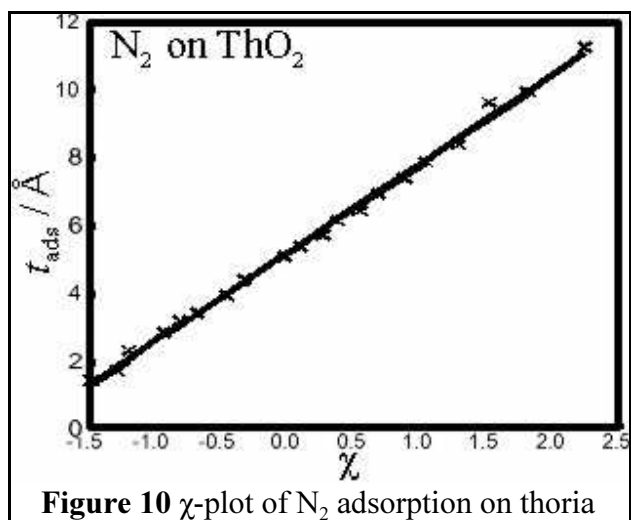
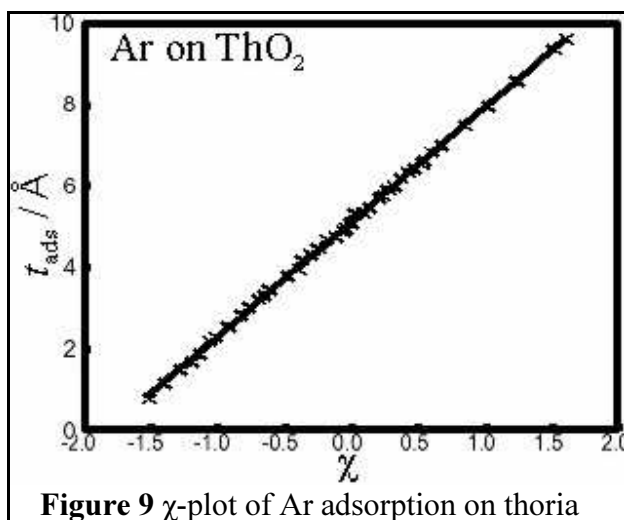
There are many problems with this approach, foremost is the reliance on the BET which throws everything off. Second is the assumption about the ranges made above. Porosity effect can start at the very beginning of the isotherm. Thirdly, Gervitsch rule is obviously correct if there is an insignificant amount of external surface area and one can assume that all the adsorbate is in pores. But if there is significant external surface area, the isotherm goes to infinity as  $P/P_{\text{vap}} \rightarrow 0$ . There are some ways to extrapolate this, most notably the Dubinin, et al., transformations. These isotherm equations provide a long straight portion suitable for extrapolation. However, the theoretical reason for this is lacking.

**Example #1: Thoria Standards[11]**

adsorbate: Nitrogen, Oxygen and water

Thoria treatment: High fired - 1000°C, then backwater added

(Isotherms were obtained for high fired without backwater also.)



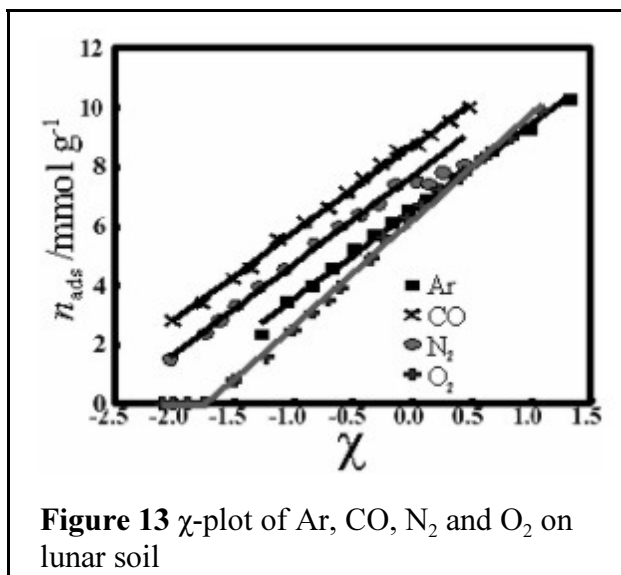
Output parameters:

Ar:  $\chi_{\zeta} = -1.816 \Rightarrow \bar{E}_a = 4.498 \text{ kJ mol}^{-1}$ ,  $P_{\zeta} = 2.14 \times 10^{-3}$ ,  $t_m = 2.81 \text{ \AA}$ ,  $T$  isotherm = 78 KN<sub>2</sub>:  $\chi_{\zeta} = -1.989 \Rightarrow \bar{E}_a = 4.741 \text{ kJ mol}^{-1}$ ,  $P_{\zeta} = 6.70 \times 10^{-4}$ ,  $t_m = 2.62 \text{ \AA}$ ,  $T$  isotherm = 78 KH<sub>2</sub>O  $\chi_{\zeta} = -1.855 \Rightarrow \bar{E}_a = 15.84 \text{ kJ mol}^{-1}$ ,  $P_{\zeta} = 1.68 \times 10^{-3}$ ,  $t_m = 2.45 \text{ \AA}$ ,  $T$  isotherm = 298 K

**Figure 12** illustrates the concept  $\Delta\chi$ . The previous 3 graphs have  $\chi$  as the abscissa, whereas in **Figure 12** the value of  $\chi_{\zeta}$  ( $-\ln(\bar{E}_a/RT)$ ) is subtracted from  $\chi$ . The intuitive advantage of this representation is that the abscissa becomes a measure of the monolayer equivalence.

**Example #2: NASA lunar soil standards[12][13]:**

In **Figure 13** are for the NASA standard curves for lunar soil. The  $\chi$ -plot is clearly linear. These samples were collected in a obviously very high vacuum and in a highly out-gassed state. They were returned to Earth in a special ultrahigh vacuum box, which was opened and loaded in the instrument in extremely clean environment. (They are probably the cleanest samples ever measure by this technique. The UHV microbalance used in Oak Ridge was solidly anchored to a very large concrete slab and was normally very stable and immune to outside vibration. However, Oak Ridge is in a geologically active area suffers from an occasional small earth quakes which upsets the operation of the balance. This is evident here in the nitrogen isotherm toward the end of the run where a weigh loss is recorded. This is obviously impossible and typical of an earth quake recording.)



**Figure 13**  $\chi$ -plot of Ar, CO, N<sub>2</sub> and O<sub>2</sub> on lunar soil

Output parameters:

Ar:  $\chi_c = -2.186 \Rightarrow \bar{E}_a = 5.70 \text{ kJ mol}^{-1}$ ,  $P_c = 1.37 \times 10^{-4} \text{ bar}$ ,  $n_m = 2.96 \text{ mmol g}^{-1}$

CO:  $\chi_c = -2.591 \Rightarrow \bar{E}_a = 11.97 \text{ kJ mol}^{-1}$ ,  $P_c = 4.94 \times 10^{-9} \text{ bar}$ ,  $n_m = 2.94 \text{ mmol g}^{-1}$

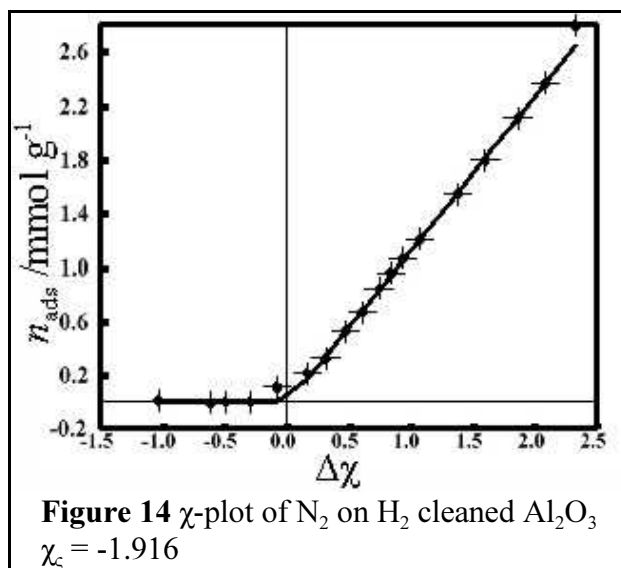
N<sub>2</sub>:  $\chi_c = -2.564 \Rightarrow \bar{E}_a = 8.31 \text{ kJ mol}^{-1}$ ,  $P_c = 2.30 \times 10^{-6} \text{ bar}$ ,  $n_m = 2.99 \text{ mmol g}^{-1}$

O<sub>2</sub>:  $\chi_c = -1.796 \Rightarrow \bar{E}_a = 3.57 \text{ kJ mol}^{-1}$ ,  $P_c = 4.07 \times 10^{-3} \text{ bar}$ ,  $n_m = 3.62 \text{ mmol g}^{-1}$

Notice here that the oxygen isotherm starts out at the low end at  $n_{\text{ads}} = 0$  and evidences the threshold pressure. (Display #1 for BET disproof)

**Sub-lesson #2: Threshold Pressure:****Example #3: N<sub>2</sub> on H<sub>2</sub> cleaned Al<sub>2</sub>O<sub>3</sub>:**

In **Figure 14** is the  $\Delta\chi$ -plot (illustrating the  $\Delta\chi$  presentation) for alumina cleaned (NBS 8571) in a hydrogen atmosphere[14]<sup>1</sup>. Again the  $\chi$ -plot is linear and the threshold pressure is present at  $\chi_c = -1.916$ . With the  $\Delta\chi$  presentation, one needs to specify the  $\chi_c$



**Figure 14**  $\chi$ -plot of N<sub>2</sub> on H<sub>2</sub> cleaned Al<sub>2</sub>O<sub>3</sub>  
 $\chi_c = -1.916$

<sup>1</sup> The experiments with diamond and alumina were initiated by Thompson and reported by Fuller

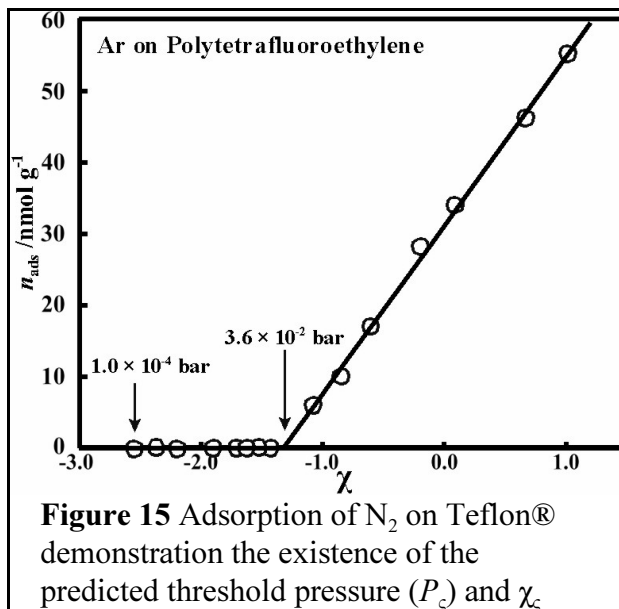
(Display #2 for BET disproof - there will be more routinely.)

Output parameters:

Ar:  $\chi_c = -1.916 \Rightarrow \bar{E}_a = 4.407 \text{ kJ mol}^{-1}$ ,  $n_m = 1.143 \text{ mmol g}^{-1}$ ,  $P_c = 1.12 \times 10^{-2} \text{ bar}$

#### Example #4: The First Tests of the Threshold Pressure:

In the development of the theoretical aspects of the Quantum Mechanical calculation of physisorption, it became apparent that it predicted a threshold pressure,  $P_c$ . We realized that the threshold pressure if it existed would be well in the vacuum range for the energies that we were observing. The researchers at ORNL<sup>1</sup> speculated that adsorption of either Ar or N<sub>2</sub> on polytetrafluoroethylene (a Teflon®.) Therefore, they performed an experiment on some of this material following up on the initiative by Thompson[15], an independent researcher who had access to the UHV microbalance system.



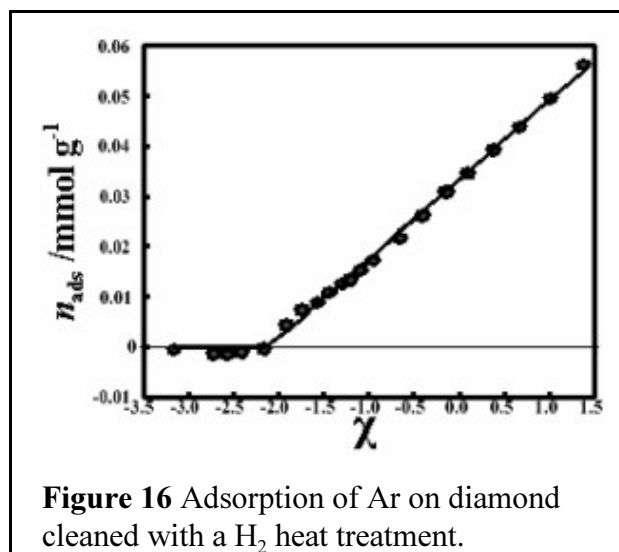
#### Example #5: N<sub>2</sub> on polytetrafluoroethylene

Looking at the low pressure in **Figure 15** it was obvious that there exists a threshold pressure at about  $3.6 \times 10^{-2} \text{ bar}$  (27 torr), well above the assumed required high vacuum range. This was the first time that the threshold pressure was observed and clearly existed. This is, therefore, the first definitive disproof of the concept of “Henry’s law,” (along with the BET, the Langmuir, the Freundlich and several other isotherms, as applied to physical adsorption. It then seemed that not only was the “Henry’s law” not the “Gold Standard of validity” but rather the “Gold Standard of falsehood..”

Output parameters:

N<sub>2</sub>:  $\chi_c = -1.261$ ,  $\Rightarrow \bar{E}_a = 2.29 \text{ kJ mol}^{-1}$ ,  
 $P_c = 2.9 \times 10^{-2} \text{ bar}$ ,  $n_m = 25.4 \mu\text{mol g}^{-1}$

Ar:  $\chi_c = -1.321$ ,  $\Rightarrow \bar{E}_a = 2.43 \text{ kJ mol}^{-1}$ ,  
 $P_c = 2.3 \times 10^{-2} \text{ bar}$ ,  $n_m = 23.6 \mu\text{mol g}^{-1}$



<sup>1</sup> ORNL = Oak Ridge National Laboratory plus other Oak Ridge installations.

Other tests Thompson performed include the  $\chi$ -plot Ar on H<sub>2</sub> cleaned diamond shown in **Figure 16**, which shows the Ar isotherm.

Output parameters:

Ar:  $\chi_{\zeta} = -2.082$ ,  $\Rightarrow \bar{E}_a = 5.87 \text{ kJ mol}^{-1}$ ,  $P_{\zeta} = 3.28 \times 10^{-4} \text{ bar}$ ,  $n_m = 16.2 \text{ } \mu\text{mol g}^{-1}$

Another example include oxygen adsorption on lunar soil in **Figure 13**. Examples of other threshold pressures will be presented in the log-law section.

#### **Sub-Lesson #4: Older “Standard Curves”**

There are several “standard curves” that have been devised in the past. It is questionable that they are useful. For these reasons:

- 1) Even if the bulk chemistry of two adsorbent are identical, there is no guarantee that the surface compositions are identical. Indeed, the whole idea is to make different arrangements between the standard and a new adsorbent.
- 2) The surface area analyzed by the BET is now obviously incorrect. This means, that even assuming identical surfaces, the answers are incorrect.
- 3) Most standard curves of the past violated one or more of the “**Big Errors**” mentioned earlier. This was not out of negligence or ignorance, but it had not yet been determine how important these factors were. Many researchers did excellent work, but the quality is not consistent or accurate enough.

The standard curves mention above were produced with a knowledge of the pitfalls. However, they are not useful for anything past ascertaining if samples are identical. Why they are presented here is to illustrate two points

- 1) For samples that are presumed non-porous and homogeneous, the  $\chi$ -plot is an excellent fit, with two parameters that cannot be determined any other way. These parameters are:

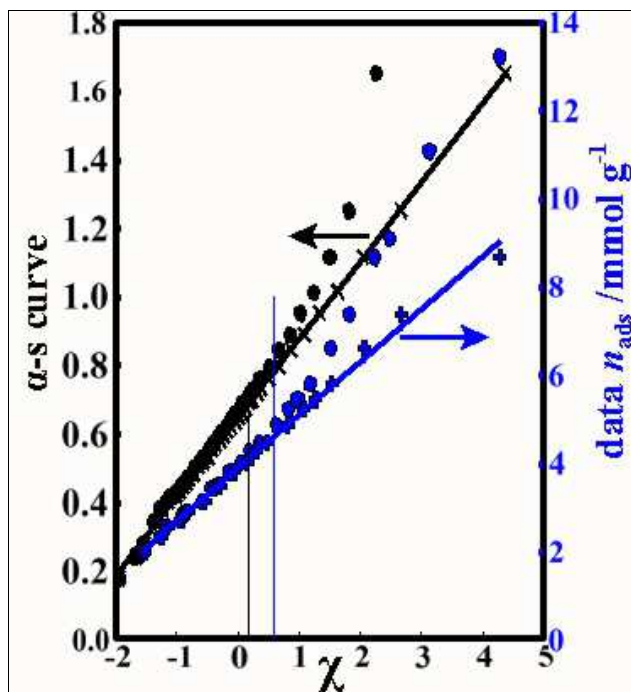
$\bar{E}_a$ : the energy of adsorption of the very first molecule adsorbed specified by  $\chi_{\zeta}$ .  
 $n_m$ : the monolayer equivalence, which could be interpreted as related to surface area.

- 2) The threshold pressure is a real phenomena, something predicted by the  $\chi$ -hypothesis and is impossible by any theory that yields “Henry’s law” as applied to physisorption.

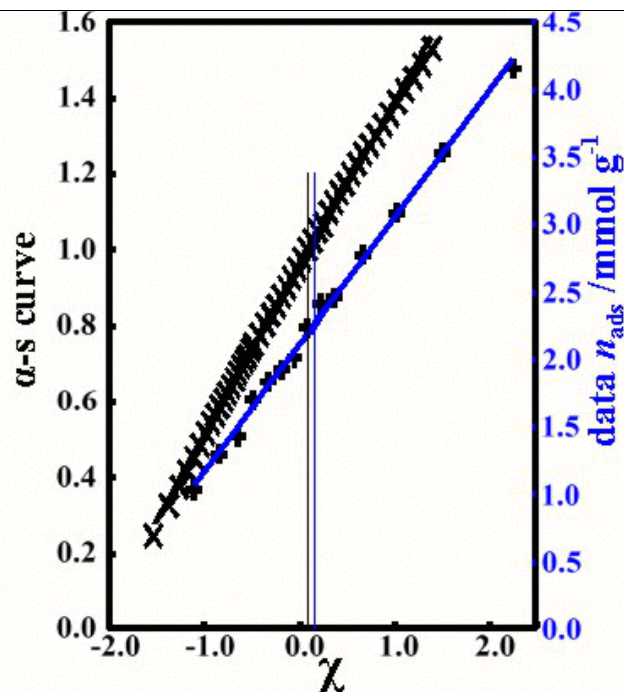
Using “standard curves” will not create a tragedy but only something that yields meaningless output parameters and their relationship to physical quantities, that is surface area and energy.

#### **Example # 6: Sing $\alpha$ -s curves**

The most widely used standard curves are the Sing  $\alpha$ -s curves. These curves are for N<sub>2</sub>[16], **Figure 17**, and Ar, **Figure 18**, on silica samples. Below are the respective examples of the plot of



**Figure 17** The  $\alpha$ -s  $N_2$  curve for silica. Symbols: top is  $\alpha$ -s transformed data,  $\bullet$ , the top T corrected transformed data,  $\times$ , and fit, (line.) The bottom is original data,  $\bullet$ , the T corrected data,  $+$ , and fit, (line.) Vertical lines are the respective 0.40 bar pressure.



**Figure 18** The  $\alpha$ -s  $N_2$  curve for silica. Symbols: top is  $\alpha$ -s transformed data,  $\times$ , and fit, (line.) The bottom is original data,  $+$ , and fit, (line.) Vertical lines are the respective 0.40 bar pressure.

the actual data use and the standard curves obtained.

In **Figure 17**, there seems to be a temperature error of about 0.5 K, so a temperature corrected curve is shown as the bottom sets for both the original data and the  $\alpha$ -s spline fit and transformed points and line. In **Figure 18**, there is not any temperature correction. The  $\alpha$ -s transformed data[17] and the original data[18] are shown as was. It might be that the original data and  $\alpha$ -s representation are from different experiments since they show up in separate publications. However the  $\chi_c$  values are very close indicating they are the same set.

Other standard curves are much older and less reliable. The isotherms by Sing, et al. are probably the most reliable and the latest of these isotherms.

### Sub-Lesson 6: More modern data plus high resolution:

#### Example #7 Standard Curve of Jeroniec, Krug and Olivier:

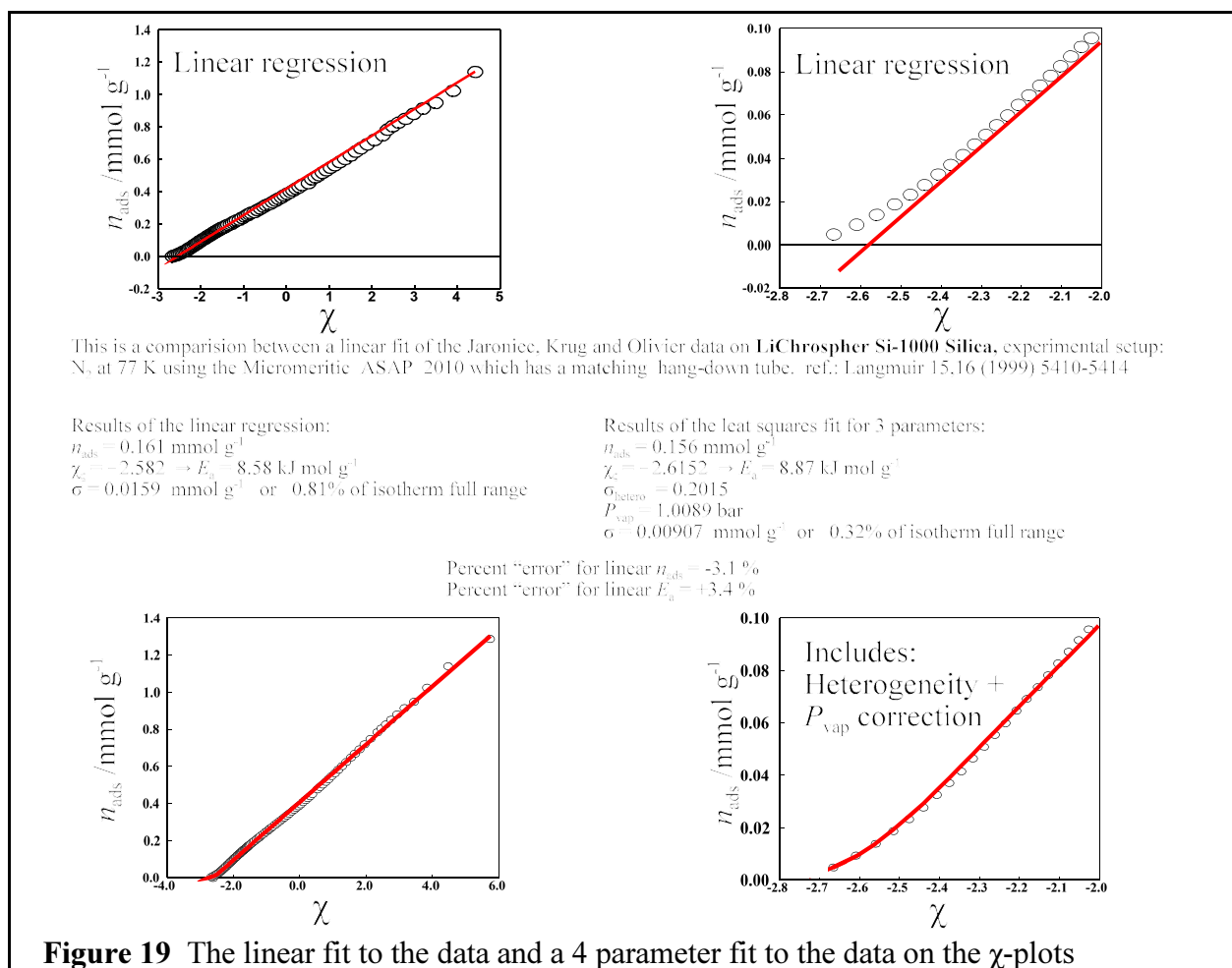
A good example of a modern isotherm is that by Jeroniec, Krug and Olivier[19]. The data is for nitrogen adsorption on Li chlospher Si-2000 Silica. The machine used was the Micromeritics ASAP 2010 volumetric system. It had three Pressure ranges 1 torr, 10 torr and 1000 torr with a lowest pressure reading to  $1 \times 10^{-7}$ . The lowest pressure recorded was  $5.55 \times 10^{-7}$  bar. (The linear

extrapolation yielded a threshold pressure of  $5.13 \times 10^{-7}$  bar which may be why the lower pressure were not recorded even though it is apparent that the transducers were capable to  $1 \times 10^{-9}$  bar)

The data indicated that there was some heterogeneity and a higher temperature than was believed to exist. The system had a twin hang-down tube, which indicates that this arrangement is not sufficient. However, the data in general is very good with only a calculated temperature off set of +0.079 K.

Two analyses of the data were preformed. One was a linear regression analysis for which the parameters are  $n_{\text{ads}}$ , and  $\chi_c$ . The second one was a non-linear least square using 4 parameters:  $n_{\text{ads}}$ ,  $\chi_c$ ,  $P_{\text{vap}}$  and  $\sigma$  the width of the heterogeneity distribution. The graphical results are shown in Figure 20. First notice is that the error using the linear regression was surprisingly low, although 3 % can throw later calculation off by quite a bit.

There is another observation, that is the wavy form or the data about the fit. This type of behavior is due to changes in the temperature of the cooling bath, probably due to room atmospheric pressure changes. The residuals show this deviation more clearly, plus that fact that the highest two points contributed disproportionately to the standard deviation. This is shown in .

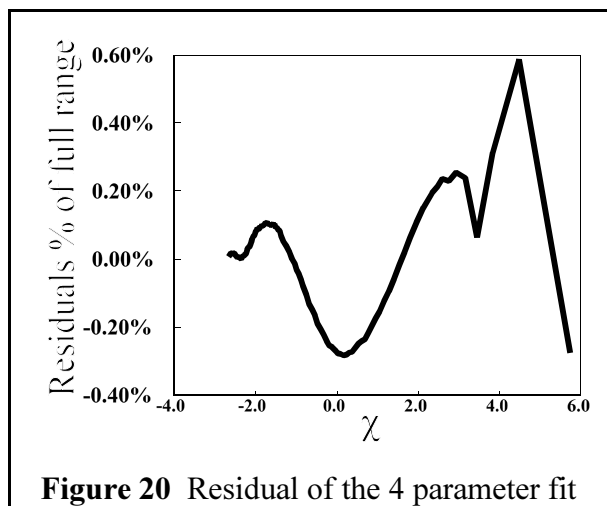


**Figure 19** The linear fit to the data and a 4 parameter fit to the data on the  $\chi$ -plots

## Summary of lesson VI and some comments

There are several more examples that are presented in the textbook. One cautionary note: Many older standard curves suffer from lack of good temperature control and measurement. This is not intended to be a criticism of the author, some of which made break-through discoveries. It is an indication of the progress in understanding of the problem.

Presented in this section are some better known investigations. All other attempted creations of standard curves yielded isotherms that support the  $\chi$ -hypothesis, especially when a temperature correction was added (The **Big error #2** is today known to be a problem) and these are in the minority. All the modern isotherm unequivocally support the  $\chi$ -hypothesis. As far as I know, no other theory of adsorption, for nonporous, homogeneous surfaces, can fit the entire isotherm within 1% with only two meaningful parameters<sup>1</sup>. This should create some interest in the field, but for 43 years very few investigators have taken up the challenge.



**Figure 20** Residual of the 4 parameter fit

One could object to the increased number of parameters that will be added to the  $\chi$ -hypothesis, but this objection is disingenuous when a comparison is made to other proposals. The big test to begin with are using the non-porous, homogeneous adsorbents and “simple” adsorbates. If a theory cannot fit many such isotherms with only 2 parameters, it’s in trouble.

Of course if a sample is not homogeneous or is not porous, it should be obvious that new meaningful parameters are needed. By definition nonhomogeneous samples have a distribution in  $E_a$ . This distribution could be distinct values or, more likely, a continuous distribution of energies, such as a normal distribution. This latter distribution, if present, adds another parameter, which is the distribution width which is the standard deviation of the normal distribution. The other parameters are already specified by the  $\langle E_a \rangle$  and  $n_m$  that is in common with the homogeneous representation. The normal distribution of energies probably always show up in the very lowest pressures (and are not observed in most instruments.) Thus, for a most nonporous,

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<sup>1</sup> For example, the BET does have 2 parameters, but the isotherm fit is bad and the “C” constant is meaningless. Freundlich isotherm, considered at the time only empirical, has two parameters one of which is meaningless and does not fit the isotherm well. The Langmuir isotherm does not even come close to fitting the entire isotherm. All other “Henry Law” isotherms have more than 2 parameters and are either combinations of other isotherm or modification of the BET, thus in both cases yielding meaningless parameters.

The Dubinin class of isotherms do not work well on nonporous surface and the extrapolation to the  $P = P_{\text{vap}}$  does yield a decent value for the pore volume (which according to  $\chi$  if there is very little external surface area, is correct.) The minimum number of parameters for these is 3 and there is considerable question about the meaning of these parameters.

heterogeneous samples, this variation is easily handled. In the next section, the nonporous, heterogeneous adsorbents will be addressed.

### Lesson VII Heterogeneity:

The word "heterogenous" for physisorption refers to the energies, and specifically for  $\chi$  the value of  $E_a$ , that vary from place to place on the adsorbent. What this due to is not specified, but could be different crystallographic faces exposed on the surface, or impurities. Nano-Luggin prob investigations in water, indicates that the potential varies for metals for different exposed plains and within plains. Other possibilities, also seen in water solution, is the presence of inclusions or other impurities on the surface.

What is the form of the energy distribution. There probably some reasons for some form of distribution of energies, but (at least to me) it's not obvious what it should be. After some preliminaries, a normal distribution will be assumed. So far the normal distribution for energy seems to work quite well, but a reason for this has not been found.

#### Sub-Lesson #1. Preliminaries about adding isotherms:

First, let's look at some very fundamental mathematics. It starts out boringly simple but ends up with something several reviewers have rejected, believe it or not.

Normally, data points on the graph are specified by the letter  $x$  and  $y$ , with the  $x$  values specified by the abscissa and the  $y$  values specified by the ordinate. So this informal convention is followed here. The  $x$  values is the set for the independent variables, whereas, the  $y$  values is the set for the dependent variables

If one has two sets of real  $y$  that depend upon the same  $x$  set then it should be obvious that the  $y$  sets can add:

**Table 2** Example of relationship between graphing sets.

common $x$ set,	$y$ set #1	$y$ set #2	$y$ set #3 = $y$ set #1 + $y$ set
1	7	2	9
2	2	5	7
3	5	1	6
4	3	4	7

...or maybe:

**Table 3** An example where the dependent sets can add for form a new valid set.

common $x$ set,	$y$ set #1	$y$ set #2	$y$ set #3 = $y$ set #1 + $y$ set
<b>ln(1)</b>	7	2	9
<b>ln(2)</b>	2	5	7
<b>ln(3)</b>	5	1	6
<b>ln(4)</b>	3	4	7

Notice it does not matter what the  $x$  set is for one to add the  $y$  sets. Furthermore, the values of the  $y$  sets (#1, #2 or #3) do not need to be monotonic (except for physisorption.) Also there is a complication if two values of the  $x$  set are the same. (It's not necessary to go there.) This means that if the  $x$  set includes all the real values over a range, then the  $x$  set must be monotonic, that is, it cannot increase and then decrease or vis-a-versa throughout its range. In this case it increases only. This means that one can apply any function to the  $x$  values, as long as it maintains the monotonic ordering either increasing or decreasing, and it does not affect the addition of the  $y$  sets. However, the same is not true for the  $y$  sets. In other words. Functions of the sets of  $y$  do not add to yield the function of the sums. For example:

**Table 4** Example where the dependent sets cannot add.

common $x$ set,	$y$ set #1	$y$ set #2	$y$ set #1 + $y$ set #2, $\neq y$ set
1	<b>ln(7)</b>	<b>ln(2)</b>	<b>ln(7) + ln(2) <math>\neq</math> ln(7+2)</b>
2	<b>ln(2)</b>	<b>ln(5)</b>	<b>ln(2) + ln(5) <math>\neq</math> ln(2+5)</b>
3	<b>ln(5)</b>	<b>ln(1)</b>	<b>ln(5) + ln(1) <math>\neq</math> ln(5+1)</b>
4	<b>ln(3)</b>	<b>ln(4)</b>	<b>ln(3) + ln(4) <math>\neq</math> ln(3+4)</b>

These preliminaries are so obvious that it's hardly ever pointed out. However, it seems that in the area of physisorption they are sometimes not followed.

**Thus, a principle:** taking a monotonic function of the dependent variable retains the order of the  $x$  values either monotonic increasing or decreasing which is all that is necessary for the dependent variable, but in order to add the independent variable, a functional transformation (other than multiplication by a constant) is not allowed before the addition.<sup>1</sup>

Let's look at the transformations that are used. The BET plot transforms the ordinate to:

---

<sup>1</sup> (This argument has been rejected by reviewers even though to violate this simple rule for chemistry the implication is that either the law of mass conservation is not true or that the surface areas do not add.)

$$y = \frac{P}{n_{\text{ads}} (P_{\text{vap}} - P)} \quad (77)$$

The inverse function of  $n_{\text{ads}}$  alone disqualifies addition. For the Dubinin transformations:

$$y = \ln \left( \frac{n_{\text{ads}}}{n_{\text{m}}} \right) \quad (78)$$

Addition of the  $y$ s in both cases are not allowed. However, the equations can be given in a form where  $n_{\text{ads}}/n_{\text{m}}$  can be solved for and can therefore be added. The problem, at least for the BET, is that determining the parameters runs into serious difficulties, due to the requirement that the individual  $y$  sets must go to (0,0) and messy math.

If transformations in the  $y$  set are problematic, why do it? It's not problematic to transform the  $x$  values, only if the  $y$  values are transformed. The  $y$  values are normally transformed to yield a graph with a straight line. With today's computers, this might seem unnecessary when a curve fit can be performed in seconds instead of days, but at the time when the various isotherms were being developed this was the normal practice.

If this is the case, why use the  $\chi$ -transform? Answers:

Firstly, for homogeneous, nonporous samples the transform should fit the entire isotherm as a straight line.

Secondly, the slope of the transformed isotherm yields the monolayer equivalent and the  $x$  intercept yields the energy of the first molecule adsorbed relative to the liquid state.

Thirdly, heterogeneous adsorbents, as to be shortly demonstrate, are easily analyzed and the same is true for porosity.

Fourthly, the abscissa is an indication of how many monolayer equivalence are potentially possible.

The third and fourth reason will be subsequently become clear.

### **Sub-Lesson #2. Addition of 2 isotherms with different $E_a$ s:**

Let's assume that we decide to mix two powder together to create a new adsorbent. Obviously, if the two powders yield the same  $\bar{E}_a$  the two isotherms would be identical except for scaling, so to demonstrate the powders with well separated  $\bar{E}_a$ s will be chosen. Looking at the isotherms above, the adsorption of Ar on H<sub>2</sub> treated Al<sub>2</sub>O<sub>3</sub> and on cleaned diamond look like good candidates for illustration. This could also be easily done experimentally since the pre-treatments are about the same.

The following are the parameters from above. (Only  $\chi_\zeta$  and  $n_{\text{m}}$  are needed, the others are redundant.)

Alumina:  $\chi_\zeta = -1.916 \Rightarrow \bar{E}_a = 4.407 \text{ kJ mol}^{-1}$ ,  $n_{\text{m}} = 1.143 \text{ mmol g}^{-1}$ ,  $P_\zeta = 1.12 \times 10^{-2} \text{ bar}$

diamond:  $\chi_\zeta = -2.082 \Rightarrow \bar{E}_a = 8.02 \text{ kJ mol}^{-1}$ ,  $n_{\text{m}} = 16.2 \text{ } \mu\text{mol g}^{-1}$ ,  $P_\zeta = 3.28 \times 10^{-4} \text{ bar}$

Since the same pressure points were not used for the two sample, they will be simulated using the fits that were determined<sup>1</sup>. Also, since the monolayer equivalence are considerably different  $n_{m,s}$ , the mixture is made to be diamond/alumina = 20:1 in terms of adsorbent mass for scaling.

The resulting  $\chi$ -plot is shown in **Figure 21**. In this case a broken straight line results.

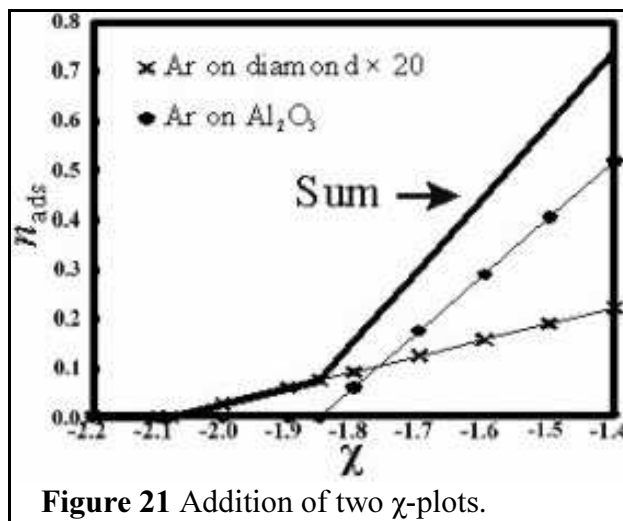
This two energy situation is unusual (with a special case to be explained later.) It is more likely that a distribution of energies is present. How does one handle that?

First we would like to know what the energy distributions are for this situation. Looking at the form of isotherm of each of these adsorbents, each is from the simple  $\chi$ -equation, i.e. equation (66) p38. If one differentiates equation (66) one gets a step function as a result of the  $U$  function and the step increments are the slopes of these lines. These slopes are the values  $n_{m,1}$  and  $n_{m,1} + n_{m,2}$ . For the 1<sup>st</sup> step the height is  $n_{m,1}$ . For the 2<sup>nd</sup> step the height is an additional  $n_{m,2}$ . Thus the total value to step #2 is the sum of  $n_{m,1} + n_{m,2}$ . Thus, to get the magnitude of  $n_{m,2}$ , the magnitude of the 1<sup>st</sup> step,  $n_{m,1}$  is subtracted from the overall magnitude of the second to yield  $n_{m,2}$  as illustrated in **Figure 22**.

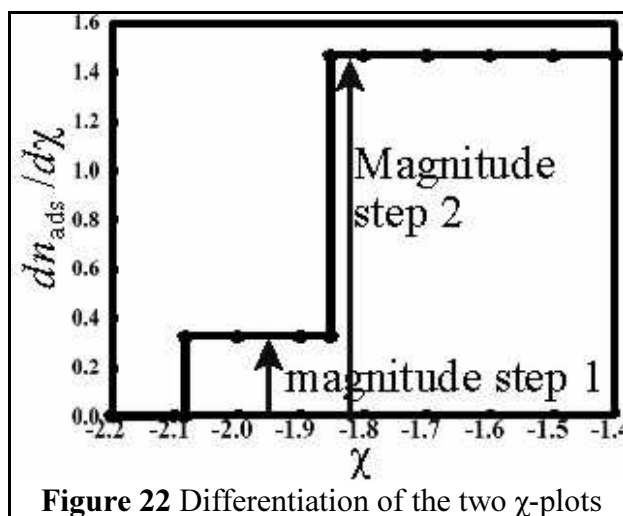
To get the distribution one differentiates once more. This is shown in **Figure 23**. The height of the bars shown are proportional, but obviously not absolute since, theoretically, the absolute heights are infinite.

**Figure 23** is the energy distribution for the two  $\chi$ -plot shown in **Figure 21**. This particular type of distribution seems to be rare.

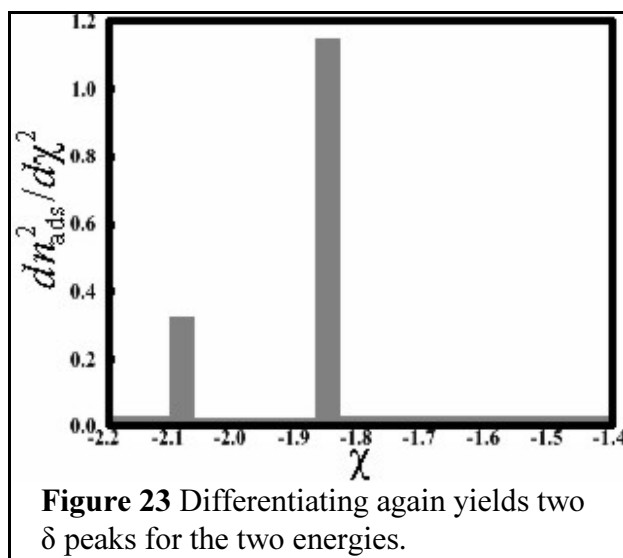
So what type of distribution is the most



**Figure 21** Addition of two  $\chi$ -plots.

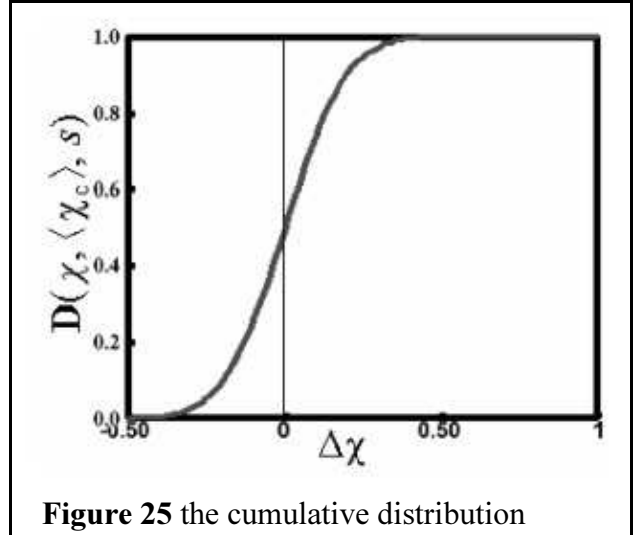
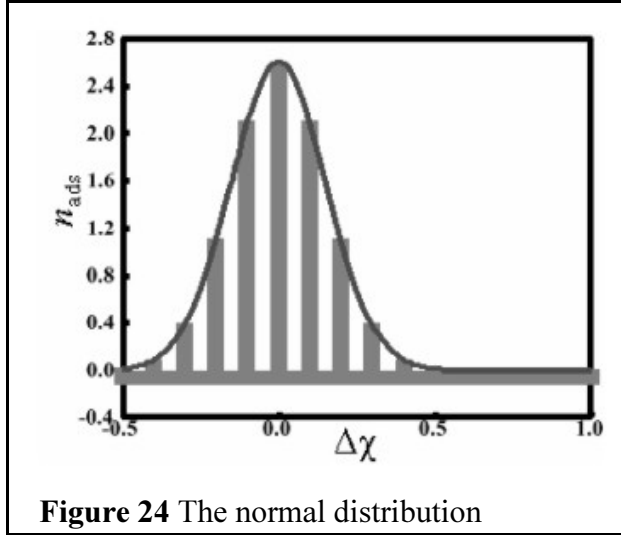


**Figure 22** Differentiation of the two  $\chi$ -plots



**Figure 23** Differentiating again yields two  $\delta$  peaks for the two energies.

<sup>1</sup> Something similar needs to be done for other addition attempts. The fitting routine is not important so long as the entire fit is within 1 % without gyrations.



common case? This common case would be a distribution of many small aliquots of surface with, perhaps, a random distribution of energies. The most obvious would be a normal distribution of energies or perhaps a log-normal distribution, that is normal in  $\chi$ . These two distributions are in practice nearly indistinguishable here. The normal distribution in  $\chi$  is the simplest, so that is what will be used here. The distribution need not be either one of these, and perhaps with better experimental data, the subtleties will become apparent.

### Sub Lesson #3. Heterogeneity by an Energy Distribution

In **Figure 24** is an example of the normal distribution. The abscissa is given as  $\Delta\chi$  since the center of the energy distribution is logically a  $\chi_c$ . The normal distribution has the formula:

$$\mathbf{N} = \frac{1}{\sqrt{2\pi s^2}} \exp\left(-\frac{(x-\mu)^2}{2s^2}\right) \quad (79)$$

The integral of the normal distribution is the cumulative normal distribution function (CDF) and is related to the error function. It is:

$$\mathbf{D}(x, \mu, s) = \int_{-\infty}^{+\infty} \mathbf{N}(x, \mu, s) dx \quad (80)$$

The integral of **D** is the (normal) statistical area function (SAF), given the letter **Z** obtained by integration by parts:

$$\mathbf{Z}(x, \mu, s) = (x - \mu) \mathbf{D}(x, \mu, s) + \frac{2s^2}{\sqrt{\pi}} \mathbf{N}(x, \mu, s) \quad (81)$$

and

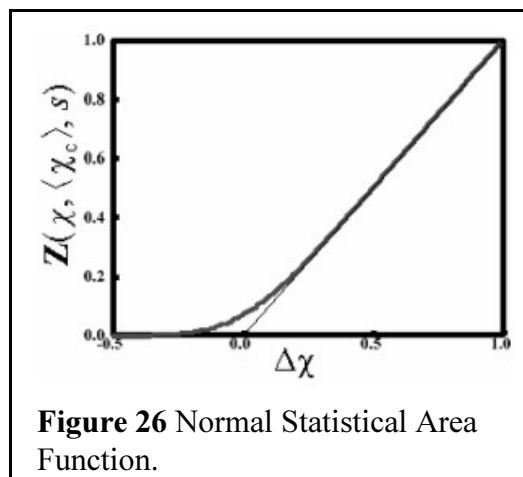
$$\therefore n_{\text{ads}} = n_m \mathbf{Z}(\chi, \langle \chi_c \rangle, \sigma) \quad (82)$$

The graphs given here show these functions:

Notice that the peak in the normal distribution, **Figure 24**, is at  $\Delta\chi = 0$ .

In **Figure 25**, the cumulative distribution, the inflection point is at  $\Delta\chi = 0$ .

In the statistical Area Function **Z**, **Figure 26**, the extrapolation from the straight line goes to  $\Delta\chi = 0$ .



### Lesson VIII - “Layering:”

The foundation of the  $\chi$ -hypothesis has been presented with evidence of its validity. If one believes that the experiments performed were correctly, unbiasedly and honestly performed<sup>1</sup> and reported, the conclusion must be that the quantum mechanical derived equations is the best description of physical adsorption yet created. The former conditions and the phenomena reported have been observed by several investigators, who performed and reported without the knowledge of other similar work. A good example of this are experiments and theoretical development by Churaev, Starke and Adolphs[20]. Other work will be cited further on.

The question now becomes, is there a way of calculating porosity and if so what physical parameters are in the output or is there some arbitrary parameters to do fitting that have little meaning. As you will see in these next two lessons, the answer is the former choice.

#### Sub-Lesson #1 The equations

There are two formulation that yield complementary information. The one presented in this lesson is the “layering” approach. The basis is equations (68), (69) and (70). For review they are presented here:

$$\theta_1 = 1 - \exp(-\Delta\chi) \quad (83)$$

$$\theta_2 = 1 - \exp(-\Delta\chi + \theta_1) \quad (84)$$

$$\theta_n = 1 - \exp\left(-\Delta\chi + \sum_{m=1}^{n-1} \theta_m\right) \quad (85)$$

The first of these equations leads to the log-law, equation (72), applicable to the first monolayer: This law is repeated here:

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<sup>1</sup> Other than the unscientific statements such as, “everyone knows this is incorrect,” all three of these reasons have been use to reject publication on the subject.

$$\theta_1 = 1 + \frac{RT}{E_a} \ln \left( \frac{P}{P_{vap}} \right) \quad (86)$$

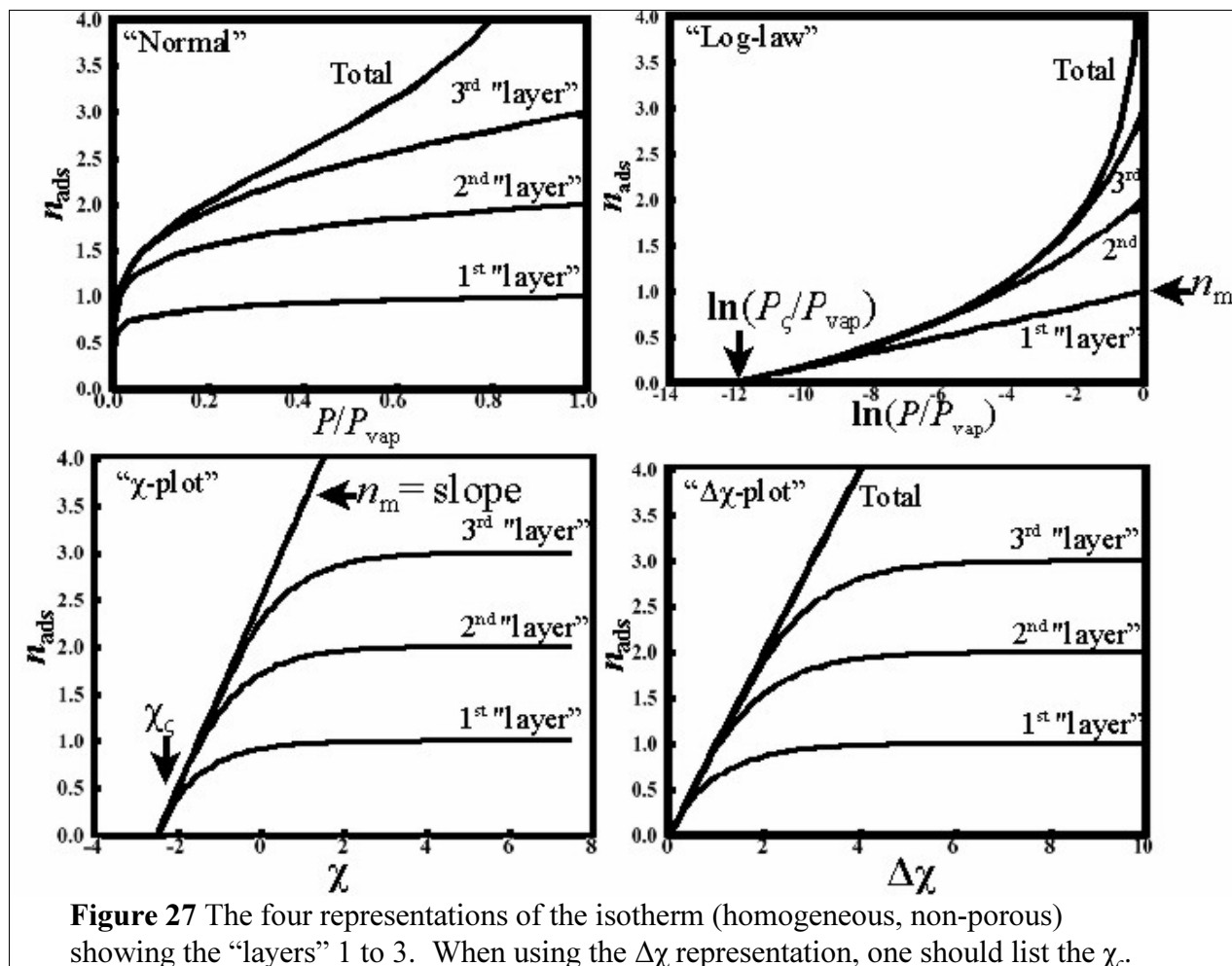
One of the principles that can be derived is that there will always be a first “layer,” according to Lemma #1, page39. At  $P = P_{vap}$  the first “layer” will be 100% dense and the value of this first “layer” is  $n_m$ :

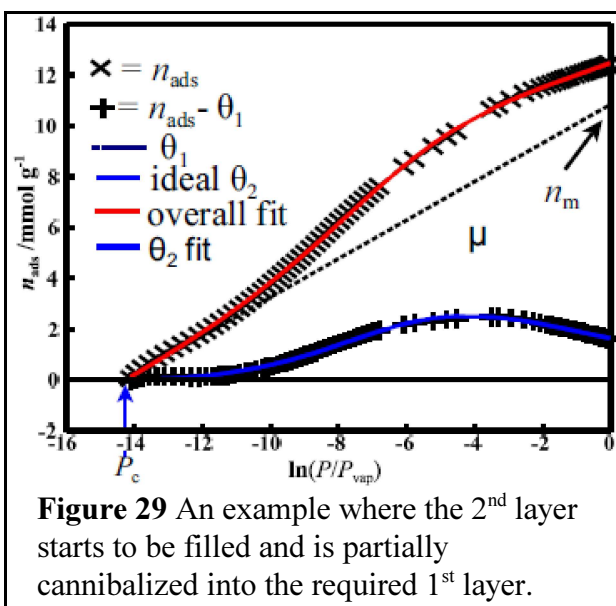
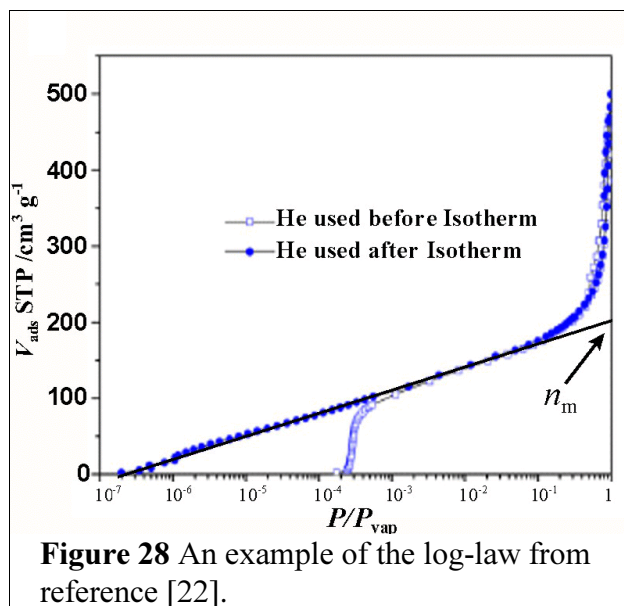
$$\theta_1 := n_{ads,1}/n_m \quad \therefore \lim_{P \rightarrow P_{vap}} (n_{ads,1}) = n_m \quad \therefore n_{ads,1} \leq n_m \quad (87)$$

Assuming a rigid adsorbent and no inter-particle condensation, this will always be true. (I can't think of any exceptions.) Thus one can draw a straight line from  $P_\zeta$  to the final  $P_{vap}$  in the log-law plot, to indicate the maximum amount allowed in the first “layer” and, thus, the maximum value for  $n_m$ . Anything above this line is in the layer 2 and higher. It is instructive to look at how the various layers form using the log-law and the  $\chi$ -plot.

### Sub-Lesson #2 What “layering” densities look like

The graphs in **Figure 27** illustrate the difference between the full  $\chi$ -plots and the layering equations.





In **Figure 28** is an experimental isotherm that is nearly a perfectly restricted to a monolayer thickness for the pore. This graph represents N<sub>2</sub> adsorption on carbon samples, LMA233 by J. Silvestre-Albero, A. M. Silvestre-Albero, P. L. Llewellyn and F. Rodrigues-Reinoso[21]. This sample had some measurable external surface area as evidenced by the upswing in the curve as  $\ln(P/P_{\text{vap}})$  approaches 0. The authors avoided the **Big Errors** and especially #3 regarding the He dead-space gas. If this had not been avoided, there would be a serious question whether this research was useful.

In reference [22] with DD52 is an illustration of going beyond a monolayer thickness for adsorption. **Figure 29** indicates partial adsorption in the 2<sup>nd</sup> “layer” and a phenomenon called “layer cannibalization” where the first “layer” takes adsorbate molecules from the 2<sup>nd</sup> “layer” to fulfill Lemma #1. The 2<sup>nd</sup> “layer” distribution follows  $\chi^{-1}$  extremely well. The distribution  $\chi^{-1}$  is similar to the normal distribution and is discussed in Lesson X, very well.

“Layering” concept will be very useful for porosity calculations along with the  $\chi$ -plot analysis, which uses  $\chi^{-1}$  function. However, first the thermodynamics of physisorption as applied to  $\chi$ -hypothesis is treated.

### Sub-Lesson #3 Rules for “layering”

Notice that if the 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup>, etc. are disallowed by the pore walls being too narrow for them to form completely, the density, according to quantum mechanics, does not change from that predicted. In other words the isotherms shown in **Figure 29** are following the predictions of n **Figure 27** until the amount is physically inhibited. This leads to

**Lemma #2:** Each “layer” density starts filling even if the amount cannot be accommodated by the pore structure. If fractional filling can be accommodated this will take place. This can lead to the cannibalization of some amounts in layers other than the first.

**Lemma #3: This principle applies to subsequent layers with, for example, the 2<sup>nd</sup> layer taking filling in preference to the 3<sup>rd</sup> but the 3<sup>rd</sup> will always follow the density line unless inhibited by the 1<sup>st</sup> and 2<sup>nd</sup> layer. Etc.**

Thus in **Figure 29** the second layer starts filling with an amount because there is room for it to fulfill the density. However, as the first layer continues to fill up, it takes precedence over the 2<sup>nd</sup> layer and the second layer has to give up its “space” until the first layer is complete.

## Lesson IX - Thermodynamics:

### Sub-Lesson #1: Some symbolism and definitions:

Some of the symbolism used in the thermodynamics has been specified before. Some new symbolism has been used specifically for the  $\chi$ -hypothesis since the normal IUPAC symbols do not cover the phenomenon. First is the definition of the “system,” that is what are the boundaries of the material which is being considered and next the comparison system, usually referred to as the “standard state.”

The definition of the system is not as critical at low pressures as it is at pressures approaching the critical point of the adsorbate. The system at low pressures obviously includes the adsorbent whose boundaries seldom change during adsorption (yes, there are rare exceptions) but it also includes the adsorbate. One could wonder where the boundary is between the adsorbate and the adsorbent. This is a problem that Gibbs’ proposed a relatively simple solution to which is difficult to apply in a practical way to adsorption<sup>1</sup>. However, the density of the adsorbate and adsorbent at the low pressures are very different so one can assume that the “missing” volume of gas in the volumetric experiment is part of the system and the weight gain, corrected for buoyancy, is the weight of the adsorbate and is part of the system. It is further assumed that the volume of the system changes very little and therefore the energies under consideration are the Helmholtz energy and the internal energy. With the possibility of the addition of adsorbate to the system, the function is referred to as the grand potential and the grand canonical partition function is the appropriate molecular description.

The normal IUPAC standard state for gasses is 1 bar ( $1 \times 10^5$  Pa or  $\sim 1$  atm) and the symbol to indicate a standard state is the superscript “<sup>o</sup>” (the subscript plimsoll.) This is a unicode character (U+2296) but is not available on most word processors. (Often a superscript circle character, such as the degree sign ( $^\circ$ ) is used. A good substitute is the Cyrillic letter old fita,  $\Theta$  or  $\theta$ , or circle negative,  $\ominus$ .) If the plimsoll or something similar is not present, then a convention other than the IUPAC is being used. This convention is usually the change from the liquid adsorbent to the adsorbate at the temperature of the adsorbent. For example  $\Delta \bar{H}_l^a$  is the change of the enthalpy function from the liquid phase to the adsorbate phase at 78 K. Usually the temperature will not be listed because the temperature will be given elsewhere. Notice some things about this symbolism:

1. The bold letter. **H**, indicates it is a function
2. There is a bar over the **H**, as  $\bar{H}$ , indicating the units are  $\text{J mol}^{-1}$  or  $\text{kJ mol}^{-1}$
3. The  $_l^a$  indicate that the change is from the liquid phase to the adsorbate phase.

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<sup>1</sup> Indeed, theoretically nearly impossible to accept as an approximation even at low pressures. For the quantum mechanical definition of the boundaries of the system, one needs to expand the meaning of boundary to include the probability functions used in quantum mechanics. So what is wrong with a “fuzzy” boundary. If one defines adsorbate appropriately, there is no problem. I hear the howls of disapproval now from the researchers stuck on classical mechanics, because the adsorbate boundaries are in constant fluctuations. However, on a time average, the amount of adsorbate remains constant if the conditions remain constant.

Below in **Figure 29** are some symbol definitions used in this presentation. They are repeated in **Table 1**.

<b>Table 5</b> some energy terms used in this lesson		
Symbol	Designates	Standard State
$\bar{E}_a$	The “molar internal energy” of the first adsorbate molecule	$\chi, P_{\text{vap}}$
$\bar{\mathbf{E}}(y)$	$(\bar{\mathbf{E}}_1^a(y))$ The molar internal energy function as a function of $y$ .	$\chi, P_{\text{vap}}$
$\Delta\bar{\mathbf{S}}(y)$	$(\bar{\mathbf{S}}_1^a(y))$ The molar entropy function as a function of $y$	$\chi, P_{\text{vap}}$
$\ominus$	indicates the standard state is $10^5$ Pa (1 bar)	IUPAC
$q = \bar{\mathbf{E}}^\ominus(y)$	Differential heat of adsorption	IUPAC*, 1 bar
$Q$	Integral heat of adsorption	IUPAC*, 1 bar
$\Delta Q$	Steps in the integral heat needed for experimental purposes.	**
$\Delta_l^a \bar{\mathbf{S}}$	entropy change from the liquid to the adsorbed state	$\chi, P_{\text{vap}}$ ***
$\Delta_l^a \bar{\mathbf{E}}$	energy change from the liquid to the adsorbed state	$\chi, P_{\text{vap}}$ ***
$\Delta \mathbf{S}_1$	$(\Delta_l^a \bar{\mathbf{S}}_1)$ - the entropy change from the liquid state to first “layer” adsorbate at $T$ of adsorbent	$\chi, P_{\text{vap}}$
$\mu_x$	Chemical potential of x	IUPAC, 1 bar
* IUPAC does not distinguish between the differential and integral heat in the “Green book,” so this distinction, which is traditional in some quarters, used. Also $q \approx \Delta Q / \Delta n_{\text{ads}}$		
** traditional		
*** Since the topic is adsorption and standard pressure is $P_{\text{vap}}$ the $l^a$ will be often be left off.		
$y$ is $\chi$ if not otherwise designated in the parenthesis.		

**Sub-Lesson #2: Basic thermodynamic applied to  $\chi$ :**

Now that the “layering” is presented, a short lesson in thermodynamics as applies to physisorption is in order. Firstly, from basic thermodynamics:

$$\mu_{\text{ads}} - \mu_{\text{liq}} = RT \ln \left( \frac{P}{P_{\text{vap}}} \right) \quad (88)$$

The comparison state for the thermodynamics according to the GPF, equations (55) through (59) is that there is no entropy term, in other words the adsorbate is very similar to the bulk liquid in configuration. This is not entirely true since the first “layer” is missing one degree of freedom. Whereas, the “layers”  $> 1$  can move up or down, the first “layer,” which is composed of the following mole fraction of the total adsorbate:

$$X_1 = \frac{1 - \exp(-\Delta\chi)}{\theta} \quad (89)$$

where  $X_1$  is the mole fraction of adsorbate confined to the adsorbent surface. (Any motion away from the surface is cancelled by the 2<sup>nd</sup> “layer” motion to the surface, on average.) This amount of change from equation (87) is normally quite insignificant:

$$\Delta S_1 = \frac{1}{2} n_m X_1 RT = \frac{n_m RT (1 - \exp(-\Delta\chi))}{2\theta} \quad (90)$$

Also in dealing with simple molecules, one would not expect changes in vibration or rotational modes. This leads to the statement, which is the Dubinin[23],[24] “thermodynamic criteria.” :

$$\Delta_l^a S = S_{\text{ads}} - S_{\text{liq}} = \Delta S \approx 0 \quad (91)$$

Since the volumes of both the liquid and adsorbate do not change significantly the enthalpy and internal energy are very nearly equal. Thus, one can rewrite equation (86) as<sup>1</sup>:

$$\frac{\bar{E}}{RT} = -\ln \left( \frac{P}{P_{\text{vap}}} \right) \quad (92)$$

Where  $\bar{E}$  ( $< 0$ ) is the standard internal energy function expressing the difference between the bulk liquid and adsorbate at the temperature of the adsorbent for both. The value of  $\bar{E}^\ominus$ , i.e.  $(\bar{E} + \bar{\epsilon})$ , is the calorimetric (i.e., differential) standard internal energy values, whereas  $\bar{E}$  is the isotherm values. The difference between the two is that the standard state for calorimetry is 1 bar, whereas, for the isotherm calculated heat is relative to the heat of vaporization at the temperature of the adsorbent.

Given the difference between the standard state used for the isotherm equation and 1 bar for the calorimetric heat, one must added  $\epsilon$  to the isotherm calculated heat to yield the calorimetric heat. Overlooking this has caused much trouble in the literature with many contortions to make the calculations come close to agreeing with experiments.

---

<sup>1</sup> A reminder, both  $\bar{E}$  and  $\bar{\epsilon}$  are negative and so far only  $\bar{E} < \bar{\epsilon}$  (or  $|\bar{E}| > |\bar{\epsilon}|$ ) has been addressed. This make the overall process exothermic.  $\bar{E} > \bar{\epsilon}$  will be addressed later.

**Side bar- some notes about calorimetry:**

There are a variety of “heats.” In calorimetry one obtains the heat of adsorption in short piecewise integral form. From these pieces one then calculates a piecewise differential heat by assuming that the heat within each piecewise portion is the integral of a line between the starting stoichiometry and the ending stoichiometry, which is a straight line relationship. We know this is incorrect because of the exponential decay curve that the heat evolution follows, so the calculation is a little different than the reality. This is best visualized graphically.

(92) (page 63) is a simulation of a the energy of adsorption on a homogeneous, nonporous adsorbent. The solid line is the calculation from the isotherm outputs. The measurement of the heat is made by adsorbing the adsorbate from point A to point B. The instantaneous differential heat cannot be measure but rather the total. One then measures the heat produced by going from A to B and divides by the number of moles used and to obtain an “average” heat. However, point A is not available. The problem is that it is normally assumed that the differential heat is given by the X between the two points. This, however could be quite wrong by a significant amount, especially where the differential heat is changing rapidly. At the beginning, depending upon the method, the measurement is very far off from the real value. As the experiment approaches the heat of vaporization, the error becomes (in a absolute sense) less.

Assuming that point A is known, the potential error demonstrated here is about 12% for the differential heat. However, an interpolations from the first data point yields a low value for -12% to about 24%, depending on the method selected. If by chance the investigator guesses that the function is exponential decay for adsorption from the start, the real value might be calculated.

**Figure 30** (page 63) is a simulation using the same parameters for the total integral heat, that is the sum experimental segments up to the value of  $n_{ads}$  specified. This is a better approach since the fit used should pass through the data points generated. The equation for  $\chi$  to fit this is an exponential decay rise plus a linear increase. The first part is the value for integral of  $E_a$  and the second part is a linear increase associated with  $\epsilon$ . This means that a nonlinear least squares routine is need to make a fit.

The parameters used for these graphs were  $E_s = 20$  and  $\epsilon = 3$ . The differential fit would be a good starting point for the integral heat, or one could simply use the  $\chi$ -plot parameters. In this simulation the relative error for the first point is 13%. If the piece-wise method is used on the integral heat as in the relative error for the first point is assuming a perfect experiment. Thus, the best strategy is to fit the integral heat to a reasonable curve and differentiate that fitted curve. This would be true even if one did not know the form of the equation.

Once one has measured the isotherm, then the output parameters  $E_a$  and  $n_{ads}$  are available, so one can plot  $\bar{E} - \varepsilon$  versus  $n_{ads}$  (obtained from equation (66)). The value  $\varepsilon$  is available from the literature for most common liquids. This equation is:

$$\bar{E}(n_{ads}) = -RT \ln(P) + \bar{\varepsilon} \quad (93)$$

or:

$$\frac{\bar{E}(n_{ads})}{RT} = E_a \exp(-\Delta\chi) + \frac{\bar{\varepsilon}}{RT} \quad (94)$$

This method and others are confirmed in the publication on the heats of adsorption for physisorption[25] which explains the various “heats” and provides several examples. A couple examples will be provided here.

First there are some definitions to review. These are the difference between the differential and the integral heat of adsorption. Usually, the calorimetric heat are perform “adiabatically.” On the other hand it is also convenient to do isothermal measurements. There are several complications and correction made in calorimetry. (For example, the use of the first and second calorimetric international calculations) Such detail is not given here but the method of obtaining the values are important.

One starts by exposing to a certain amount of adsorptive. One then measures the heat released and allows the sample temperature to return to the starting temperature. One then from the heat capacity of the adsorbate<sup>1</sup>, calorimeter and adsorbent calculates the heat that has evolved. The normal thing to do is the assume that this heat evolved over the entire span of the pressure increase. To obtain the per mole amount of heat as an average is divided by amount of adsorbate taken up. The point for the adsorption amount is then set for the average of amounts adsorbed. One also needs to assume that the adsorbate in the range of this aliquot is also an average.

Take the first step as an example, an assume 2 mmol were adsorbed and the heat produce was 10 J. The over average would be calculated then as 10 J/2 mmol or 5 J mmol<sup>-1</sup>.

One then continues, leaving by leaving the adsorbate as is and increase the pressure for the next reading. (In the mean time one needs to keep track of the adsorption just as one would for a volumetric measurement.)

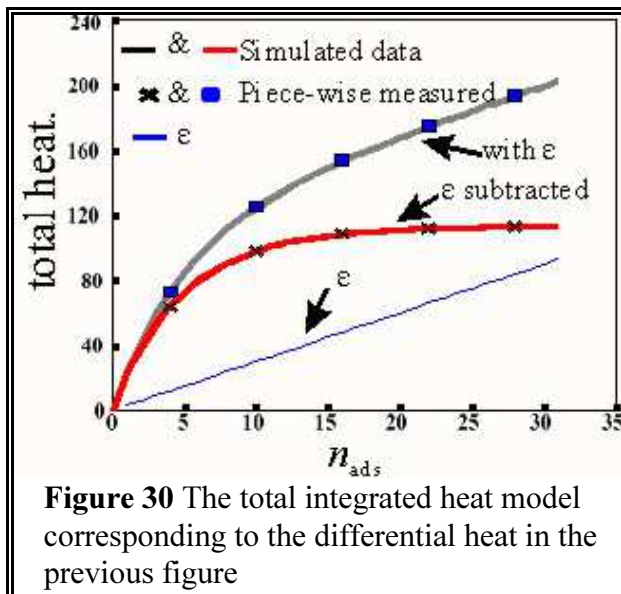
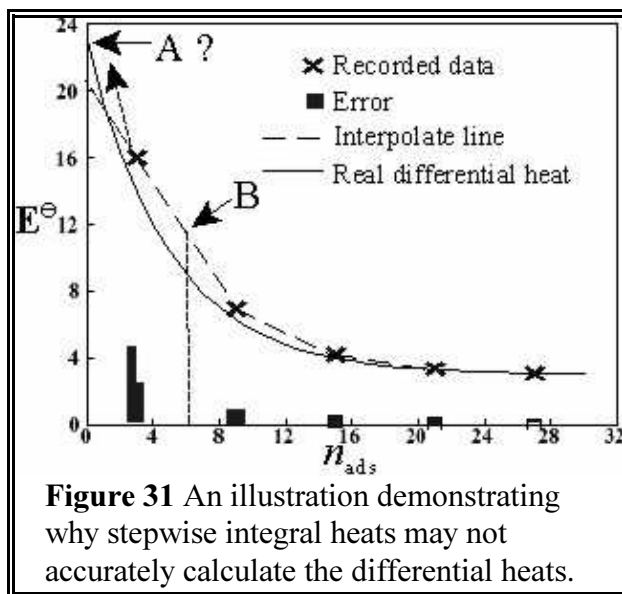
This calculation seems reasonable, but it assumes a straight line adsorption, which is incorrect. The heat capacity might be a smaller problem if the adsorbent is the primary large depository for the heat. However, it might be a good approximation, but the worst error is at the very beginning of the adsorption. In (92) is a schematic of this problem. Using these interpolate values only, without any knowledge of the form of the isotherm, one obtains a starting  $E_a$  which will probably be low.

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<sup>1</sup> Ho, Ho! Notice one has to measure the heat capacity of the adsorbate before even beginning. See the thesis by Berg to see how it is done. It is a lot of work, which might discourage researcher that need some quick answers.

A better method might be to use the step-wise integral heat as illustrated in **Figure 30** simulation. In this case, the total integral heat is the running total of each step-wise integral heat. This then needs to be fitted with a decreasing exponential function with the addition of a constant,  $\epsilon$ , the heat of vaporization. (Recall the shift in heat definition between the calorimetric and the isotherm.)  $\epsilon$  is either the literature value or the asymptotic value in (92) which should end up being a very good approximation.

Although both the differential heat with an exponential decay has high errors for the starting heat. For the integral heat, at least in principle, should have a very low error, provided the correct form is used.

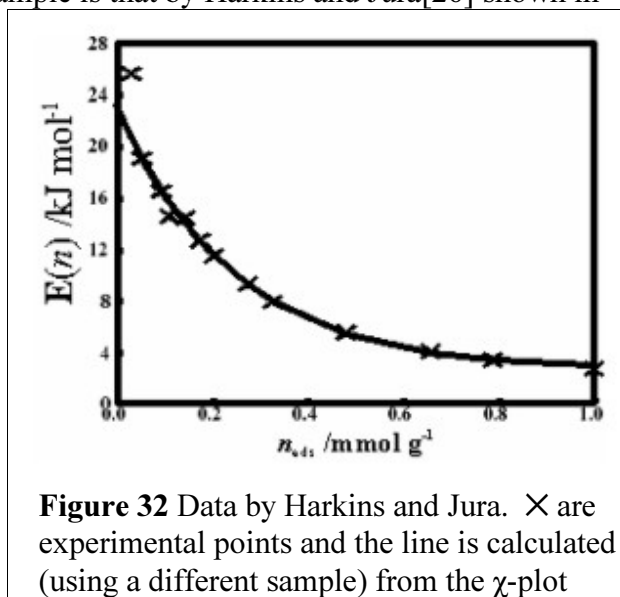


### Sub-Lesson #3 - Examples:

#### Example #1 Harkins and Jura data.

It has long been known that the differential heat of adsorption has a tendency to be an exponential decay function of amount adsorbed. An early example is that by Harkins and Jura[26] shown in **Figure 32**. (Note the high approximation for the starting  $E$ .) The experiment was performed by pre-adsorbing water to a certain level and the dropping the sample in liquid water to determine by difference what the  $\Delta E$  is. (The last point at  $1.0 \text{ mmol g}^{-1}$  is for the saturated surface  $n > 1.0 \text{ mmol g}^{-1}$ )

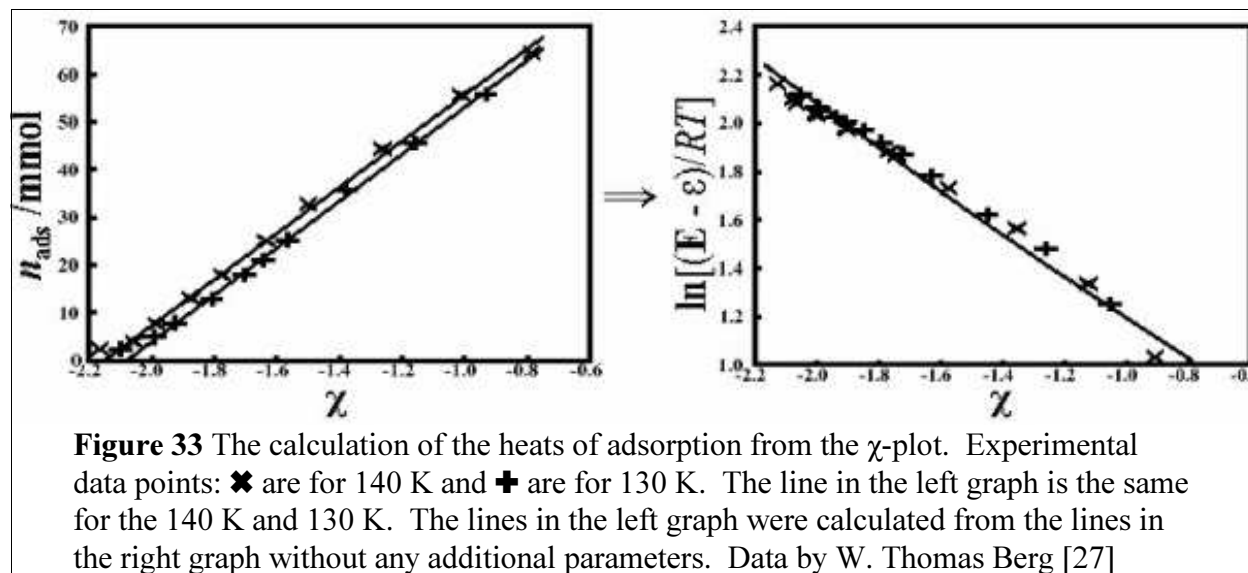
For most of the work on heats of adsorption, the calorimetry and the isotherm measurements have been of different samples. Attempts were made to make sure the samples were identical, but there could be several problems with this approach.



**Figure 32** Data by Harkins and Jura.  $\times$  are experimental points and the line is calculated (using a different sample) from the  $\chi$ -plot

#### Example #2 Berg's Data

The solution is to use the same sample in the same apparatus to obtain both the isotherm and the heat of adsorption. This is unusual. An exception is that by Berg[27] (See also [28],[29],[30] ) shown in **Figure 33**. No parameters were added in the obtain the graph to the right. It is, therefore, referred to as “parameter-less.” (The calculated two lines for the right graph were indistinguishable.)

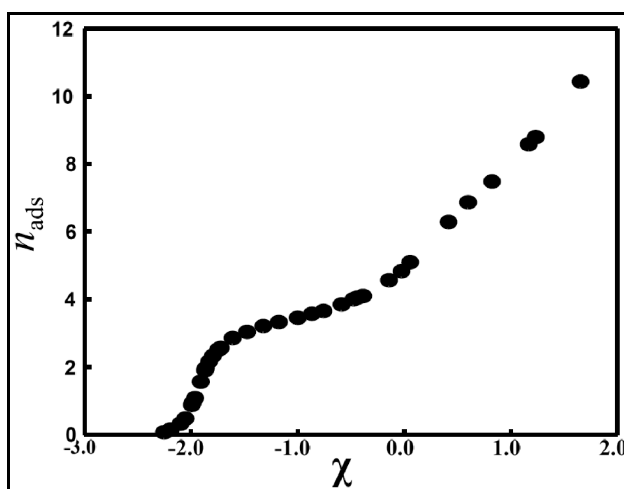


**Figure 33** The calculation of the heats of adsorption from the  $\chi$ -plot. Experimental data points:  $\times$  are for 140 K and  $+$  are for 130 K. The line in the left graph is the same for the 140 K and 130 K. The lines in the left graph were calculated from the lines in the right graph without any additional parameters. Data by W. Thomas Berg [27]

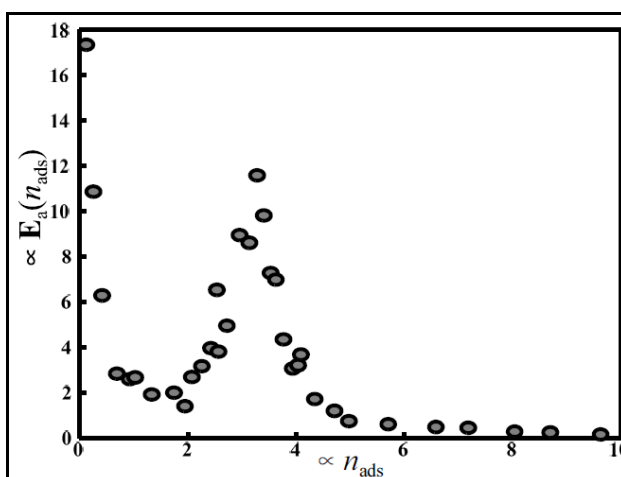
#### Sub-Lesson #4: Results of 2 or more $\langle E_a \rangle$ s:

The differential heat of adsorption is not monotonic. (The integral heat is a monotonically increasing function of adsorption. This should be obvious.) For a nonporous homogeneous surface it is a decreasing exponential function of amount adsorbed. However, for a surface that has two or more  $\langle E_a \rangle$ s there could be a decrease in  $E(n_{\text{ads}})$  followed by one or more temporary increases. (Such a deviation could also be seen with the pore filling phenomenon, but the characteristics are somewhat different.)

This phenomenon has been observed in several system with a clear example by Istrikyan and Kiselev[31]<sup>1</sup>. In **Figure 34** and **Figure 35**. Although **Figure 35** does not look exactly like the graph in the publication it looks similar. The peak in this calculation is much sharper than what appears for the calorimetry.



**Figure 34** Isotherm of *n*-hexane on carbon observed by Isirikyan and Kiselev [31, 32]\*



**Figure 35** differential heat of adsorption calculated from Isirikyan and Kiselev [31, 32]\*

There are several problems to make this calculation including uncertainty in the units' meanings and their dependence upon the BET calculation.

<sup>1</sup> The units are uncertain since they rely upon the BET and some normalization.

This phenomenon has been observed in several system with a clear example by Istrikyan and Kiselev[32]<sup>1</sup>. In **Figure 34** and **Figure 35**. Although **Figure 35** does not look exactly like the graph in the publication it looks similar. The peak in this calculation is much sharper than what appears for the calorimetry.

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<sup>1</sup> The units are uncertain since they rely upon the BET and some normalization.

to be continued ...

**Sub-Lesson #5: Distribution  $E_a$ s:**

At the moment, available in the text book.

**Sub-Lesson #6: ESW and disjoining theory**

The Excess Surface Work (ESW) hypothesis depends upon the concept of disjoining pressure. This is a classical fluid dynamics concept, that a liquid film consist of three parts:

1. One side (Call it “A”) surface of the film. It is characterized by a surface energy with the symbol  $\sigma_A$ .



2. The liquid between the two surfaces. This is characterized by the tensor  $\mathbf{\Pi}$ .
3. The other side surface (Call it “B”) surface of the film. It is characterized by a surface energy with the symbol  $\sigma_B$ .
4. The total film tension is given the symbol  $\gamma$ .

The surfaces A and B often of different phases, For example, one surface may be a water-air surface and the other a water-metal surface.

The disjoining pressure,  $\mathbf{\Pi}$ , is a little-known, well-established concept proposed by Derjaguinand Kusakov, M. M in 1936. [33]. The concept says that there is a function of thickness,  $\tau$  defined by:

$$\mathbf{\Pi}(\tau) = \left. \frac{\partial \mathbf{F}(\tau)}{\partial \tau} \right|_{\tau} \quad (95)$$

Where  $\mathbf{F}$  is the Helmholtz free energy. This leads to the equation for the chemical potential change from the vapor as:

$$\bar{V}\mathbf{\Pi}(\tau) = -\Delta\mu \quad (96)$$

The “excess surface energy” function,  $\Phi$ , leads to the equation:

$$\Phi(\tau) = -\tau\bar{V}\mathbf{\Pi}(\tau) \quad (97)$$

Here now is where an assumption enters in. As reasonable as it seems. as the gas ideal law is to gas behavior, it is still a non-thermodynamic assumption.  $\mathbf{\Pi}$  can be expressed as a function of  $t$  by the equation:

$$\Pi(\tau) = \Pi_0 \exp\left(-\frac{\tau}{\lambda}\right) \quad (98)$$

Intuitively, it behaves like the well know Beer's law. Making the substitution:

$$\Phi(\tau) = -\Pi_0 \bar{V} \tau \exp\left(-\frac{\tau}{\lambda}\right) \quad (99)$$

differentiating to find a minimum:

$$0 = \frac{d\Phi(\tau)}{d\tau} = -\Pi_0 \bar{V}_m \left[ \exp\left(-\frac{\tau}{\lambda}\right) - \frac{\tau}{\lambda} \exp\left(-\frac{\tau}{\lambda}\right) \right] \quad (100)$$

This can be true only if  $\tau = \lambda$ . It is now assumed that the derived  $\tau$  is the monolayer coverage.

That is:

$$t_m = \lambda \quad (101)$$

Given the  $P_{\text{vap}}$  is the comparison state. The chemical potential is:

$$\Delta\mu = RT \ln\left(P/P_{\text{vap}}\right) \quad (102)$$

One can show that (I leave this up to the student to show - no fair looking at the textbook):

$$-\ln\left(-\ln\left(\frac{P}{P_{\text{vap}}}\right)\right) = \theta - \ln\left(-\frac{\bar{V}\Pi_0}{RT}\right) \quad (103)$$

Which is the same as the  $\Delta\chi$  equation.

It's possible to show that the assumption of the exponential function is the only function that yields the equation (98). This leaves the assumption the  $\lambda$ , the half distance, is the same as the monolayer equivalent. The connection equation (101) demonstrates that the assumption is correct, provided  $\chi$  is correct. Furthermore, it is obvious that  $\bar{E}_a = \bar{V}\Pi_0$ . In other words, the change in  $\bar{E}$  is due to more of the adsorbent surface being covered by the adsorbate as stated in the section on "layers."

In the textbook a classical mechanical justification is given for equation (98). It is always an iffy proposition to explain something that is due to a quantum mechanical derivation by using an analogous situation in the classical mechanical world, but it might help the intuition to understand what is happening. Remember, molecules are best described as waves in this situation.

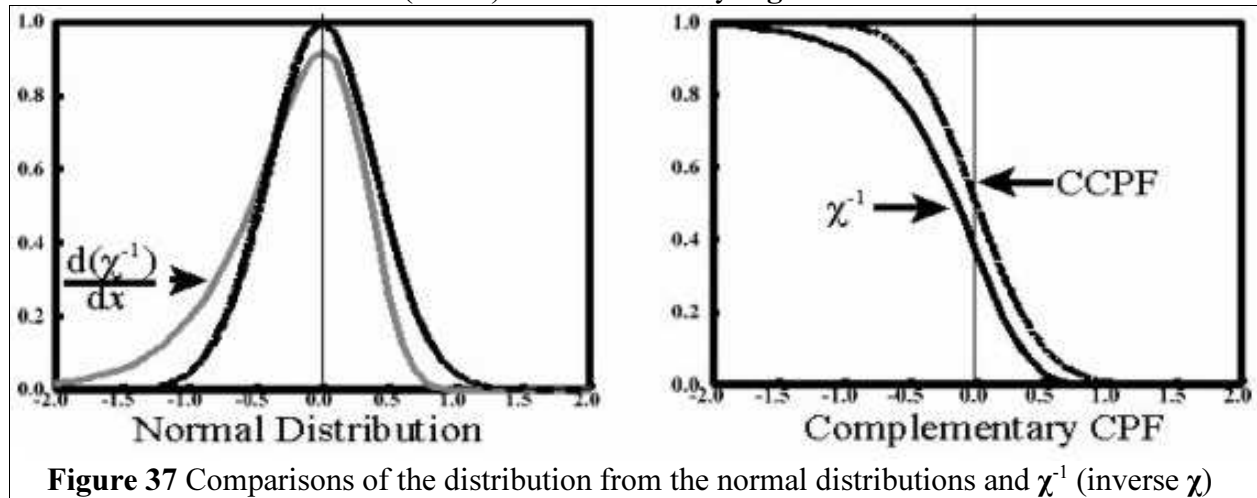
## Lesson X - Introducing the inverse $\chi$ function:

### Sub-Lesson #1 - properties of $\chi^{-1}$ :

In lesson I the inverse  $\chi$  function was defined as:

$$\chi^{-1}(x) = \exp(-\exp(-x)) \quad (104)$$

You may have wondered, “Why?” The answer is that this is the function that terminates the  $\chi$ -function if there is a barrier to adsorption. The function looks a lot like a complementary cumulative normal distribution (CCPF) as can be seen by **Figure 37**.



**Figure 37** Comparisons of the distribution from the normal distributions and  $\chi^{-1}$  (inverse  $\chi$ )

Notice the peaks of the normal distribution and the derivative of the  $\chi^{-1}$  are the same, the inflection points are not the same, due to the skewness of  $\chi^{-1}$ .

The argument of  $\chi^{-1}$  is similar to the argument in the normal distribution, except it is not squared. So the argument of **Figure 37** was:

$$\frac{x - \mu}{s} \quad (105)$$

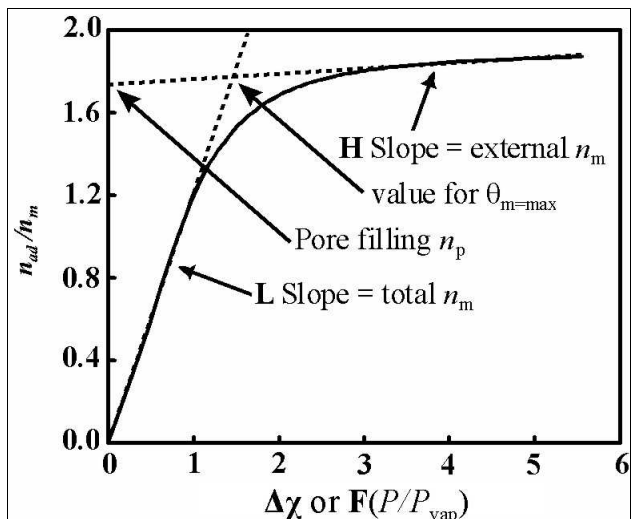
where  $x$  is the independent variable,  $\mu$  is the analogue to the mean and  $s$  is the analogue to the standard deviation. For the figures, the values were  $\mu = 0$  and  $s = 0.4$ . The  $\chi^{-1}$  and  $N$  are related mathematically. If one replaces the “2” in the argument of  $N$  with a variable and let it approach  $\infty$ , one obtains  $\chi^{-1}$  with a shift in  $s$ . (This is an interesting mathematical fact for which other than here there doesn’t seem to be much practical use.)

### Sub-Lesson #2 - application to porosity.

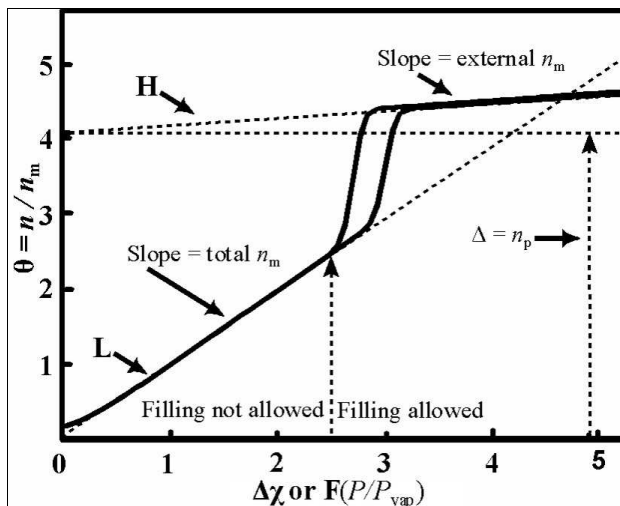
It should make sense that the inverse of the  $\chi$  function would cancel out the  $\chi$  function itself, the question is where should it in the isotherm be applied. A little “classical” porosity isotherms is in order.

There are two types of isotherms for porosity which apply to “classical” standard isotherm interpretation and  $\chi$ -hypothesis. (Recall that the  $\chi$ -plot is similar to the classical standard isotherm

except a standard is not needed.) These two types are microporous and mesoporous illustrated by **Figure 38** and below.



**Figure 38** Schematic of a micropore adsorbent isotherm



**Figure 39** Schematic of a mesopore adsorbent isotherm.

The main difference is that the microporous sample adsorption, except for heterogeneity, never has a positive curvature, whereas the mesoporous sample does. The hysteresis loop, may or may not show up in mesoporosity. If one examines these curves there is more similarity between them than initial impression yield. For both, the initial slope is the total monolayer equivalence, the back extrapolated high linear portion to ordinate intercept yields the pore volume and the final slope is the external monolayer equivalence. The positive curvature, and the possible hysteresis, is referred to as prefilling. It is assumed that something, perhaps balance in energy with the formation of the liquid-gas interface, fills the pores with the liquid adsorptive. After all, as adsorption progresses,  $E(\chi)$  decreases exponentially and there is bound to be an energy cross-over to favor the formation of a sharp adsorbate-gas interface. Thus the surface tension energy will finally win out in the mesopores.

What is important, at this point, is how the fit the initial slope, how to fit the final slope and how to model the transition between these two. It is this latter point at which the  $\chi^{-1}$  function is useful. (The statistical area function could also be used as well as the cumulative normal distribution. These functions works quite well, but  $\chi^{-1}$  seems to work better.)

The minimum number of parameters needed to fit these is 6. Each parameter has a meaning:

1.  $\chi_c$  specifying the  $E_a$ , (or  $\langle \chi_c \rangle$  specifying the  $\langle E_a \rangle$ ) molecule
2.  $\sigma$  for  $\langle \chi_c \rangle$
3. The total monolayer equivalents including pores and external area.
4. The external monolayer equivalents.
5.  $\chi_c$  specifying the  $E_a$ , energy of adsorption of the first adsorbate molecule
6.  $\Delta\chi_p$  specifying the mean of the distribution,  $\mu$
7.  $\sigma_p$  specifying the spread of the pore sizes,  $s$
8.  $n_p$  the pore volume.

Those are a lot of parameters, but they are all justified by the reality of the sample geometry and the adsorbate used. (This is way fewer than some other treatments use.)

These number of parameters, to be solved by a minimum search routine, is quite a few and a computer is definitely needed. Therefore, an example will be provided here with the spreadsheet column formulas.

Column 1:	$P/P_{\text{vap}}$		parameter to adjust
Column 2:	$V(\text{g}) / \text{mL g}^{-1}$	(maybe)	
Column 3:	$\chi = -\ln(-\ln(P/P_{\text{vap}}))$		
Column 4:	$n_{\text{ads}} / \text{mmol g}^{-1}$	$V(\text{g}) \div 22.4 \text{ mL mmol}^{-1}$	
Column 5:	$\Delta\chi = \chi - \chi_c$		$\chi_c$ parameter 3
Column 6:	$A := \text{low fit} = \Delta\chi \times n_m$		$n_m$ parameter 1
Column 7:	$B := \text{high fit} = \Delta\chi \times n_{\text{ext}} + n_p$		$n_m$ parameter 2 $n_p$ parameter 6
Column 8:	Cumulative distribution using $\chi^{-1}$		
	$(\text{calculated } n_{\text{ads}}) = A + (B - A)\chi^{-1}$		$\Delta\chi_p$ parameter 4
	$= (\text{low fit}) - [(\text{high fit}) - (\text{low fit})] \times [1 - \exp(-\exp(-\{\Delta\chi - \Delta\chi_p\}/\sigma))]$ , $\Delta\chi_p (= \mu)$ and $\sigma_p (=s)$		$\sigma_p$ parameter 5
Column 9:	$\text{SS} = [n_{\text{ads}} - (\text{calc. } n_{\text{ads}})]^2$	minimize and use for standard deviation.*	

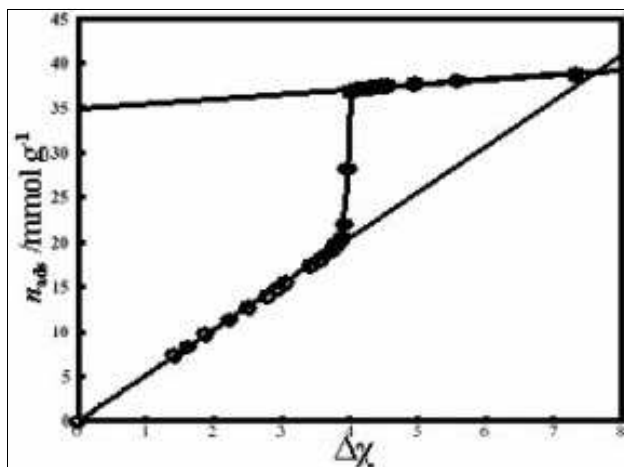
Obtain the minimum standard deviation to 1 ppm for each parameter. A 1 % fit full range seems to be sufficient for most fits. The  $Z$  function could substitute for the  $\chi^{-1}$ . The meaning, however, is different. This will be discussed with the combination of microporosity and a distribution of  $E_a$  that is binary. The above spreadsheet does not include heterogeneity. Heterogeneity would require one more parameter.

The problem with curve fitting with literature data is that the temperature control and/or measurement is lacking in most publications. This requires a fix that include multiplying the stated temperature, or  $P_{\text{vap}}$ , by a correction value. **Thus, a 7<sup>th</sup> parameter.** (Usually the temperature is stated as 77 K or 78 K indicating that such measurement of either  $T(\text{adsorbent})$  or  $P_{\text{vap}}$  was not made. The temperature needs to be controlled and read to at least 0.01 K and the pressure to at least 0.001 bar for a liquid nitrogen bath. The optimistic spec of 0.01 K for refrigerated cooling is usually incorrect, especially considering radiative heating. So, don't believe it!)

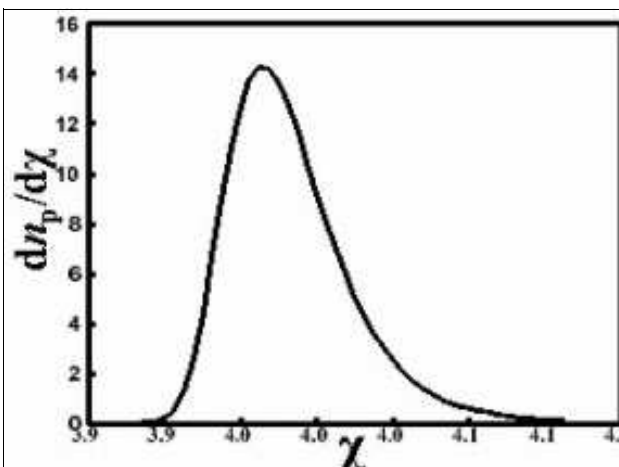
This could be included by modifying the low fit provided there is sufficient separation between the distributions. For microporosity this could be a problem, but it can be handled by using the "layering" method.

**Example #1 mesoporosity:**

The following is an example of mesoporosity by R. Guillet-Nicolas, M. Wainer, L. Marcoux, M. Thommes, F Kleitz[34] who performed adsorption of Ar and N<sub>2</sub> on SBA-15 and KIT-g silica to measure mesoporosity. **Figure 40** is the fit to the data within 0.50% if full range,



**Figure 40** N<sub>2</sub> adsorption on KIT-6 silica (K(100)48) from reference [34] using  $\chi^{-1}$



**Figure 41** The distribution from  $\chi^{-1}$  for the prefilling for the sample from **Figure 40**

In **Figure 41** is the distribution that turns of part of the  $\chi$ -plot. The parameters for the overall fit are:

$$n_m = 5.101 \text{ mmol g}^{-1}$$

$$\chi_c = -2.684$$

$$n_{\text{ext}} = 0.552$$

$$n_p = 34.887$$

$$\Delta\chi_p = 3.970$$

$$\sigma_2 = 2.570 \times 10^{-2} \approx 0.028 \text{ nm}^1$$

This approach seem quite successful, so why present the alternative with the “layering” method. The answer is as follows. Since the first layer will always be  $\theta_1 = 1 - \exp(-\Delta\chi)$ , the  $\chi^{-1}$  function cannot operate on it to stop. The  $\chi^{-1}$  function can only operate when it is free to specify to total amount, which leads to a phenomenon call “cannibalization.” In the above case, there are 3 underlying “layers” before the  $\chi^{-1}$  comes into play. There is litter “need” to cannibalize layers above #1 since layer #1 is 97% dense at the onset of the prefilling. Thus, if there is enough adsorbed in layers higher than the first “layer” to accommodate the  $\chi^{-1}$  function, then it will specify the additional amount beyond the first.

Modeling confirmed that the closer the onset of the porosity effect is the  $\chi_c$  the more likely there

<sup>1</sup>  $\sigma_2$  combines  $\sigma_c$  and  $\sigma_p$  by law of variance addition, however  $\sigma_p$  is not necessarily the pore distribution but rather reflects the cut-off of the various levels unevenly. In this case, the value of  $\sigma_2$  is very low implying  $\sigma_c$  is also very low and the sample must be homogeneous.

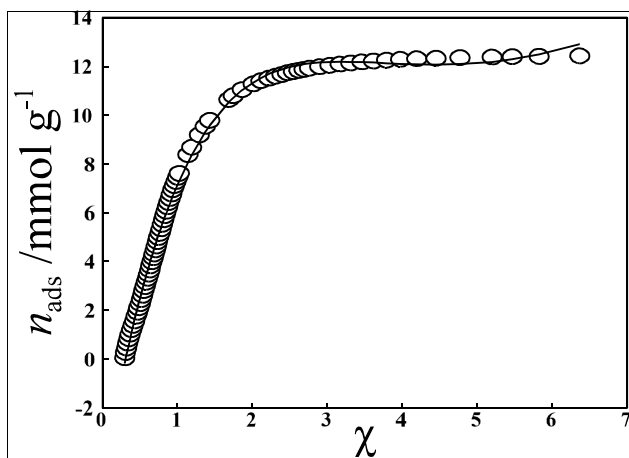
will be a distortion in the amounts calculated by the method of using  $\chi^{-1}$  to describe the porosity[35]. Another way of viewing this is that the distribution for the pores overlap the initial determination of the determination of the total monolayer equivalency. However, this problem happens when the adsorption is nearly described by the log-law, either a monolayer coverage or partial 2<sup>nd</sup> layer coverage. An example is in order.

### Example #2 microporosity:

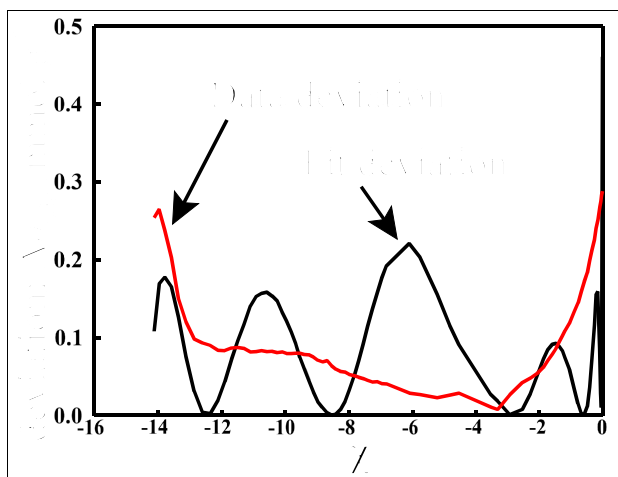
The Ar adsorption on activated carbon by Madani, Kwong, Rodríguez-Reinoso, Biggs and Pendleton[36] is a good example (which appears to have avoided the **Big Errors**.) First, one could check out the use of  $\chi^{-1}$  function. This is shown in **Figure 42**. This fit is a disaster. Firstly, the fit shows a turn-around in a position were the fit should be flattening out. However, ever worse, the values of  $n_m$  and other parameters were completely of from any logical numbers. For example, simply taking the early slope, yields an  $n_m$  of about 10.5 mmol g<sup>-1</sup>, whereas this fit yielded 66.0 mmol g<sup>-1</sup>, a totally unreasonable value. The standard deviation of the fir was also very poor at 1.8 % of full range.

The comparison of the individual deviations for the fit and the reported standard deviation from multiples runs is shown in **Figure 43**. The deviation comparison between the data standard deviation (from multiple experimental runs) and the standard deviation of the fit from the data, make it obvious that this treatment was a failure. (The calculation should also be monotonic and clearly is not.)

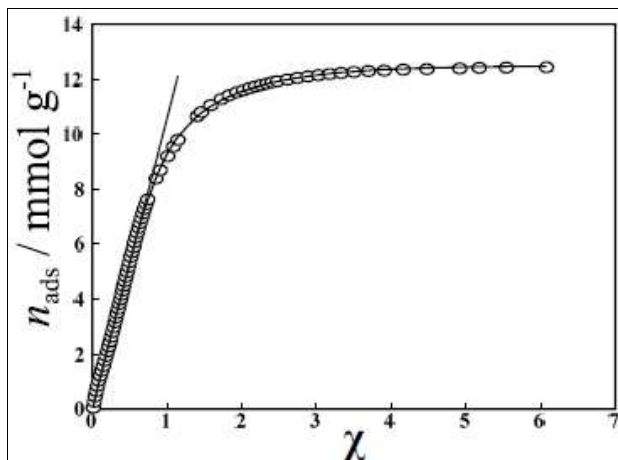
Recall the Lemma #1. It states that “first layer” cannot be anything but specified by Lemma #1 equation (74) (page 39). Thus, applying the  $\chi^{-1}$  cannot be allowed until the 1<sup>st</sup> “layer” is nearly dense. (Perhaps at  $\Delta\chi > 3$ , with  $\theta \approx 95\%$  is perhaps sufficient. At a lower level, an approximate answer might be possible, but the “layering” method should be used to check the answer.)



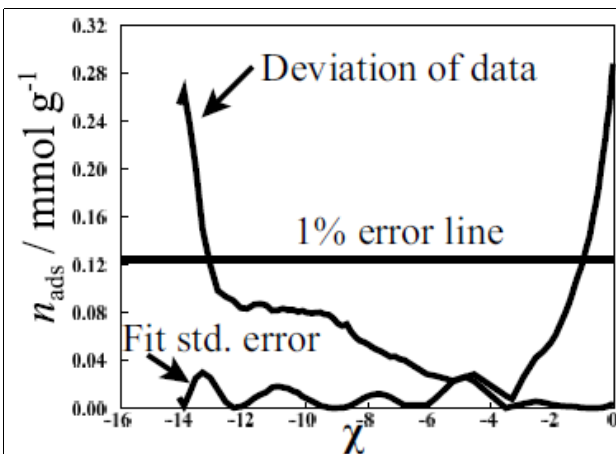
**Figure 42** Application of  $\chi^{-1}$  to the entire amount adsorbed. Ar on carbon by Reference [36]. This obviously fails.



**Figure 43** The fit deviation (solid) versus the data deviation (dashed) using  $\chi^{-1}$  on full isotherm. Ar on carbon by Reference [36].



**Figure 44** Fit to data applying the  $\chi^{-1}$  to “layers”  $> 1$  Ar adsorption on carbon by Reference [36].



**Figure 45** comparison of data deviation and fit deviation. Ar adsorption on carbon by Reference [36].

Using the technique for “layering” and applying the  $\chi^{-1}$  function to “layer” yields the total  $\chi$ -plot shown in **Figure 44** with the deviations in **Figure 45**. This fit is very good with a total deviation of 0.47% of full range.

In **Figure 46** is the “layering” of the isotherm. In this figure the first “layer” is always according to equation (74) which is a straight line in the log-law. The second “layer” would come up and meet the first “layer” if there were no physical restriction. The second “layer,” however, cut off according to the  $\chi^{-1}$  function and fits the difference between the 1<sup>st</sup> “layer” and the overall data. (The use of the cumulative normal distribution also does a decent job of fitting

Notice that the second “layer” decreases as the first continues to increase. This indicates that the first “layer” cannibalizes the second layer to keep in accord with the log-law equation (74).

Output parameters

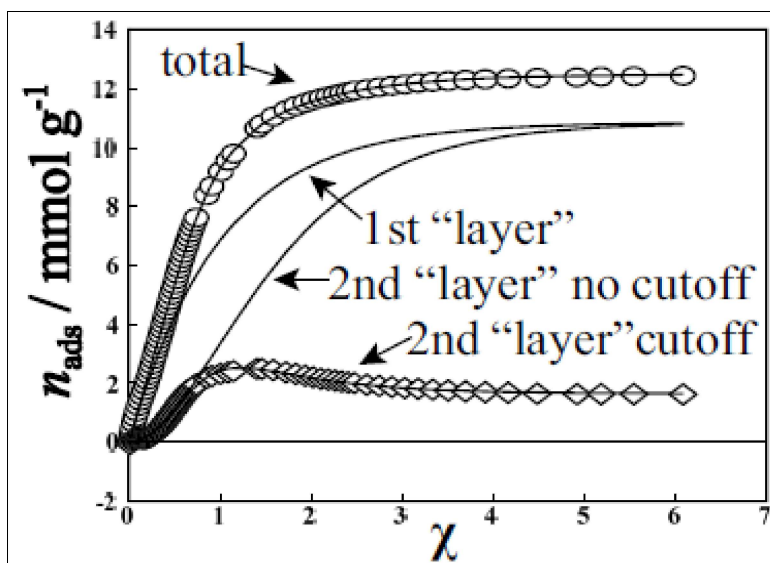
$$s = 2.604$$

$$\mu = -4.665$$

$$\chi_c = -2.6581$$

$$n_m = 10.91 \text{ mmol g}^{-1}$$

$$n_{\text{ext}} = -0.02 \text{ mmol g}^{-1}$$



**Figure 46** The overall fit of data from Reference [36] Ar on carbon. Graph shows component “layers.” Ar on carbon.

The conventional interpretation of these parameters are given in **Figure 46**.

Some notes about the analysis:

- 1) The fit without allowing external area yielded  $n_m = 10.84 \text{ mmol g}^{-1}$
- 2) The fit allowing external area yielded a negative  $n_{\text{ext}}$  which is not possible
- 3) The maximum for the adsorption was  $12.41 \text{ mmol g}^{-1}$  using the log-law (Gurvitch rule.) indicating good agreement if  $n_{\text{ext}}$  were = 0.

$n_m = 10.91 \text{ mmol g}^{-1}$		$A_{\text{total}} = 938.2 \text{ m}^2 \text{ g}^{-1}$
$n_{\text{ext}} = -0.027 \text{ mmol g}^{-1}$		$A_{\text{ext}} \geq \sim 0$
$n_{\text{pore}} = 10.91 \text{ mmol g}^{-1}$		$A_{\text{pore}} \geq 929.5 \text{ m}^2 \text{ g}^{-1}$
$n_{\text{ext}}^* = +0.032 \text{ mmol g}^{-1}$		$A_{\text{ext}} \leq 2.8 \text{ m}^2 \text{ g}^{-1}$
$n_{\text{pore}}^* = 10.88 \text{ mmol g}^{-1}$		
$n_{\text{pore,V}}^\dagger = 12.39 \text{ mmol g}^{-1}$	$V_{\text{pore}} = 0.355 \text{ mL g}^{-1}$	
$E_a = 10.36 \text{ kJ mol}^{-1}$		
* $n_{\text{ext}}^*$ and $n_{\text{pore}}^*$ is from the fit at high $P/P_{\text{vap}}$ , $n_{\text{ext}}$ is from overall least squares fit.		
$\dagger n_{\text{pore,V}}$ is from the ordinate intercept to the high fit - anti-Gurvitch rule		

It appears at this point that the layer method is a more reliable technique since the adsorption is forced to be monotonic with  $P$ . More research is needed, especially data, to support (or disprove) this method.



**Lesson XI: The trade-off  $\Delta_1^a E$  vs  $\gamma$  to specify mesoporosity<sup>1</sup>:****Sub-lesson 1 Combining Classical Film equations with QM:**

The energy of

$$\mathbf{E}_{\text{liq}}^{\text{ads}}(n_{\text{ads}}) = \mathbf{E}_{\text{liq}}^{\text{ads}}(\Delta\chi) = E_a \mathbf{exp}(-\Delta\chi) \quad (106)$$

adsorption from QM is given by equation for the a homogeneous and non-porous adsorbent:

For porous materials, this applies to the external surface and to the pores before the outer surface forms. Heterogeneity modifies this equation as well with a distribution in  $E_a \mathbf{exp}(-\chi)$ . This means that the pore distribution will be a combination of the normal distribution for the  $E_a$  and the inverse  $\chi$  function ( $\chi^{-1}$ ). As  $\Delta\chi$  gets into the mesopore range, however, it is likely for heterogeneous adsorbents that the distribution in  $E_a$  which will often be a normal distribution is much large that  $\chi^{-1}$  so the effective pore distribution can be approximated with a normal distribution, centered however on the  $\chi^{-1}$  distribution:

$$\sigma_{\text{p,obs}}^2(\chi) = \sigma_{E_a}^2 + \sigma_{\chi^{-1}}^2 \approx \sigma_{E_a}^2 \quad (107)$$

but

$$\mu_{\text{p,obs}} = \mu_{\chi^{-1}} \quad (108)$$

where the  $\mu$ s are the means ( not free energy.) The difference between the mean for the normal distribution and  $\chi^{-1}$  is big enough to be significant in calculating the relationship between the energy relationship of (104) and the equation for the formation of the dense liquid-vapor interface. This could be, for example, the Kelvin (or Ostwald–Freundlich) equation:

$$\mathbf{E}_{\text{liq}}^{\text{ads}} = \frac{h\gamma\bar{V}}{r} \quad (109)$$

The  $h$  is the geometrical factor, 2 for cylindrical pores (2 radii) and 1 for slit pores. The main problem with this equation is  $r$ . It obviously is not the "wall" to center radius since at these small geometries the "thickness" of the adsorbate molecules is not insignificant. There are other considerations. For example, how does one account for the way the "layers" pack and is there the predicted compression effect from the adsorbent-adsorbate. These questions lead back to the problem of interpreting atomic scale phenomenon in macroscopic terms and if left to others to argue about.

One thing is fairly certain, at 2 "layers" or less or  $\Delta\chi \leq 2$ , pore filling will not occur but is best described by a combination of the log-law and the  $\chi$ -plot. If there is more than one monolayer available distance and less than two, one will observe to cannibalizing effect. At the moment it is not clear what is happening if  $2 < \Delta\chi < 3$  since to pore fill something might be cannibalized. It seems unlikely that the first layer would be and doing so to the 2nd layer would leave a film with a depleted middle layer, which is a contradiction.

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<sup>1</sup> Revised since the book

Here is a bit of a thought process exercise:

Notice that theoretically at  $\Delta\chi = 2$ , for slit pores when fully filled there are at least 2 first "layers" and one or two second "layers." In the former case, as the isotherm progresses, the filling of the second "layer" proceeds normally until the first "layer" requires the space taken up by some 2nd "layer" molecules, at which time the cannibalization require by the Lemma 1 takes place. If the space could only accommodate 3 "layers," then there would be only one second "layer."

Notice that just as the 2nd "layer" can start filling and then be cannibalized to a lower layer, the same holds true for all the other "layers." However, the pore filling is likely to happen before this happens. Theoretically this is possible, if the adsorbate-adsorbate attraction are very small compared to  $E_a$ .

At the beginning of mesoporosity there are two measures of the radius of the of the pore. The first is the value of  $\Delta\chi$ . The distribution using  $\chi^{-1}$  yields the position in  $\Delta\chi$ , thus yielding the monolayer coverage at which the mesoporosity begins. The other is combining equation (104) with equation (107):

$$r = \frac{h\gamma\bar{V}}{E_a \exp(-\chi_p)} \quad (110)$$

Assuming  $r/\omega = \Delta\chi$  where  $\omega$  is a constant:

The constant  $\omega$  is the conversion is from SI units to monolayer thickness. The value for this is a question. Some things to consider would be the IUPAC convention or the van der Waal radius. What the value of  $r$  means is also a question. From where and to where it is measured.

Classically, the "pore size" edge should be the middle of the first adsorbed layer which brings up the problem of "Where is the middle of the first layer?" If the adsorbate molecule are on a flat surface it is the plain which passes through the middle of the molecules. If there is a curved surface, it is not so clear. Many authors simply say that it is  $\frac{1}{2}$  the thickness of the first layer subtracted from the pore radius. This does not account for possible compression not in many cases, using  $N_2$  adsorptive, does it account for the approximately 30% difference for the prone versus the standing position.

The basic problem is that these considerations are attempting to calculate nanoscale phenomena, which logically should be analyzed with quantum mechanics, by using macroscale classical mechanics.

### Sub-Lesson 2 Checking the Equations against Experiment:

To check if the equations work, what is needed is a porous adsorbent with a sharp peak in the pore distribution. **Figure 41** on page 72 appears to be a good candidate for the calculation. The onset of **mesoporosity** is very sharp so the  $\chi^{-1}$  distribution should be valid. Here are the parameters obtained:

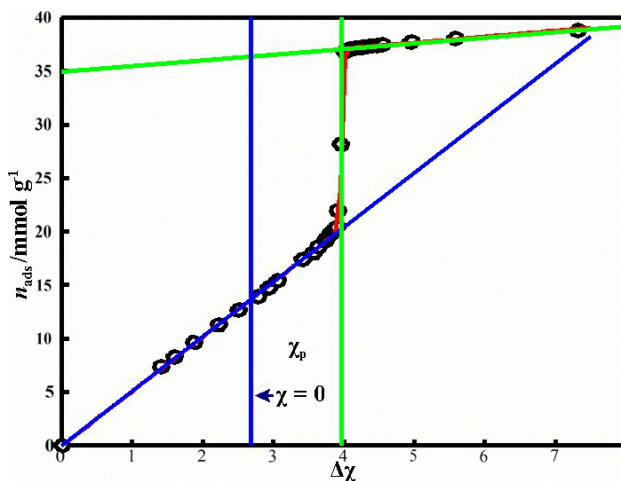
$$\begin{aligned}
 n_m &= 5.101 \text{ mmol g}^{-1} \\
 \chi_c &= -2.684 \\
 n_{\text{ext}} &= 0.552 \\
 n_p &= 34.887 \\
 \Delta\chi_p &= 3.970 \\
 \therefore \chi_p &= 1.286 \\
 \mathbf{E}(\chi_p) &= 179 \text{ J mol}^{-1} \\
 \sigma_2 &= 2.570 \times 10^{-2} \approx 0.028 \text{ nm}
 \end{aligned}$$

The question is what is  $\omega$ ? For the IUPAC convention, Nitrogen would 0.3522 nm. The numbers given above are for the adsorption branch. The measurement for the desorption branch was estimated to be  $\chi_p \approx 0.95$  due to the data being obscured by other data. The following are the results of the calculation from equation (108):

From equation (108) for adsorption:  
 $r = 1.71 \text{ nm} \Rightarrow \Delta\chi_p = 4.84$   
 for desorption:  
 $r = 1.23 \text{ nm} \Rightarrow \Delta\chi_p = 3.46$   
 From the chi plot distribution peak  
 for adsorption:  
 $\Delta\chi_p = 3.97$   
 for desorption:  
 $\Delta\chi_p = 3.64$

The answers are in the neighborhood, with an unsatisfactory error. Notice that the difference for the values obtained by equation (108) is 1.38 whereas, the difference in the peaks of the distribution is 0.33. What the cause of this discrepancy is unknown at this time. Some possibilities:

1. The overall hypothesis is wrong (what are the chances at this point?)
2. This section is wrong
3. There is a mathematical error
4. The value for  $\chi_c$  is wrong. Both calculations depend upon a good determination of  $\chi_c$ , but different functions.
5. The use of  $\chi^{-1}$  is wrong (However, using the normal distribution would not be much different.)
6. The adsorbate cross section is not the IUPAC and/or depends upon orientation.
7. Experimental error in either  $P$  or  $n_{\text{ads}}$ .
8. Something I haven't thought about.



**Figure 47** The isotherm used to illustrate the onset of mesopore calculation. This is the same as **Figure 41**

### Sub-Lesson 3 - What Happens when $|\epsilon| > |E_a^{\ominus}|$ ? Adsorptive-phobia?

There appears to be a problem when  $|\epsilon| > |E_a^{\ominus}|$  which make the value of  $E_a$  positive instead of negative. This make the second **ln** function impossible. Thus:

$$-RT \ln\left(\frac{P}{P_{\text{vap}}}\right) = -E_a \exp(-\Delta\chi) \quad (111)$$

at the threshold pressure  $\Delta\chi = 0$  and:

$$\left(\frac{P}{P_{\text{vap}}}\right) \leq 1 \quad \therefore -\ln\left(\frac{P}{P_{\text{vap}}}\right) \geq 0 \quad \therefore \ln\left(-\ln\left(\frac{P}{P_{\text{vap}}}\right)\right) \in \Re \quad (112)$$

$$\text{if } E_a < 0 \quad \therefore \ln(-E) \in \Re \quad (113)$$

$$\text{but if } E_a > 0 \Rightarrow \ln(-E) \in \Im \quad (114)$$

Switching the sign for the whole equation obviously does not help since that makes the left side imaginary. Evaluating the **ln** with  $E_a > 0$  yields a complex number:  $\ln(E_a) + i\pi$ . Rather than trying to figure out what that means, return to the basic model.

This seems to indicate that there is a second possibility for a critical point based on  $\theta$  being a particular value. The value of:



**Lesson XII - adsorption of more than one adsorbate:**

This topic is still under development. In the text book there is a derivation which may or may not be correct. The Grand Partition Function is difficult to sort and the question of how the interactions in the QM derivation is handled is a question. This seems like fertile ground for some graduate student.

**Sub- Lesson #1: What is logical?**

- 1) The adsorbate with the highest  $|E_a|$  should adsorb first.
- 2) The adsorbate with the lower  $|E_a|$ , even though it is not adsorbed in the first “layer” to any great extent, will be attracted to the first adsorbed layer as it would be in solution.
- 3) At the point of  $\chi_c$  for the second layer will adsorb in the area designated by  $1-\Delta\chi$  by the first layer, in other words, by the “bare” adsorbent surface.

This seems to be the case reported in the textbook for the data by Arnold. It isn't quite perfect by this description, but the data is probably not quite right either. In some case, this approach is quite far off. The Arnold method is quite eloquent and it is puzzling why others have not taken up on the technique. (Another grad student needed?) Arnold called the technique a flow system, but it is not at all related to what is called a flow system today. With modern vacuum systems and mass spectrometers, his technique could be more rapid and powerful.

Other data looks at the

So what data looks good to analyze? The trials of binary phase diagram seems to be a fertile area. Given the above analysis, one could make a first approximation by say that only the high energy adsorbate determines the progression of the adsorption. So here are some step-by-step rules for this approximation:

**Sub-Lesson #2: Binary Adsorption - strategy**

It appears that calculations from the pure adsorbate to mixed adsorbate is relatively simple, especially if there is a large mismatch in the adsorbate,  $E_a$ s.

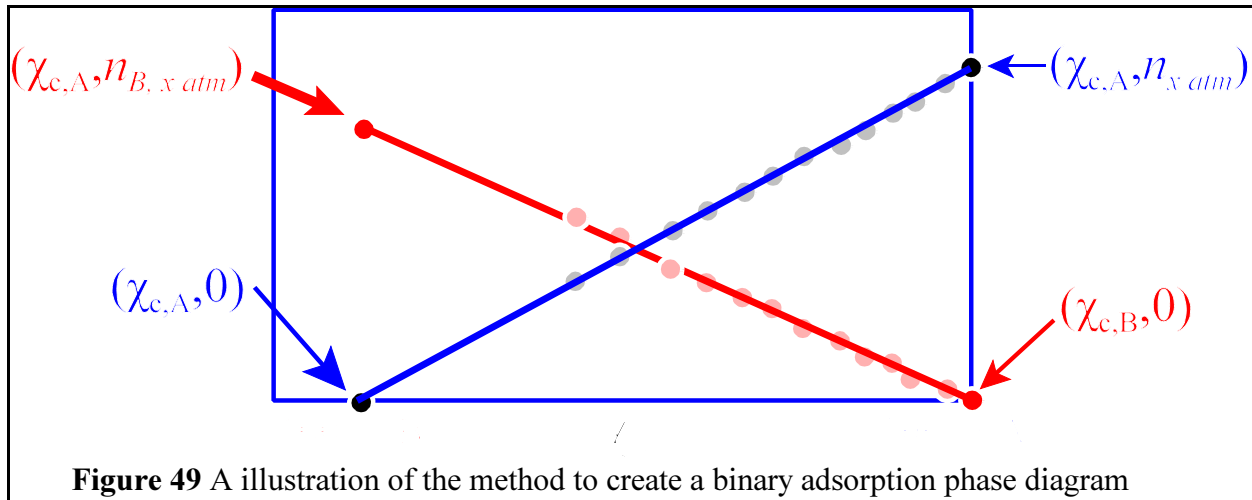
1. The adsorbate (label #1) with the highest  $|E_a|$  (recall that  $E_a < 0$ , and  $E_a > 0$  is not fully developed.) will adsorb before the adsorbate with the lower (#2)  $|E_a|$ 
  1. since the pressure of adsorptive #2 is below its  $P_c$ .
  2. However, #2 can adsorb in “layer” 2 by some binary 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  $\chi_c$ s of the adsorbate, the stronger will be the dominance of #1\*

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\* This is the basis of the so-called Henry's law dominance for the carrier gas method. This is assuming that the diagram is not extending into the UV range.

5. If the  $\chi_c$  of the two adsorbate are nearly identical, then they may adsorb together.†
6. †However, the particle pressures must be used in this calculation.

The diagram below illustrates the method



In the single adsorbate isotherms, component A has the lowest  $\chi_c$  (largest exothermiadsorption energy) so the abscissa is specified by it.

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

The data points are matched pairs in the binary experiment. The abscissa could be either values of  $\chi$ , 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.)

### Sub-Lesson #3: Step-by-Step instructions for binary adsorption:

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

1. Do the  $\chi$ -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  $\chi$ -plots, determine which adsorbate has the lowest value for  $\chi_c$ . It may be difficult to do this, so try determining the value of  $\chi_c$  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  $\chi$  values of A over the range from  $\chi_c$  to the value of  $\chi$  at  $p'$ .

6. Draw straight lines from for
- 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:  $\chi = \chi_c(A!)$  and  $n_{\text{ads}} = n_{\text{ads}}(p'(B))$  to  $\chi = \chi(p'(A!))$  and  $n_{\text{ads}} = 0^*$

**Examples of binary adsorption:** Once this is done then the percent for each point can be plotted but so can the lines that have been created, to yield the phase diagram and the fit. Here are some examples from Danner and Wenzl[37]. In the  $\chi$ -like plots the black lines are fits, whereas the blue and red lines are calculated only from the pure adsorbate isotherms. First is 5A zeolite adsorbent:

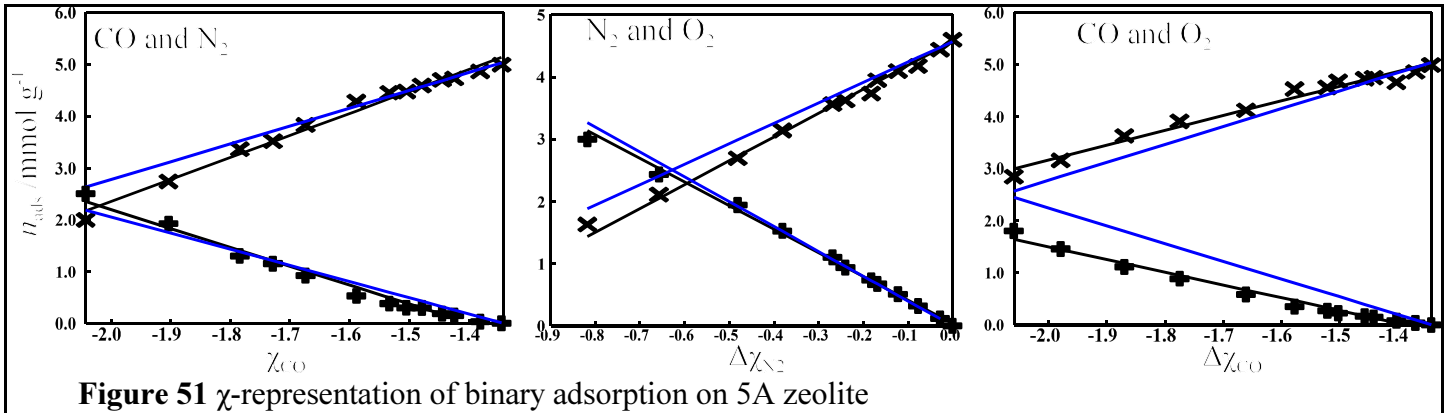


Figure 51  $\chi$ -representation of binary adsorption on 5A zeolite

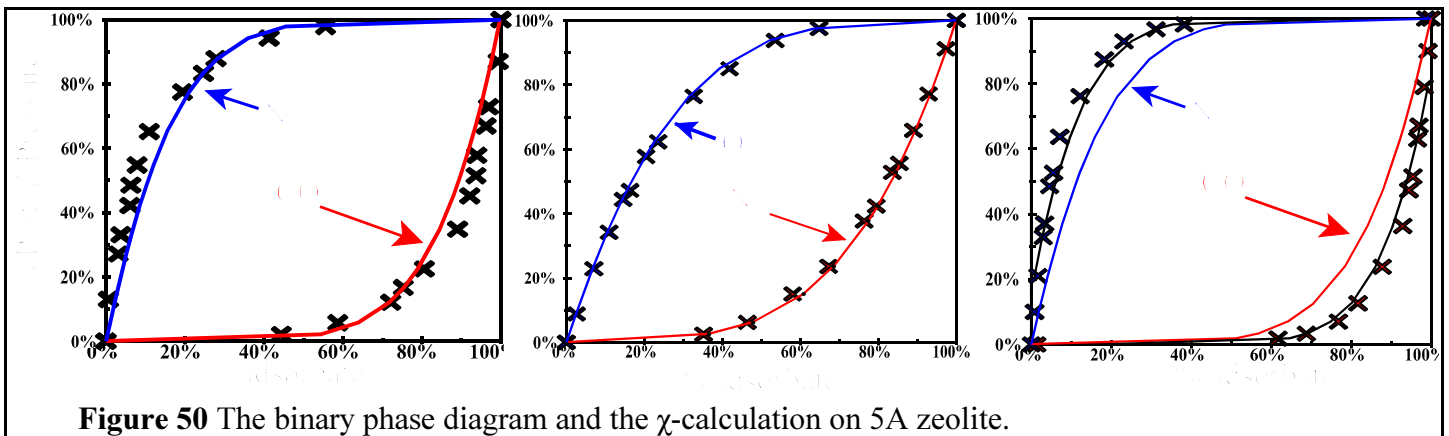
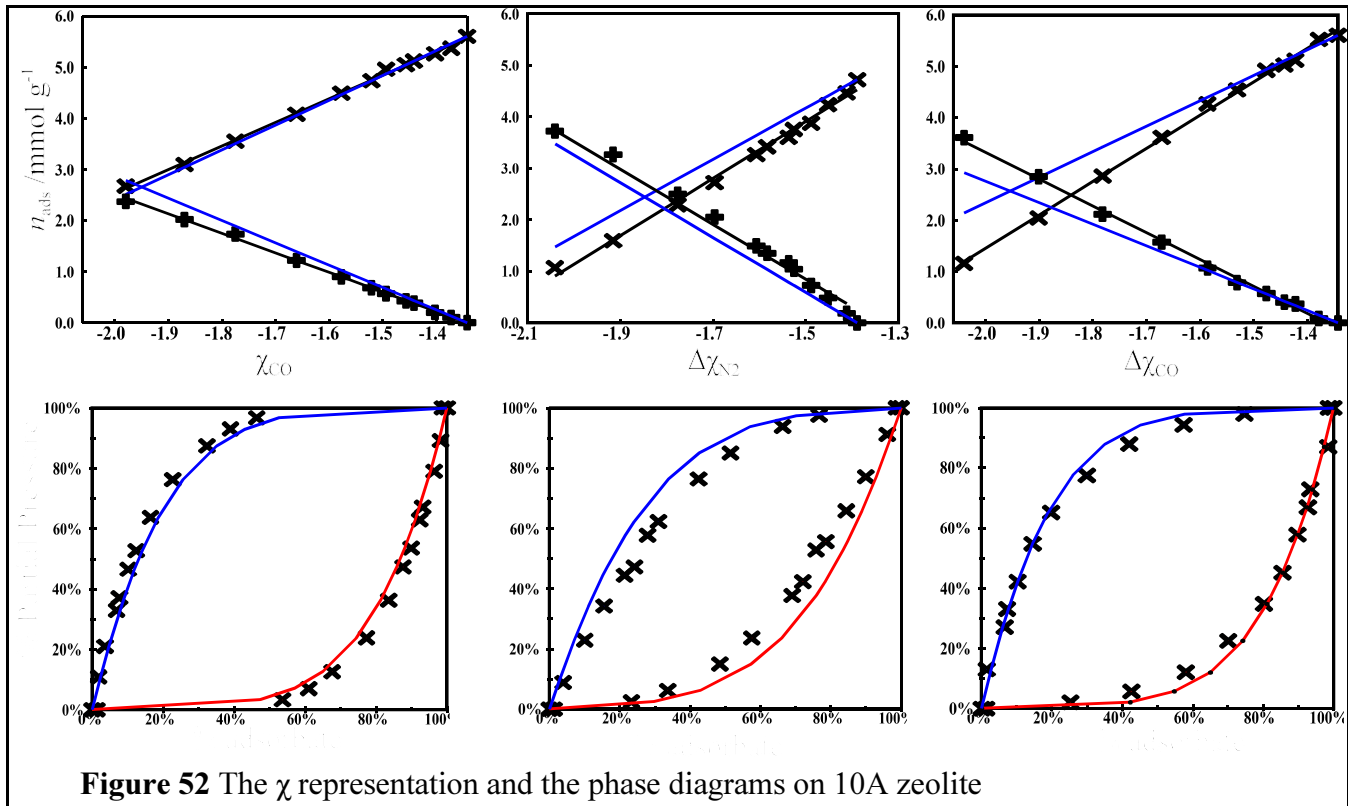


Figure 50 The binary phase diagram and the  $\chi$ -calculation on 5A zeolite.

The next ones are the same gasses on **Figure 51** on 10X zeolite.

One can see that the calculation are in some cases very good while others are somewhat iffy. The N<sub>2</sub>-CO on 5A and the N<sub>2</sub>-O<sub>2</sub> on 10X are particularly out of order. This is, however is based upon very crude assumptions. If the hypothesis is correct, there is much potential for improvement. Furthermore, as good as this data is, it must be remembered that such experiments should be repeated with modern instruments, to provide a good test of this hypothesis.

\* The “!” is placed here to emphasize that one uses only the  $\chi$  values for A.



## Concluding remarks

Well there you have it, at least a good start. What you have seen here is 40 years of off-and-on work by at least two people with two others pitching in upon occasion. The two people who were lead people were myself and Dr. E. Loren Fuller, Jr., who is now deceased. Loren and I are both physical chemist who work at the Oak Ridge Labs. This is a problem for using the data that we knew about, including perhaps thousands of isotherm, micrographs, etc. All of this data is archive at the Department of Energy, I hope, but was born classified. We did a lot of work that one would normally consider unclassified, but it's very hard to convince DOE that this is the case. After all, they have no idea what they are reading.

The entrance of the theoretical developments here has generally been bared from the open literature. I was successful in publishing a few articles and by using the KBW argument, instead of perturbation theory, figuring that the reviewer would not be familiar with the technique, got the essence of the theoretical development slipped through and published. Loren was able to publish quite extensively by disguising by plotting  $\ln(-\Delta E_t^a / RT)$  instead of  $-\ln[-\ln(P/P_{\text{vap}})]$ . Since it is one step removed from the deBoer-Zwicker equation, the reviewers did not know they were the same thing (recall the Dubinin thermodynamic criterion.). When Elsevier asked me to

The other two people at the Oak Ridge Labs that I need to mention are Dr. John Kirkpatrick and Dr. W. Thomas Berg. Dr. John Kirkpatrick was a top notch mathematician, one of the best in Oak Ridge. John provided much advise and mathematical computations. He proved that the BET had an inherent anomaly when applied to anything but the simplest case. Tom Berg supplied some critical data, the most thorough data relating the isotherm to calorimetry. He also had many discussion with me about

possibilities in the theoretical development. His observation of delocalized adsorption below the melting point is very interesting, but not covered either here or in my book. (Question: would this be more common than believed?) Both John and Tom are now deceased which leaves myself as the only member of the senior staff that worked on this project. I myself am in the red zone, so soon there will be no one to consult with if there is a need to learn what is now known. If this is not taken up by some graduate students soon, it will have to be rediscovered and reworked, and that is not likely to be easy.

**A personal note:**

Polanyi in his last letter to Science magazine did not write about his many worthwhile accomplishment, but rather his frustration about physical adsorption. I was at the ACS conference where Arthur Adamson cursed the Colloid and Surface session for their narrow-mindedness over with their refusal to consider something other than BET. I was horrified by the snickers, laughter and viciousness ensued in the room and outside. To me it's amazing that after, perhaps 60 years of failure, the BET and Langmuir isotherm was alive and kicking, hard.

This is a demonstration how science can be derailed by authorities and tradition. It is a demonstration how a few people can get in position to dictate what others may say and do. This is not the only area of science that is stuck in the past errors and incorrect theories. Another area of disaster is corrosion research and I am sure there are others. It is a good thing that the arts in these fields are extensive to allow engineering to do a decent job.

Loren and I were, naively sure, that once researchers saw the advantage of the QM approach they would take up the chase, or at least try to disprove it. We became disappointed that after several publications, no one answered the challenge. It apparently was either not understood, dismissed with little thought, or possibly the thought was, "...this is the deBoer-Zwicker theory (dBZ) that was disproved long ago." For the latter of course it is not the dBZ, but one of the equations used is the same empirical form. I believe that the evidence for it, including monolayer porosity, mesoporosity fitting, heterogeneity, binary fitting, and other phenomena indicates at least it is going in the right direction, whereas the BET is presenting verifiable inaccuracies and imprecision over and over. To even get a reasonable answer the criteria for a valid BET answer has, at last count, six restrictions, which apparently using an AI-like program and as the use of little as 10% of the full isotherm. Where else in a physical science does such a situation exist? These known inaccuracies, restrictions, imprecision, and contradictions with thermodynamics, not to mention the disproofs, would not be acceptable in hardly any other discipline, with the exception of Soviet Union Lysenkoism. It's time to move on.

**Appendix I: Mesopore calculations:**1) K(100)48, N<sub>2</sub> using  $\chi^{-1}$ 

Parameters and statistics:

$n_m = 5.101$
$\chi_c = -2.684$
$n_{ext} = 0.552$
$n_{pore} = 34.9$
$\Delta\chi_p = 3.970$
$\sigma_2 = 0.026$
curve fit stats:
$\sigma = 0.19282$
<b>% full = 0.50%</b>

Constants used:

density N <sub>2</sub>	0.809 g cm <sup>-3</sup>	
$M =$	28.01 g mol <sup>-1</sup>	
$V =$	34.623 cm <sup>3</sup> mol <sup>-1</sup>	0.0346 cm <sup>3</sup> mmol <sup>-1</sup>
$V =$	$3.46 \times 10^{-5}$ m <sup>3</sup> mol <sup>-1</sup>	
$A =$	97.7 m <sup>2</sup> mmol <sup>-1</sup>	
$r =$	$3.54 \times 10^{-10}$ m	<b>0.3544 nm</b>
$t_{mono} =$	1.0781 nm	
$\Delta H_{vap} =$	5.56 kJ mol <sup>-1</sup>	
$T =$	77 K	
$\gamma =$	8.85 dyne cm <sup>-1</sup>	$8.85E^{-3}$ N m <sup>-2</sup>

Calculated quantities from the parameters:

	adsorption	desorption
$E_a =$	9.50 kJ/mol	
$\chi_p =$	1.286	0.95 (est.)
from $\Delta\chi_p =$	3.97 monolayers	3.64 monolayers
$r_p =$	1.41 nm	1.29 nm
from $\chi_p =$	adsorption	desorption
$E_p =$	179.21 J/mol	250.10 J/mol
$r_p^* =$	<b>1.71 nm</b>	<b>1.23 nm</b>
$\Delta\chi_p =$	<b>4.82 monolayers</b>	<b>3.46 monolayers</b>

\* $h$  is assumed to be =1The  $\chi_p$  for desorption is estimated to due to interfering data.

Waiting for more data.

## References:

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