# Modern Hypothesis for Physical Adsorption

## How to analyze physisorption data - method based on Quantum Mechanics - an easy introduction

by Dr. James B. Condon
Prof.  Emeritus of Chemistry

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## Preface

I start by paraphrasing the prefix of a book written by my friend Dr. Terry Louch, "The whole point of these notes is to explain how to perform *PA-QM* calculations. They are written for anyone with a modest background in *QM* and the most elementary aspects of the theory of *PA*."[1]

*PA* = physical adsorption
*QM* = quantum mechanics.
The italics for Terry were:
*PA* = "APW" (Augmented Plane Wave)
*QM* = "Bloch electron in an ideal crystal."

We were both teachers and knew the importance of meeting the students at their level. Thus, it is with this book. If you have had some background in quantum mechanics, indeed a little, and have performed or supervised someone who performs a physical adsorption isotherm to get a sample's "surface area," you should be able to understand what is written in this book.

Unfortunately, the new concepts presented in this book are very foreign for most who work with physical adsorption and for some it is heretical, which brings on a strong reaction. This is because almost everything they have learned about physical adsorption is disputed.

The main problem is the continued use of the BET theory. In other attempts, I have tried to address this problem head-on, pointing out flaws in the BET. There are many attempts by others to "correct" many problems. For example, some have used multiple additions of BETs. Some others the have used exponents on the various parts, or mixing in the Langmuir isotherm, etc. The list is rather long. They all have flaws, which are very apparent with modern equipment, and these flaws are impossible to explain away. One of these flaws, is critical disproof in the BET and related theories. However, the kind of presentation found in this book is not convincing to the die-hard disciple and is a waste of reading time for those not open to something new. Therefore, I have not include the disproof of these theories in the main body. Instead, the disproof of these theories, with the misnomer "Henry's Law," are presented in Appendix II at the end of the book. Appendix I is reserved for definitions and symbols.

The book starts with the derived equations, with the derivations in Appendix III. The following Appendices are unnecessary for understanding the theoretical portions, however, they answer questions that might be of interest to the reader, such as the history of quantum mechanics being introduced to physical adsorption from my viewpoint. The reader might wonder, "who is this author," and, "What were the roles did personnel in the Oak Ridge National have in the discovery of the quantum mechanics application." Thus, the role that Dr. Loren E. Fuller, chemistry, and Dr. Kenneth Thompson, mathematics is explained. Another appendix is my curriculum vitae. It is quite boring reading but perhaps is needed to lend credence that I am indeed a believable scientist.

The equations that are used for physical adsorption-quantum mechanics are provided up-front, followed with a few examples of physisorption of pure solid samples with pure adsorbing gases. Such calculations are provided early and the technique to obtain the relevant output parameters is provided.

As the text continues, various words and definitions are provided. In Appendix I are all the symbols and definitions used. They are listed alphabetically with English symbols first and Greek symbols second. Other symbols not being either English or Greek are presented last. Some symbols are different from those commonly seen. However, as far as possible the SIO/IUPAC symbols or perhaps their approved alternative symbols are used. The reason for this is there are internal conflicts in the SIO/IUPAC especially between Physical Chemistry and Physical Adsorption. Since this was originally written before the 4th IUPAC, the 3rd IUAC is used so some symbols may be out of date, but widely used anyway. However, there are some symbols that have never before been used anywhere except in the physical adsorption-quantum mechanics and this is pointed out.

Following the introduction chapter, a list of possible experimental errors are addressed. This is **extremely important** because firstly, these are common errors, and secondly these errors can radically change the answers one gets. The errors are unfortunately implicit in some commercial instruments - It is good to check these out in the instrument before you buy! If you already have an instrument, you need to find ways to cure the problems and some suggestions are given. The presence of experimental errors produces false features in the adsorption isotherm (that is, the data plot of gas adsorbed versus pressure at constant temperature.) These errors, by the way, have been past used in the past to discredit the physical adsorption-quantum mechanics hypothesis. Of course, no other hypothesis or theory could account for these distortions either.

The book then continues with heterogeneity of the solid surface and the way to account for it. Later topics address pores called micropores with related pores, and mesopores. The introduction of these are an addition to the basic theoretical framework and can be confusing, so a methodology is given to follow. These should help to obtain the correct answer. The final chapters address two-gas adsorption (binary adsorption) and the relationship between the heats of adsorption calculated with no information other than the isotherm.

The QM is not the only modern hypothesis for physisorption based on preexisting science. The hypothesis call Excess Surface Work (ESW) based on the disjoining pressure theory, a thermodynamic adjunct using hydrodynamics, was also developed about the same time as QM. (See Jürgen Adolphs, references 12 through 14.) to the problem of physisorption reinforces the validity of both.

One last thought: I call this **“Modern Hypothesis**” and not “Theory” because very few people have attempted to test it. Indeed, the material that has been used in this publication and others supporting the Modern Hypothesis has been largely by others who either knew nothing about it or were hostile towards it. Recent exceptions, by recent is meant the last 47 years, includes publications by Dr. Jürgen Adolphs and Dr. Loren E. Fuller.

So, good luck and do not be discouraged by anything, including contrary advise either by authorities or your own mind.

JBC - June 29, 2025

# Modern Hypothesis of Physical Adsorption

## Contents:

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## 1. The Ideal Equations with Examples:

The derivation of the equations are presented starting with the Hellmann-Feynman (HF) theorem (in Appendix III.) Although not often used, this is the simplest way to derive them. If the perturbation theory were to be used the 1st approximation is good enough, due to the very small size of the perturbation compare to the surface aliquant. If you prefer other techniques, these equations have been derived in a book[2] using the perturbation and in a publication using the WKB approximation[3]. (WKB works, but is not advised.) Digital calculation have also been preformed to check out the methods. The answer is also intuitive to some.

These statements should not disturb you and they are placed here to indicate that indeed to final resulting equation are based on solid grounds. If there is any question about this, consult with the nearest physicist at a University or College.

### *1.1 So, here are the equations for the simple case*:

For an adsorbent[a] that is homogeneous[b], non-porous and not sterically hindered[c,d] this is "the simple case."

$$\Delta\chi := \chi - \chi_\varsigma \tag{1}$$

where the QM quantity $\Delta\chi$ is related to the physical quantity $\theta$ by:

$$n_\mathrm{a} / n_\mathrm{m} := \theta = \Delta\chi \tag{2}$$

and where $n_\mathrm{a}$ is the amount of adsorbate[e], $n_\mathrm{m}$ is the monolayer equivalence[f] and $\theta$ is classically called the "coverage."

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[a] Def (=Definition): Adsorbent: The solid material upon which the gas adsorbs.

[b] Def: Homogeneous: the surface of the adsorbent is chemically uniform in all ways that might affect the adsorption.

[c] Def: Steric Hindrance: hindrance of chemical action ascribed to the arrangement of atoms in a molecule.

[d] Def: the symbol ":=" means by definition

[e] Adsorbate: the amount that is adsorbed and is the same component as the gas phase.

[f] Def: A monolayer is the amount of adsorbate that, if it were all in contact with the adsorbent, would exactly cover the surface

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The following are the definitions of the QM quantities $\chi$ and $\chi_\varsigma$. The subscript with the Greek terminal sigma subscript, $\varsigma$, indicating what is call a threshold quantity.

$$\chi = -\mathbf{ln}\left\{-\mathbf{ln}\left(\frac{P}{P_{\text{vap}}}\right)\right\} \quad \Rightarrow \quad \chi_\varsigma = -\mathbf{ln}\left\{-\mathbf{ln}\left(\frac{P_\varsigma}{P_{\text{vap}}}\right)\right\} \qquad \mathbf{(3)}$$

(OK we have just lost half our readers.) The symbols are:

$P_{\text{vap}}$ = the vapor pressure of the adsorptive[a] at the temperature of the adsorbent.

$P_\varsigma$ = the threshold pressure. The concept that the low end of the isotherm extrapolates to $(P,n_{\text{a}}) = (x, 0)$ where $x > 0$ and not to (0,0) as once thought to be required. See Appendix II and III for details.

The relationship of the energy of vaporization, $\varepsilon$, to adsorptive pressure is

$$\mathbf{ln}\left(P_{\text{vap}}\right) = \overline{\varepsilon}/RT \qquad \mathbf{(4)}$$

Where the over-line is the indicates molar quantities (the alternative SI designator used here to avoid conflict with "$_{\text{m}}$" for "monolayer equiv"[b]) After defining $E_{\text{a}}$ as the threshold energy:

$$\mathbf{ln}\left(\frac{P_\varsigma}{P_{\text{vap}}}\right) = -\frac{\overline{E}_{\text{a}}}{RT} \quad \text{or} \quad P_\varsigma = P_{\text{vap}}\,\mathbf{exp}\left(-\frac{\overline{E}_{\text{a}}}{RT}\right) \qquad \mathbf{(5)}$$

From these equation the following are true:

$$-\mathbf{ln}(P) = -\frac{\overline{E}_{\text{a}}}{RT}\mathbf{e}^{-\theta} + \frac{\overline{\varepsilon}}{RT} \qquad \mathbf{(6)}$$

The thermodynamic internal energy function $\Delta_l^{\text{a}}\mathbf{E}$[c,d] is the energy change

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[a] Def: Adsorptive: the gas phase in contact with the adsorbent. The adsorptive and adsorbate are the <u>same</u> thermodynamic <u>component</u> in QM theory and so in physical adsorption. They are not in the same state. See the next footnote

[b] equiv = abbreviation for equivalence

[c] $\Delta_l^{\text{a}}\mathbf{E}$ is the change in the internal energy of the system, the adsorbent plus adsorbate, from the liquid state to the adsorbed state

[d] I make an exception to IUPAC convention here with the letter "*l*" being italic rather than Roman. From sad experience, I have learned the text editors confuse l vs. 1. Can you blame them? It looks like a 1 pixel difference.

from the liquid phase at temperature of the adsorbent to the adsorbed state (the adsorbate.) If one needs the standard energy, i.e. referenced to 1 bar, which is what is found in calorimetry, then[a]:

$$\Delta_{\mathrm{g}}^{\mathrm{a}}\mathbf{E}^{\ominus} := \Delta_{\mathrm{g}}^{\mathrm{a}}\mathbf{E} = E_{\mathrm{a}}\,\mathbf{exp}\left(-\chi\right) \tag{7}$$

For those wondering about Gibbs' energy being missing out of all these equation, here is a very interesting relationship, Unless there are internal and molecular change or rotational changes then:

$$\Delta_{l}^{\mathrm{a}}\overline{\mathbf{S}} = -RT\left\{1-\mathbf{exp}\left(-\Delta\chi\right)\right\} \approx 0$$

means that the entropy change is insignificant. It also means that the adsorbate is a liquid phase of a different <u>average</u> density. Of course, from the gas phase there is the entropy of condensation. This is the basis for the Dubinin "thermodynamic criterion."

### *1.2 The Schichten equations and the log-law*:

The other equations which the QM yield is called the "schichten"[b] equations. A schicht in classical meanings as a "level," "layer," spot in a "chain." In QM one could think of it as the distribution of the density of the molecules according to normal (geometric) position. To break from classical thinking this word will be used since in geology there is some similar characteristics. So, the following are the Schichten equations. The subscripts indicate the schicht:

$$\theta_1 = 1-\mathbf{exp}\left(-\Delta\chi\right) \tag{8}$$

$$\theta_2 = 1-\mathbf{exp}\left(-\Delta\chi+\theta_1\right) \tag{9}$$

$$\theta_3 = 1-\mathbf{exp}\left(-\Delta\chi+\theta_1+\theta_2\right) \tag{10}$$

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[a] Def: $\Delta\mathbf{E}_{\mathrm{g}}^{\mathrm{a}\ominus}$ is the change in the internal energy from the gas state at 1 bar to the adsorbed state. The symbol $^{\ominus}$ means standard state.

[b] Trans: Schichten translates as strata (singular: Schicht.) The work "layers" is used classically, but I have had to continually put quotes around it because there is an implication that 1) dense layers build one on top of another, or 2) the Brunauer concept of each layer has the same equilibrium ratio to the previous layer, confusing amount with concentration.

So for the (n +1)th schicht:

$$\theta_{n+1} = 1 - \mathbf{exp}\left( -\Delta\chi + \sum_{m=1}^{n} \theta_m \right) \qquad \textbf{(11)}$$

and it can be proved that:

$$\therefore \theta = \sum_{n=1}^{\infty} \theta_n = \sum_{m=1}^{\infty} 1 - \mathbf{exp}\left( -\Delta\chi + \sum_{m=1}^{n} \theta_m \right) \qquad \textbf{(12)}$$

The schichten equations can be used when steric hindrances are present. For example, if there is only room to stack one molecule in the normal direction from the surface, only equation, **(8)**, will apply. All other schichten are blocked.

Equation **(8)** can be rearranged to:

$$n_1 = n_m + \frac{n_m RT}{E_{\mathrm{a}}} \mathbf{ln}\left( \frac{P}{P_{\mathrm{vap}}} \right) \qquad \textbf{(13)}$$

This is the log-law and is seen quite often. This is a straight line of amount adsorbed versus the **ln** of pressure and indicates that only one schicht is being used. Note that when $n_1 = 0$ the abscissa intercept is the threshold pressure, $P_\varsigma$ and when $P$ is at $P_{\mathrm{vap}}$ then $n_1 = n_{\mathrm{m}}$. Extrapolation to the ordinate axis yields the monolayer equiv and the extrapolation to the abscissa yields $P_\varsigma$, which yields $E_{\mathrm{a}}$ according to **Equation (5)**.

### *1.3 Calculating the unlimited multischichten case*:

Using equation **(1)** with the definitions equation **(2)** and **(3)**, one is able to find $n_{\mathrm{m}}$ and $E_{\mathrm{a}}$ from a straight fit of a curve $n_{\mathrm{a}}$ versus **-ln**{**-ln**($P/P_{\mathrm{vap}}$). In this representation, the abscissa intercept is $E_{\mathrm{a}}$ and the slope is $n_{\mathrm{m}}$. This plot is called a $\chi$ plot.

The question can come up, “What if an isotherm is limited by 2 or 3 schitchen. This is relatively simple to address with some calculation steps:

1. Calculate the $n_{\mathrm{m}}$ for an initial slope if it is straight enough. As will be seen later in section 4.2.2 there is an interesting thing that happens if the last schicht to begin a significant density and “reverses” its

adsorption, given the name "cannibalization."

2. One can start adding schichten in a spread sheet following the rules given in equations **(8)** through **(11)** for filling of the schichten and the determination of the error that a single schicht cannibalization incurs.
3. With a little more calculation this error can be corrected.

A total schichten filling is shown in **Figure 1**.

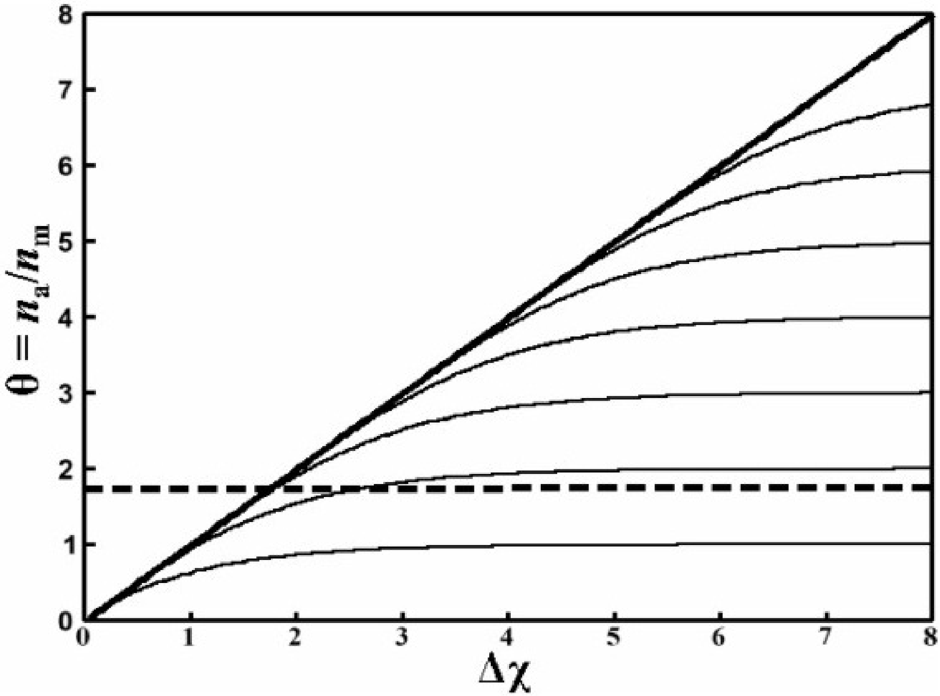

**Figure 1** The addition of schichten with filling. If the maximum filling is designated by the dotted line Then when the 2nd schicht crosses the line it not only stops filling, but reverses (drops) to allow the 1st schicht to continue to fill to $n_a$.

Since all schichten start to fill above $P_ς$ , there is a small amount to be sacrificed in the higher layer as well as the one that is above the main filling schicht. For example in the **Figure 1**, the 2nd schicht will have to give up some adsorbate for the 1st schicht to continuing to fill. 3rd one needs to release its adsorbates to the 1st and 2nd, but it should be noticed that it is probably experimentally insignificant.

This graph demonstrate also how all densities in each schicht fills with respect to other schichten and is set with these values for any particular micropore size.

### *1.4 Examples of a $\chi$ plot, log-law plot and $\Delta\chi$ plot:*

Below are some examples of a $\chi$-plot and a log-law plot. It is important to able to distinguish between a $\chi$-plot and a log-law plot. A $\chi$-plot is useful if there is no steric hindrances and the log-law is for porous material where only a single schicht is adsorbed. They look quite different.

#### 1.4.1 example of a $\chi$-plot:

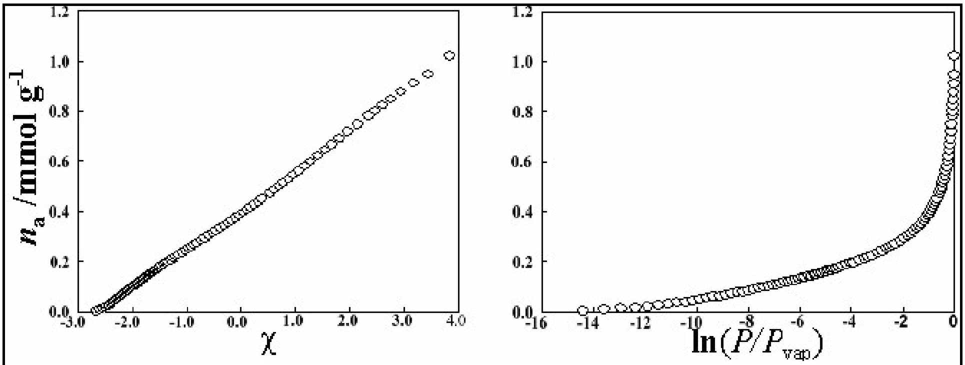

**Figure 2** Comparison of the $\chi$-plot against the log-law plot, Data by JKO by permission from the American Chemical Society.

In **Figure 2** are plots are by Jaroniec, Krug and Olivier[4] (JKO.) The data is used with permission from the American Chemical Society. It is plotted on the left as a $\chi$-plot and on the right as a log-law.

The question is then, which one is the closest to a straight line? It would seem intuitive that the left graph is nearly a straight line. Ignoring the bumps in this graph, the output parameters are in **Table 1.**

The fit to the straight line using a simple linear regression is very good.

To be able to compare various isotherms[a] a criterion must take into account the different amount of specific adsorbate. The FDR means "Full Date Range." It is the standard deviation of the $n_a$ fit divided by the range on the $n_a$ data. This is a very approximate way to cross-compare isotherms. It is also a way of determining the if fit is "good enough." Arbitrarily this author has set 1% as the maximum FDR to accept the results, especially for modern equipment. The criterion is loosened if the increase in the $n_a$ is very steep, which can cause an artificially high $\sigma_{\text{fit}}$ in the steep zone, as indicated in the mesopore section.

It is obvious with this definition that poorly scattered data might never qualify by this 1% rule regardless how well the isotherm fit is. Furthermore, repeat experiments, which are recommended, can detect problems by comparing the data itself.

**Table 1** Output parameters obtained by linear regression of JKO $\chi$-plot

| Name | Symbol | Value | Std. Dev. | units |
|---|---|---|---|---|
| monolayer equiv | $n_m$ = | 0.15553 | $\pm 5.2 \times 10^{-4}$ | mmol $g^{-1}$ |
| threshold $\chi$ | $\chi_\varsigma$ = | -2.6213 | $\pm 8.4 \times 10^{-3}$ | |
| starting energy* | $E_a$ = | 8.92 | ± 0.07 | kJ $mol^{-1}$ |
| $\sigma_{\text{fit}} = \pm 9.14 \times 10^{-4}$ or 0.089 % FDR (full data range) | | | | |
| * indicates a derive value from the output parameter. $\chi_\varsigma$. | | | | |

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[a] Def: Isotherm is literally "at constant temperature." Since this data was taken at constant temperature. The graphs of this type, that is, the abscissa transform is a function of $P$ only and the ordinate is a function of $n_a$ only are mathematically correct, but the $\sigma$ needs to be calculated from the original data.

### 1.4.2.The $\Delta\chi$-plot.

The $\Delta\chi$-plot is nearly the same as the $\chi$-plot except the value of the threshold of $\chi$, $\chi_\varsigma$, is subtracted. There is a very convenient way of looking at a plot with the abscissa as $\Delta\chi$. In the simple case, the abscissa is also a measure of monolayer equivalence. Some of the added features upset this convenient arrangement but it is still useful.

On the other hand, the $\chi$-plot is an energy plot according to **Equation (7)**. This is a plot which makes mesoporosity, hysteresis and thermodynamics more intuitive.

### 1.4.3 An example of the log-law:

Another isotherm for illustration is presented two ways in **Figure 3**. This data is by Nguyen and Do[5] (ND) of $N_2$ on microporous carbon (Takeda ACF). Now on the left is the log-law and on the right the $\chi$-plot. In this case it is obvious that the log-law plot is the linear plot and the one to analyze. The linear analysis is presented in **Table 2.**

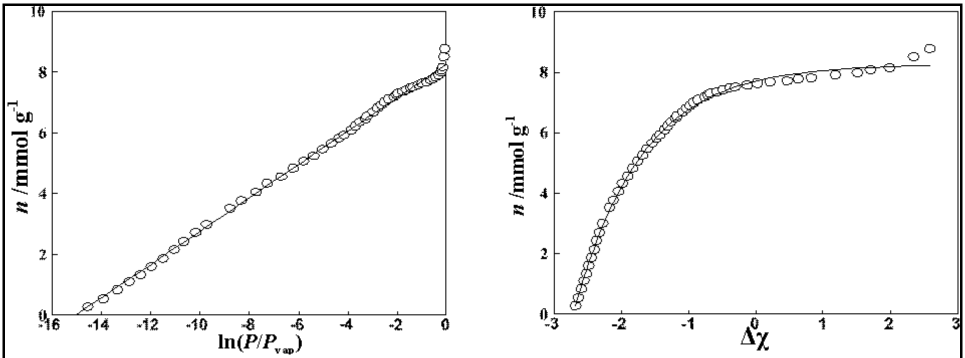

**Figure 3** Data by Nguyen and Do (ND) with permission from Pergamon Press, publishers of Carbon.

Both of these examples will be used again to point out some subtle features[a].

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[a] Notice that no graphs of the $n_a$ versus $P$, the "usual isotherm," is presented. Why? because it is useless.

The lesson here is that is the $\chi$-plot describes the isotherm then the isotherm is not sterically hindered and if the log-law fits it is hindered to one schicht.

What about an intermediate case, may be 1 ½ or 2 shichten. This is presented later along with other interesting isotherms.

A more complete analysis drops the $\sigma_{FDR}$ below 1%. This is demonstrated in Appendix IX.

**Table 2** Output parameters obtained by linear regression of NO log-law

| Name | Symbol | Value | Std. Dev. | units |
|---|---|---|---|---|
| monolayer equiv | $n_m$ = | 8.251 | ± 0.032 | mmol $g^{-1}$ |
| threshold **ln**($P_\varsigma/P_{vap}$) = | | -15.0555 | ± 0.0459 | |
| threshold $P$* | $P_\varsigma/P_{vap}$ = | $2.894\times10^{-7}$ | | |
| threshold $\chi$* | $\chi_\varsigma$ = | -2.7117 | | |
| starting energy | $E_a$ = | -9.72 | ± 0.07 | kJ $mol^{-1}$ |
| $\sigma_{fit} = \pm 8.94 \times 10^{-4}$ or 1.10 % FDU (full data range) | | | | |
| * indicates a derive value from the two output parameters. | | | | |

## 2. Quality of Conclusions = Quality of Experiments:

It may seem strange that this section is included in a series that is mostly theoretical. However, theory must always come from the observations that scientists make and if the observations are faulty, it is likely the hypotheses formed will also be flawed. Sadly, this is what has happened in the field of physisorption. All the following errors have contributed to false assumptions and conclusions, but the one that is most problematic is Error 1.

It is extremely important to have good equipment and good technique when measuring the isotherm. One should not overlook this section. Measurement of the isotherm is the primary measurement made for physical adsorption and the easiest. The problem is that it may be too easy, and the pitfalls are ignored. Furthermore, there are two primary methods to measure the isotherm, either gravimetrically or volumetrically. A well-designed gravimetric system is less prone to error, but it is generally more expensive. The volumetric system on the other hand is usually more affordable but very highly error-prone, and some of the errors are built in. This is especially true for most commercial instruments. The first two common errors essentially can yield useless data, although there may be ways to recover from disaster. The other errors can have similar disastrous results, but these are less common.

### *2.1 Error 1 vacuum requirements*

Error 1 is using a system that does not pump down at least to high vacuum, HV, and preferably into the ultrahigh vacuum, UHV. This has been thought of as unnecessary since originally the BET analysis ignored all data below an $X := P/P_{\text{vap}} = 0.01$, even if it existed. (...or perhaps this may be because the isotherm starts to deviate from the expected trend.) In some of the older literature, the isotherm begins after a monolayer equivalence is already present. Furthermore, without these vacuum capabilities there is little assurance that the surfaces of the adsorbent are contaminant free. Capability does not seem to be the reason for the lack of attention nor does politics, which seems rife in the field. The ability to obtain and measure these low pressures was available, why they were ignored is outstanding question.. At any rate, one seldom sees isotherm data below this 0.01 limit until recently.[a]

Why is this important? You have already learned the value of the quantity $E_a$, around which the entire calculation centers, is usually found in the HV or UHV range. Furthermore, the log-law, an important sub-law found in QM, is difficult to determine above $X = 0.01$. It is easily mistaken for the Langmuir isotherm. The log-law is also needed to determine if there is microporosity (as defined in section **2.**) since it is more obvious with HV or UHV systems.

Another reason mentioned in the article by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[6] (SSLR) is that out-gassing of the sample in HV appears to be a requirement for some adsorbent-adsorbate combinations. For volumetric systems, which require a dead-space calibrating gas, it is best to have a good vacuum system to reach these levels, HV or UHV. This problem is illustrated in **Figure 4**.

Possible avoidance: If there is absolutely no porosity, then measurement above $X = 0.01$ will yield an average $n_a$ and peak value for $E_a$. If this is all that is require, that would be OK, but one needs to do several high resolution isotherms to determine if this short-cut will work. If one has no instrument to read below $X = 0.01$, then some samples need be outsourced to someone who has the proper equipment.

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[a] Early work by Hobson and others were quite reproducible, but do not agree with the BET. They were, thus, ignored. One qualifier must be stated, the material was very heterogeneous and deviated form the linear in (today) the QM style equations. However it was a big deviation from the BET or other "Henry's Law" isotherms, therefore there was no chance of making an analysis using these theories..

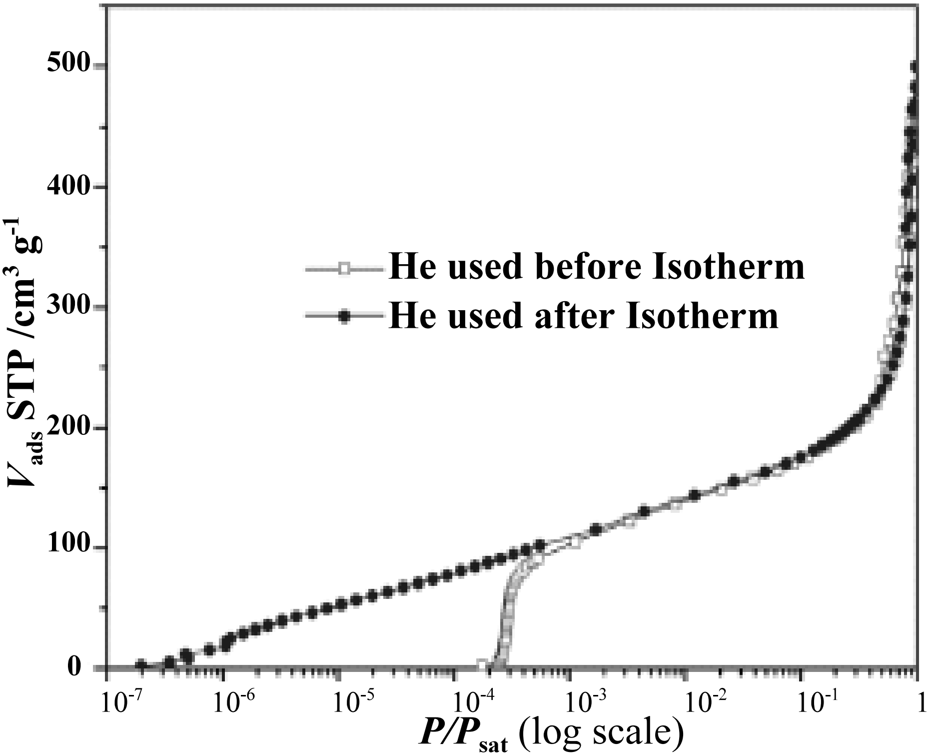

**Figure 4** log-law plot by SSLR of $N_2$ on Carbon. ● are data after the first run. ○ are data on the first run after a 473K out-gas. Presented with the permission of American Chemical Society.

*2.2 Error 2 temperature control and measurement*:

Error 2 is poor measurement and control of the adsorbent temperature and the adsorptive gas immediately over it. This is a very common error, especially with inexpensive volumetric systems. This correction is so common that most of the standard curves until very recently had this problem. This author was very naïve in the first edition of his book and the conclusions and usefulness provided in the "Standard Isotherms" section is mostly incorrect, except for data by Fuller some by deBoer[a].

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[a] It is rather shocking to realized that so many standards were incorrect. DeBoer was aware of the temperature problem and Fuller used the best equipment made in-house in Oak Ridge, which was fortunate since the samples for the lunar soils is rather rare.

The solution that is commonly advertised is the dual hang-down tubes. This is better but not as good as it could be.

The reasons for this are:

- There is usually radiative heating problems, especially for a cryogenic bath. Even though the sides of the cooling chamber are well above the sample, there is room temperature radiation from above. Shielding using metal foils will help, but usually, unless there are bends in the tubes, there could still be some heat gain.
- If the adsorbent is a dark color or black this radiative heating problem would be worse.
- It is insufficient to assume that a cryogenic bath is at a constant temperature . The temperature of the bath is dependent upon the atmospheric pressure and not taking this into account, which the dual tubes should do, the answer can be wildly wrong.
- Even if attempts are made to measure the temperature for the isotherm, it may vary with time. This is especially true with cryogenic baths due to atmospheric pressure changes. Keeping track using a liquid-gas thermometer reading is advised for a post-experiment correction .

Possible corrections:

The temperature effect has not been fully researched. However, it was recognized as a problem early in the work by deBoer and Zwikker, but since they were in general “discredited,” almost no one paid attention to this publication (until recently.) Given little guidelines, it is best to play it safe and do everything possible to control and correctly measure $P_{vap}$. The control and measurement of the temperature to 0.01K is minimal for a liquid nitrogen temperature. If a liquid cryostat is being used, selection of a nice steady weather day to get data is advised. Also, keeping an eye on the barometer and recording the uncorrected atmospheric pressure. This is another quality control. Uncorrected changes in $P_{vap}$ causes a wavy $\chi$ -plot, which have lead some researchers to incorrect conclusions.

If temperature control can be maintained but with questions about the actual pressure, then one can use an extra parameter to find the $P_{vap}$ value. That was the technique that deBoer and Zwikker used. However, it is best to use a liquid-gas thermometer in good contact or close to the adsorbent.

If you have a dual hang-down arrangement, wrap the sample tube and the liquid thermometer tube in copper (best) or aluminum foil. This still leaves direct overhead radiation to shine on the sample, so if you have room, bend the glass tubes to eliminate the direct line of sight.

In gravimetric systems this is easily handle with internal baffles in the tube and on the hang-down wire. A more thorough discussion is provided in the fore-mentioned book[2].

*2.3 Error 3 Knudsen Effect*:

Error 3 is a problem for the low end of the HV pressures. This is the point where liquid nitrogen temperature measurements have a problem with the Knudsen effect. This is very hard to handle with a volumetric system where the tube size cannot be arbitrary because of the sample size. One would have to use adsorbent sample sizes of kilograms instead of typically grams and a much larger scale up to about the kilogram scale. Characteristic of this error is the occurrence of a "double dogleg " at the lowest pressures.

Langmuir solved this problem by calibrating each individual hang-down tube. However, great care is needed to avoid powder sticking to the side of the hang-down tube, since it is the micro-topography which determines the magnitude of the correction. This presents a funneling problem to be solved. For the best information on this problem see the Vacuum Technology book by Roth[7].

With gravimetric systems the hang-down tube diameter and length can be increased to eliminate the problem. Gravimetric systems can adjust the diameter and length of the hand-down tube to avoid the problem. A tube diameter of ~3 cm will eliminate most Knudsen effects through HV. This probably will be suitable for silica samples that have a low $P_\varsigma$, but look for the dog-legs. It is not only the diameter that is important, but also the length. One might end up with quite a large system beyond the 3 cm diameter, since the larger tube length would also require lengthening to accommodate the longer temperature-transition zone. A 1 meter length with properly place baffles and temperature transition is probably OK.

*2.4 Error 4 Residual dead space gas or buoyancy gas*:

Error 4 is residual dead space/buoyancy probe gas in the sample. This is especially bad with porous samples. It appears to be a common cause of hysteresis especially IUPAC types H3 - H5, but not the only one. Furthermore, the contamination can have a very large effect upon hysteresis. Not much research has been done on this but an excellent paper on this subject is the one by SSLR[6]. In this publication they emphasize the importance of either a high temperature out-gas of the dead space gas or doing the dead space calibration last or repeating the isotherm measurement two times. (By good analytical practice convention, which is rarely done in physisorption, a measurement should be repeated thrice and if one of the three measurements disagrees, one continues to repeat more times for reproducibility or attempt to resolve the experimental problem.)

The SSLR publication is very important for several reasons and reading it is strongly advised.

*2.5 Error 5 kinetics*:

Error 5 is kinetic problems.: This problem varies with the sample – porous versus nonporous, tightly packed versus loosely packed and other factors. Most instruments are automatic, but the researcher should not go brain-automatic. Set the wait time for different settings and see if it makes a difference. The length of time to settle "enough" depends upon where in the isotherm the measurement is being made, so keep track of this phenomenon throughout the measurement to get an indication of the wait time versus pressure. The criteria based on the exponential advance to a constant pressure used in some instrument might yield more consistent results, but multiple runs using different decay constants for a particular adsorbate-adsorbent pair is advised. This will give an indication of how long one should wait.

### *2.6 A final request:*

Please, keep good records especially of data and experimental details. Data should include, but not limited to, pressure and amount of weight gained but also $P_{\text{vap}}$ readings, base vacuum, out-gassing procedure, instrument specifications, starting total weight, gas purity, adsorbent preparation or specifications from preparer, adsorbent characterization and the list of the readings of at least three experimental runs. If the make and model of the instrument is given, any modifications should be listed. If any of these data are missing, that should be reported. It may be that the lack of information will disqualify the validity in the future. For ease of reading put information in tables or lists. Be kind to your colleagues and either list all the data in digital form or make it available to the public.

The more information you provide, the better. If the journal restricts your length, or does not have archive ability, archive information somewhere accessible to the public.

Thank you.

## 3 Heterogeneity:

The QM hypothesis can be easily modified to accommodate heterogeneity. The reason is that the independent variable, $P$, or a transform of it is the only thing used in the plots for the abscissa. The same is the case for $n_{\mathrm{a}}$, the dependent variable, for the ordinate for the isotherm plots. This means that the for a variety of energy surfaces the $n_{\mathrm{a}}$s add. For two $n_{\mathrm{a}}$, 1 and 2:

$$\left\{ n_{\mathrm{a}}(1) + n_{\mathrm{a}}(2) \equiv n_{\mathrm{a}}(1+2) \right\} \Big|_{\mathbf{F}(P)} \qquad \textbf{(14)}$$

This property is illustrated in **Figure 5**.

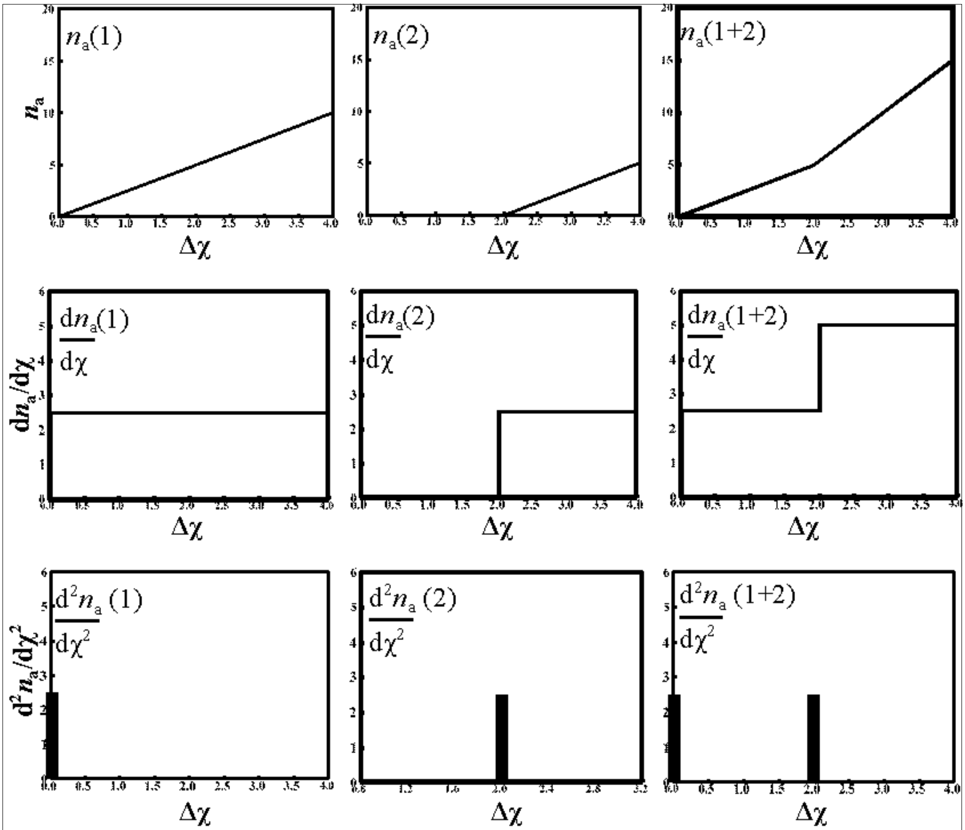

**Figure 5** Simulation of the addition of two isotherms of differing $E_{\mathrm{a}}$s. The two left columns are the two isotherms, the third column is the summation of the isotherms. Top row are the experimental, the middle row the first differentials, and the bottom row the second differentials.

### *3.1 Using the insight of* ***Equation (14)****:*

The isotherms add even with the abscissa transformed, which is something most isotherm hypotheses, including the BET, are not capable of doing. In are schematics this situation this is illustrated in **Figure 5**. By rows and columns:

- The top row is the isotherms in the first two columns. They add to yield the isotherm in the last column.
- The second row are the first derivatives of those in the first column and the third row are the second derivatives.
- Thus, the bottom row yields the distribution, the ratios of how large the amount of powder in each type and the columns starting point pressure, $P_ς$s or energies, $E_a$s.

Thus, a heterogeneity with two a samples that has two distinct straight line fits. The first line is treated as the simple case, but one should subtract the extrapolated line of the first from the rest of the isotherm to yield the second line with a different $E_a$.

This type of behavior does not seem to be common except for a log-law starting isotherm followed by a $\chi$-plot for higher pressures. More common is the case where the $\chi$-plot starts up as a slightly positive curvature. In this case there needs to be a continuum distribution. A normal distribution is a logical choice, only because Nature seems to favor it. Others might work better or some skew, kurtosis or both might prove better. Another distribution that should be considered is the inverse, $\chi^{-1}$, although this was derived to specifically deal with sharp pore distributions.

If one assumes a normal distribution so that the sum becomes the double integral of the normal distribution, or the **Z** function or statistical error area function:

$$n_{\mathrm{ads}} = n_{\mathrm{m}}\,\mathbf{Z}\left(\chi, \left\langle \chi_{ς} \right\rangle, \sigma_{c}\right) \qquad \textbf{(15)}$$

If one uses the statistical functions in a computer, this is usually written:

$$\mathbf{N}(x,\mu,s)=\frac{1}{\sqrt{2\pi s^2}}\mathbf{exp}\left(-\frac{1}{2}\left(\frac{x-\mu}{s}\right)^2\right) \tag{16}$$

$$\mathbf{D}(x,\mu,s)=\frac{1}{\sqrt{2\pi s^2}}\int_{-\infty}^{\tau=x}\mathbf{exp}\left(-\frac{1}{2}\left(\frac{\tau-\mu}{s}\right)^2\right)d\tau \tag{17}$$

$$\mathbf{D}(x,\mu,s)=\int_{-\infty}^{\tau=x}\mathbf{N}(x,\mu,s)\,d\tau \tag{18}$$

$$\mathbf{Z}(x,\mu,s)=\int_{-\infty}^{\tau=x}\mathbf{D}(\tau,\mu,s)\,d\tau \tag{19}$$

$$\mathbf{Z}(x,\mu,s)=(x-\mu)\,\mathbf{D}(x,\mu,s)+\frac{2s^2}{\sqrt{\pi}}\mathbf{N}(x,\mu,s) \tag{20}$$

$$\therefore n_{\mathrm{a}}=n_{\mathrm{m}}\,\mathbf{Z}(x,\mu,s) \tag{21}$$

Where **N** is the normal distribution and **D** is the cumulative normal distribution. Thus for heterogeneity, the fit is expanded to 3 output parameters. To see what this look like, In **Figure 6** is an example of a **Z**($\chi$, $E_a$, $s$) and the **N** from which it is derived.

T = 78 K:

$\mu = \langle \chi_\varsigma \rangle = -2.0$* $\therefore E_a =$ 4.97 kJ mol$^{-1}$ $\therefore P/P_{vap} = 6.18 \times 10^{-4}$

($n_a$ = 1.0)*

$s$ = 0.5*

* an output parameter.

The brackets ⟨⟩ indicates an average amount. The new parameters are $\mu \equiv \langle \chi_\varsigma \rangle$, $n_a$ and $s$. Notice that the extrapolated line from higher pressures intersects at the normal **max.** The $s$ = 0.5 is not normal for an isotherm. It is usually $s$ < 0.2.

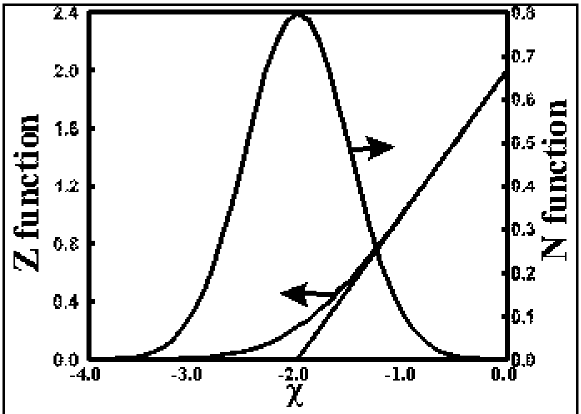

**Figure 6** An example of the **Z** function and the **N** from which it is generated.

### *3.2 How do I fit the **Z** function for heterogeneity?*

Thus two of the output parameter have basically the same meaning, See **Table 3**:

Therefore, for beginning with a starting estimate for calculating the **Z** function by the least squares routine, make the *s* parameter extremely small in **Equation (21)**.

**Table 3** comparing the **Z** function with linear fit

| **Z** | single $\chi_\varsigma$ |
|---|---|
| $\langle \chi_\varsigma \rangle =$ | $\chi_\varsigma$ |
| $n_a =$ | $n_a$ |
| $s =$ | nonexistent |

- To obtain starting parameters use a linear regression of moderately higher data points to obtain the slope , *m*, and intercept, *b*, in the equation $y = mx+b$.
- Let $n_a = m$,
- Let $\langle \chi_\varsigma \rangle = m/b$.
- Let $s$ =~0 but not exactly 0, say $1 \times 10^{-20}$.

### *3.3 How to compensate for a bad vapor pressure reading*

This output parameter is on the vapor pressure value. Most data assumes the vapor pressure at the temperature of the adsorbent is the listed value. There are many experimental problems with this convention ( See the Errors section *2.2*) The $P_{vap}$ error can be a multiplicative factor greater than 1 or less that 1. The only restriction is it may not yield a calculated $P/P_{vap}$ greater than 1 for any data point. This will generate an ERROR code, and depending on the program, will not allow a calculation. Go back and see what error has been made, either in the analysis or in the experiment, which is quite probable.

#### 3.3.1 Example: The JKO isotherm again

A low amount of heterogeneity was detected in the JKO's standard isotherm. Heterogeneity was not used in **Figure 2** since in the view of the overall isotherm it was not obvious. However on closer inspection at low pressure, presented in **Figure 7**, it is clearly there.

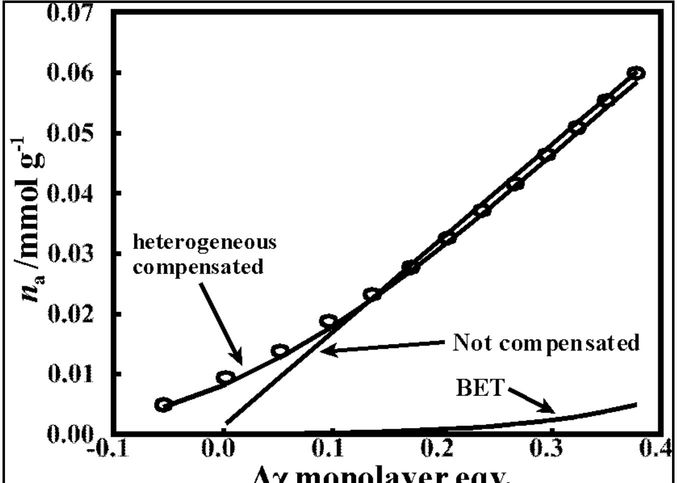

**Figure 7** Low pressure of the JKO isotherm. Labels are in graph.

The output parameters obtained from **Figure 7** are presented in **Table 4** for the heterogeneous compensated fit. Notice that this fit has one more parameter compared to the fit of the fit that is not compensated.

**Table 4** The parameters of the JKO data compensated for heterogeneity.

| Parameter | Value |
|---|---|
| $n_a$ / mmol g$^{-1}$ = | 0.1561 |
| $\mu = \langle\chi_\varsigma\rangle$ = | -2.6123 |
| $s$ = | 0.2408 |
| $\sigma_{fit}$ /mmol g$^{-1}$ = | $2.1 \times 10^{-4}$ |
| $\sigma_{FDR}$ / % = | 0.016 |

The parameters are present here. The parameter μ, = $\langle E_a\rangle$ is similar to $E_a$ except bra-kets (⟨⟩) are being used to indicate it is a average (peak) value. $s$ is therefore the new symbol and this parameter indicates the standard deviation of the normal distribution of the $\chi_\varsigma$ or **-ln**($-E_a/RT$) s.

Looking back at the linear regression, **Figure 2** and the listed values in **Table 1**, the improvement in the $\sigma_{FDR}$ is at lease a factor of 4, but the change was small for the output parameters.

## *3.4 The pressure correction - an ignored parameter:*

The pressure correction is to compensate for the error in $P_{\mathrm{vap}}$. This is the temperature of the adsorbent. If measured it is usually done with a liquid-gas thermometer. Assuming a liquid $N_2$ coolant bath, it is often simply stated to be 78K (to one part in ~80.)

With a coolant bath, the temperature may be far from what one believe, due to the effect of atmospheric pressure. The connection, of course, can be calculated with the Clausius Clapeyron equation[a]. The ΔH of vaporization of $N_2$ is well known, $\Delta_l^g H(N_2) = -7.1\ \mathrm{kJ\ mol^{-1}}$. Thus, a one degree change in temperature yields a $P_{\mathrm{vap}} = 1.47$ bar! Or this is nearly a 50% error!

It is amazing that this error has largely been ignore until recently (due partly to Fuller's influence.) The usual control with volumetric systems is the dual hang-down arrangement. It is assumed that the twin hang-down tubes are at the same temperature, but this is not necessarily true. See Error 2 (2.2.) Of course, creates a funneling problem. (3.3.1.).

With a coolant bath, one should always keep track of the atmospheric pressure. An uncorrected barameter (not compensated for elevation) should be part of the record not just at the beginninng of the experiment but also during the experiment in order to compensate for the waviness that is often observed.

The best solution is as mentioned in section *3.3.1*.

One can correct for the pressure error apres experiment, which will be demonstrated here with the JKO data. To do so, first run the program without the correct as a starting approximation. In **Figure 8** on the right is fit which was fount in *3.3.1* showing the full isotherm. Notice that the data moves away from the fit at the higher pressures, which is an indication that the assumed vapor pressure was higher than the vapor pressure over the adsorbent. Thus, there need to be a correction factor, $G \approx 1$

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[a] Something my first year chemistry students would be very aware of !!

$$P_{\mathrm{vap},\mathbf{R}} = GP_{\mathrm{vap},\mathbf{M}}, \left|G-1\right| > 0.010 \ \&\ \forall P < P_{\mathbf{R}} \qquad \textbf{(22)}$$

Where **R** stards for the real and **M** stands for the measured. The added parameter, *G*, is inserted into the equation by mulltillying the pressure by it. The qualification for *G* means that any correction less than 1% is probably not significant, never-the-less this does not disqualify it. The other qualification is that there is an error some place if a pressure reading goes above $P_{\mathbf{R}}$**,** but the program will show as an error anyway.

In **Figure 8** one can detect the correction by comparing the left graph, the recalculated fit to the fit without the *G* parameter on the right. In **Table 5** are the output parameters. The changes in the first three output parameters are not significant.

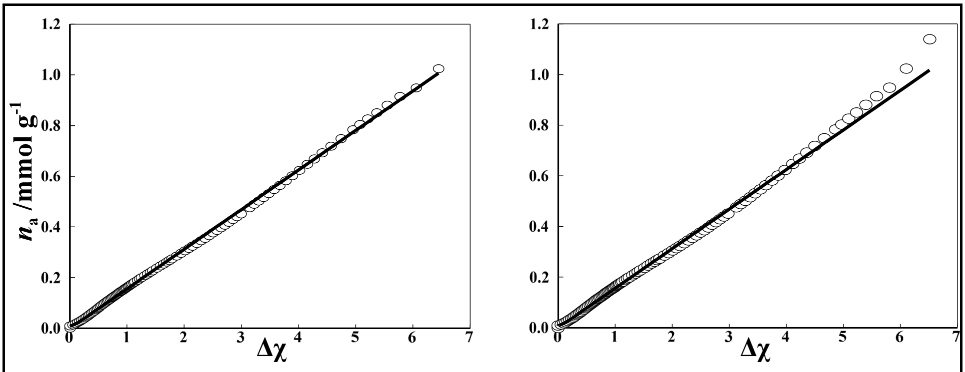

**Figure 8** The pressure compensated isotherm on the left and the non-compensated isotherm on the right. The heterogeneous was previously compensated above in **Figure 7**.

**Table 5** the output parameters for the 4-parameter fit for the JKO data.

| | |
|---:|---|
| $\mu \Rightarrow \langle E_\mathrm{a} \rangle =$ | -2.6123 |
| $n_\mathrm{a} =$ | 0.1561 mmol g$^{-1}$ |
| $s =$ | 0.2048 |
| $G \times P_\mathrm{M} = \boldsymbol{P_R}$ , $G =$ | 1.0089 |
| $\sigma_\mathrm{fit} =$ | $7.63\times10^{-5}$ mmol g$^{-1}$ |
| $\sigma_\mathrm{FDR} =$ | 0.0059 % |

Notice that there is still a little bit of wavyness in the data relative to the fit. This is probably due to slight change in temperature. As listed in the **Table 5**, the temperature correction was quite small and did not make much difference in the output parameters, yet a big difference in the $\sigma_\mathrm{fit}$ of a factor of about 2.7. The multiplying factor, *G* was barely under the the stated maximum of 1.01. So, for very careful work one should try to obtain the temperature to 0.001 K, which is hard to do.

By and large the JKO standard curve is ideal. The problem, of course, is if it is used with the BET as a calibration it is useless. This is the normal use for the "standard curve," but here it is an important test for the QM. Here it is being used as an example of a very carefully performed experiment with an excellent adsorbent. A very rare occurrence indeed!

### *3.5 Conclusion for Section 3*

In this section you have been presented the instructions and reasoning for fitting the isotherm using the equations derived from quantum mechanics. You may have wondered, "Why can't one derive these equation from classical mechanics, specifically from chemical thermodynamics?"

Even if one assumes total mobility on the surface, classically there is no reason that a molecule entering a bare part of the surface should have a difference from others that strike the surface. Hard as you may try, it doesn't work, and you should always end up with a "Henry's Law" isotherm. Even Fuller's classical explanation sounds reasonable, but here is the truth: Fuller knew of the real reason for the success of his writings, which is QM. This may be why IUPAC disallowed isotherm that were not "Henry's Law". (Although they allowed for the Dubinin group of isotherms since that pass through [0,0].)

How come then does QM work? Although it probably can not be used to demonstrate these reason, it is because of the scale

1. The particles are indistinguishable both in position and energy!
2. The property the easily operates at this level is superposition
3. Thus, this liquid phase does not behave as individual particles but as a group ensemble and it is likely that the schichten are also acting as ensembles of various densities.

If you have been convinced at this point, that there is some truth to the QM method, you are following a century of work, ridicule and failed attempts at publication. Carry on! You are now able to analyze non-porous materials, with the first stages of complications, heterogeneity and temperature correction. Get some sleep now, and later continue on to "4 Microporosity."

## 4 Microporosity

### *4.1 Microporosity with nonporous external area*

The phenomenon of microporosity has already been provided in section 1.2 and 1.4.1. Those are about the schichten equation and the log-law:

$$n_1 = n_m + \frac{n_m RT}{E_\mathrm{a}} \mathbf{ln}\left(\frac{P}{P_\mathrm{vap}}\right) \qquad \textbf{(23)}$$

The data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[6] (SSLR), demonstrate the log-law and the threshold pressure. The fit is shown in **Figure 9**.

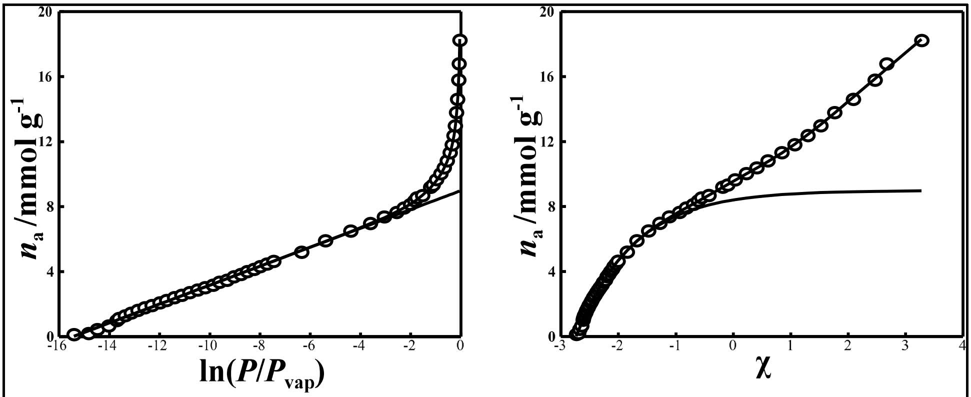

**Figure 9** Adsorption of $N_2$ on Carbon at 77.4 K on activated carbon LMA233 BY SSLR On the left is the log-law and on the right the χ-plot

The linear fit looks good up to about **ln**($P/P_\mathrm{vap}$) ≈ 4 not past that. Does this disprove the QM hypothesis? No, not if there is an answer provided by QM. This case is typical for a microporous solid with a significant external area. On the right the χ-plot is showing a fit with the addition of the external area. To get the parameters as non-linear least squares (NLLS) fit is used. The output parameters and the standard deviation of the fit is presented in **Table 6**. This plot looks like the IUPAC round-robin investigations on Sterling FT and Vulcan G carbons which could not be correctly analyzed due to lack of the low-pressure range.

To start the fitting, first the log-law could be used on the lower pressures.

This is then subtracted from the overall isotherm and the remainder fit with the $\chi$-plot. The fit for this case was extremely good (0.47 % FDR) even without a least squares fitting. The data for this isotherm in is **Table 6**.

**Table 6** Data for N2 adsorption on microporous C by SSRL

| quantity value Units | Description/meaning |
|---|---|
| $n_1^* = 0.581$ mmol g$^{-1}$ | Slope of the 1st schicht line (homogeneous fit) |
| $\ln(P_\varsigma/P_{\mathrm{vap}})^* = -15.445$ | energy term relative to reference state |
| $E_a^D = -10.02$ kJ mol$^{-1}$ | differential energy at the start, (Threshold energy) |
| $\chi_\varsigma = 2.7379$ | threshold |
| $n_{m,1}^* = 8.99$ mmol g-1 | ordinate intercept for the 1st schicht |
| $n_{\mathrm{ext,m}} = 2.967$ mmol g-1 | monolayer equiv of a monolayer for "1st layer" schicht |
| $\chi_{\varsigma,p}{}^* = -0.6493$ | position of the pore distribution peak in the $\chi$-plot |
| $\Delta\chi_p = 0.770$ | position of the pore distribution peak in the $\Delta\chi$-plot |
| $<E_p> = 4.1$ J mol-1 | Average energy of the pore – peak value |
| $s_p^* = 0.649$ J mol-1 | The "spread" parameter of the Z function, 1$\sigma$. |
| $G^* = 1.025$ K | Pressure correction due to higher than recorded T |
| $\sigma_{\mathrm{fit}} = 0.0856$ mmol g-1 | The standard deviation for the entire isotherm, 1$\sigma$. |
| $\sigma_{\mathrm{FDR}} = 0.47$ % | $\sigma_{\mathrm{FDR}} = \sigma_{\mathrm{fit}}/\mathbf{max}(n_a) =$ |
| * ouput parameters all other values are derived from these or the fitted isotherm. | |

One might criticize the number of parameters being calculated here, but there are only 6. Two are for the log-law, three for the $\chi$-plot with included heterogeneity and one for the pressure correction, which was of marginal significant.

## *4.2 Micropore-Cannibal Hybrid*

It is important to be able to recognize when one has mesoporosity and not. For certain if there is a late positive curvature (past $\chi = 0$ especially) then there is mesoporosity. If there is hysteresis, it seems to be it's a slam dunk.

In this next example, the pore filling slightly past the monolayer filling. It has been postulate that meoporosity is not possible below $\chi = 2$ or even 3. This is because for mesoporosity there needs to be enough space in the pores to accommodate the liquid-gas interface separate from the solid-liquid phase.

There is no reason that there is exactly two types of pores, monolayer pore, called micropores here, or mesopores. Or, what would it be like to have a restricted volume could accommodate a little more or a fraction of another layer? This may be where the investigator needs to remember not to go brain-dead. "What should this be called?" For now, it will be called a "hybrid analysis" using the log-law and the $\chi$ analysis.

### 4.2.1 The First Lemma that is quite obvious:

**Lemma 1 and cannibalization:**

Schicht #1 will always go to $n_{m,1}$ even at the expense of higher schichten.

Lemma 1 forces the filling on a straight line from $n_a = 0$ to $n_a = n_{m,1}$. in the log-law, In doing so, some of the 2nd schicht may have to lose some of its density. This will be referred to as "cannibalization." One could imagine this to be due to the development of addition steric interference in "stacking."

### 4.2.2 An Example of Cannibalization

An example of this is calculate here with micropores that contains at saturation a 1st layer plus some room for the 2nd "layer," plus a small amount of external surface. The following is from original data by: Madani, Kwong, Rodríguez-Reinoso, Biggs, Pendleton[8] (MKR-RBP) and

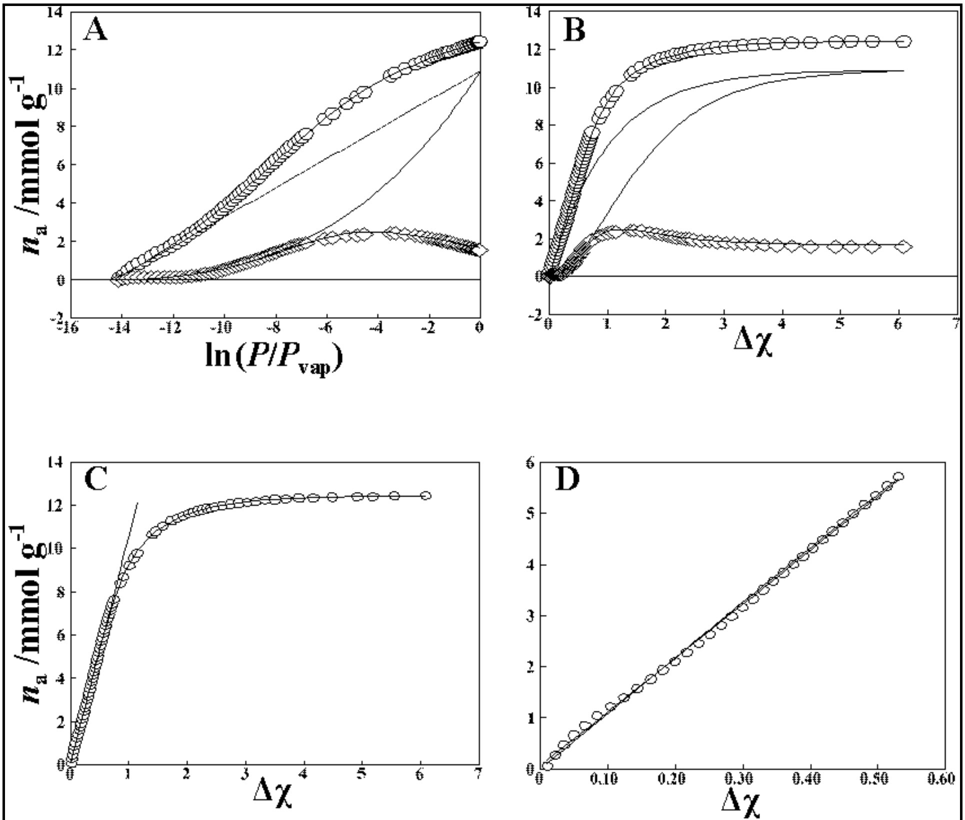

**Figure 10** The data by graphed by low-law and $\Delta\chi$ to show how the analysis of this type of hybrid analysis can be accomplished. Original digital data and permission provided by Professors Madani and Pendleton. Digital data available from Prof. Madani.

was kindly provided by Professors Madani and Pendleton. The adsorbent for this study was microporous carbon (poly-furfuryl alcohol based activate carbon) and the adsorptive-adsorbate was argon. This is shown in four graphs in **Figure 10**.

In graphs A and B the dashed line is the 1st schicht filling according to Lemma 1. The question could be, “How did you know that this was the proper line?” Of course, the fit was finally made using a least squares routine, but there was an advantage with having a partial amount of 2nd schicht. That advantage was there was enough 2nd schicht to allow a straight line to fit the initial area of the $\Delta\chi$-plot demonstrated by C and D.

**Table 7** Output parameter for the MKR-RBP data.

| | | | |
|---|---|---|---|
| $\chi_\varsigma^*$ = | -2.6591 | $\ln(P_p/P_{vap})^*$= | −4.596 |
| $\ln(P_\varsigma/P_{vap})$ = | −14.283 | $<\chi_p>$ = | −1.525 |
| $E_a$ = | −10.37 kJ mol-1 | $<E_p>$ = | −53.7 J $mol^{-1}$ |
| $n_{m,1}^*$ = | 10.84 mmol g-1 | s* = | 2.5410 |
| $\sigma_{fit}$ = | 0.059 mmol g-1 | *original fitting parameters. Others are derived from them. | |
| σ = (%FDR) | 0.47% | | |

The following are the description of the input parameter:

$\chi_\varsigma$ = the treshole pressure for both schicht 1 and 2
$n_{m,a}$ = the monolayer equivalence for schicht 1
**ln**$(P_p/P_{vap})$ = the $\boldsymbol{\chi}^{\mathbf{-1}}$ distribution peak for schicht 2 (similar too the normal distribution.)
s = the width of the 2nd schicht (denominator in arg of $\boldsymbol{\chi}^{\mathbf{-1}}$.
$n_{ext}$ = external surface monolayer equivalance was 0 in this case.

This is an alternative way to obtain $n_{m,1}$. To see how linear the plot becomes in low $P$, in **D** the start of the $\Delta\chi$-plot is shown.

Very little heterogeneity was detected, so it is a 4-parameter fit. Both the $\chi$-plot and the log-law plot are useful for this situation. The final least squares fit is a 4-parameter fit There was no detected adsorption on the external area, there was no detectable heterogeneity and there was no detectable pressure correction. Schicht 1 and 2, of course, have the same $\chi_\varsigma$ as required. The 4-parameters are in **Table 7** along with some derived quantities.

## 5. Mesoporosity and Hysteresis -

There is no question that the QM characterization is easy to do and easy to interpret compared to other techniques. However, the important question of prediction has not yet been addressed. It seems probable that a combination of QM and ESW will yield some answers especially for hysteresis. QM may not at this point answer all question, but it does do is to supply some physical meaning to a minimal number of fitting parameters. Some parameter meanings are clear, for example the slope and abscissa intercept of the $\chi$-plot are clearly the monolayer equivalence and the measurement of the isotope starting energy. Microporosity is also fairly clear.

We not come to a phenomenon where the meaning of the fit is not quite so clear. The mesoporosity can be fit with three new parameters. Using the statistical functions, the cumulative distribution is used here. This has three parameters, the position of the normal distribution (i.e. the peak of the differential of the cumulative,) the spread of the distribution and the ending value. The ending value has a slope that is apparently the value for the external surface area.

What has not been demonstrated is how to calculate the position of the peak and the spread. Furthermore, these parameters change when the isotherm is reversed, yielding the hysteresis phenomenon. This needs very much more research.

### *5.1 Mesoporosity*

In previous sections, the definitions of physical adsorption with the use of the QM formulation does not necessarily follow the SIO/IUPAC definitions. The IUPAC definitions of micropores and mesopores were classified according to the radius or pore wall separation. For the modern definitions, this is replaced by questions of what the interactions are between the absorbent, adsorbate and adsorptive. This interaction is between $E_p$ (↑ or ↓)[a] for the pore radii and the $\boldsymbol{\Delta}_{l}^{a}\mathbf{E}$. It seems based upon

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[a] ↑ means adsorption and ↓ means desorption.

competing energies that determine the classification of micropore versus mesopore.

### *5.2 Recognizing Mesoporosity*

Either the log-law or the $\chi$ -plot will settle to be a straight line after the pressure is high enough for the effect for heterogeneity. After $\Delta\chi \approx 1.5$ it is likely to be negligible.

Beyond the heterogeneity in the $\chi$-plot, mesoporosity causes a positive curvature. This is followed by a negative curvature resolving in a final linear portion for the $\chi$-plot. This final slope is less than the initial slope.

The linear portion of the log-law indicates microporosity. This portion of the plot is signaling steric hindrance. Very often there is then an extra amount adsorbed on the external area, which is a normal $\chi$-plot. These two need to be added.

The first case above is illustrated by the schematic in **Figure 11**. This is an idealized isotherm diagram of an adsorbent sample that involves the features of heterogeneity and mesoporosity. (The ordinate intercept of $n_{\mathrm{ext}}$ yields the anti-Gurvitsch rule for mesopore quantity.)

There has been much discussion about the origin of hysteresis in literature. This section only provides a method of curve fitting to provide parameters to characterize the mesoporosity. This can fit both branches of the hysteresis. Later are some tentative proposals for the origin for mesoporosity and hysteresis will be provided.

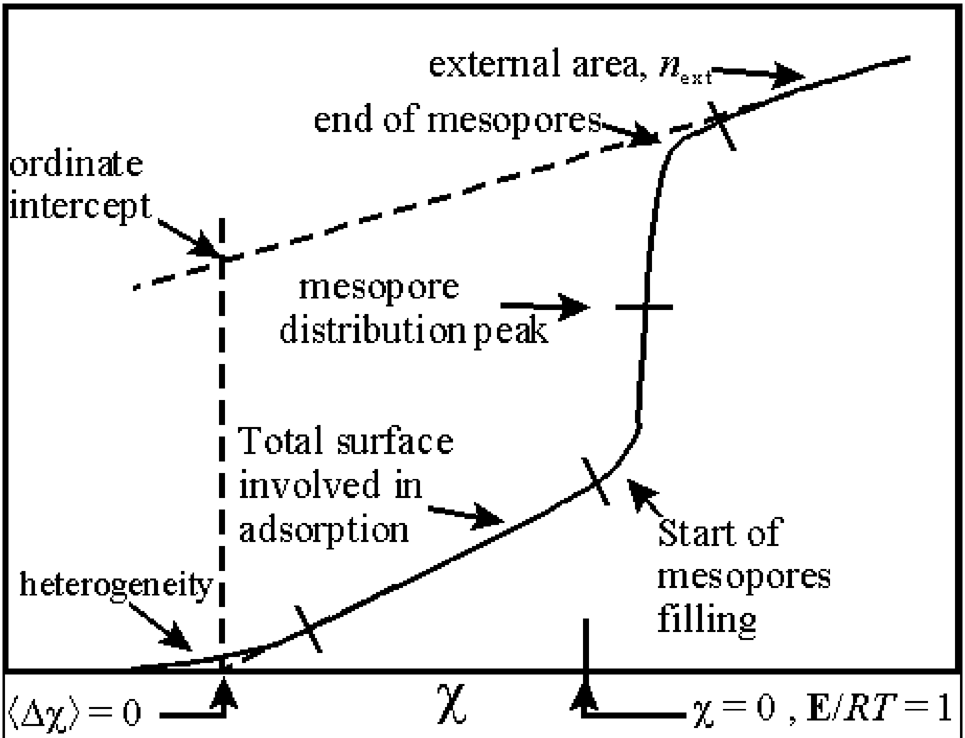

**Figure 11** Schematic of an isotherm of an adsorbent with mesoporosity.

### *5.3 The **D** function again and a new function $\chi^{1}$:*

The **D** function, commutative normal distribution. has been give above The new function $\chi^{-1}$ describes the ending of the QM fitting. It is simply the inverse function, displaced and distributed. It is given in **Equation (24)**.

$$\chi^{-1} = \mathbf{exp}\left\{-\mathbf{exp}\left(\frac{\chi-\chi_{\mathrm{p}}}{s_{\mathrm{p}}}\right)\right\} \qquad \textbf{(24)}$$

The equations to do the analysis uses the following equations. These apply either the χ-plot or the Δχ-plot, depending upon preference. Here it is shown for the Δχ-plot. The bold **n**s are for the linear functions or if there is heterogeneity the corrected function for heterogeneity.

Using the **D** function to modify the χ or Δχ-plot is **Equation (25)**

$$\begin{aligned}&\mathbf{n}_{\mathrm{a},\Sigma} = \mathbf{n}_{\mathrm{a},1} + \left(\mathbf{n}_{\mathrm{f}} - \mathbf{n}_{\mathrm{a},1}\right)\mathbf{D}\left(\Delta\chi,\Delta\chi_{p},s_{\mathrm{p}}\right)\\ &\text{where: } \mathbf{n}_{\mathrm{a},1} = \Delta\chi n_{\mathrm{m}} \text{ and } \mathbf{n}_{\mathrm{f}} = \Delta\chi n_{\mathrm{ext}} - n_{\mathrm{p}}\end{aligned} \qquad \textbf{(25)}$$

or using the $\chi^{-1}$ function **Equation (26)**:

$$\mathbf{n}_{\mathrm{a},\Sigma} = \mathbf{n}_{\mathrm{a},1} + \left(\mathbf{n}_{\mathrm{f}} - \mathbf{n}_{\mathrm{a},1}\right)\left\{-\mathbf{exp}\left(-\mathbf{exp}\left[\frac{\Delta\chi-\Delta\chi_{p}}{s_{\mathrm{p}}}\right]\right)\right\} \qquad \textbf{(26)}$$

(Obviously, the heterogeniety correction would apply to $\mathbf{n}_{\mathrm{a,i}}$.) To demonstrate the use of these equation a Δχ-plot is shown in **Figure 12**.

#### 5.3.1 An Example by Guillet-Nicolas, Wainer, Marcoux, Thommes, Kleitz

These data were measured by Guillet-Nicolas, Wainer, Marcoux, M. Thommes, F. Kleitz[9] (GWMTK) on KIT-6, a porous silica heat treated for 48 hr at 373 K. **Figure 12** is the least squared minimized fit to the data.

Both the inverse chi function, $\chi^{-1}$, and the cumulative distribution function, **D,** were used to fit the data. This was done to compare the two approaches. Both adsorption and desorption were fit. In comparing the fits, $\chi^{-1}$ was only slightly better compared to **D** as is indicated in **Table 8**.

Once one has the rough estimates for the parameters, a least squares routine is used to get sharper results. The quantities in **Table 8** are:

$n_{\mathrm{m}}$ = monlayer equivalence early portion,
$n_{\mathrm{exp}}$ = monolayer equivalence of last portion,
$\Delta\chi_{\mathrm{p}}$ = the peak of the normal distribution or in **Figure 12** the steep increase, and
$s_{\mathrm{p}}$ = the spread in the normal distribution for **D** but
$\Delta\chi$ = $\chi - \chi_\varsigma$ so,
$\chi_\varsigma$ = another parameter used for $\mathbf{n}_{\mathrm{a},1}$.
$\mathbf{n}_{1,\Sigma}$ = the resultant summation of the adsorbate is the total isotherm.

Most of the fits were well within the 1 % FDR except the desorption using the normal distribution. It is too early to draw a conclusion about this, but certainly indicates addition work would be welcomed.

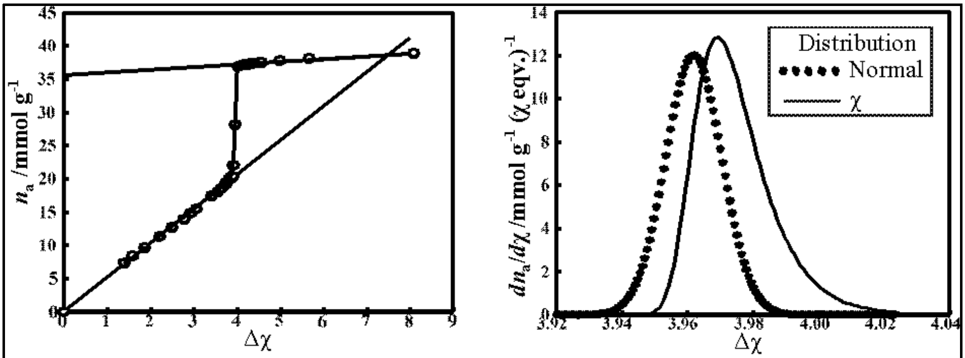

**Figure 12** $N_2$ adsorbed on KIT-6 after heat treatment by GWMTK, Sample K(100)48_N2. Left is the isotherm and right are the normal pore distribution and the $\chi^{-1}$ distribution. $\chi^{-1}$ is used. Data used was bought from Science Direct Elsevier Publishing through CCC..

**Table 8** parameters and quantities using the data by GMK of $N_2$ adsorption/desorption on KIT-6 silica that demonstrate the $\boldsymbol{\chi}^{\mathbf{-1}}$versus **D** distribution and hysteresis value.

| physical quantity | Adsorption $\chi^{-1}$ | Adsorption **D** | Desorption $\chi^{-1}$ | Desorption **D** |
|---|---|---|---|---|
| $n_m$ /mmol $g^{-1}$ = | 5.310 | 5.282 | 5.206 | 5.201 |
| $\chi_\varsigma$ = | -2.9870 | -3.0145 | -3.0129 | -3.0178 |
| $n_{ext}$ mmol $g^{-1}$ = | 0.661 | 0.679 | 0.680 | 0.715 |
| $\Delta\chi_p$ = | 4.259 | 4.275 | 3.997 | 3.995 |
| $n_p$ /mmol $g^{-1}$= | 39.197 | 39.153 | 39.165 | 39.036 |
| $s_p$ = | 0.0275 | 0.0304 | 0.0165 | 0.0227 |
| Goodness of fits: | | | | |
| $\sigma_{fit}$ /mmol $g^{-1}$ = | 0.402 | 0.540 | 0.453 | 0.312 |
| $\sigma_{FDR}$/ % = | 0.91 | 1.28 | 0.72 | 0.71 |
| $r^2$ = | 0.9990 | 0.998 | 0.9995 | 0.9995 |
| Derived physical quantities: | | | | |
| $\chi_p$ = | 1.272 | 1.260 | 0.9682 | 0.9774 |
| $n_{m,p}$ /mmol $g^{-1}$ | 4.65 | 4.60 | 4.53 | 4.49 |
| $E_a$ /kJ $mol^{-1}$ = | -12.69 | -13.05 | -13.02 | -13.09 |
| $E_p$ /J $mol^{-1}$ = | -181.7 | -183.9 | -242.2 | -244.0 |
| $A_p$* /m= | 454.3 | 449.4 | 442.6 | 438.3 |
| $V_p$ ($\rho l$) /mL $g^{-1}$ = | 1.357 | 1.356 | 1.356 | 1.352 |
| $2V_p/A_p$ /nm = | 5.97 | 6.03 | 6.13 | 6.17 |
| $E_p{\downarrow}:E_p{\uparrow}$= | 1.33 | 1.33 | | |

* By IUPAC convention conversion to area.
↓ = desorption ↑= adsorption

## *Wait a minute! 5.3 How does one get an initial estimate?*

I'm glad you asked. Below are some figures to make this clear.
In the following step is a typical fit (GWMTK KIT-6 **Figure 12**)

STEP 1: Obtain the $\chi$-plot (suggestion convert amounts the molar units) by using the $\chi$-transform for the abscissa and amount as ordinate.

STEP 2: Use a linear regression on the low pressure data and a separate linear regression for the high pressure data. In some spread sheets it is the function @linest(y, x, yes, yes) and plot the results on the original plot. (Conventional $y = mx + b$ is used here.)

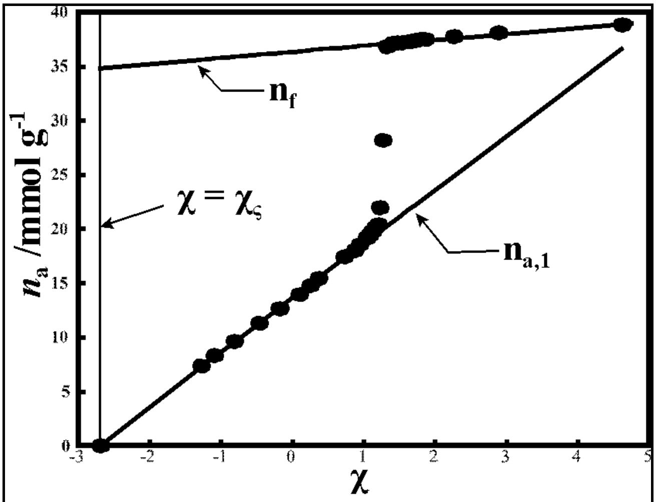

**Figure 13** Determination of the estimate for $\boldsymbol{n}_{a,1}$ and $\boldsymbol{n}_f$ to yield $\chi_\varsigma$, $n_m$, $n_p$ and $n_{ext}$

| $m = n_m$ ↘ | $b$ ↘ |
|---|---|
| **4.9748** | 13.6272 |
| 0.0485 | 0.0363 |
| 0.9991 | 0.1201 |
| 10507 | 9 |
| 152 | 0.1299 |

$-b/m = \chi_\varsigma$ **-2.7392**

| $n_{ext}$ ↘ | $n_p$ ↘ |
|---|---|
| **0.5294** | **36.4397** |
| 0.0250 | 0.0583 |
| 0.9825 | 0.0726 |
| 449.4 | 8 |
| 2.3715 | 0.0422 |

This yields the estimate of the four parameters list.

STEP 3 Shift the abscissa by subtracting the $\chi_\varsigma$ (< 0 usually.)

STEP 4:

Estimate where the most steeply part of the isotherm. This is the estimate for **D** for $\chi^{-1}$ distribution peak, $\Delta\chi_p$. Use the distribution to transition between $\mathbf{n}_{a.1}$ and $\mathbf{n}_f$.

STEP 5: Assume a very small $s_p$ (= 1 ×$10^{-10}$)[a] in either **Equation (25)** or **Equation (26)**. In this case the normal distribution is shown

To illustrate the effect of $s_p$ this is set to 0.1 in place of ~0.02

After running the resulting equation through the least squares routine **Figure 16** is obtained.

The desorption branch is perform the same way.

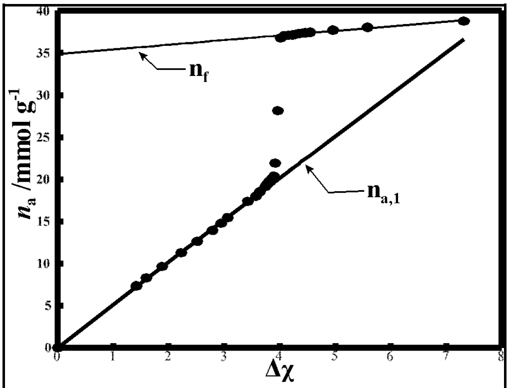

**Figure 14** Change the abscissa to Δχ.

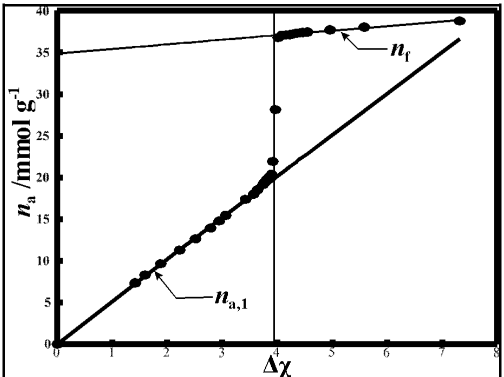

**Figure 15** Estimate $\Delta\chi_p$

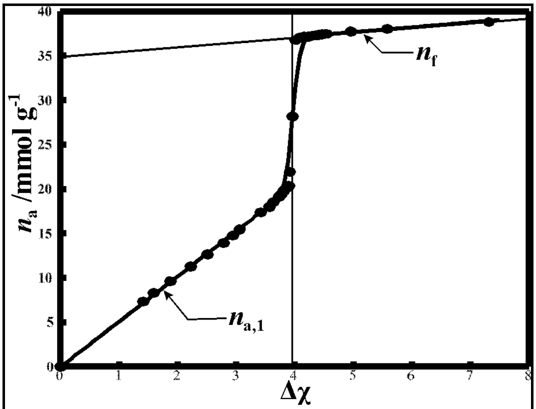

**Figure 16** the fit with estimate values

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[a] Most least squares programs yield an error if $\sigma_p$ is set to exactly 0.

### *5.4 Possible ways to calculate hysteresis*

The following is speculation based on a few observations.

One of the discoveries that the QM model presented is the importance of the $E_a$ and the "Fuller magic point," $\chi = 0$ or $P = P_{vap} \times 0.3678\ldots$, in the calculation of the desorption isotherm. Firstly, the $E_a$ is the zero point for the $n_a$, whereas $\chi = 0$, is the reference point for the energy. $\chi = 0$ is also the inflection point for the isotherm. At the "magic point" the QM model has an energy of $-648.5$ J mol$^{-1}$ for $N_2$ at 78 K (or $RT$). The "magic point" is an important point in column operations. Basmadjian[10] has pointed out that since the second derivative in the isotherm plots changes from negative to positive at this point, so does the analysis change. This is in agreement with the ESW approach by Adolphs, et al.[11,12,13,14]. This is also the point for the maximum in the ESW transform to yield $n_m$ and the slope in the untransformed isotherm at this point is $n_m$ (See reference 2 for error analysis since one is dealing with data points and not a continuous expression.) This is always the case for any physisorption, barring some interference such as porosity. With this information one could speculate on the origins of hysteresis.

It is unlikely that the hysteresis will be below the magic point since the energy is becoming so (negatively) high. There is evidence that mesoporosity happens at or near this point, but not hysteresis.

The concept of a monolayer when there are schichten to consider is problematic. For example, say there is a steric hinderence that allows the 3rd schicht. When there 2 monolayer equiv, the 3rd schicht is quite well along in filling and the missing 4th schicht cannot fill at all. So how much is in the 3rd schicht? Of course that question can be solved but not straight forward. So to make things simple the assumption that the break from QM to classical applies to all schichten at once.

A very important thermodynamic competition is present. If it is assumed that the mesoporosity is pore filling due to the liquid surface tension, which most investigators assume, then the there are is a counter mechanism to QM controlled by the Kelvin (Oswald-Freundlich) or similar equations:

$$-\Delta_{\text{a}}^{\gamma/\text{g}}E = RT\,\mathbf{ln}\left(X\right) = \frac{m\gamma\bar{V}}{r_{\text{c}}} \qquad \textbf{(27)}$$

This written as the formation of the interface, so it is exothermic. $r_c$ is the radius of the "core," defined by the state that the liquid-gas interface is formed. In other words, ideally, if the total amount $n_a$ were compacted evenly as a liquid to the sides of the pores, then there would be an empty space in the center. The radius of this virtual space is the core radius. There is then a virtual thickness through the virtual collapsed film, defined as the thickness, *t*. Thus, $t + r_c = r_p$ were $r_p$ is the pore radius "measured" in the adsorbent.

There is another consideration. The QM measures from charge center to charge center. The DFT convention used a hard sphere core plus a potential, like a Lennard-Jones potential added to that. It then assumes an external potential at the pore wall surface. The center-to-center convention yields a smaller number by the value of *t* for the pore diameter or ½t for the radius.

Anything, more subtle than the above is getting into the weeds of,"What is the radius of an atom," etc.

In **Equation (27)**, *m* is a constant depending upon the geometry of the pore. Ideally , *m* is 1 for a cylindrical core, and 2 for a semispherical core. However, pores are not always ideal and even if they were it does not mean their openings are. What if the pore is at a slant to the surface and not perpendicular?

In **Equation (27)**, the symbol $\Delta_{\text{a}}^{\gamma/\text{g}}E$ is an attempt at consistency with IUPAC to designate the energy of the formation of the gas-adsorbate interface energy release. The transition from the schichten diffuse situation, where there is no defined interface, to the compaction of all schichten into a liquid for the formation of this interface is what is meant by this symbol. The starting phase is adsorbate, a, and the final state is the liquid-gas coexistence delineated by an interphase compact boundary,$\gamma/$a. In this case, the Gibbs' free energy of the transition also includes an entropy term. This is a big question of how to calculate this. It may be the biggest problem in the following calcuations made, because at this time it is being ignored.

Also, to be considered is the schichten density and steric hindrances that dictate what the possible volume of liquid can be produced. For example a pore could be large enough to warrent a collapse to make the *l*-g interface but the schichten are too small due to steric hindrance to produce the quantity of liquid required.

Given all these uncertainties, there might still be value in going through the exercise of comparing energies to yield " pore size"

The first concern is the value of *m*. If the interface geometry changes from adsorption to desorption, as one would expect from **Equation (27)**. The question is, "How could this happen." Of special concern is how can the isotherm still be in equilibrium when the answer changes. This is, believe it or not, something that is observed elsewhere. Especially, for example in the case of corrosion where the equilibrium changes are due to mechanical changes, leading to a hysteresis.

So what is the geometric change in this case. **Figure 17** is a schematic or the step and the geometric difference between adsorption and desorption. As the diffuse film fills up, the energy (again negative) of the diffuse film become smaller and smaller according to **Equation (7)**, whereas the formation of the *l*-g increases according to **Equation (27)**. At some point they are bound to cross, provided there is a large enough cross section area for the diffuse QM film can have enough virtual volume[a].

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[a] virtual volume: the volume that the diffuse film would fill if it were to collapse into a dense liquid.

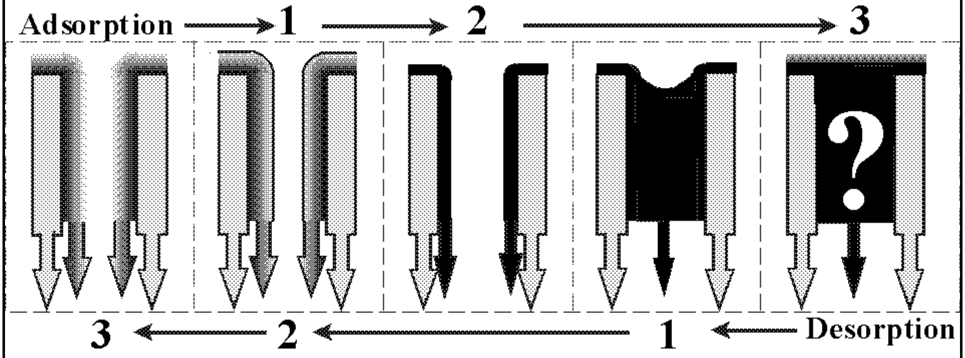

**Figure 17** The steps in the conversion between the QM dispersion (according to the schichten equations) and the compacted (classical theory) and the difference between adsorption and desorption.

However, the energy of thc collapse to densification depending on $m = 1$ and the "snap back" depending on $m = 2$ means that the ratio of the energies are 1:2 respectively. More likely, using arrow up, ↑, for adsorption and down, ↓, for desorption, from **Equation (27)** the relationship becomes:

$$\frac{E_{\mathrm{p},\uparrow} r_{\mathrm{c},\uparrow}}{E_{\mathrm{p},\downarrow} r_{\mathrm{c},\downarrow}} = \frac{m_{\uparrow}}{m_{\downarrow}} \tag{28}$$

The $E_\mathrm{p}$s can be measured. This leaves the ratios of the $r_\mathrm{c}$s to $m$s to be determined. One cannot determine this without some additional information or assumption. The virtual thickness can be calculated from the $E_\mathrm{p}s$ to calculate the effective[a] $r_\mathrm{p}$ as an anchor since it is the same for both adsorption and desorption.

These considerations are taken into account for the example calculation.

5.4.1 Example: mesoporosity SBA-15 silica:

One should be able to calculate pore size with knowledge of the surface

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[a] The word effective is used here to indicate that even though the $r_\mathrm{p}$ is reproducible, one should not give it a macroscopic definition compare to, say, X-ray value. One also needs to keep in mind the X-ray value is also an effective parameter.

tension of the adsorptive and the value of $\chi$ for the mesopore peak. The data by Guillet-Nicolas, Wainer, Marcoux, Thommes and Kleitz (GWMTK2) will be used for illustration An isotherm was selected, which the adsorptive was $N_2$ at 78 K and the adsorbent is SBA-15 calcined at 413 K for 24 hours (S(140)24_N) The following constants were used:

$\gamma_{\mathrm{lg},78\mathrm{K}} = 8.72$ mN m$^{-1}$ , $\rho_{\mathrm{N2}(l)} = 0.809$ g mL$^{-1}$ $\bar{V}_{\mathrm{N2}(l)} = 34.63$ mL mol$^{-1}$.

The nitrogen surface tension at 77K is from the UNIFAC (Dortmund) data base with several authors in agreement. **Equation (27)** was used for calculating the radius from energy.

This GWMTK2 sample was chosen because the graph was reasonably readable, and enough data points were present in critical areas. The isotherm and the pore size analysis are presented in **Figure 18**. A summary of the output data and derived quantities are presented in **Table 9**. In the NLDFT results by GWMTK is also presented for comparison. The spread in the NLDFT is much larger in the pore distribution than the QM results. However, the NLDFT assumes a hard core, plus a Lennard-Jones potential for the admolecules that should spread out the looks of the distribution, whereas the QM calculation is center-to-center.

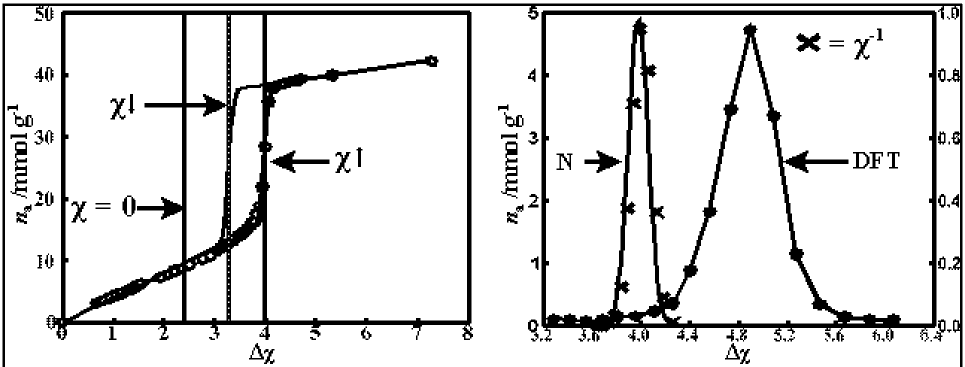


**Figure 18** - Isotherms (L) and porosity determination (R ) for data by GWMTK2 of $N_2$ on SBA-15 silica. Data used by permission From Science Direct - Elsevier Publishing.

Symbols and defintions for **Table 9**
$\langle X \rangle$ = (when not QM) aveage of $X$
↑ = for adsorption
↓ = for desorption
$r$ = pore radius measured with $d$ from adsorbent edge to opposite edge.
$r_{\mathrm{c}}$ = the "core" radius, measurement from virtual adsorbent, $d$ measured from inner edge to opposite inner edge.
$V_{\mathrm{BET}}$ = total pore volume by classical means, BET or Gurvitsch based
$A_{\mathrm{BET}}$ = area calculation by BET theory
$t$ = either classical monolayer of schitchen monolayer equiv

Virtual Monolayer: the amount of adsorbate that if all the molecules were touching the surface and if no other molecules were in the adsorbate. Not normally observe except if the steric hindrance perfectly match the size of the admolecules, it would be the value $n_{\mathrm{a}}$ at $P_{\mathrm{vap.}}$

$x$ virtual monolayers: The measure of amount of adsorbate that if compacted as liquid would have a film thickness to $x$ classical layers.

**Table 9** Output parameters and quantities for data by GWMTK of N2 on S(140)24_N sample of SBA-15 silica sample using the shut-off functions $\chi^{-1}$

| QM Values and units | | | derived from QM (*) or UPAC convention (I) | | |
|---|---|---|---|---|---|
| $n_m =$ | 3.979(a) | mmol $g^{-1}$ | $A_{tot} =$ | 388.7 | $m^2g^{-1}$ (*,I) |
| $\langle \chi_\varsigma \rangle =$ | −2.4163(a) | | $\langle E_a \uparrow \rangle$ | -7.17 | kJ $mol^{-1}$ (*) |
| $n_{ext} =$ | 1.071(a) | mmol $g^{-1}$ | $A_{ext} =$ | 104.6 | $m^2$g-1 (*,I) |
| | | | $A_p \uparrow = A_{tot} - A_{ext} =$ | 284.1 | $m^2g^{-1}$ (*,I) |
| $n_p =$ | 34.350(a) | mmol $g^{-1}$ | $V_p \uparrow =$ | $1.19 \times 10^{-6}$ | $m^3g^{-1}$ (*,I) |
| | | | $d = 4V_p / A =$ | **16.8** | nm (*,I) |
| | | | $t_m =$ | 0.709(c) | nm (*) |
| $\langle \Delta\chi_p \rangle =$ | 3.974(a) | | $t = t_m \langle \Delta\chi_p \uparrow \rangle =$ | 2.82 | nm (*,I) |
| $\langle \chi_p \rangle =$ | 1.5578(a) | | $\langle E_p \uparrow \rangle =$ | -136.6 | J mol-1 (*) |
| $\langle \chi_p \rangle =$ | | | $r_c$(c) from $\langle E_p \uparrow \rangle =$ | 2.21 | nm (*,I) |
| | | | $r = r_c + t =$ | **5.03** | nm (*,I) |
| | | | $d_p = 2r =$ | **10.06** | nm (*,I) |
| | | | $A^{(d)BE}{}_T =$ | 580 | $m^2g^{-1}$ (I) |
| | | | $V^{(d)} =$ | $1.42 \times 10^{-6}$ | $m^3g^{-1}$ (I)) |
| | | | $d \uparrow^{(d)} = 4V/A_{BET} =$ | **9.79** | nm (I) |
| | | | $d_{ads}{}^{(d)} =$ | **10.1** | nm (I) |
| $\sigma_p =$ | $6.989 \times 10^{-2}$ | $\chi$ units | $\langle E_d \downarrow \rangle =$ | -292.5 | J $mol^{-1}$(*) |
| $\sigma_{fit} =$ | 0.6127 | mmol $g^{-1}$ | $\langle \Delta\chi_d \downarrow \rangle =$ | 3.184 | (*) |
| $\sigma_{FDR} =$ | **1.45 %** | | $m\downarrow / m\uparrow =$ | 2.14 | (*) |
| (a) indicates output parameter. | | | FDR = “of Full Data Range” | | |
| (b)Measured from admolecules’ centers | | | | | |
| (c) Measured across pore admolecules’ inside edges. | | | | | |
| (d) This datum is given by GWMTK | | | | | |
| (e) Given by GWMTK using NLDFT . | | | | | |
| ↑ = the pore value for adsorption (default) ↓ = the pore value for desorption | | | | | |
| **Note: The values for the pore diameter are in bold font.** | | | | | |

In **Figure 18** the calculation of the QM pore distribution used both the **D** distribution and the $\chi^{-1}$ distribution. On the right the **N** companion distribution of the **D** function is the ✖'s line. The solid line is the $\chi^{-1}$ distribution. There is only a slight difference between the two.

In **Table 9** are the output parameters. The first thing notable is the %FDR is above the self imposed limit. This data set, however, has the advantage of more clearly recording of the desorption branch.

There is a mix in conversion to physical dimensions. The conversion to SI units uses the classical IUPAC conversions listed in the physical adsorption conventions. For example, nitrogen has the classical molar area of $9.77\times 10^4$ m$^2$ mol$^{-1}$, and the conversion from linear monolayer equivalence is IUPAC classical diameter of 0.354 nm monolayer$^{-1}$. Opposing sides, however, need to be counted. (The van der Waals $d = 0.31$ nm and the following dimensions apply to solid $N_2$: the waste is $d_w = 0.339$ nm, and the length is $d_l = 0.434$ nm. Thus, classically, it makes a 20% difference the orientation of $N_2$ to the surface.)

The QM analysis does not predict that an outer liquid-gas boundary exists. However, we know that it happens, and if it is a sudden enough formation, then there should be a peak in the observed $-\Delta H$ to indicate this. If the adsorbent is perfectly smooth, it may be that the transition is above a high $\theta$ value ( 9 monolayer equivalence, $-\Delta E \sim 1 - 2$ j mol$^{-1}$ compared to ~10 kJ mol$^{-1}$ at the start of the isotherm.) thus little heat is emitted and it is not noticed. So far, some smooth surfaces have absorbed up to 8 monolayer equivalences without any sudden shift, which contradicts the prediction by Brunauer that the phase boundary is at the high end of the pressure. Most likely, the sample becomes noticeably "wet." This ends the experiment with adsorptive dripping off the side of the sample tube.

There is a lot of information in **Table 9** and it would be helpful to spend time to see how the 6 output parameter ends up calculating the inferences.

It is important to notice that the ratio of m↓/m↑ is about 2, as one expects from ideal cylinders.
The other notice is the numbers in bold.

1. The FDR% is a little high. However the steep portion of the istherm really throws a lot of scatter into the mix,
2. The pore size by ratio of $4V_p/A$ for the QM is off by quite a bit whereas the BET seems very good. However, the BET does not subtract the external area, so it is not 9.79 nm but around 13.3 nm. At any rate this does not seem to be a way of calculating pore size probably due to cross channels in the pores.
3. It is surprizing how close the NLDFT and the QM + *t* are, about 10.1 nm, considering all the uncertainties.

### *5.5 Conclusion about mesoporosity*

So the QM description holds up fairly well for mesoporosity. The question of what the relationship is between the adsorption and desorption branches that are not due to energy shifts, seem to be promising. The nearness of the "magic point" may interrupt this picture as it has for flowing systems as pointed out by Basmadjian[10]. There are many cases in the literature where the classical method seems to work, even if the isotherm is misinterpreted.

The ratio of adsorption versus desorption for this sample seems reasonable, but for some others the ratio is lower than 2, more like 1.5. This explanation is obvious to simple. More work is needed on this.

It was not surprising that the NLDFT since the NLDFT does not need the BET to create the correct answer.

There is a need for better and more data to test.

Overall this approach seems promising. Oh, and congratulations, mesoporosity is the hardest section.

## 6 Heats of adsorption simulations

### *6.1 Some Easy Thermodynamics*

Much of this section will deal with the data by Dr. W. Thomas Berg[15], whose data was simultaneous isotherm measurement and adiabatic calorimetry. The equations used are list above in Appendix on QM,

$$\Delta_{\mathbf{l}}^{\mathbf{a}}\,\bar{\mathbf{E}} := \bar{\mathbf{q}}_{\mathrm{la}} = RT\,\mathbf{exp}(-\chi) \equiv -RT\,\mathbf{ln}(P\,/\,P_{vap}) \qquad \mathbf{(29)}$$

which is **Equation (50)** for the reference state as the adsorptive vapor pressure at the temperature of the adsorbent. For calorimetry this is modified with the heat of vaporization or **Equation (7) (see (57))**:

$$\bar{\mathbf{E}}^{\ominus}\left(\theta\right) = -\bar{E}_{\mathrm{a}}\,\mathbf{e}^{-\theta} + \bar{\varepsilon} \qquad \mathbf{(30)}$$

Where the primsoll symbol indicates the thermodynamic standard state. The treatment here assumes no heterogeneity or other complications, so this is some deviations at low pressures.

### *6.2 The Berg data[15].*

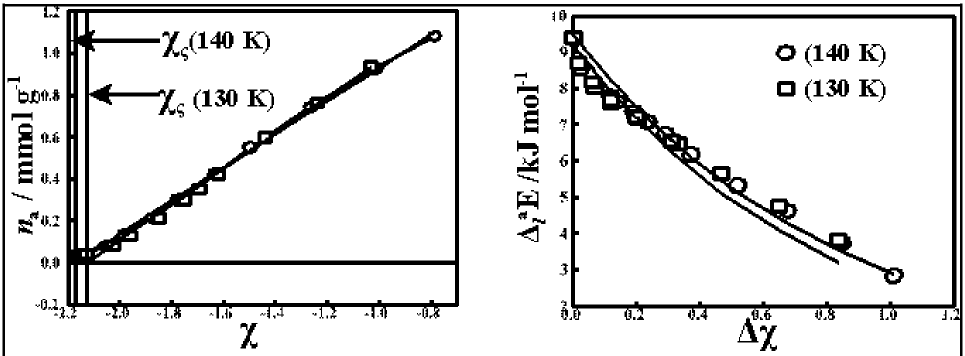


**Figure 19** Data by Berg of Kr on Anatase. On the left is the $\chi$-plot which yields 2 parameters that are use to calculate the theoretical lines on the right plot. There are no fitting parameters for the right graph.

Dr Thomas Berg measured the adsorption of Kr on anatase using calorimetry and isotherms determination on the same sample in the same instrument. The results of his experiments are given in **Figure 19**. In order to obtain the answers he also had to measure the heat capacities of the adsorbate, which is quite difficult, as well as the adsorbent.

There have been other attempts measuring the heats of adsorption that are not as convincing due to separated measurements and lack of adsorbate heat capacities. A review of these attempts has been provided in the open literature[16]. Since the preparation of the surface is critical and the duel measurements are difficult it is understandable why other measurements are inconsistent. In addition, the theoretical background was also not available.

Those familiar with calorimetry will recognize some problems with obtaining the differential heat here:

1. by taking digital differences one naturally loses one data point and there is a distortion due to this at the beginning of the data fit.
2. The assumption is made that there is a straight line segement between the data points and the average value is coupled with the average of the two data points. This assumption is basically incorrect since the line is curved. It helps somewhat to do this on a $\chi$-plot, but the mathematics is not strictly correct.
3. The isotherm indicates some heterogeneity which is not very obvious from the graphs displayed here. The heterogeneity is more obvious on the right

The entropy of adsorption for the first layer was taken into account. The entropy is for the loss of 1 translational mode for the first schicht. The other thing that is noticeable is that fits in the $\chi$-plot are identical. This because the $\chi$-plot is energy base and the $\Delta\chi$-plot is amount based.

### *6.3 Conclusions about Heat of Adsorption*:

With only one set of data measureing both the isotherm and heat of adsorption on the same sample and adsorptive simultaneously, it is hard to say this subject is settled. Hopefully, this is just a start. If this analysis is correct the correction for heterogeneity seems easy, but what about the complication of micropores, hybrid adsorbents, mesopores and the hysteresis.

The problem of the lost of information in a digital differential heat might be solve by fitting the intergral heat. This could be done with the raw data. Differentiation of the fit would then provided a better picture, but this might be a bit naive.

## Modern Hypothesis of Physical Adsorption

For mesopore adsorption there should be a short burst of heat evolution in the ~ 5-400 J mol$^{-1}$ region given off by the conversion for schichten to film transition. The presence of the forming film should contribute to this burst. The broadness of the burst should depend upon the $s_\mathrm{p}$.

## 7 Binary isotherms

There is much room for further research in the area of binary adsorption.. Presented here is some suggestions for analysis, but the literature seems to lack good data to test against. The first suggestion is to approach it like the flowing systems analysis. In the flowing systems case the use of the Langmuir isotherm fit is used, the there is an assumption that one of the adsorptives predominate in the energy consideration. This adsorptive is called the "Henry's Law" adsorptive. (Although the "Henry's Law" has been proven incorrect, the suggestion seems to be a good guidance.) Although, the idea of a threshold pressure was not known at the time, it would make sense that it would usually predominate for the construction of the abscissa.

The logic is as follows:

- The adsorbate with the greatest exthermic heat (most negative thermodynamic heat from the system) starts at its threshold pressure to adsorb before the other adsorptive
- By the time the threshold pressure for the second adsorbate is reached, the first one has some density of adsorbate in the 1st schicht, but some in the 2nd and small amounts in higher schichten.
- This changes the adsorption energy for the second, thus also changing the threshold pressure for the second. This effect one should be able to calculate if one knew how shifted the $E_a$, similar to the effect of contamination of impurities being on the surface.
- For the rest of the adsorption, this initial adsorption predominates with smaller variations due to the second and higher schichten play and influence.
- This continues until the effect of the surface become negligible and the bulk interaction energies dominate.
- So, if the 1st schicht is the dominating energy interaction, it will be controlling the adsorption.

The predominence of the higher energy adsorbate is the basis of the proposed "Henry's Law" for binary adsorption[10]. It was proposed on the basis of observation and not on theoretical aspects.

## *7.1 Calculating the isobaric binary isotherm with the 1st schicht dominating:*

Logic above would indicate that the onset of adsorption and its continuation is governed by the more exothermic of the two adsorbates. In The following list is a procedure to take advantage of this for binary mixtures where the $E_a$s are different enough. This procedure would apply to a given total pressure and variation of stoichiometry. Notice that only the $\chi$-values associated with the lowest $\chi_\varsigma$ value, listed as the "A" adsorbate, is used for plotting.

List of steps to calculate the binary diagrams when $\chi_\varsigma(A) < \chi_\varsigma(B)$, 1st schicht.

1. Do the $\chi$-plot for both adsorbates.
2. Create a graph with the abscissa as the $\chi$ for A.
3. Determine what total pressure you wish to have the phase diagram for. (call this p'.)
4. From the $\chi$-plots, determine which adsorbate has the lowest value of $\chi_\varsigma$. If this is difficult to determine, try determining the value of $\chi_\varsigma$ from the log-law plot.
5. The adsorbate with the lowest $\chi_\varsigma$ is adsorbate "A," labelled "$\chi_\varsigma$(A)"
6. Determine the value of $n_a$ from both isotherms of the adsorbates at pressure p'. Designated these $n$A(p') and $n$B(p')
7. Draw straight lines for A from ($\chi_{\varsigma,A}$,0) to ($\chi_{\varsigma,B}$ (p'), $n_A$(p'))
8. and for B from - ($\chi_{\varsigma,B}$ (on A!*),0) to ($\chi_{\varsigma,A}$ (p' (on A!*)),$n_B$(p'))

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

This appears a bit confusing, so there is a diagram below to illustrate.

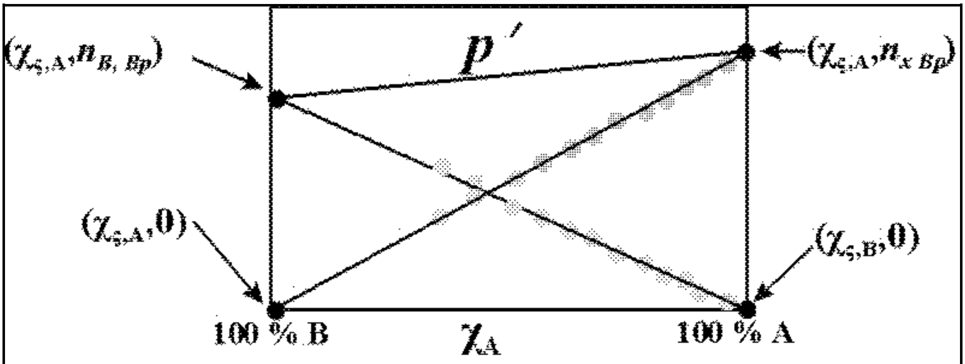


**Figure 20** An illustration of the technique described in the list above to analyze a binary adsorption phase diagram for the first schicht.

Faux data points are placed on the lines created. (Of only every analysis were so good.) Thus an isotherm for A and for B is all that is needed to make a prediction of the entire relationship in the phase diagram, that is to fill in the real data point for the faux. The big gap from the left most single point to the pure isotherm of B is quite typical. The reason will be obvious when one looks at the final binary diagram. (Just for fun try to using the $\chi_B$ as the abcsissa.)

This is not normally the way the diagram is shown. So, some manipulation is yet to be done.

*7.2 Isobaric by Danner and Wenzl*[17] *- Illustrating the method*:

The data by Danner and Wenzl is reasonably precise to make some tests. The data being analyzed by Danner and Wenzl was for the gases CO, $N_2$ and $O_2$ on 5A and 10X zeolite. The temperature was 144.3 K. The $P_{vap}$ was calculated from data by Clayton and Giauque[18] for CO2 and Streng[19] for $O_2$, which has some uncertainty. For $N_2$ the Dortmund data base, mentioned previously, was used.

There are, however, some uncertainties about the extrapolated $\chi_\varsigma$, but they are good enough to tell which one is dominate. The binary phase diagrams were obtained at 1 atm, which is probably within the range where a one monolayer equivalent is being adsorbed. Thus, to find the $\chi_\varsigma$s, a log-law

might be useful. Therefore, both the $\chi$-plot and the log-law were used and a judgement as to which is clearer in the determination was made.
The graph in **Figure 21** used the real data from Danner and Wenzl for $N_2$ and $O_2$ on 5A zeolite for illustration. Other combinations were similar. The binary diagrams were created at one atmosphere, but $P_{vap}$ for the adsorptives were quite high at the temperature used of 144.7 K:

$P_{vap}(O2) = 29.96$ atm
$P_{vap}(N2) = 55.28$ atm
$P_{vap}(CO) = 45.97$ atm

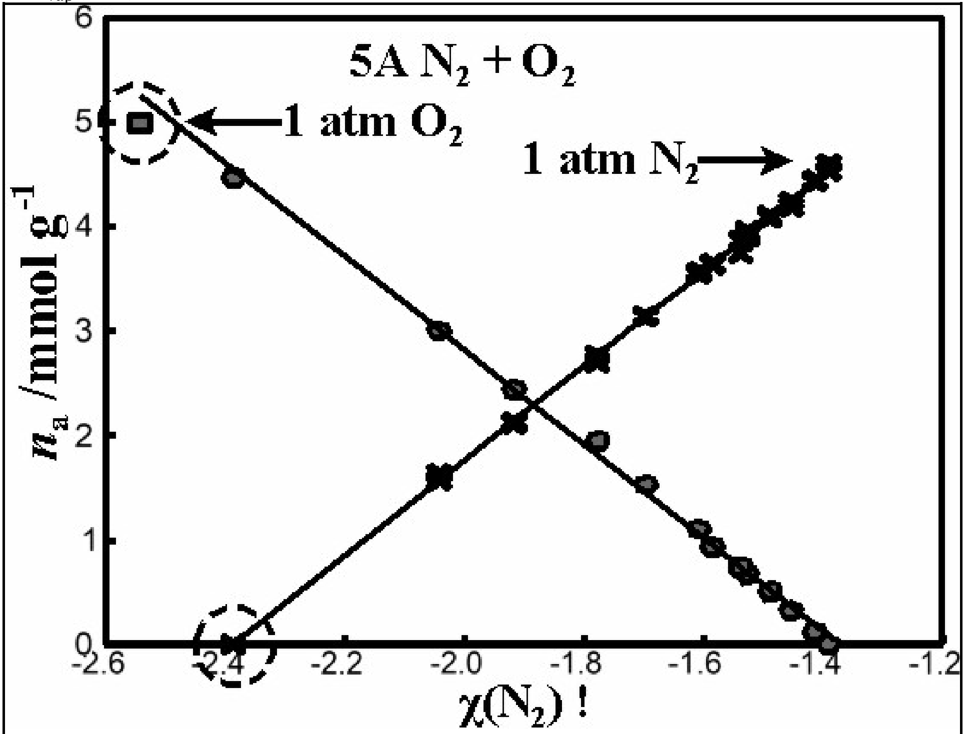


**Figure 21** Data by Danner and Wenzl of $N_2$ and $O_2$ adsorbed on 5A Zeolite. From data by permission from AIChE Journal, Wiley Press.

In **Figure 21** the rearranged binary data plotted on a $\chi$-plot using only $N_2$, the adsorbate with the lowest $\chi_\varsigma$ as the abscissa. This yields two straight-line fits to the data. Normally, the line could be defined solely by the value at the upper pressure and the $\chi_\varsigma$s. (Data used with permission from AIChE.)

Thus, this data was undoubtedly below mesopore considerations and there was no indication of observed mesoporosity. Indeed, the isotherms up to 1 atm is for only about one monolayer equivalence. In **Figure 21** the straight lines are determined by a linear regression to the data. This is not the normal method but rather an illustration by **Figure 22**.

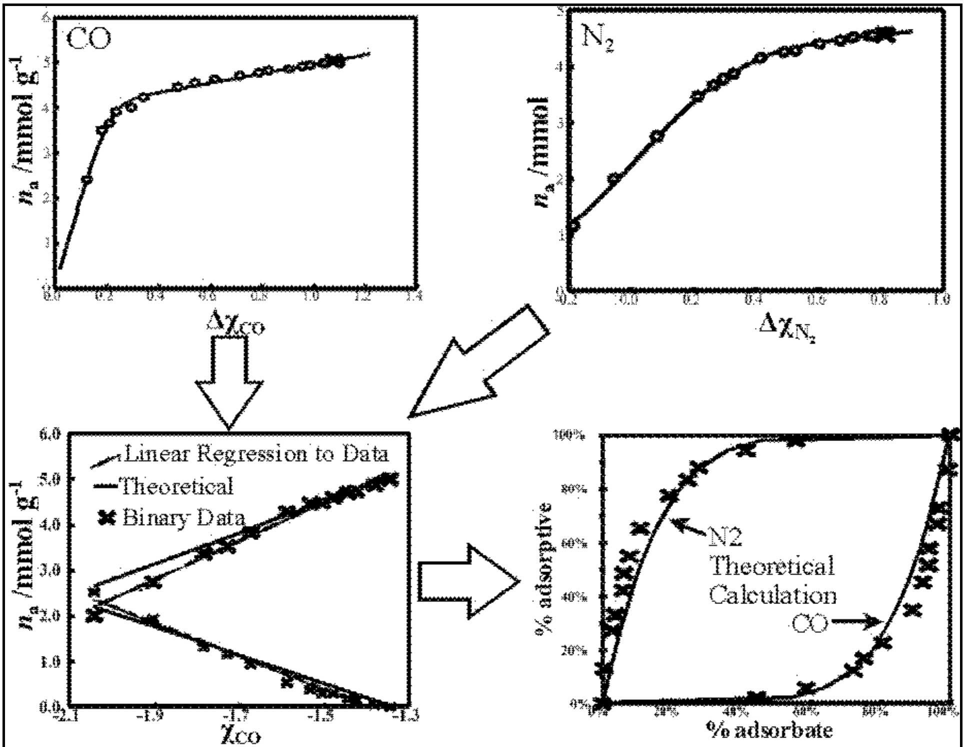


**Figure 22** Description of how the individual predictions are redisplayed into a phase disgram. CO and $N_2$ adsorbed on 5A Zeolite by Danner and Wenzl.

**Figure 22** is the full experimental method using the 5A zeolites and adsorbing CO and $N_2$. The lowest $\chi$ values are left off in this figure, but the high and low values are all that is needed to yield the straight line, as evident in **Figure 22**. Thus, the only points that need to be measured is the adsorption at the designated pressure, in this case 1 atm, and the determination of the $\chi_\varsigma$s. However, these points are difficult to determine with just the observation without the isotherm, especially the $\chi_\varsigma$s.

Probably, the extrapolation of several data points in the low-pressure region is needed. (Although, there might be a yet-to-be-exploited experimental method to find these values quicker. Up to now, there does not seem to be a reason to do so.)

**Figure 22** Shows how to construct the binary adsorption isotherm from the individual isotherms. The black lines are the $\chi$-prediction and the grey lines are for the linear regression. Here the isotherms of $N_2$ and CO are used to calculate the binary phase diagram at 144.7 K and 1.00 bar. The log-law is used for both to make it easier to extrapolate to yield the $\chi_\varsigma$s.

In **Figure 22** the six steps are shown for the method to measure the isotherms for $N_2$ and CO. Using the maximum and minimum points (black lines) one extracts the values, pressures and amount (as in **Figure 21** and **Figure 22** ) and plot them on the binary diagram. If one has the full isotherms plotted for the lower left, one can get a more accurate binary diagram by using a regression analysis for this figure. However, this may not be available, so the final high and low points must suffice, that is, the 4-point method, is used.

Notice that in **Figure 22** the $\chi$-plot values for the 4-point binary diagrams are normally a little imprecise when combined to the binary. On the other hand, the linearity of both regression plots on the bottom-left are fair, with a standard deviation of about 1.3 % FDR. This is slightly out of the $\chi$ imposed criterion of 1.0 % FDR, but it is certainly an advance over past efforts. There is, however, considerable data scatter, especially for the $O_2$ isotherm as is evident in **Figure 22** upper left. One would not expect high precision starting with low precision data. Without high resolution with the starting individual isotherms, the results are only crudely approximate. However, the improvement in the scatter when the binary plots are made is an interesting phenomenon, which provides hope for improvement.

### *7.3 The whole data set from Danner and Wenzl*

Using the entire data set from Danner and Wenzl[17], one can see how precise the present state of the art is. In **Figure 23** and **Figure 24** below then is all six of the binary experiments. Most of the predictions were fairly good except for $N_2 + O_2$ on 10X.

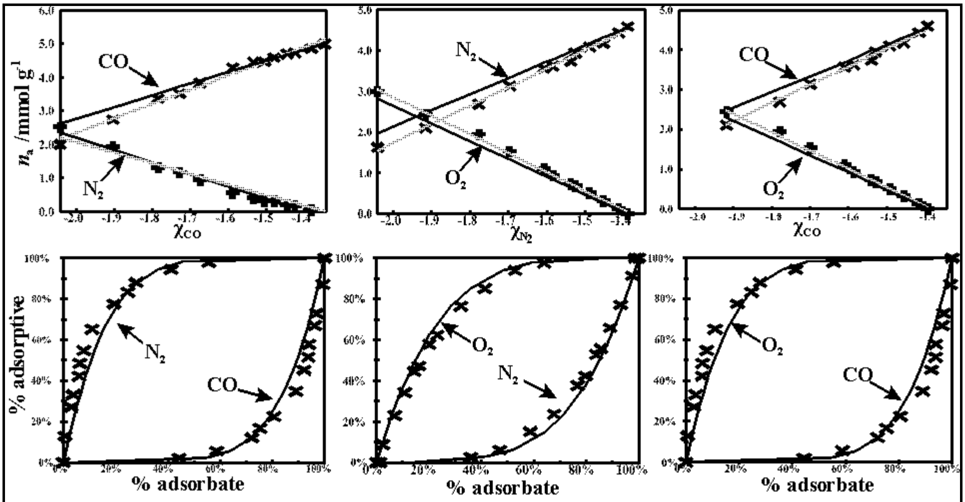


**Figure 23** The binary analysis for CO, $N_2$ and $O_2$ on 5A Zeolites. Data is by Danner and Wenzl.

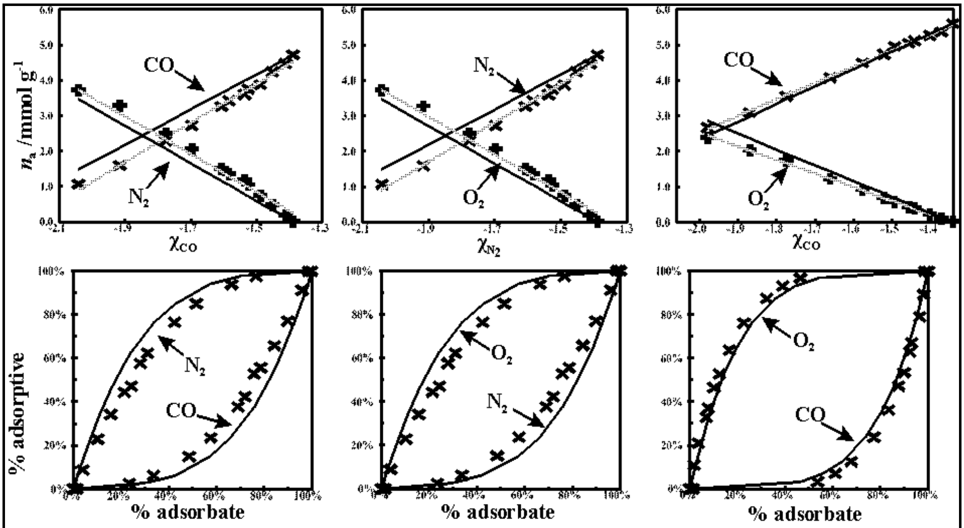


**Figure 24** The binary analysis for CO, $N_2$ and $O_2$ on 10X Zeolites. Data is by Danner and Wenzl.

This method works fairly well but there is no question that these are monolayer equivalent or less adsorption. It probably does not work this way for higher coverages when the adsorption layer is more like the bulk mixed liquid. Perhaps that needs to addressed schicht by schicht.

## Conclusion:

This method works fairly well but there is no question that these are monolayer equivalent or less adsorption. It probably does not work this way for higher coverages when the adsorption layer is more like the bulk mixed liquid. Perhaps that needs to addressed schicht by schicht.

This is all for now. For those of you who are taking this seriously, congratulations. You truly have an open mind and you probably will successfully discover new ways to calculate physisorption. If you stick with it you will discover:
- many things that are not explained here,
- perhaps many concept made here and/or
- many new uses and substitutes and quicker ways of approaching the solutions.

I wish you all the best and good luck.

JBC

## A1 Appendix I Definitions and Symbols:

### *A1.1 Definitions:*

Adiabatic: Measurement made with no net loss or gain of heat.

Adsorbate: The material adsorbed from the gas. Adsorbate and adsorptive are the same component.

Adsorbate: the amount that is adsorbed and is the same component as the gas phase.

Adsorbent: The solid material upon which the gas adsorbs.

Adsorptive: The gas phase that is the same component as the adsorbate.

Adsorptive: The gas phase of the component that is adsorbing

Calorimeter: An instrument used to follow heat transport from the surroundings to the system. Can be adiabatic or isothermal.

Core radius: The radius of the empty volume that is formed after the QM - classical collapse, $r_\mathrm{p}$

Grand Canonical Partition Function: The energy exchange calculation for an open system. (GCPF)

Gravimetric: Measurements made using a balance

Homogeneous: the surface of the adsorbent is chemically uniform in all ways that might affect the adsorption.

Isotherm: The output of an isothermal experiment.

Isothermic: (or isothermal) Measurements made at constant temperature.

Knudsen effect = an effect that a temperature gradient has on the pressure of a gas. Usually noticed with small diameter vacuum tubing.

Microbalance: A balance that can detect changes in mass to one part in a billion of the sample weight. The total mass is usually measured before loading the sample on the microbalance.

Monolayer: is the amount of adsorbate that, if it were all in contact with the adsorbent, would exactly cover the surface

Monolayer equivalence (equiv): The unit for the amount in terms of monolayers - CAS standard not IUPAC

Open System: A system with interchange with surroundings of heat, work and matter is possible.

Potential thickness: The classical thickness, *t*, that a dispursed film were to have after compaction to a layer that has the density of the liquid adsorpent (at the temperature of the adsorbent.)

Pore radius: The radius of the pore from one wall of the adsorbent pore to the opposite wall, $r_p$

Schicht number: The schicht cardinal number is determined by how many adsorbate molecule are between it and the surface minus 1. The molecule on the surface is in the 1st schicht. A molecule touching a 1st schicht molecule is in the 2nd.

Schichten: Translates here as strata (singular: Schicht.) In classical physisorption the word "layers" is used implying dense layer are formed. A schicht in QM means density compared to $n_m$.

System: (Thermodynamics) a delineated place in physical space defined to be consistent with a logical item, in this case it is adsorbent plus adsorbate.

Steric Hindrance: hindrance of chemical action ascribed to the arrangement of atoms in a molecule.

## Modern Hypothesis of Physical Adsorption

Symbol **:=** means “by definition”

Surroundings: The physical space around a system that can interact with the system. For physisorption the surroundings includes the adsorptive. Other surrounding components may not be relevant.

System: A defined closed physical volume upon which the experimental measurements are arranged from the surroundings, For physisorption the system is the adsorbent plus adsorbate.

Virtual monolayer: The measure of amount of adsorbate that if compacted as liquid would have a film thickness of a classical layer.

Virtual space: The space that is devoid of adsorbate if the schichten were to collapse into a dense liquid (at the temperature of the adsorbent.)

Virtual thickness: Same as potential thickness.

Virtual volume: the volume that the diffuse film would fill if it were to collapse into a dense liquid (at the temperature of the adsorbent.)

*A1.2 Symbols:*

A1.2.1 English: Change in quantities using Δ are in the Greek.

$A$ = ("Specific" if per gram) surface area using the IUPAC convention to convert from $n_a$
$A_{BET}$ = area calculation by BET theory
**D** = The Normal Cumulative distribution function
$E$ = (QM) The total energy of a particle (adsorbate molecule)
$E_a$ = The preëxponential in the heat of adsorption function
$\overline{E}_a$ = The preëxponential in the molar heat of adsorption function usually in kJ mol$^{-1}$ but occasionally in J mol$^{-1}$ especially above $\Delta\chi = 0$.
$E_p$ = The energy for the mesopore peak
$E_p\uparrow$ = " " " " " " for adsorption
$E_p\downarrow$ = " " " " " " for desorption
$E_N$ = the energy of adsorption of the N$^{th}$ molecule.
$\mathbf{E}^{\ominus}$ = The thermodynamic internal energy at 1 bar (standard internal energy)
$G$ = Correction parameter for an incorrect reading for $P_{vap}$.
$\hat{H}$ = The Hamiltonian operator
$R$ = The gas constant - units J mol$^{-1}$ K$^{-1}$ or kJ mol$^{-1}$ K$^{-1}$
$n_a$ = amount adsorbate - usually in mmol g$^{-1}$ or µmole g$^{-1}$
$n_j$ = amount of adsorbate in the j$^{th}$ schicht.
$n_m$ = amount adsorbate in a monolayer equivalence, units "
**N** = The normal Distribution Furnction
$P$ = pressure units bar
$P_{vap}$ = Vapor pressure of adsorptive at the temperature of the adsorbent
$P_\varsigma$ = The threshold pressure
$\mathbf{q}_{la}$ = the differenetial heat of adsorption referenced to the liquid stata at the temperature of the adsorbent.
$r_p$ = pore radius measured from adsorbent edge to opposite edge of the adsorbent
$r_c$ = the "core" radius, measurement from virtual adsorbent inner edge to opposite inner edge.
$s$ = The spread of the normal distribution, in statistics its called the standard deviation
$V_{BET}$ = total pore volume by classical means, BET or Gurvitsch based
$t$ = Either classical monolayer of virtual monolayer thickness

**Z** = The stitistical “area” function, the integral of the cumulative normal distribution function

### A1.2.2 Greek:

$\delta$ = a very small increment
$\varepsilon$ = Heat of vaporization of the adsorptive at the temperature of the adsorbent
$\Delta\chi = \chi - \chi_\varsigma$
$\Delta_l^{a}\mathbf{E}$ = The internal energy function change from the liquid state to the adsorbed state at the temperature of the adsorbent
$\Delta_{a}^{\gamma/lg}E$ = the energy at which the Kelvin (or other) equation and the $\chi$ energy match.
$\Delta_l^{g}H(N_2)$ = Enthalpy of vaporization of $N_2$
$\Delta_l^{a}\mathbf{S}$ = The entropy change in the system going from a liquid to adsorbate.
$\Delta\chi = \chi - \chi_\varsigma$
$\varepsilon$ = energy of vaporization,
$\overline{\varepsilon}$ = molar heat of vaporization
$\theta$ = The coverage, $n_a/n_m$
$\theta_N = n_N/n_m$ the amount in the Nth schicht compared to 1 monolayer equiv
$\chi$ = **-ln(-ln**$\{P/P_{vap}\}$) a vaiable
$\chi_\varsigma$ = **-ln(-ln**$\{P_\varsigma/P_{vap}\}$) a parameter
$\psi$ = (QM) the wave function
$\psi^*$ = (QM) the complex conjugate of the wave function $\psi$
$\sigma$ = standard deviation.
$\sigma_{fit}$ = standard deviation of the isotherm fit
$\sigma_{FDR}$ = standard deviation as a percent relative to the full range of the data.

### A1.2.3 Other:

$\langle X\rangle$ = (when not QM) aveage of $X$
$\langle X|Y\rangle$ = vector multiplication
↑ = for adsorption
↓ = for desorption

### A1.2.4 Subscripts

m = “monolayer equiv”

n. = *n*th schicht

A1.2.5 Superscripts:
$^{\ominus}$ (primsoll) = designates the thermodynamic standard state.
¯ (overline) = designates the quantity is molar (IUPAC alternative)

A1.2.6 A&A (Acronyms and Abbreviations):

BET = Brunauer, Emmitt, Telle
FDR = (percent of) Full Data Range
GCPF = Grand canonical Partition Function.
HV = High Vacuum ($1.3\times10^{-3}$ to $1.3\times10^{-6}$ Pa or $1\times10^{-5}$ to $1\times10^{-8}$ Torr)
IUPAC = International Union of Pure and Applied Chemistry
JKO = Jaroniec, Krug and Olivier
NASA = National Aeronautics and Space Administration
NLLS = Non-Linear Least Squares
ND = Nguyen and Do
QM = Quantum Mechanics
SSLR = Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso
UHV= Ultrahigh Vacuum ($1.3\times10^{-7}$ to $1.3\times10^{-9}$ Pa or $1\times10^{-9}$ to $1\times10^{-11}$ Torr)

## **A2 Appendix II: The disproof of the "Henry's Law"** isotherm theories and some others.

### *A2.1 Henry's Law*

First, it must be stated that "Henry's Law" for physical adsorption has no relationship to Henry Law, which is normally applied to solutions. The words "Henry's Law" was arrogated from solution thermodynamics and must have a companion law "Raoult's Law" that is coupled by thermodynamics. Thus "Henry's Law" is not appropriate for physical adsorption. The psychological effect of its application is to require it for any theory, and indeed at times was specified by SIO/IUPAC as a requirement until SIO 2022.

So what is "Henry's Law" for physical adsorption. This states that the isotherm of $n_a$, amount adsorbed, and the pressure, $P$, of the adsorptive are at low pressure proportional and $P$ goes to 0 is and only if $n_a$ goes to 0.

$$P/n_a = C \text{ and } \lim_{n_a \to 0}(P) = 0 \qquad \textbf{(31)}$$

Another way of saying this is the isotherm theory must pass to [0,0]. To get away from the misnomer the symbolism [0,0] will now replace the words "Henry's Law"

The list isotherm theories that require this is quite long, most prominent are the BET and Langmuir theories. However there are many more including modification of these two, addition of separate isotherm, raising some or all of the terms to a power (exponent). Several of these last proposals violated the consistency of units.

### *A2.2 How to disprove a theory:*

There are three principal way of disproving a theory. They are:

1. In light of a new theory, which yields the same output parameters or fewer, the theory is statistically much worse. The word "much" is meant to means that by any statistical measure or test the old theory turns out to be obvious worse and not just worse by statistical tests, such as the "F" test , etc
2. The theory predicts something that experimentally is not true. In this

case the [0,0] law is predicted.

3. The theory predicts an anomaly.

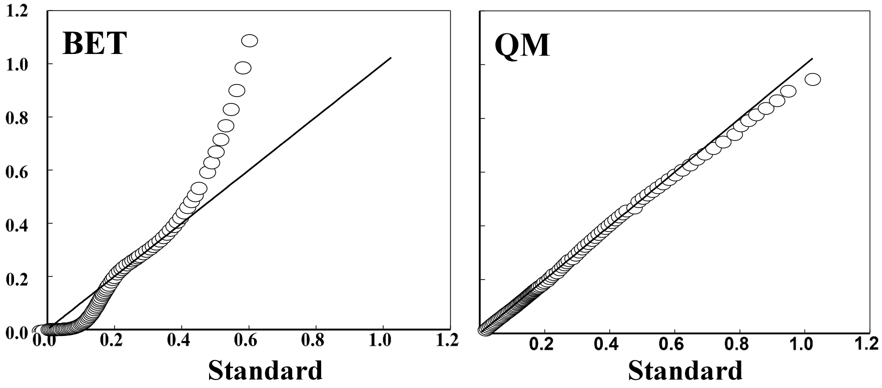
The third option does apply here but the mathematics is a bit difficult and complicated. Only the first two will be addressed.

*A2.2.1 #1 Statistics*:

Standard Curves for physical adsorption have been used since 1928. The idea is to find a pure, nonporous adsorbent and carefully measure the isotherm. This will be used as a “standard” against which other isotherms will be compared. It seemed obvious that any material of the same chemical composition would behave very close to identical in the isotherm. Therefore if a sample is identical chemically but the size of the particles are different, then a ratio be the sample to standard is the ratios of there surface area. There are some glitches in this idea but it is not important here for what is presented

What is presented is the comparison of theoretically calculated fits of the isotherm against the standard. Obtaining a good standard is not an easy task and eliminating all the experiment errors is also surprisingly difficult. However a recent standard produced by Jeroniac, Krug and Olivier4 (KJO) seems to be well done with the temperature control problem solved.

If one were to plot the standard against itself, obviously what you get would be line where the abscissa values ($x$) and the ordinate values ($y$) are



The comparison of the BET vs. QM fitting a standard curve.

the same. A good theoretical fit should do about the same with a line going nearly through the sample line. The better to do this, the better are the statistics. In **Figure 25** are two graphs. One on the left is the fit of the BET and the one the right is the QM fit as described in this book. Both of these are the 2 parameter fits. The BET cannot be expanded past this, whereas the QM can be.

The very large deviation of the BET after 0.3678... is well known and is discounted using some criteria to find where it deviates. The deviation below about 0.2 is not so well known, at least in the literature. Between 0.2 and 0.3678... the line does a fair job of fitting, but not as well as the QM. However using the BET "transform" on the ordinate yields a better fit. This, however, is mathematically illegal since over a certain range it effectively plots the abscissa against itself.

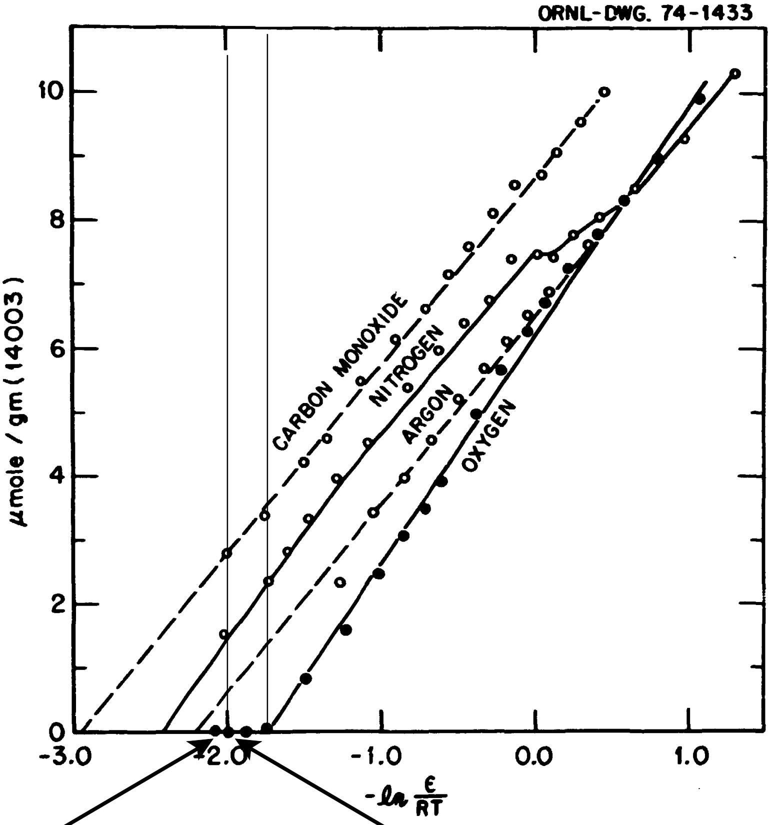
Thus, the BET fit is only statistically close over 16 % of the data, the other 84% is discarded either deliberately or some artificial criteria which has changed over the years to produce a lower standard deviation, in other words with mathematical trickery. It is hard to find any other discipline in science were such is allowed.

Notice, nothing has been determined about whether the BET answers are correct or not. Many experiment have be preformed in the past to determine this and that answer has always been high by a factor of 2 to3 when above 0.2. However, below 0.2, the answers are always low by a factor of 2 to 3. Looking at the graphs, one can see why.

*A2.2.2 #2 the [0.0] fallacy:*

Obviously to see the problem at [0,0] one needs to go to $n_a = 0$. (Langmuir in his famous paper[6] reported a positive offset in $n_a$ for $P = 0$. This is clearly impossible and must have been experimental or extrapolation error.)

If one can find even one isotherm that yields a finite pressure when $n_a = 0$ then all [0,0] isotherms are disproved. This is the case with several isotherms recorded in the literature. The first example is by Fuller and Agron of common gases on lunar soil from the Apollo moon shot. The graphs shown in **Figure 26** were constructed before there was knowledge of the QM theory or any other explanation. As a fact, the puzzlement over the oxygen line was the beginning of Fuller's quest to find out about what was wrong with the BET.



**1.2 x $10^{-3}$ atm**
**~0.09 torr**

**~0.5 torr - BET low *P* criterion**

Fig. 3. Vapor sorption on 14003 at -196°C.

**Figure 26** the Figure 3 in the NASA report ORNL-5129. Reproduced with permission of Oak Ridge National Laboratory.

## Modern Hypothesis of Physical Adsorption

There had been many contradictions in Fuller's Lab[*] regarding the BET. He started to report all his results with the abscissa being **-ln**(*E/RT*) in agreement with Polanyi and deBoer/Zwikker. The reason that this worked was the realization that it is what one would expect from the admolecules would successively be perturbations. Thus, the adsorption from the liquid state had to have and entropy change of zero, as postulated in the Dubinin "thermodynamic criterion." In other words, the threshold pressure is the start of the liquid phase.

The arrows and pressure values in **Figure 26** are added for clarity. This points out that the reading were below the normal isotherm readings of 0.01 atm or 7.6 torr. This data was obtained with a microbalance system. (The glitch in the $N_2$ adsorption is probably due to an earthquake, not an uncommon occurrence in East Tennessee. This may have shaken some of the sample off the pan.) Thanks to some bureaucrat who set up the specs for the experiment, something unusual happened. Every step on every aspects of Appolo was overseen by at least two people with check sheets, so to be sure, the pressure range was fixed "too low.".

4. One example is not enough to convince most people so two more will be presented here. Although there are many examples from Oak Ridge, an accusation of bias is not unreasonable. There are others not associated with ORNL. These are reported in a book[2][**]. Furthermore above are two publications where the threshold pressure is obvious.

   There are three examples in the data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[6] (SSLR.)

   a. $N_2$ on at 77.4 K on activated carbon LMA233 with $X_\varsigma = 2.0 \times 10^{-7}$
   b. $N_2$ at 77.4 K on activated carbon DD52 with $X_\varsigma = 6.5 \times 10^{-7}$
   c. $N_2$ at 77.4 K on silica SBA-15 with $X_\varsigma = \sim 3.5 \times 10^{-6}$. This last one has two data points that are clearly $n_a = 0$

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[*] I have no idea how many isotherms Fuller's lab ran. I must be at least in the thousands. They also used many other certification methods including electron microscopic tomography, poresimetry, etc.

[**] See especially the hydrogen cleaned carbon and aluminia. The Teflon® experiment is also easy to do and also needs some cleaning routine.

d. The data by Nguyen and Do[5] (ND) in **Figure 33**. The $\chi$ plot is obviously headed to $n_a$, since in order for heterogeneity to create a quick a very sharp positive curvature a very unrealistic value of $s$ would be required.

e. Madani, Kwong, Rodríguez-Reinoso, Biggs, Pendleton (MKR-RBP) in **Figure 10** where the $\Delta\chi$-plots are shown with the value of -2.6591for the offset for $\chi_\varsigma$.

The evidence of the threshold pressure seems to actually widely visible in the literature, but totally overlooked. (That is, ignored in plain sight.)

A2.2.3 #3 *Another fallacy to contemplate.*\

The thermodynamic energy function $E = -RT\mathbf{ln}(P/P^{\ominus})$. The energy becomes lower and lower if there were no threshold pressure, and approaches -∞ if there is no entropy term to keeping it to doing so. So what is the entropy that qualifies for this continually negative approaching energy? Or, does the universe explode?

## A3 Appendix III Derivation of the resultant equations from QM

### *A3.1 Assumptions:*

The $\chi$ assumption, a specific use to QM, is reasonable for any theoretical chemist. The following is the simple case of only one type of adsorptive is measure. Going to binary mixtures gets a little more complicated although there are examples of simple cases. The assumption are that the wave function of an adsorbate particle may be separable into two geometrical parts is:

> Part 1 is parallel to the plane of the surface (*x,y*). This is the most important part and generates the isotherm. It specifies the amount of adsorbate molecules directly in contact with the surface and the amount in subsequent "layers." This term is in quotes because the word is a classical interpretation, but molecules are not distinguishable. It yields $n_m$, the monolayer equivalence from the isotherm directly without modeling or the use of standard plots. Furthermore, the heats of adsorption obtained from $\chi$ equations are in excellent agreement with those obtained by calorimetry.
>
> Part 2 is the wave function normal to the surface (*z*). From the "layer" amounts, one obtains an estimate of the amount that fills the pores from each "layer." This is calculated from Part 1. For actual vertical distance from the surface, one needs to assume an intermolecular potential, such as a Lennard-Jones potential to get the distribution between the "layers."

Notice that the Part 1 involves no input parameters. For a nonporous homogeneous surface, if the resulting equations are fit to the isotherm then there are two output parameters, $n_m$, and $E_a$. If porosity exists, Part II is used to convert the extra output parameters to radii and volumes.

### *A3.2 Part 1: The wave function parallel to the surface (x,y).*

First a reference to the thermodynamics of the situation. The thermodynamic system in question is the adsorbate plus adsorbent. Everything else is the surroundings, including the gas phase. The system is an open system, thus the grand canonical partition function needs to be used to obtain the thermodynamics and other properties.

**Figure 26** illustrates the potential used for the calculation of the [x,y]-wave functions. The energy for the adsorbate is referenced to a liquid reservoir at the same temperature. With the adsorption of the first molecule, the energy difference between the reservoir and the bottom of the potential well of depth $V$ is with a ground state $W^0(0)$. For simplicity it will be assume that $W^0(0) = 0$ (not necessary.) and a first perturbation at $E_1$ ($E_0$ - ε), which is designated by the letters "αa/$A$".

The simple QM starts with the Hellmann-Feynman theorem (HF) to yield the monolayer equivalence, $n_a$, and the internal energy function $\Delta_{la}\mathbf{U}(n_a)$. The first assumption is the a the commonly used "non-local" adsorption due to superposition. That is the potentials from the adsorbed (adsorbate) molecules and the periodic potentials of the solid adsorbent are represented by an overall average potential on the surface. The second assumption is the wave functions on the surface are separable into a two-dimensional function in the plane of the surface ($x,y$) and one normal to the surface ($z$.) Adsorbate molecules become part of the potential in both. Each new adsorbate molecule modifies the surface with its potential as seen in . This is a simple particle-in-a-box with a tooth instead of a supplementary hole.

There will be three shifts in the reference state for the energy. The first reference is the infinite box wall. The tooth perturbation, the first molecule adsorbed has an energyof β above $E_0$. subscripts indicate the energy level and number in parentheses for the entering molecule. There is no perturbation for this first molecule.

1. The 2nd adsorbed molecule see the potential as modified by the 1st. The size of the perturbation is the cross-section area of the 1st adsorbate molecule, $a$. Thus the perturbation is $a\beta$.
2. The 3rd by the combination of the 1st and the 2nd .
3. The 4th by the 1st , 2nd and 3rd , etc.

The admolecules are free to cove the whole surface as indicated by experiments that support the QM characteristics of large molecules.

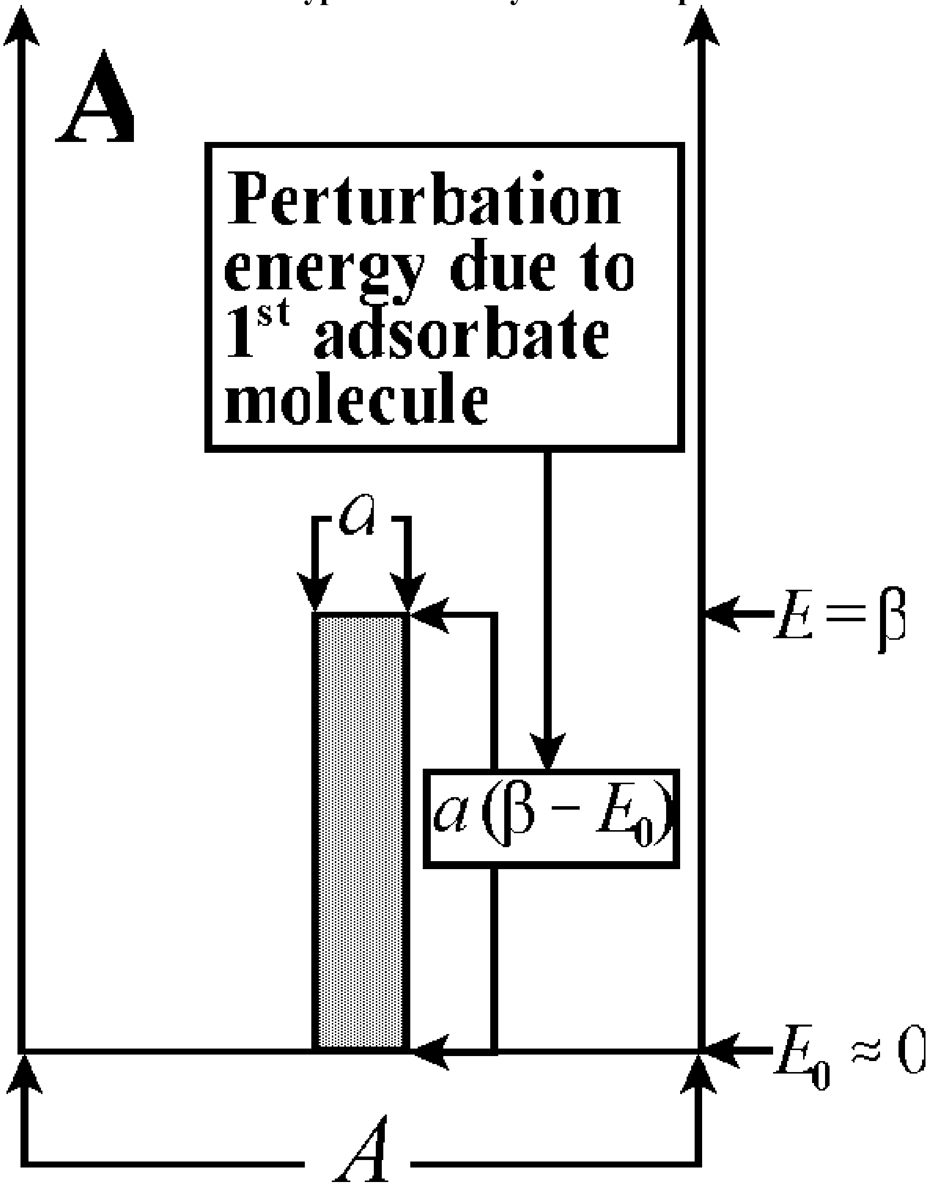
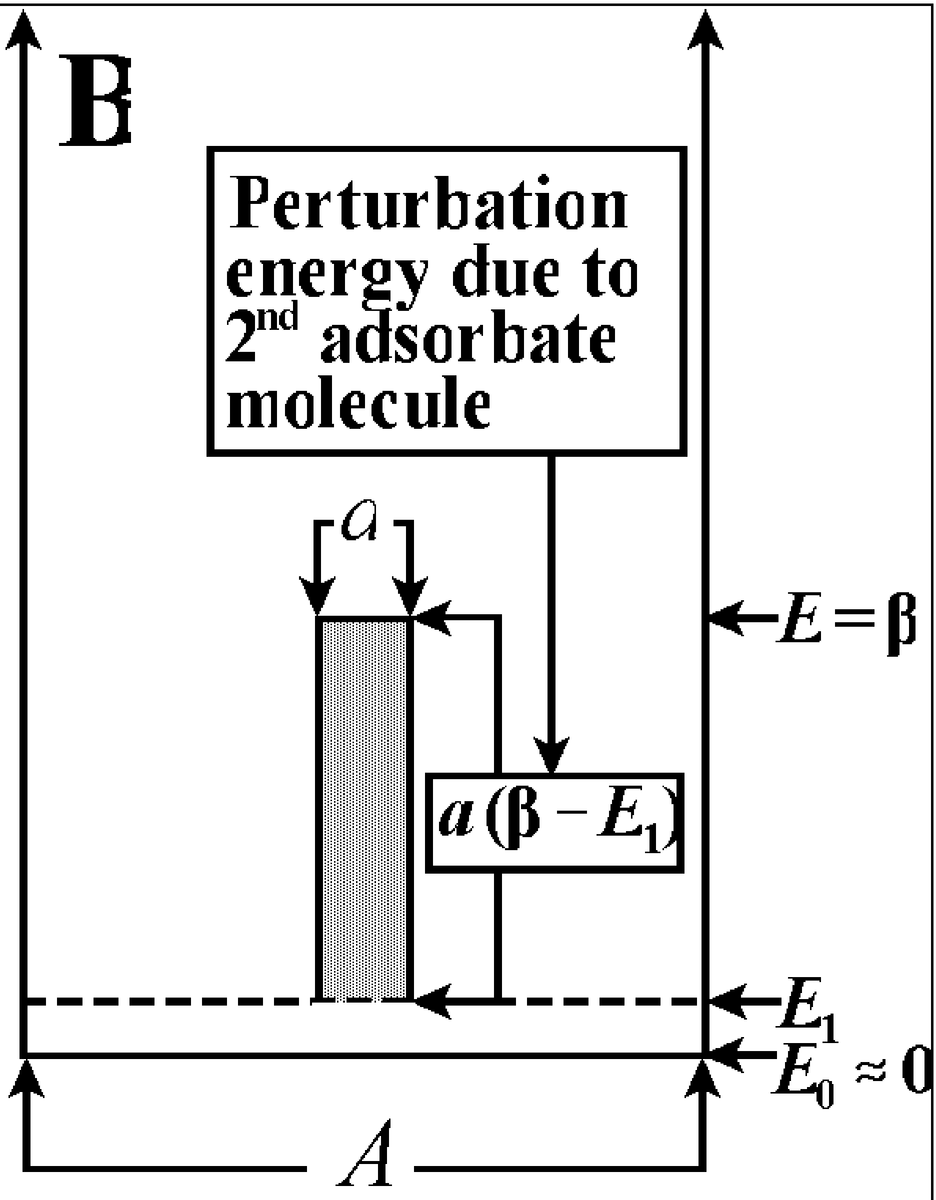
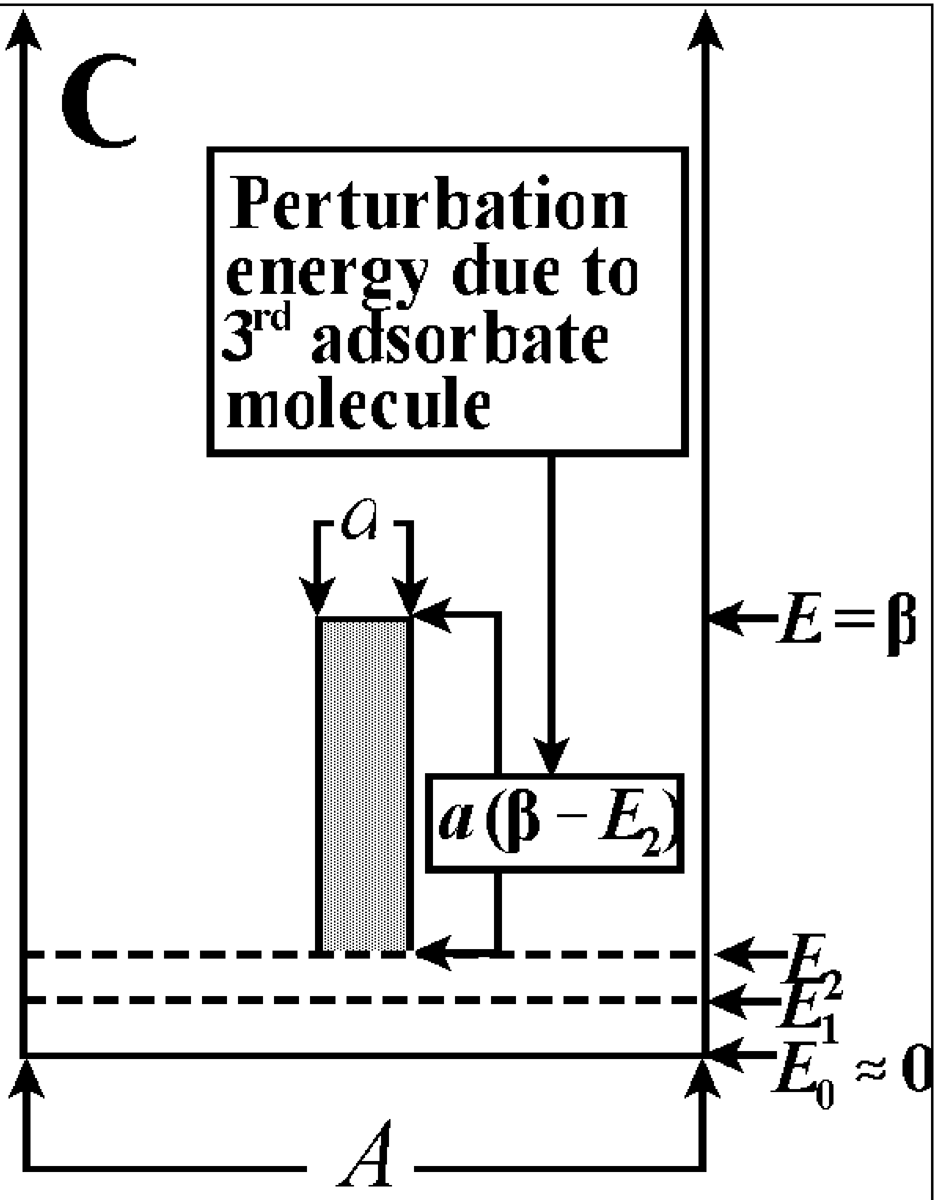


**Figure 27** The QM model with reference energy at the well bottom. The base energy for the first molecule is the base energy   It causes a perturbation of the amount in the box for the next molecule.



$$E_1 = E_0 + a(\beta - E_0)/A$$

**Figure 28** The base energy is higher because of the perturbation by the 1st molecule according to the above equation.



$$E_2 = E_1 + a(\beta - E_1)/A$$

**Figure 29** The 2nd molecule provides addition perturbation upon the base energy of $E_1$. This moves the base energy up some more.

The cross-sectional area of the admolecule, $a$, compared to the surface aliquots, $A$, is $a << A$, typically, $< 1:10^6$ the HF is applicable for the perturbation. Thus,

$$\langle \psi^* | \{E + \delta E\} | \psi \rangle = \langle \psi^* | \hat{\mathbf{H}} + \delta \mathbf{H} | \psi \rangle \tag{32}$$

and

$$E + \delta E = \frac{\langle \psi^* | \hat{\mathbf{H}} + \delta \mathbf{H} | \psi \rangle}{\langle \psi^* || \psi \rangle} = \hat{\mathbf{H}} + \frac{\langle \psi^* | \delta \mathbf{H} | \psi \rangle}{\langle \psi^* || \psi \rangle} \tag{33}$$

Looking at ? $\delta\mathbf{H} = \delta E$ and the total universe for this derivation is restricted to $A$, thus:.

$$E_1 := E_0 + \delta E = E_0 + \beta\alpha/A \cong \beta\alpha/A \tag{34}$$

But $E_2$ (3rd molecule) is ("completing the squares" to get the final answer):

$$\begin{aligned} E_2 &= E_1 + \alpha(\beta - E_1)/A = (\alpha/A)\beta + (\alpha/A)\beta - (\alpha/A)^2\beta \\ E_2 &= \beta - \beta(1 - \alpha/A)^2 \end{aligned} \tag{35}$$

Repeating this for the 4th molecule, one obtains:

$$E_3 = \beta - \beta(1 - \alpha/A)^3 \tag{36}$$

So, by induction:

$$E_N = \beta - \beta(1 - \alpha/A)^N \tag{37}$$

By definition, the "coverage," $\theta = n_a/n_m$, and since $N$ is a very large number, $N + 1$. $N$. By substituting $x = -A/\alpha$ and making it justifiably very large, and by definition of the **e** function[I]:

$$E_N = \beta - \beta\left\{(1 + 1/x)^x\right\}^{-\theta} = \beta - \beta\,\mathbf{exp}(-\theta) \tag{38}$$

This can be substituted into the Grand Canonical Partition Function (GCPT) since the normal physisorption experiment is a thermodynamic open system.

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[I] For the uninformed reviewer, this is right. Try plugging a few values into the $x$ in the {} and you will get closer to 2.718...the higher the number. Please excuse me, no intention of an insult, it just seems to be a stumbling block.

(For simplicity, the count has been shifted down.) Noticing that: $\theta = na/A_\mathrm{a}$ and usually the number of adsorbate molecules are at least in the range of nanomoles or O(1 × $10^{14}$) molecules, then the summation may, with a very insignificant error, be written as an integral. Furthermore, $A$/a is very large and the number of adsorbate molecules, $N$, is also very large. By definition $\theta = N\mathrm{a}/A$ which means $N = \theta A/\mathrm{a}$, thus by the definition of the **exp** function[I]:

$$\sum_{m=1}^{n} \mathbf{E}_n = \beta + \beta \int_{\tau=0}^{N} \mathbf{exp}(-\theta) d\tau \qquad \mathbf{(39)}$$

The question of the open "uncovered" surface now becomes for any particular $N$: (If you check this, remember this is exothermic and therefore the signs of the energies are negative.)

$$\theta_{MT} = \mathbf{exp}(-\theta) \qquad \mathbf{(40)}$$

The term $E_0$ is still quite small so shifting the standard state here to use the thermodynamic standard state with $\mathbf{E}^{\Theta}$ it makes little difference.

$$\Delta_l^a \mathbf{E}(N) \approx E_\mathrm{a} \int_{x=0}^{N} \mathbf{exp}(-\theta) dx \quad . \qquad \mathbf{(41)}$$

This shifts the standard state from the normal thermodynamic state to that used for the isotherm presentations. This will be more obvious with the Grand Canonical Partition Function, but here only the energy of adsorption portion of the equilibrium was given.

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[I] Yes, this equation is correct. When this gets plugged into the Grand Canonical Partition Function, the low values of $N$ do not apply and only $m$ near $N$ are important. So, anyone claiming that this approximation is incorrect needs to retake calculus.

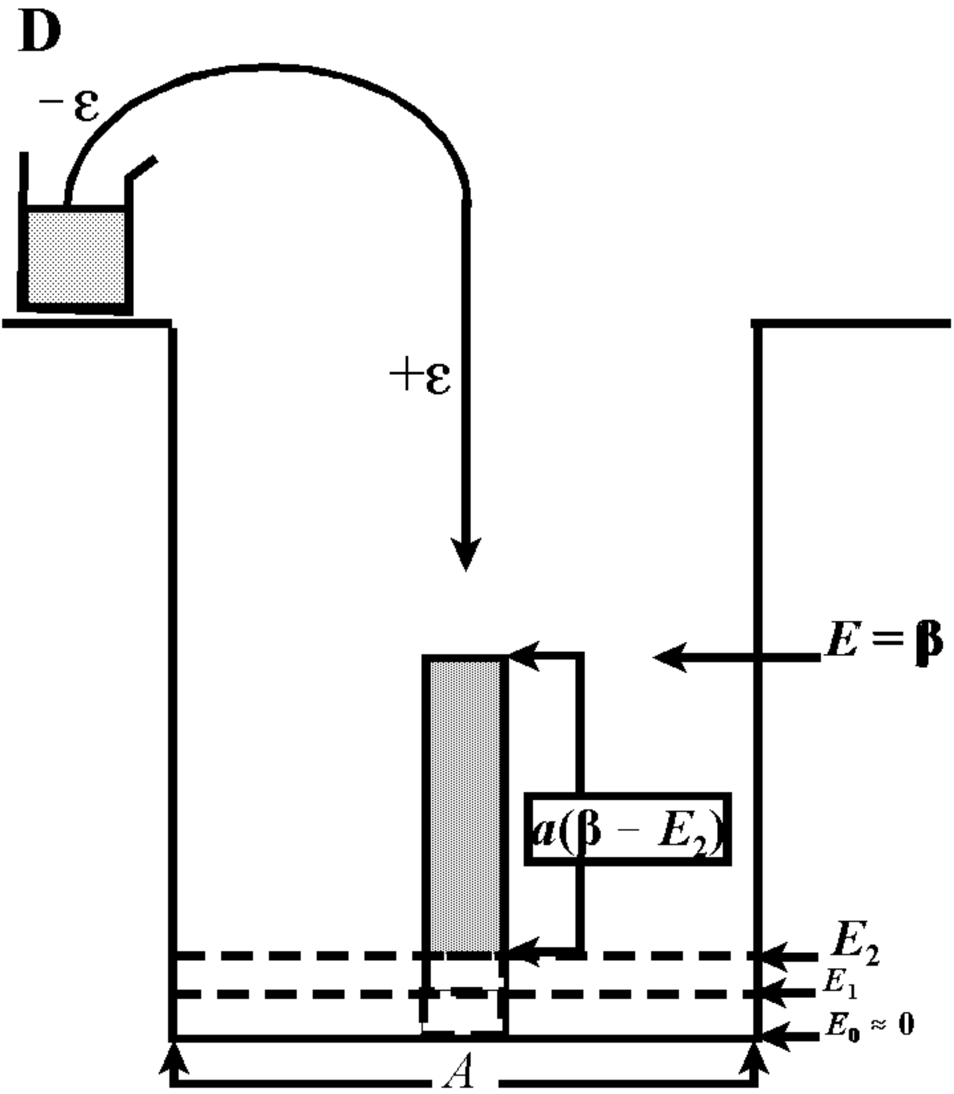

**Figure 30** The final energy reference shift. The other shift is from a vapor pressure of 1 bar, used for calorimetry.

### *A3.3 The Grand Canonical Partition Function (GCPF):*

Since there are no further QM problems to derive, the classical GCPF is used here. By including the canonical partician function in the GCPF, the shift to the vapor pressure for the relevant comparison state is implied as indicated in **Figure 30**.

The GCPF, which is appropriate for an open system, is:

$$\Xi = \sum_{N} (\lambda Z)^{N} \,\mathbf{exp}\left[ -\left( E_{\mathrm{a}} \int_{0}^{N} \mathbf{exp}(-\theta)\, dx - N\varepsilon + \tfrac{1}{2} NkT \pm N\,\mathbf{f}(T) \right) \Big/ kT \right] \mathbf{(42)}$$

The following are the meaning of the terms:

term 1: $\lambda Z$ this is the canonical partition function for the adsorbent = $\mathbf{ln}(\tilde{p})$, $\tilde{p}$ = fugasity but will be replaced here with standard pressure.
term 2: with the integral is equation **(41)**
term 3: $N\varepsilon$ - the interaction between adsorbate particles - assumed to be the same as liquid state
term 4: ½NkT - the loss in translation mode to 2D instead of 3D. This needs to be restricted to those molecule touching the adsorbent surface. This is very small but might be observed, but it needs modification to be restricted to the first "layer" by the calculation of $\theta_1$ - an advanced topic.
item 5: $N\mathbf{f}(T)$: changes in internal adsorbate modes such as rotation and vibration. This is mostly also for the first "layer."

A further consideration for calculating the surface area is the orientation of the adsorbate molecules, if they are not symmetrical.

Items 4 and 5 are ignored here. They are for advance topic consideration if at all.

Proceeding by differentiating the max term of the GCPF and setting to 0 to get the most probable state:

$$0=\frac{\partial\,\mathbf{ln}\left(\Xi_{\text{max term}}\right)}{\partial N}=\mathbf{ln}\left(\tilde{p}\right)+-\left\{E_{\text{a}}\,\mathbf{exp}\left(-\theta\right)-\varepsilon+\tfrac{1}{2}kT\pm\mathbf{f}\left(T\right)\right\}/\,kT \tag{43}$$

converting to molar amounts then and moving the pressure term to the left:

$$-\mathbf{ln}\left(\tilde{p}\right)=-\frac{\overline{E}_{\text{a}}}{RT}\mathbf{e}^{-\theta}+\frac{\overline{\varepsilon}}{RT} \tag{44}$$

As θ → ∞ the exponential term approaches zero and the last term approaches the **ln** of the vapor pressure. Thus, using $P$ in place of $\tilde{p}$ :

Substituting this information back into equation 45 and taking the **ln**:

$$-\mathbf{ln}\left(P_{\text{vap}}\right)=-\frac{\overline{\varepsilon}}{RT} \tag{45}$$

The point that disturbs most reseachers is that as θ →0, $P$ approaches a finite value. Thus, the QM derivation predicts that there is no change in the component, but there is a phase change at low pressures that is the precursor for the bulk liquid adsorptive. This phase change occurs when:

$$\mathbf{ln}\left(\frac{P_{\varsigma}}{P_{\text{vap}}}\right)=-\frac{\overline{E}_{\text{a}}}{RT}\quad\text{or}\quad P_{\varsigma}=P_{\text{vap}}\,\mathbf{exp}\left(-\frac{\overline{E}_{\text{a}}}{RT}\right) \tag{46}$$

with $P_{\varsigma}$ being referred to as the “threshold pressure.”

These equation can be expressed by the χ-transform of the abscissa,

$$\chi=-\mathbf{ln}\left\{-\mathbf{ln}\left(\frac{P}{P_{\text{vap}}}\right)\right\}\quad\Rightarrow\quad\chi_{\varsigma}=-\mathbf{ln}\left\{-\mathbf{ln}\left(\frac{P_{\varsigma}}{P_{\text{vap}}}\right)\right\} \tag{47}$$

with a definition of:

$$\Delta\chi=\chi-\chi_{\varsigma} \tag{48}$$

It can be written

$$\frac{n_{\text{a}}}{n_{\text{m}}}:=\theta=\Delta\chi\quad\Delta\chi\geq 0 \tag{49}$$

The subscripts “a” and “m” indicate “adsorbate” and “monlayer equivance” respectively. Obviously Δχ cannot be less than 0. This is a simple straight-forward equation with a simple straight line with the abscissa as χ or Δχ and $n_{\text{a}}$ for the ordinate. It does not fulfill the definition of segmented line as some have claimed, it is simply discontinued at $n_\mathrm{a} = 0$.

Equation **(40)** has further implication. If this equation specifies the portion of the adsorbent surface that is available for further adsorption, then the proportion of the surface that must be covered by at least the first "layer" is:

$$\theta_1 := \frac{n_1}{n_m} = 1 - \mathbf{exp}\left(-\Delta\chi\right) \qquad \textbf{(50)}$$

where the subscript "1" indicates the 1st layer and the subscript "m" stands for the monolayer equivalent. This can be rearranged to

$$n_1 = n_m + \frac{n_m RT}{\bar{E}_\mathrm{a}} \mathbf{ln}\left(\frac{P}{P_\mathrm{vap}}\right) \qquad \textbf{(51)}$$

which is the log-law. This shows in its purest form in a plot only if the micropores are restricted to allow only one monolayer equivalent from the onset of adsorption to $P = P_\mathrm{vap.}$ It will therefore not follow a straight from the start of adsorption, but rather a logarithmic curve - i.e. the log plot. If there is a 2nd layer, or a partial 2nd layer the $\chi$-plot will start out linear up to the distance where the 2nd layer is inhibited further. (This is assuming that the external surface area is insignificant.)

**Lemma 1: $n_1$ always approaches $n_\mathrm{m}$ in the log-law linearly even if to do so $n_1$ preempts adsorption in $n_2$, $n_3$,$n_4$...etc. and they decrease to make accommodation. This phenomenon is referred to as "cannibalization.**"

The series for the other layers follow the same pattern, for the same reason, and yields the following:

$$\theta_2 = 1 - \mathbf{exp}\left(-\Delta\chi + \theta_1\right) \qquad \textbf{(52)}$$

$$\theta_3 = 1 - \mathbf{exp}\left(-\Delta\chi + \theta_1 + \theta_2\right) \qquad \textbf{(53)}$$

$$\vdots$$

$$\theta_{n+1} = 1 - \mathbf{exp}\left( -\Delta\chi + \sum_{m=1}^{n} \theta_m \right) \qquad \mathbf{(54)}$$

$$\Downarrow$$

$$\therefore \theta = \sum_{n=1}^{\infty} \theta_n = \sum_{m=1}^{\infty} 1 - \mathbf{exp}\left( -\Delta\chi + \sum_{m=1}^{n} \theta_m \right) \qquad \mathbf{(55)}$$

The last equation can be proven correct for non-porous adsorbents. The easiest was to demonstrate it to ones satisfaction is digitally. Mathematical proof is difficult. This series of equation may be obtained by assuming any molecule in layer “*n*” sees and average energy for layers <“*n*’ along with the “empty” surface. This is one of the disprovables that this hypothesis possesses. How to test this is left for future researchers.

Historically, an identical equation which include equations **(46)** through **(49)** was derived by Churaev, Starke and Adolphs[11,12,13,14,20], although written differently. The first definition was assumed to be correct because of a minimum in excess surface work, or ESW, as a function of coverage which is the result of the half-life of the potential from the surface as the monolayer equivalence. However, the quantum mechanical derivation proves this assumption is correct.

Equation **(44)** yields Fuller’s(21) and Dubinin’s(22) observation that:

$$\Delta_l^{\mathbf{a}}\,\bar{\mathbf{E}} := \bar{\mathbf{q}}_{\mathrm{la}} = RT\,\mathbf{exp}(-\chi) \equiv -RT\,\mathbf{ln}(P/P_{\mathrm{vap}}) \qquad \mathbf{(56)}$$

This equation expresses the internal energy function change, $\Delta_l^{a}\bar{\mathbf{E}}$, for the change from the liquid at the temperature of the adsorbent to the adsorbate state. In this equation $\mathbf{q}_{l\mathbf{a}}$ is the instantaneous heat of transfer[I] or the “differential” heat. The second term in this expression is the Fuller expression and the last term is the Dubinin “thermodynamic criterion,” which was not acceptable in the literature because of the implication that $\Delta_1^{a}S = 0$, that is, the entropy from liquid state is 0. This criterion is correct according to $\chi$ hypothesis, with the exception of the loss of one degree of

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[I] Traditional but not present day IUPAC translational freedom ( ½*RT)* for molecules in direct contact with the surface. As mentioned above, this latter exception is usually a small, and unobservable, correction. Although, the data by Berg(*15*) seems to show this. For calorimetry, the normal thermodynamic internal energy function is use, $\overline{\mathbf{E}}^{\ominus}$, with the standard state as 1 bar pressure.

$$\overline{\mathbf{E}}^{\ominus}\left(\theta\right)=-\overline{E}_{\mathrm{a}}\,\mathbf{e}^{-\theta}+\overline{\varepsilon} \qquad \textbf{(57)}$$

*A3.4 Is this evidence of entanglement?*

The admolecules, once adsorbed, are indistinguishable. Thus, all the molecules will respond according to the Equation **(56)**. In other words, they are entangled. This is consistent with resent a publication by Wu, Fassioli, Huse, Scholes[23] on the subject where confined molecules are entangled in cavities. This has implication of how one views interactions near surfaces and pores. More studies are obviously needed along these lines, both for surfaces and for pores.

## A4 Appendix IV a short history of QM applied to physisorption

So, what's behind this book? It is a story that lasted 50 years starting in the mid 1980's, when the fitting problem was solved and the meaning of the new parameters became clear, until today because of journal rejections.

This book is based upon my experience, knowledge and discoveries regarding physical adsorption. I worked as a collaborators with Dr. E. L. Fuller, Jr.†, whose group ran perhaps of a thousand isotherms[I] or more isotherms, which were use for production quality control. It was Fuller who noticed that the BET not only did not work, but yielded the wrong answers for the surfaces area, which seemed to have no correlation to anything. Dr. Fuller determined that the Polyani theory did fit a majority of the time, even though the theoretical basis as uncertain and the surface area parameter was not obtainable. He started publishing on the basis of energy instead of relative pressure so the reviewers did not know what he was trying to get across. Thus, there is a record of some of his work in the open literature. When I had to use the BET and it created weird results, I consulted Dr. Fuller about it and also Dr. John Kirkpatrick, a world famous mathematician. Dr. Kirkpatrick discovered and anomaly in the BET, which meant that it had to be abandoned. When I wrote about the anomaly in an attempted publication, the reaction of the reviewer was, "This is ridicules." I agree the statement but not the target. Unfortunately, there did not seem to be an answer to my problem so it was not used in

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[I] In this respect, JBC engineered and constructed the UHV capable microbalance system used by the laboratory analytical labs for physisorption. Incorporated into the system are method to avoid the first five **Big Errors.** Thus, the vacuum obtainable was $10^{-12}$ bar for UHV, the hang-down tube was 1 m long to avoid problems with the temperature gradient zone, the temperature detector was a gas-liquid thermometer close to the sample, baffles were used place in such a way that radiant heat could not shine on the surroundings of the adsorbent and multiple diaphragm pressure detectors reading 0.1% were used for reading $10^{-6}$ bar to 10 bar were used. A computer was used to record pressure, temperature, weight gain and other diagnostics. Importantly, earth quake detectors were available and connection to the office that keeps track of blasting in the area was maintained. The lab ended up with one microbalance that weighed a 1g sample and 5 microbalance that weighed 10g that were also capable of pressure up to 25 bar. Each balance had the sensitively of $1:10^9$ (1 ppb).

the since I have multiple micrographs of the material proposed publication.

In summer 1986 I met with Dr. Fuller when we were both attending a conference in Los Alamos. During dinner at a local Santa Fe restaurant, Dr. Fuller asked me why would the amount adsorbed be an exponential decay. I had some previous experience with QM and it immediately occurred to me that perturbation theory should work instead of classical chemical[I] thermodynamics. When I performed the operations, QM followed by Grand Canonical Partition Function (GCPF,) not only did it work but it was easy. He then was able to explain multiple isotherms with the theory giving the name "Auto-Shielding Physisorption," (ASP.)

Later, Dr. Fuller introduced me to Dr. Jürgen Adolphs who determine that the multilayer adsorption equation from disjoining pressure theory (DP) was the same as the QM equation. The equation that Dr. Jürgen was using was derived from DP. I determined that disjoining pressure can be derived from QM. thus proving that the slope of the DP derived equation was indeed $n_a$ as assumed. Thus, there are two basic derivations from well tested theories to support the validity of the analysis provided in this book.

One can never prove a theory, but for a well based theory one should is advised not betting against it, unless there is an identified problem and another solution. With the BET versus QM and DP, I would take that bet. However, this is also a lesson for scientist: no theory is sacrosanct, this includes the quantum mechanics of physisorption.

End of story - almost, or will it continue?

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[I] Classical Chemical Thermodynamic deals mostly with changes in components, that is chemical equilibrium. It, of course, must take into account other aspects, such a phase change, etc., uses them more or less as an adjunct to the main stage.

## A5 Appendix V- Data by Fuller and by Thompson in Oak Ridge

This a critical test for the BET and for any other isotherm or isotherm combinations that predict Henry's. law.

There are several examples provided previously, so here only two clear examples will be presented. Remember, only one example is all that is needed to disprove a theory, provided there is nothing wrong with the example.

Although the above should be sufficient. it is very difficult to find evidence in the open literature. violation of "Henry's Law" is a publications killer, something Polyani obliquely pointed in Science Magazine. [24]

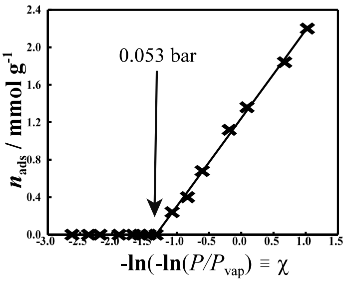

**Figure 31** Adsorption of Argon on Teflon® by Thompson.

**Table 10** is data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[7] (AALR). his is Nitrogen adsorption on activated carbon LMA223. There are several features about this isotherm that deserves discussion, but the important feature in the discussion is the line leading down in pressure a reaching zero adsorption at a finite pressure. Yes, the pressure is small, but it is still real.

The following feature can be observed in the microporous representation:

In the Microporosity (log-law) presentation the straight line fit intersects the abscissa at about $2 \times 10^{-7}$. line. There are other very important features here and this is a very important experiment for several reasons.

This should suffice as a QED but provide here are some more. Observe where the low pressure seems to intersect. Since one experiment is not convincing, presented here are a few more.

In **Figure 32** is the isotherm of oxygen on some soil returned from the moon in a high vacuum box. The sample was handled by NASA in the best argon boxes available and measured in a system that was out-gassed to a high vacuum. The data is by Gammage, Holmes, Fuller and Glasson($^{25}$). (It is probably the best out-gassed sample ever measured.)

Notice that there are 4 data point actually on the zero line. Measuring and recording the isotherm down to the $10^{-4}$ bar range was a requirement of the NASA contract. Otherwise the researcher probably would not have done this.

The next one has a very important point. The threshold pressure is high enough that even with the crudest instruments it can be observed. This is Teflon® as the adsorbent, which should have a very low energy of adsorption, and argon with an argon bath. This is by Thompson($^{26}$) who also found a threshold pressure for hydrogen cleaned $Al_2O_3$. The $H_2$ cleaning was to remove unknown contaminants on the surface. He also found that diamond that had the graphic carbon removed from the surface same hydrogen cleaning had a strong indication of a threshold pressure.

There are several more examples in reference *(?)* some of which are not obvious but are also disprovable with a different test. This test is to select a low pressure point (but not the lowest) and draw the Henry's law curve from [$n_{ads}$,$P/p_{vax}$] = 0. Theoretically by Henry's law this line should pass through several other points, when in fact it will pass through only 2 (or 1 if the point is on a tangent.).

This data was presented at a DOE conference on Surface Chemistry and Physics. The author did not attend but

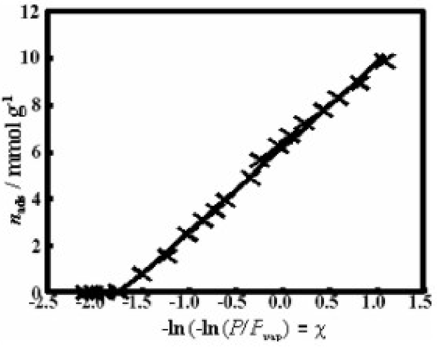

**Figure 32** Oxygen adsorbed on lunar soil NASA samples.

## **A6 Appendix VI short history** of quantum mechanics applied to physisorption

So, what’s behind this book? It is a story that lasted 50 years starting in the mid 1980's.

This book is based upon my experience, knowledge and discoveries regarding physical adsorption. He worked as a collaborators with Dr. E. L. Fuller, Jr.†, whose group ran perhaps of a thousand isotherms[I]. It was Fuller who noticed that the BET not only did not work, but yielded the wrong answer for the surfaces area that seems to have no correlation to anything. Dr. Fuller determined that the Polyani theory did fit a majority of the time, even though the theoretical basis as uncertain and the surface area parameter was wrong. He started publishing on the basis of energy instead fo relative pressure so the reviewers did not know what he was trying to get across. Thus, there is a record of some of his work in the open literature. When I had to use the BET and it created weird results, do I consulted Dr. Fuller about it and also Dr. John Kirkpatrick, a world famous mathematician. Dr. Kirkpatrick discovered and anomaly in the BET, which meant that it had to be abandoned. When I wrote about the anomaly in an attempted publication, the reaction of the reviewer was, “This is ridicules.” I agree the statement but not the target. Unfortunately, there did not seem to be an answer to my problem so it was not used in the since I have multiple micrographs of the material proposed publication.

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[I] In this respect, JBC engineered and constructed the UHV capable microbalance system used by the laboratory analytical labs for physisorption. Incorporated into the system are method to avoid the first five **Big Errors.** Thus, the vacuum obtainable was $10^{-12}$ bar for UHV, the hang-down tube was 1 m long to avoid problems with the temperature gradient zone, the temperature detector was a gas-liquid thermometer close to the sample, baffles were used place in such a way that radiant heat could not shine on the surroundings of the adsorbent and multiple diaphragm pressure detectors reading 0.1% were used for reading $10^{-6}$ bar to 10 bar were used. A computer was used to record pressure, temperature, weight gain and other diagnostics. Importantly, earth quake detectors were available and connection to the office that keeps track of blasting in the area was maintained. The lab ended up with one microbalance that weighed a 1g sample and 5 microbalance that weighed 10g that were also capable of pressure up to 25 bar. Each balance had the sensitively of $1:10^9$ (1 ppb).

# Modern Hypothesis of Physical Adsorption

In summer 1986 I met with Dr. Fuller when we were both attending a conference in Los Alamos. During dinner at a local Santa Fe restaurant, Dr. Fuller asked me why would the amount adsorbed be an exponential decay. I had some previous experience with QM and it immediately occurred to me that perturbation theory should work instead of classical chemical[I] thermodynamics. When I performed the operations, QM followed by Grand Canonical Partition Function (GCPF,) not only did it work but it was easy. He then was able to explain multiple isotherms with the theory giving the name "Auto-Shielding Physisorption," (ASP.)

Later, Dr. Fuller introduced me to Dr. Jürgen Adolphs who determine that the multilayer adsorption equation from disjoining pressure theory (DP) was the same as the QM equation. The equation that Dr. Jürgen was using was derived from DP. I determined that disjoining pressure can be derived from QM. thus proving that the slope of the DP derived equation was indeed $n_a$ as assumed. Thus, there are two basic derivations from well tested theories to support the validity of the analysis provided in this book.

One can never prove a theory, but for a well based theory one should is advised not betting against it, unless there is an identified problem and another solution. With the BET versus QM and DP, I would take that bet. However, this is also a lesson for scientist: no theory is sacrosanct, this includes the quantum mechanics of physisorption.

End of story - almost, or will it continue?

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[I] Classical Chemical Thermodynamic deals mostly with changes in components, that is chemical equilibrium. It, of course, must take into account other aspects, such a phase change, etc., uses them more or less as an adjunct to the main stage.

## A7 Appendix VII Experimental Errors :

### The BIG two errors:

*A7.1 #1 Temperature:* The first and most prevalent error is not measuring the temperature of the adsorbent and/or controlling the temperature steady.

On the latter problem, if one uses a evaporation cryostatic fluid system, be aware that the temperature of the bath depends upon the atmospheric pressure. Some simple calculations can reveal the problem:

Assume one is using a liquid nitrogen bath. Assume that the bath is at 1 bar pressure and the adsorbent is 0.1 K warmer than the bath. This can easily happen if there is no protection from outside light shielding, especially infrared from the room temperature instrument above the sample and perhaps from other origins if the sample the tubing is transparent. A simple application of the Clausius-Clapeyron equation then yield an over-pressure of $N_2$(27). This yields are difference of 1.2%. Considering that when working with the QM modeling, it has traditionally required that the fit standard deviation be less than 1% of the full range, this will likely indicate that one should reject any conclusions in the analysis. If the temperature difference is greater, the error is naturally greater. **Table 10** shows how the proplem gets worse with increased temperature error. It would be best to keep the pressure/temperature error below 0.05 K for liquid $N_2$.

The atmospheric pressure has a great effect upon the temperature of the bath. For experiments well above sea level this is a problem. Even at sea level it is good to keep an eye on a non-compensated (no correction to sea level) barometer.

**Table 10** *P* error as function of *T* offset

| *T* offset | Error in $P_{vap}$ |
|---|---|
| $\Delta T$ /K | % error |
| 0.1 | 1.2% |
| 0.5 | 6.0% |
| 1.0 | 14% |

*A7.2 #2 Insufficient vacuum:*

To do a proper job of measuring the

isotherm, one needs to read pressure in the HV or even better in the UHV range[I]

The reason this is important is that most threshold pressures are below $10^{-3}$ mbar. Without a good measure the the energy of the threshold pressure other implication of the isotherm are lost. For example, where should the mesoporosity begin. Without the $E_a$ this cannot be calculated. This will be clear with some calculation that come later. Suffice it to say here that the measurement of the threshold pressure is a stating point for many of values of the isotherm.

### Other problems to consider:

*A7.3 #3 Knudsen Effect:*

Most investigator never observe this problem because they don't overcome the first two. Langmuir noticed this, in spite of his poor measurements. If one is measuring into the HV or UHV range, then the Knudsen effect is important for most volumetric system. These systems, due to their small tubing in the temperature transition, are definitely susceptible to this problem. Small tubing is needed to allow higher sensitivity. For properly constructed gravimetric systems this problem can be avoided by using appropriately large tubing. With such tubing the temperature problem is also solved with appropriate internal baffles in the cold zone. Langmuir, with a small tubing instrument, solved this problem by calibrating each hang-down tube individually. For the matching tube for $P_{vap}$ there is no need to make this calibration.

*#4 Residual gases from dead space or buoyancy calibration*

This error is insufficient attention to sample out-gassing and failure to check the isotherm with rerun without re-measuring the "dead space." The publication by is data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso (AALR) of Nitrogen adsorption on activated carbon LMA223 illustrates the point clearly. This is shown in **Table 10**.

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[I] HV = high vacuum = $10^{-3}$ to $10^{-7}$ mbar, UHV = ultrahigh vacuum - $10^{-7}$ to $10^{-12}$ mbar.

This publication has an example of a log-law fit derived by QM. Here is is used to illustrate the importance of getting rid of the dead-space gas, in this case He. It may be that a thermal treatment is not good enough as seen by the circles, and one way is to do the "dead apace" calibration last. Another way is to do the isotherm over to see if it is reproducible. This is a good idea anyway. Normal procedure in an analytical laboratory is to repeat the experiment two times. If all the measurement agree within an acceptable limit, this is evidence that it is probably correct. If not, several more run are required to eliminate the outlier. If that is not the case, then more effort needs looking into on the experimental plan.

The publication from which this graph was taken is a very important publication, all researchers in the area should read it. The paper also is cited since it reveals other twists in adsorption analysis

## A8 Appendix VIII: Who is this author?

Curriculum vitae for Dr. James B. Condon, Prof. Emeritus .

The author as undergraduate attended Eastman School of music and then Binghamton University - Harpur College. He graduated first in his chemistry class. For graduate work, he attended Iowa State University and studied physical chemistry under a well known surface chemist Prof. Robert Hansen. His thesis disprove the multiplet theory of bezene chemisorption.

After graduate school he was hired by the Oak Ridge Labs as a surface scientist consultant to solve what was thought to be a surface problem. He discovered it was not a surface limited reaction, so he was retained as a consultant for several fields of physical chemistry. He is the inventor of the modern hydrogen in/on metals instrument. This insturment is still used today in the Oak Ridge Laboratory's analytical labs and also world-wide in perhaps thousands of laboratories. In the days of reprint requests, the laboratory received over 700 requests. He received the 1985 award from the contractor for the Oak Ridge complex for the "Invention of the Decade" for this instrument. He consulted on multiple practical problems involving various aspects of surface chemistry, corrosion reaction, hydride reaction, electrochemistry and other physical chemistry questions. Very often the problems he consulted on had more to do with personnel problems than an unknown science. In that regard, he was licenced and presented courses in self-esteem. While working in the Oak Ridge labs, he also was an adjunct full professor of chemistry at the University of Tennessee in Knoxville.

Other accomplishment at the time, were:

- His work with corrosion preempted a serious problem with missile system saving billions of dollars. For this he receive an award from DOD and DOE.
- He was the founder of ZYP Coating, Inc., a manufacturer of high temperature paints and coatings. ZYP is today the only company making these coatings and has expanded into providing on-site or in-house application services.

After leaving the DOE facilities, he switched to full time professor at a nearby community college and performed research as a Gest Wissenschaftler as Physikert at the Institut der Festkörper Forschung (IFF, Institute for Solid State Research) in the Forschung Zentrum Jülich.

Dr. Condon has over 100 open literature publication mostly dealing with corrosion but a few for physisorption and nine other topics. He has also authored more than 600 presently classified reports. He also has 2 unclassified patents dealing with low pressure diamond production and several other patents, which are classified.

## A9 Appendix IX Further analysis of the Nguyen and Do data.

As is probably true for most isotherm there is a touch of other features operating in an isotherm. This is true of the Krug, Jaroniec and Olivier isotherm, as good as it is, with heterogeniety and $P_{\text{vap}}$ corrections. Only when one gets the basics correct can one discern the more subtle features

**Table 11** the parameters yielded by the 2 and the 4 parameter fit for ND

| | | | |
|---|---|---|---|
| Quantity | linear LS | non-linear LS | units |
| $n_{\text{m}} =$ | 8.251* | 8.448 * | mmol $g^{-1}$ |
| $\ln(P_\varsigma/P_{\text{vap}})$ | -15.0555 * | -14.9055 * | |
| $P_\varsigma/P_{\text{vap}} =$ | $2.894\times10^{-7}$ | $3.362\times10^{-7}$ | |
| $\chi_\varsigma =$ | -2.7117 | -2.7017 | |
| $E_{\text{a}} =$ | -9.76 | -9.70 | kJ $\text{mol}^{-1}$ |
| $n_{\text{ext}} =$ | | 0.0834 * | mmol $g^{-1}$ |
| $\chi_{\varsigma\text{,ext}} =$ | | -2.2768 * | |
| $E_{\text{a,ext}} =$ | | 6.32 | kJ $\text{mol}^{-1}$ |
| $\sigma_{\text{fit}} =$ | **0.0894** | **0.07289** | |
| $\sigma_{\text{FDR}} =$ | **1.10%** | **0.893%** | |

So it is with the Nguyen and Do data. In **Table 11** is the analysis of the data with the linear regression previously determined with two parameters, and the data analyzed with a non-linear least squares routine that has four parameters. Notice there are differences in the common parameters and for the standard deviation of the fit.

The amount of external surface area is very small compared to the pores, but never-the-less, it seems real.

Statistically, the ratios of the σs is 1.23 which is not sufficient to reject the 2 parameter fit over the 4 parameter(F = ~1.4. However, recall that there is more to consider than statistics. The 2 parameter fit would normally be rejected on the basis of the 1 % FDR rule, but the 4 parameter fit would not be. Inspecting the **Figure 33** compared to **Figure 3** it seems intuitive that the 4 parameter fit should be selected, but again this is not an unbiased decision.

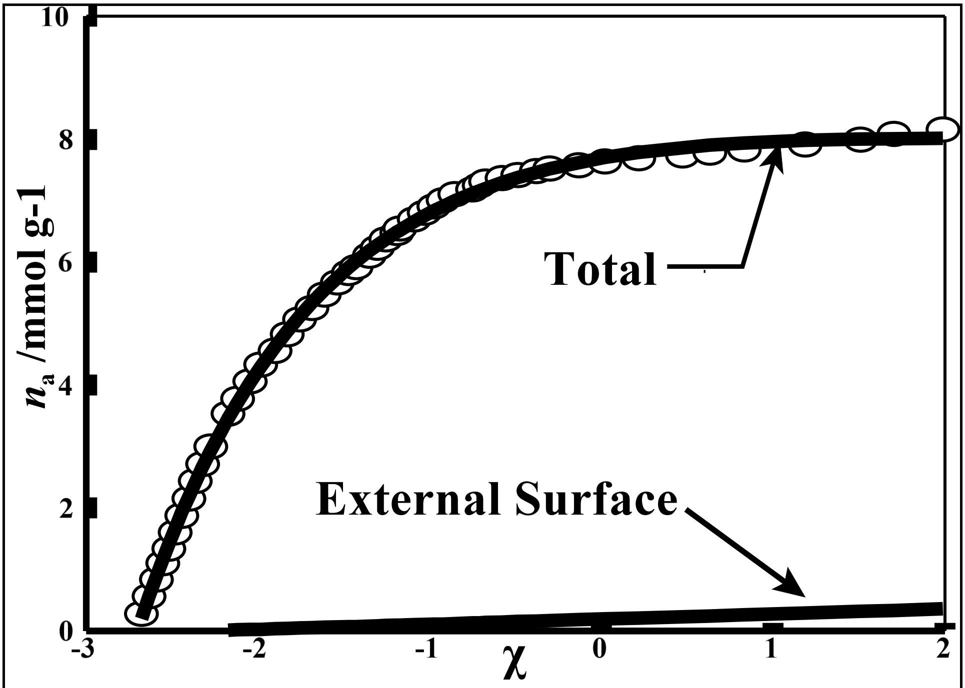

**Figure 33** The fit to the ND data including the log-law, mainly, followed by the linear fit for external adsorption. The χ-plot is used to show both high and low pressure reagions. Compare this to **Figure 3**

## A10 Appendix X Some data tables

The following are some of the data tables used. The JKO data is listed in their publication.

### *10.1 KIT-6 data Sample K(100)48_N*

These tables have been added to avoid copyright infringement. Actual data cannot be shown even though such, as data, cannot be copyright protected by US law. See the original paper for the data listed in a graph.

KIT-6 Sample K(100)48_N: $\chi$-plot results

| $P/P_{vap}$ | $\chi$ | $n_a$ /mmol/g | overall fit | Residuals |
|---|---|---|---|---|
| 0.02811 | -1.273 | 7.357 | 7.202 | -0.1552 |
| 0.05132 | -1.088 | 8.312 | 8.143 | -0.1694 |
| 0.1058 | -0.809 | 9.643 | 9.567 | -0.0760 |
| 0.2045 | -0.462 | 11.299 | 11.338 | 0.0386 |
| 0.3049 | -0.172 | 12.656 | 12.816 | 0.1596 |
| 0.4046 | 0.100 | 13.946 | 14.203 | 0.2567 |
| 0.4612 | 0.256 | 14.759 | 15.000 | 0.2413 |
| 0.5029 | 0.375 | 15.455 | 15.605 | 0.1496 |
| 0.6192 | 0.735 | 17.411 | 17.443 | 0.0325 |
| 0.6618 | 0.885 | 18.027 | 18.205 | 0.1784 |
| 0.6801 | 0.953 | 18.545 | 18.554 | 0.0092 |
| 0.7052 | 1.052 | 19.152 | 19.059 | -0.0926 |
| 0.7137 | 1.087 | 19.455 | 19.243 | -0.2125 |
| 0.7232 | 1.127 | 19.808 | 19.475 | -0.3331 |
| 0.7326 | 1.167 | 20.112 | 19.818 | -0.2936 |
| 0.743 | 1.214 | 20.393 | 20.885 | 0.4926 |
| 0.7464 | 1.229 | 21.951 | 21.741 | -0.2097 |
| 0.7561 | 1.274 | 28.170 | 28.140 | -0.0298 |
| 0.767 | 1.327 | 36.799 | 36.978 | 0.1788 |
| 0.7817 | 1.401 | 37.071 | 37.141 | 0.0698 |
| 0.7954 | 1.474 | 37.129 | 37.182 | 0.0521 |
| 0.8082 | 1.547 | 37.170 | 37.221 | 0.0518 |
| 0.8191 | 1.612 | 37.259 | 37.257 | -0.0016 |
| 0.8288 | 1.673 | 37.326 | 37.291 | -0.0350 |
| 0.8366 | 1.724 | 37.375 | 37.319 | -0.0559 |
| 0.8451 | 1.782 | 37.415 | 37.351 | -0.0639 |
| 0.8562 | 1.863 | 37.473 | 37.396 | -0.0774 |
| 0.902 | 2.272 | 37.737 | 37.621 | -0.1152 |

| | | | | |
|---|---|---|---|---|
| 0.9462 | 2.895 | 38.058 | 37.965 | -0.0928 |
| 0.9903 | 4.631 | 38.821 | 38.923 | 0.1014 |

$\sigma_{\text{fit}}$ = **0.15752**
$\sigma_{\text{FDR}}$ = **0.43%**

Transition zone: 1.229 - 1.327
$\chi_\varsigma = -2.685$

### *10.2 SBA-15 Sample S(140)24_N:*

These tables have been added to avoid copyright infringement. Actual data cannot be shown even though such, as data, cannot be copyright protected. See the original paper for the data listed in a graph.

SBA-15 Sample S(140)24_N: χ-plot results

| $P/P_{\text{vap}}$ | $\chi$ | $n_a$ /mmol g$^{-1}$ | overall fit | residuals |
|---|---|---|---|---|
| 0.003777 | -1.719 | 3.144 | 2.461 | 0.683 |
| 0.005351 | -1.655 | 3.411 | 2.727 | 0.685 |
| 0.008184 | -1.570 | 3.649 | 3.076 | 0.573 |
| 0.01416 | -1.449 | 4.034 | 3.575 | 0.459 |
| 0.02361 | -1.321 | 4.435 | 4.102 | 0.333 |
| 0.03305 | -1.227 | 4.777 | 4.490 | 0.287 |
| 0.04501 | -1.132 | 5.103 | 4.881 | 0.222 |
| 0.05445 | -1.068 | 5.308 | 5.142 | 0.166 |
| 0.06295 | -1.017 | 5.518 | 5.353 | 0.165 |
| 0.07334 | -0.960 | 5.710 | 5.587 | 0.123 |
| 0.0831 | -0.911 | 5.888 | 5.789 | 0.099 |
| 0.09128 | -0.873 | 6.080 | 5.948 | 0.133 |
| 0.1032 | -0.820 | 6.290 | 6.164 | 0.126 |
| 0.2046 | -0.462 | 7.299 | 7.642 | -0.343 |
| 0.2572 | -0.306 | 7.804 | 8.284 | -0.480 |
| 0.3044 | -0.173 | 8.366 | 8.830 | -0.464 |
| 0.3573 | -0.029 | 8.750 | 9.426 | -0.676 |
| 0.4079 | 0.109 | 9.268 | 9.994 | -0.726 |
| 0.503 | 0.375 | 10.277 | 11.091 | -0.814 |
| 0.5515 | 0.519 | 10.857 | 11.683 | -0.826 |
| 0.5993 | 0.669 | 11.598 | 12.303 | -0.705 |
| 0.615 | 0.721 | 11.911 | 12.517 | -0.606 |
| 0.6257 | 0.757 | 12.134 | 12.666 | -0.532 |
| 0.6361 | 0.793 | 12.326 | 12.813 | -0.487 |

| | | | | |
|---|---|---|---|---|
| 0.644 | 0.821 | 12.518 | 12.927 | -0.409 |
| 0.6544 | 0.858 | 12.665 | 13.080 | -0.415 |
| 0.6648 | 0.896 | 12.844 | 13.236 | -0.392 |
| 0.6752 | 0.935 | 13.054 | 13.396 | -0.342 |
| 0.6837 | 0.967 | 13.272 | 13.529 | -0.257 |
| 0.6928 | 1.002 | 13.540 | 13.675 | -0.135 |
| 0.7107 | 1.074 | 13.866 | 13.972 | -0.106 |
| 0.7233 | 1.127 | 14.192 | 14.190 | 0.002 |
| 0.7347 | 1.177 | 14.446 | 14.394 | 0.053 |
| 0.7422 | 1.210 | 14.741 | 14.532 | 0.209 |
| 0.7517 | 1.254 | 15.143 | 14.711 | 0.432 |
| 0.7608 | 1.297 | 15.527 | 14.889 | 0.638 |
| 0.7734 | 1.359 | 16.049 | 15.144 | 0.905 |
| 0.7797 | 1.391 | 16.357 | 15.276 | 1.081 |
| 0.7904 | 1.447 | 17.500 | 15.649 | 1.851 |
| 0.7998 | 1.499 | 18.853 | 17.791 | 1.062 |
| 0.808 | 1.546 | 21.862 | 22.654 | -0.793 |
| 0.8171 | 1.600 | 28.344 | 29.091 | -0.747 |
| 0.8281 | 1.668 | 35.701 | 34.594 | 1.107 |
| 0.8388 | 1.739 | 37.866 | 37.208 | 0.658 |
| 0.847 | 1.795 | 38.089 | 38.128 | -0.039 |
| 0.8577 | 1.874 | 38.429 | 38.677 | -0.248 |
| 0.8694 | 1.966 | 38.696 | 38.939 | -0.243 |
| 0.882 | 2.075 | 38.888 | 39.105 | -0.216 |
| 0.8949 | 2.198 | 39.094 | 39.252 | -0.158 |
| 0.9049 | 2.303 | 39.348 | 39.372 | -0.024 |
| 0.9484 | 2.938 | 40.058 | 40.085 | -0.027 |
| 0.9924 | 4.876 | 42.254 | 42.263 | -0.008 |

$\sigma_{\text{fit}}$ = **0.606** $\sigma_{\text{FDR}}$ = 1.46%

Transition zone: 1.229 - 1.327

$\chi_\varsigma = -2.3162$

### 10.3 Data by Nguyen and Do:

| $P/P_{\text{vap}}$ | $\chi$ | $n_a$ | overall fit | residuals |
|---|---|---|---|---|
| | **-2.7017** | /mmol g$^{-1}$ | /mmol g$^{-1}$ | /mmol g$^{-1}$ |
| 4.704E-07 | -2.6789 | 0.2835 | 0.1903 | 0.0932 |
| 8.889E-07 | -2.6343 | 0.5576 | 0.5510 | 0.0066 |
| 1.574E-06 | -2.5924 | 0.8379 | 0.8748 | -0.0369 |
| 2.528E-06 | -2.5563 | 1.106 | 1.1433 | -0.0373 |
| 3.983E-06 | -2.5204 | 1.339 | 1.4010 | -0.0620 |
| 6.193E-06 | -2.4842 | 1.607 | 1.6511 | -0.0441 |

| | | | | |
|---|---|---|---|---|
| 1.014E-05 | -2.4423 | 1.875 | 1.9306 | -0.0556 |
| 1.577E-05 | -2.4031 | 2.156 | 2.1809 | -0.0249 |
| 2.329E-05 | -2.3672 | 2.442 | 2.4018 | 0.0402 |
| 3.72E-05 | -2.3224 | 2.719 | 2.6666 | 0.0524 |
| 5.86E-05 | -2.2768 | 3.003 | 2.9243 | 0.0787 |
| 0.0001521 | -2.1737 | 3.536 | 3.4567 | 0.0793 |
| 0.0002411 | -2.1199 | 3.779 | 3.7133 | 0.0657 |
| 0.0004353 | -2.0463 | 4.065 | 4.0420 | 0.0230 |
| 0.0006902 | -1.9849 | 4.336 | 4.2982 | 0.0378 |
| 0.00123 | -1.9022 | 4.56 | 4.6187 | -0.0587 |
| 0.001963 | -1.8299 | 4.831 | 4.8776 | -0.0466 |
| 0.003033 | -1.7575 | 5.071 | 5.1182 | -0.0472 |
| 0.004536 | -1.6856 | 5.255 | 5.3403 | -0.0853 |
| 0.006567 | -1.6146 | 5.482 | 5.5441 | -0.0621 |
| 0.009508 | -1.5381 | 5.676 | 5.7474 | -0.0714 |
| 0.01273 | -1.4733 | 5.831 | 5.9074 | -0.0764 |
| 0.01547 | -1.4276 | 5.922 | 6.0141 | -0.0921 |
| 0.02099 | -1.3516 | 6.109 | 6.1807 | -0.0717 |
| 0.02486 | -1.3068 | 6.236 | 6.2728 | -0.0368 |
| 0.02981 | -1.2564 | 6.373 | 6.3716 | 0.0014 |
| 0.03693 | -1.1935 | 6.479 | 6.4877 | -0.0087 |
| 0.03941 | -1.1736 | 6.548 | 6.5229 | 0.0251 |
| 0.0511 | -1.0899 | 6.7 | 6.6631 | 0.0369 |
| 0.06049 | -1.0315 | 6.809 | 6.7538 | 0.0552 |
| 0.07069 | -0.9744 | 6.912 | 6.8374 | 0.0746 |
| 0.0805 | -0.9241 | 7.012 | 6.9069 | 0.1051 |
| 0.0953 | -0.8547 | 7.112 | 6.9967 | 0.1153 |
| 0.1196 | -0.7531 | 7.186 | 7.1170 | 0.0690 |
| 0.1301 | -0.7127 | 7.252 | 7.1613 | 0.0907 |
| 0.1407 | -0.6735 | 7.314 | 7.2024 | 0.1116 |
| 0.1676 | -0.5801 | 7.37 | 7.2938 | 0.0762 |
| 0.1959 | -0.4887 | 7.42 | 7.3746 | 0.0454 |
| 0.2319 | -0.3794 | 7.482 | 7.4611 | 0.0209 |
| 0.259 | -0.3008 | 7.523 | 7.5172 | 0.0058 |
| 0.3188 | -0.1338 | 7.579 | 7.6210 | -0.0420 |
| 0.375 | 0.0194 | 7.644 | 7.7002 | -0.0562 |
| 0.4468 | 0.2161 | 7.697 | 7.7831 | -0.0861 |
| 0.5359 | 0.4719 | 7.738 | 7.8649 | -0.1269 |
| 0.5869 | 0.6294 | 7.784 | 7.9032 | -0.1192 |
| 0.647 | 0.8315 | 7.837 | 7.9417 | -0.1047 |
| 0.7367 | 1.1856 | 7.915 | 7.9857 | -0.0707 |
| 0.8015 | 1.5084 | 7.996 | 8.0066 | -0.0106 |
| 0.8334 | 1.7024 | 8.087 | 8.0125 | 0.0745 |
| 0.8721 | 1.9889 | 8.164 | 8.0144 | 0.1496 |

$\mathbf{ln}(\chi_\varsigma) = -14.9055$

$n_\mathrm{m} = 0.5667$

$n_\mathrm{ext} = 0.0834$

$\mathbf{ln}(\chi_\varsigma)_\mathrm{ext} = -2.2768$

## A11 A Word About How Science is Supposed to Work

I taught General Chemistry, the first competency I taught was. “What is scientific knowledge and how is it obtained.” I did not say, “What is science.” because this term is fraught with misunderstanding and prejudgement. So, here is what I provided.

Scientific knowledge consists of:

- Observations that are:
  - repeatable
  - independent of observer
  - tentative and
- Explanations for the observations that are:
  - matching most of the observations with reasons for exceptions
  - they must be disproveable
  - are always tentative
- The official deference between the words for observations are.
  - Laws - laws are able to describe the observations without explanation. Example: Newton’s Laws, Chemical kinetics laws
  - Theories - are able to describe the observations and supply basic explanation for the method of describing the phenomena.
  - Hypothesis a proposal for a new law or theory as an explanation based on basic mathematic of other logic.

All Theories, Laws and Hypothesis must be disprovable, meaning there must be a way to test their veracity. This is normally done by testing possible predictions. It might also be a prediction of an anomaly. If the prediction is found to fail, then the explanation is false. However, this type of disproof must be confirmed by reproducible observations as well.

## Acknowledgments:

I wish to thank Dr. Jürgen Adolphs for his continued help and encouragement in recent years.

I acknowledge the incredible amount of work and knowledge provided by Dr. E. Loren Fuller. He was a friend and mentor and I miss him. As obvious from the history, given above, he is a key link in the passage and addition of knowledge leading to the understanding of physisorption documented in this book. This knowledge started with Polanyi and was pass on by several others to Loren and then to me.

I also acknowledge the contributions provided by Dr.W. Thomas Berg whose information provided the a critical experimental in thermodynamic that support the QM hypothesis. I miss him also.

I also acknowledge the work of Dr. John Kirkpatrick, whose mathimatical skills were vital to this area of research but also to the calculations in other areas, such as corrosion and hydride reactions.

To my ever patient wife, Gisela, who put up with many years of my frustration with this project, I say, “Wow, thank you!”

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